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Studies of Structural Dynamics in Polymer Blends
Using Rheology and Small-Angle X-Ray Scattering Techniques

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ABSTRACT

Studies of Structural Dynamics in Polymer Blends Using Rheology and Small-Angle X-Ray Scattering Techniques

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Structural dynamics in three polymer blend systems, differing largely with respect to morphology, have been investigated. The first system, composed of two immiscible homopolymers, exhibits a microstructure of micron-sized droplets dispersed in a matrix phase. We have examined small-angle x-ray scattering (SAXS) as a new approach for conducting *in situ* studies of flow-induced structural changes in these types of blends. This approach relies on Porod scattering, which is related to the interfacial properties in two-phase systems. Indeed, we have successfully performed *in situ* SAXS measurements of an immiscible blend in response to applied shear, allowing for the observation of deformation and relaxation of interface with time.

The second blend system, a bicontinuous microemulsion (B μ E), consists of two cocontinuous domains of immiscible homopolymers compatibilized by diblock copolymer at the interface. The equilibrium dynamics were characterized via x-ray photon correlation spectroscopy. These measurements were used to test rheological predictions for bicontinuous microemulsions by Pätzold and Dawson. Although the

predictions describe the *shape* of the relaxation spectrum fairly well, the theory fails to predict *absolute* values of the rheological properties. These results highlight a need for the development of more sophisticated theory to describe the dynamics of bicontinuous microemulsions. The *shear*-induced dynamics of the B μ E microstructure were interrogated using rheology, *in situ* SAXS, and optical microscopy. Optical microscopy revealed micron-sized phase-separated structures coexisting with the nano-scale B μ E phase at equilibrium. Direct comparison of this multi-phase system to a previously documented B μ E system by Bates, Lodge, and coworkers strongly indicates that the microemulsion morphology dominates the rheology and scattering behavior at linear to moderately non-linear shear conditions, whereas the phase-separated structures govern the response under more severe shear conditions.

The third system is a sponge phase, characterized by two domains of a single homopolymer separated by a continuous, multiply-connected bilayer membrane, which is formed by triblock copolymer. The flow behavior of polymer-based sponge phases has not been previously documented. Rheology and *in situ* SAXS measurements of our sponge system indicate very slow topological dynamics, which appear to give rise to unexpected, persisting anisotropy in the sponge structure that does not relax under quiescent conditions.

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CHAPTER 1.

INTRODUCTION

1.1. Overview

Blending of dissimilar polymers offers a valuable means for creating new materials whose end-use applications are determined by their ultimate properties. Blend properties, in turn, depend on a multitude of factors, including blend composition, constituent properties, interfacial properties, processing history, and the final morphology. The relationships among these factors and their impact on the ultimate properties are quite complex. As a result, the investigation of these relationships is a significant area of research today.

Perhaps the simplest and most common form of blend is a binary blend of immiscible homopolymers, which typically yields morphologies where a minor phase is dispersed as droplets in a matrix phase. The properties of immiscible blends are strongly influenced by the size and shape distribution of the dispersed droplets. Because these systems are thermodynamically unstable, dispersions with smaller than micron-sized droplets are difficult to achieve; droplet sizes tend to grow owing to both thermodynamic (coarsening) and kinetic (coalescence) factors. In addition, adhesion between the two

phases is weak. Despite these limitations, the properties of immiscible blends are suitable for meeting performance requirements for many applications. For instance, small quantities of rubbery polymer are often mixed into brittle plastics to improve impact strength [Harrats *et al.* (2006)].

Greater control over morphology and interfacial properties is possible by blending block copolymer with one or more homopolymers. In immiscible homopolymer blends, appropriate choice of a block copolymer can lower the interfacial energy and increase the interfacial strength between the two phases. For small concentrations of block copolymer added to droplet/matrix systems, the effect of lower interfacial energy allows finer dispersions to be achieved [Thomas and Prud'homme (1992)]. Higher concentrations of block copolymer can yield a variety of microstructures, such as lamellae, bicontinuous microemulsions, and ordered micellar systems, with length scales ranging from 10 – 100 nanometers [Washburn *et al.* (2000)]. Other morphologies, such as sponge phases [Falus *et al.* (2006)] and vesicles [Falus *et al.* (2005)], can be obtained in blends of block copolymer with a single homopolymer. In these systems, one block segment is miscible with the homopolymer, whereas the other (immiscible) block segment typically forms a bilayer membrane between regions of the homopolymer.

Although a large array of interesting structures can be created from homopolymer/copolymer blends, these systems are generally much less economical to produce than immiscible blend systems. The synthesis of copolymers with controlled composition and chain length is expensive. Also, since diffusion of the long polymer chains is slow, achieving the desired equilibrium structure on reasonable time scales may

require the use of environmentally-unfriendly solvents to facilitate mixing. Furthermore, a large fraction of the block copolymer chains irreversibly form micelles before reaching the interface, even at low concentrations in the blend. Consequently, homopolymer/copolymer blends are typically used for specialized applications, such as membranes, catalyst supports, and optical and conductive materials [Harrats *et al.* (2006)]. However, a couple of processes, reactive compatibilization [Beck Tan *et al.* (1996); Macosko *et al.* (2005)] and solid-state shear pulverization [Lebovitz *et al.* (2002b); Tao *et al.* (2005)], have recently shown promise as economically viable approaches in achieving sub-micron morphologies in blends. For example, solid-state shear pulverization, under appropriate conditions, can lead to *in situ* formation of block copolymer at the interfacial regions [Lebovitz *et al.* (2002b)]; the resulting interfacial activity of the block copolymers stabilizes the blends against subsequent coarsening [Lebovitz *et al.* (2002a)].

Polymer blends in the melt state exhibit diverse, complex dynamics that are highly dependent on the microstructure and the dynamics of the blend constituents. Since the manufacturing of blends often requires some level of processing in the melt state, understanding these dynamics is of great importance. If the blend dynamics are slow or similar to the time scales associated with processing, the microstructure may deform or break down, changing the final properties of the material.

Industrial processing of blends typically involves non-isothermal, complex flow fields composed of a combination of shear and extensional flow. To date, predicting the structural response of blends under such complicated conditions remains a significant challenge. To better understand the underlying physics associated with blend

microstructure, significant effort has been expended by the scientific community to study the dynamics of blends under quiescent or simple, well-defined flow conditions at constant temperatures. The focus of our work is to contribute to this broad research area by utilizing rheology and small-angle x-ray scattering (SAXS) techniques to investigate structural dynamics under quiescent or simple shear flow conditions in three types of polymer blend systems: immiscible binary homopolymer blends, bicontinuous microemulsions, and sponge phases.

1.2. Outline and Objectives

Small-angle x-ray scattering is an essential tool used to achieve our research objectives for each of the blend systems. Therefore, Chapter 2 is dedicated to introducing the fundamentals of x-ray scattering as well as to provide descriptions of the key small-angle scattering techniques employed in these studies. These techniques include (1) *in situ* SAXS experiments to probe structural dynamics during applied homogeneous shear flow in each of the three blends, and (2) x-ray photon correlation spectroscopy (XPCS) to probe dynamics in a bicontinuous microemulsion at thermal equilibrium.

To date, *in situ* techniques have not been established for probing structural dynamics in opaque immiscible blends with high concentrations of dispersed phase. In Chapter 3, we investigate SAXS as a potential tool for conducting *in situ* measurements of these systems. The droplets in immiscible blends are larger than the 10 – 100 nm length scales typically probed by small-angle x-ray scattering. However, scattering due

to electron density contrast at the phase interface, known as Porod scattering, enables measurement of changes in the orientation and quantity of interface in the blend with time, providing valuable insights into changes in blend structure. We have performed two experimental studies that establish the feasibility of characterizing structural dynamics in immiscible polymer blends via SAXS. The first experiment is a coarsening study in which droplet growth was determined as a function of annealing time. The second experiment involved characterization of droplet deformation in response to applied shear deformations.

Chapter 4 presents an investigation of the equilibrium and shear-induced structural dynamics in a polymer bicontinuous microemulsion (B μ E). Currently, only a single polymer B μ E system has been extensively characterized in this manner [Burghardt *et al.* (2002); Caputo *et al.* (2002b); Krishnan *et al.* (2002a, 2002b); Morkved *et al.* (1999, 2001)]. These previously documented studies show complex, interesting behavior related to the interconnected morphology in the system, but many of the mechanisms leading the observed behavior remain uncertain. Thus, our studies of a second polymer B μ E system contribute to the development of a greater understanding of dynamics in the bicontinuous microemulsion morphology. We have characterized the equilibrium dynamics of our system using rheology and x-ray photon correlation spectroscopy. These measurements were employed to test the predictions of B μ E rheology by Pätzold and Dawson, which are based on a time-dependent Landau-Ginzburg model. The shear-induced behavior was probed using rheology, *in situ* SAXS, and *in situ* optical microscopy.

In Chapter 5, we investigate the rheology and shear-induced structural dynamics in a polymer sponge phase, which is an intriguing and relatively new class of materials [Falus *et al.* (2004a); Laurer *et al.* (1997)]. To our knowledge, the flow behavior of these systems has not yet been characterized. Studies of *aqueous*-based sponge phases have shown a shear-induced sponge-to-lamellar phase transition at very high shear rates [Mahjoub *et al.* (1998); Porcar *et al.* (2003); Yamamoto and Tanaka (1996)]. However, the underlying mechanisms of this transition are difficult to resolve experimentally due to the fast dynamics of these small molecule systems. Studies of polymer sponge phases, which exhibit much slower dynamics due to the larger constituent molecules, may help to resolve the shear-induced processes occurring within these systems.

Finally, Chapter 6 summarizes the important findings in the studies of each blend system and provides recommendations for future work.

CHAPTER 2.

SMALL-ANGLE X-RAY SCATTERING TECHNIQUES

2.1. Introduction

X-ray scattering is a powerful tool for investigating structure in materials over a wide range of length scales, from the atomic scale to the supramolecular scale on the order of 100 nm. For the polymer blend systems used in our studies, the molecules phase separate to form structures greater than 10 nm in size. Scattering from structures in this range of length scales occurs in the small-angle regime. Small-angle scattering is classified separately from conventional x-ray scattering in part due to some differences in experimental factors. For example, since the flux of the transmitted incident beam is several orders of magnitude greater than the flux of the radiation scattered by the sample, any divergence or stray scattering from the incident beam can overwhelm scattering from the sample. Therefore, small-angle scattering requires a highly collimated incident beam while maintaining a high flux level, characteristics ideally suited for the use of synchrotron radiation. The high fluxes attainable at synchrotron sources also allow for rapid data collection, facilitating measurement of structural changes in the sample with time. The length scales and data collection rates accessible using synchrotron radiation

make small-angle x-ray scattering techniques a very suitable choice for probing structural dynamics in the three polymer blends presented in this study.

2.2. Fundamentals of X-Ray Scattering

When a sample is subjected to an x-ray beam, the electric field in incident waves causes the electrons in the sample to oscillate at the frequency of the incident radiation. As the electrons accelerate during oscillation, radiation is, in turn, emitted (scattered) in all directions. In our studies of structure during shear, we are interested in radiation that scatters elastically, where the energy (or frequency) of the scattered waves is equal to the energy of the incident radiation. The waves scattered from different locations in the sample interfere with each other constructively or destructively, producing a scattering pattern. According to Bragg's law, the interference is constructive when the phase shift between scattered waves is a multiple of 2π . This condition is given by

$$\frac{n\lambda}{2d_0} = \sin \theta \quad (2.1)$$

where n is a positive integer, λ is the wavelength of the radiation, 2θ is the angle between the incident and scattered waves, and d_0 is the distance between scatterers. The scattering pattern produced from an illuminated sample is captured using a detector, which measures intensity, I , as a function of position.

The intensity of a wave is given by the square of its amplitude A . For a wave traveling in the x direction with time t , the amplitude can be expressed as

$$A(x, t) = A_0 \cos[2\pi(\nu t - x / \lambda)] \quad (2.2)$$

where ν , λ , A_0 are the frequency, wavelength, and amplitude of the wave, respectively.

For convenience, $A(x, t)$ may be written using complex notation:

$$A(x, t) = A_0 \exp[2\pi i(\nu t - x / \lambda)] = A_0 \exp[i\omega t] \exp[-i2\pi x / \lambda] \quad (2.3)$$

where $\omega = 2\pi\nu$, and the quantity $2\pi x / \lambda$ gives the change in phase ϕ of the wave that occurs from traveling a distance x . Note that taking the real part of eqn. 2.3 yields eqn. 2.2.

Figure 2.1(a) shows an incident plane wave, traveling in the direction specified by unit vector $\mathbf{k}_0$, scattered by two points (at O and P) within a sample separated by vector $\mathbf{r}$. The phase difference $\Delta\phi$ between the scattered waves traveling in the direction specified by unit vector $\mathbf{k}$ is given by

$$\Delta\phi = \frac{2\pi}{\lambda} (\overline{QP} - \overline{OR}) = \frac{2\pi}{\lambda} (\mathbf{k}_0 \cdot \mathbf{r} - \mathbf{k} \cdot \mathbf{r}) = -\mathbf{q} \cdot \mathbf{r} \quad (2.4)$$

where $\mathbf{q}$ is the scattering vector defined as $\mathbf{q} = 2\pi(\mathbf{k} - \mathbf{k}_0)/\lambda$. The scattering vector, therefore, describes the scattering geometry (Figure 2.1(b)). The relationship between the magnitude of $\mathbf{q}$ and the scattering angle 2θ is given by

$$|\mathbf{q}| = q = \frac{4\pi}{\lambda} \sin \theta. \quad (2.5)$$

Combining eqn. 2.5 with Bragg's law (eqn. 2.1) shows that an arrangement of scattering elements with a characteristic spacing d_0 will exhibit a maximum intensity at:

$$q = q_{\max} = \frac{2\pi n}{d_0}. \quad (2.6)$$

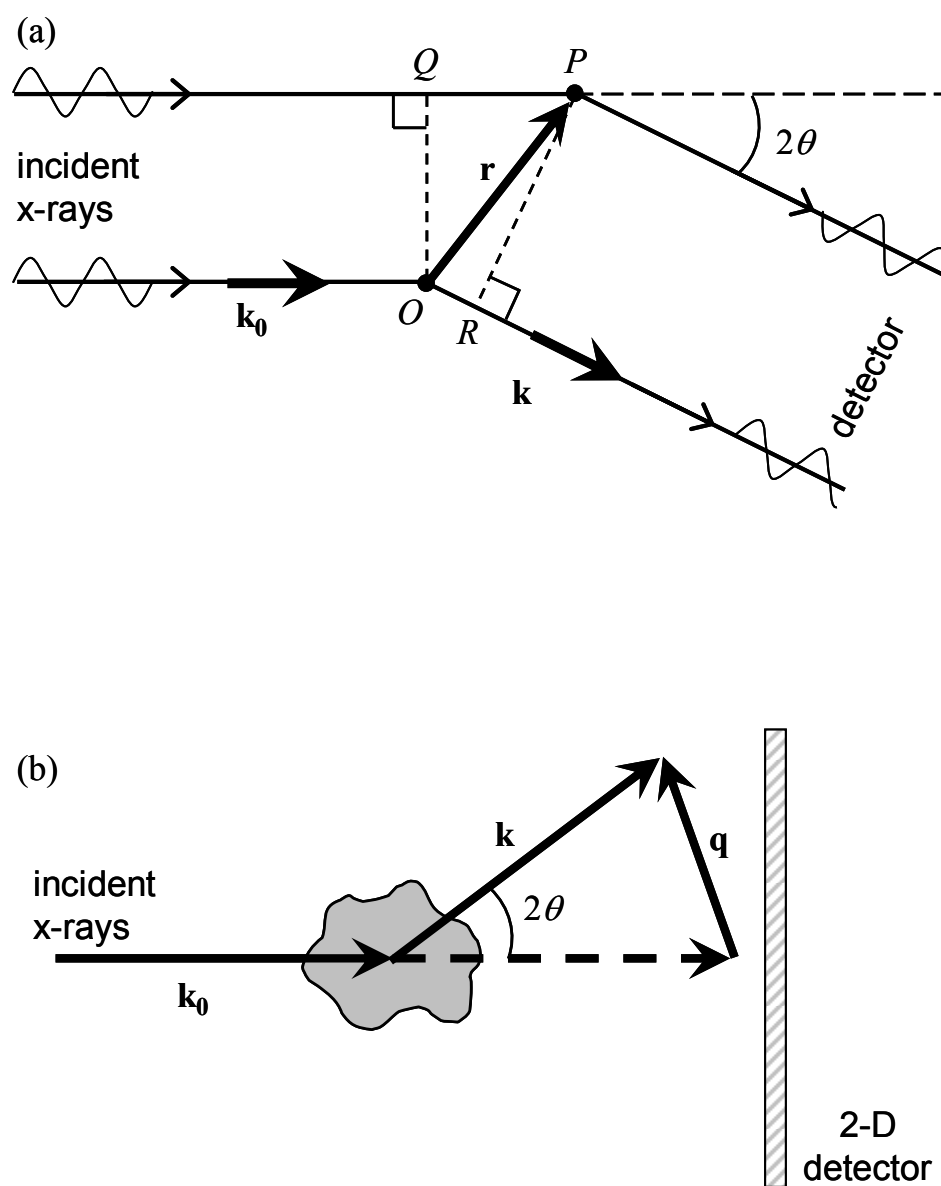


Figure 2.1. (a) Geometry of the path length difference between parallel scattered waves [adapted from Roe (2000)]. (b) Geometry of a typical scattering experiment.

Clearly, this relationship shows that arrangements with larger d_0 scatter at smaller scattering angles.

Considering eqns. 2.3 and 2.4, the wave amplitude from a single scatterer can be written as

$$A(\mathbf{q}, t) = A_0 b \exp[i\omega t] \exp[-i\mathbf{q} \cdot \mathbf{r}] \quad (2.7)$$

where A_0 is the amplitude of the incident wave, and $\mathbf{r}$ is now the position of the scatterer with respect to an arbitrary origin. b is the scattering length, describing the scattering efficiency of the scatterer. In our experiments, the scatterers are electrons, and the incident x-rays are generated from a synchrotron source. For this case, in the small-angle regime, b is approximately equal to the classical radius of the electron $r_e [= 2.818 \times 10^{-15} \text{ m}]$. For elastic scattering, the scattered frequency remains unchanged from the incident frequency. Since the quantity measured at the detector is the intensity, the time-dependent term in eqn. 2.7 can be discarded, resulting in

$$A(\mathbf{q}) = A_0 b \exp[-i\mathbf{q} \cdot \mathbf{r}]. \quad (2.8)$$

For a discrete system of N scatterers, eqn. 2.8 can then be extended as

$$A(\mathbf{q}) = A_0 b \sum_{j=1}^N \exp[-i\mathbf{q} \cdot \mathbf{r}_j]. \quad (2.9)$$

The total *intensity* scattered by the system is then given by

$$I(\mathbf{q}) = \frac{|A(\mathbf{q})|^2}{A_0^2} = \frac{A(\mathbf{q})A^*(\mathbf{q})}{A_0^2} = b^2 \sum_{j=1}^N \sum_{k=1}^N \exp[-i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)] \quad (2.10)$$

where $A^*(\mathbf{q})$ is the complex conjugate of $A(\mathbf{q})$. Here, the amplitude has been normalized by the amplitude of the incident wave. This expression shows that the intensity only depends on the *relative* difference in the path length between waves scattered from

different locations. Hence, the phase angle ϕ associated with each scatterer is not represented in the intensity.

As $N \rightarrow \infty$, the system of scatterers can be treated as a continuous distribution, and the amplitude can be written as

$$A(\mathbf{q}) = A_0 \int_V \rho(\mathbf{r}) \exp[-i\mathbf{q} \cdot \mathbf{r}] d\mathbf{r} \quad (2.11)$$

where V denotes that the integration is performed over the volume of sample that is illuminated by the incident beam. $\rho(\mathbf{r})$ is the scattering length density distribution and is equal to the electron density distribution $n(\mathbf{r})$ multiplied by b . Again, the intensity is computed by taking the square of the amplitude:

$$I(\mathbf{q}) = \frac{|A(\mathbf{q})|^2}{A_0^2} = \iint_V \rho(\mathbf{u}') \rho(\mathbf{u}) \exp[-i\mathbf{q} \cdot (\mathbf{u}' - \mathbf{u})] d\mathbf{u}' d\mathbf{u} . \quad (2.12)$$

Invoking a change of variables by replacing $\mathbf{u}'$ with $\mathbf{r} = \mathbf{u}' - \mathbf{u}$ yields

$$\begin{aligned} I(\mathbf{q}) &= \iint_V \rho(\mathbf{r} + \mathbf{u}) \rho(\mathbf{u}) \exp[-i\mathbf{q} \cdot \mathbf{r}] d\mathbf{r} d\mathbf{u} \\ &= \int_V P(\mathbf{r}) \exp[-i\mathbf{q} \cdot \mathbf{r}] d\mathbf{r} \end{aligned} \quad (2.13)$$

where $P(\mathbf{r}) = \int_V \rho(\mathbf{r} + \mathbf{u}) \rho(\mathbf{u}) d\mathbf{u}$ and is called the autocorrelation function of $\rho(\mathbf{r})$.

Note that the amplitude $A(\mathbf{q})$ is the Fourier transform of the scattering length density distribution $\rho(\mathbf{r})$ (eqn. 2.11), whereas the intensity $I(\mathbf{q})$ is the Fourier transform of the *autocorrelation function* of $\rho(\mathbf{r})$ (eqn 2.13). Since $\rho(\mathbf{r})$ describes the structure of the sample, it is the quantity of interest. If the amplitude is known, $\rho(\mathbf{r})$ can be directly obtained from the *inverse* Fourier transform of $A(\mathbf{q})$. However, scattering experiments

measure the *intensity*. In the squaring of $A(\mathbf{q})A^*(\mathbf{q})$ to give $I(\mathbf{q})$, the phase angle information associated $\rho(\mathbf{r})$ is permanently lost. Consequently, only the autocorrelation function $P(\mathbf{r})$ can be recovered from $I(\mathbf{q})$.

The interpretation of the measured $I(\mathbf{q})$ or $P(\mathbf{r})$ is generally carried out in one of two ways, depending on the sample type. For materials having crystalline structure, one is interested in determining the locations of the structural components within a unit cell. In this case, the absolute value of $A(\mathbf{q})$ is computed by taking the square root of the measured $I(\mathbf{q})$, and then the phase angle information is determined using additional known physical information or other experimental techniques. For non-crystalline materials, such as polymers, $I(\mathbf{q})$ or $P(\mathbf{r})$ is usually interpreted in terms of a model that is based on some assumptions made about the nature of the sample, which can be determined by additional experimental techniques. By fitting the model to the experimentally measured $I(\mathbf{q})$, one can extract values for structural parameters defined by the model. Clearly, the latter analytical treatment applies to the polymer blends used in our studies. The scattered intensity written in terms of a model is sometimes referred to as the static structure factor, $S(\mathbf{q})$.

The general concepts of x-ray scattering presented here also apply to light and neutron scattering, which are common techniques for probing structure in polymeric materials. Whereas the interference among scattered x-rays is determined by the electron density profile within a sample, neutron scattering relies upon the scattering cross section of atomic nuclei. Neutron scattering probes similar length scales as x-ray scattering, but typically requires selective deuteration of one of the components in the system to create

sufficient contrast. Also, the high flux levels available at x-ray synchrotron sources, which enable time-resolved measurements, are not attainable at neutron facilities. In light scattering, on the other hand, interference effects result from variation in refractive index within the sample. Light scattering probes structures on micrometer length scales, which are larger than many of the structures of interest in our studies. In addition, our samples are nearly opaque and thus nearly impenetrable to visible light. This is frequently true in light scattering from two-phase samples unless they are very dilute or very closely index-matched in refractive index to reduce multiple scattering.

2.3. Scattering from Polymer Blends

In a polymer blend, the blend constituents (for example, homopolymers A and B) have different electron densities. Scattering from blends, therefore, arises from the electron density contrast between regions of different homopolymer concentration. The characteristic spacing between these regions (or microdomains) and the orientation of the phase *interface* determine the distribution of the scattered intensity within three-dimensional q -space (also known as reciprocal space). A two-dimensional slice of the scattering profile may be measured using a 2-D detector appropriately positioned relative to the sample.

Connections between anisotropic structure in two-phase systems and scattering in reciprocal space can be illustrated for the extreme case of a highly segregated, highly aligned lamellar system with symmetric alternating domains of A and B shown in Figure

2.2(a) [as presented by Caputo (2002a)]. Here, the unit vector $\mathbf{n}$ represents the normal to the lamellar layers (*i.e.*, interface). When $\mathbf{n}$ is within the plane perpendicular to the incident beam, the lamellae exhibit scattering peaks that are oriented parallel to $\mathbf{n}$. Alternatively, one can state that the scattering peaks are perpendicular to the orientation of the layers. The location of these peaks relative to the transmitted beam are related to the domain spacing d_0 according to Bragg's law ($q_{\max} = 2\pi n/d_0$ with $n = 1, 2, 3, \dots$).

Consider the situation where the lamellae are subjected to flow, resulting in rotation or reorienting of the lamellar layers (and, therefore, the interface). Rotation of the lamellae such that the interface normal ($\mathbf{n}$) remains in the plane perpendicular to the beam will be observed in the scattering pattern (Figure 2.2(b)). If applied flow results in interface rotation such that the normal rotates out of the plane, the scattering peaks will also rotate out of plane and will not be observed experimentally (Figure 2.2(c)). For a sample containing many grains of randomly oriented lamellae, the scattering peaks will be observed as isotropic rings located at $q_{\max} = 2\pi n/d_0$.

The higher order scattering peaks ($n = 2, 3, \dots$) from the lamellar system in Figure 2.2 are observable due to the high degree of order and high degree of segregation between the domains. For this type of system, $\rho(r)$ can be represented as a step function as shown in Figure 2.3. As the degree of segregation between the domains decreases, $\rho(r)$ becomes a sinusoidal function. This corresponds to a decrease in the amount of electron density contrast in the system and, therefore, a decrease in the absolute intensity of the peaks. As the domain size distribution broadens and/or the domains become less

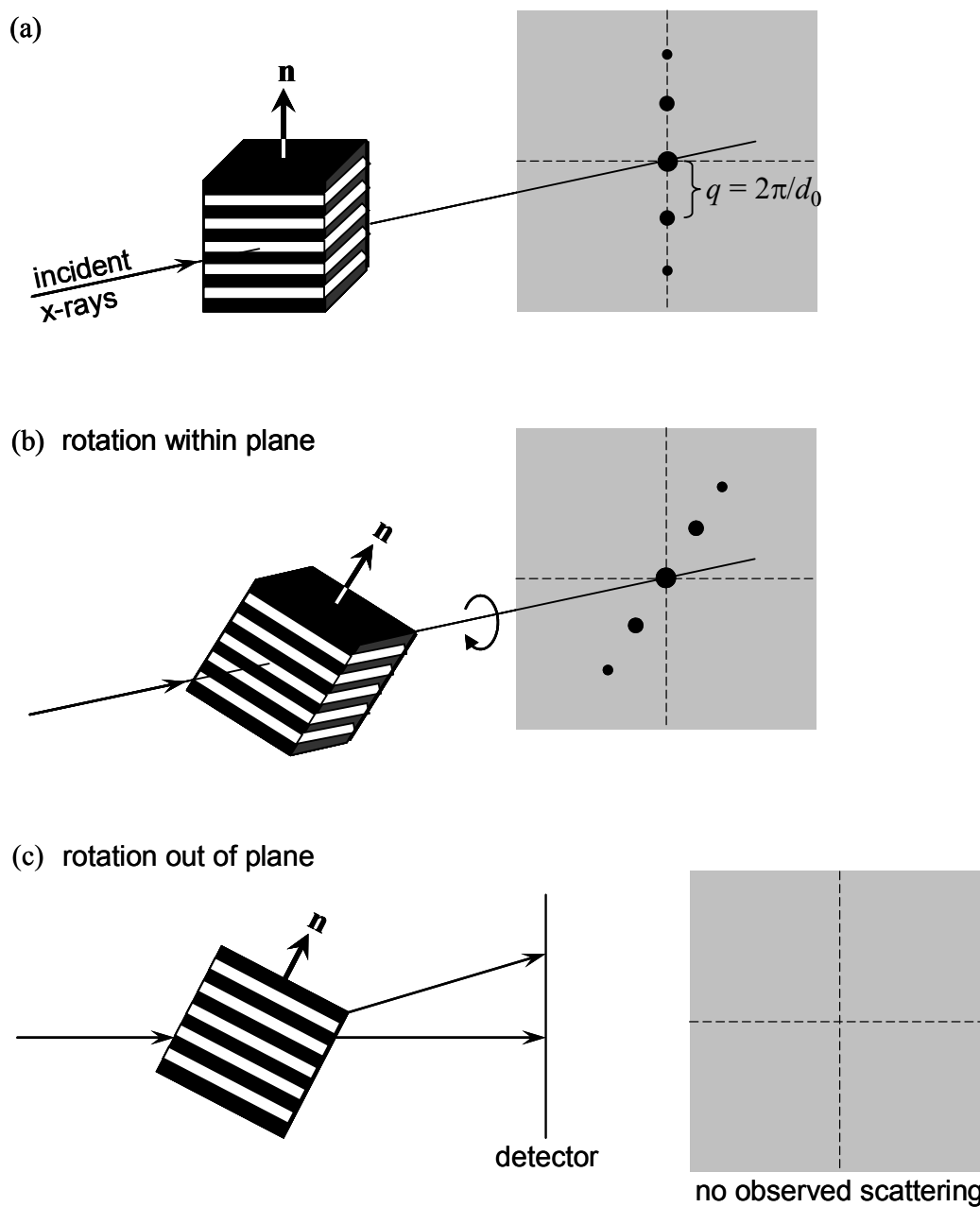


Figure 2.2. Illustration of the effect of the orientation of interface (with respect to the incident beam) on the observed small-angle scattering pattern [adapted from Caputo (2002a)]. Unit vector $\mathbf{n}$ represents the normal to the interface in the lamellar structure.

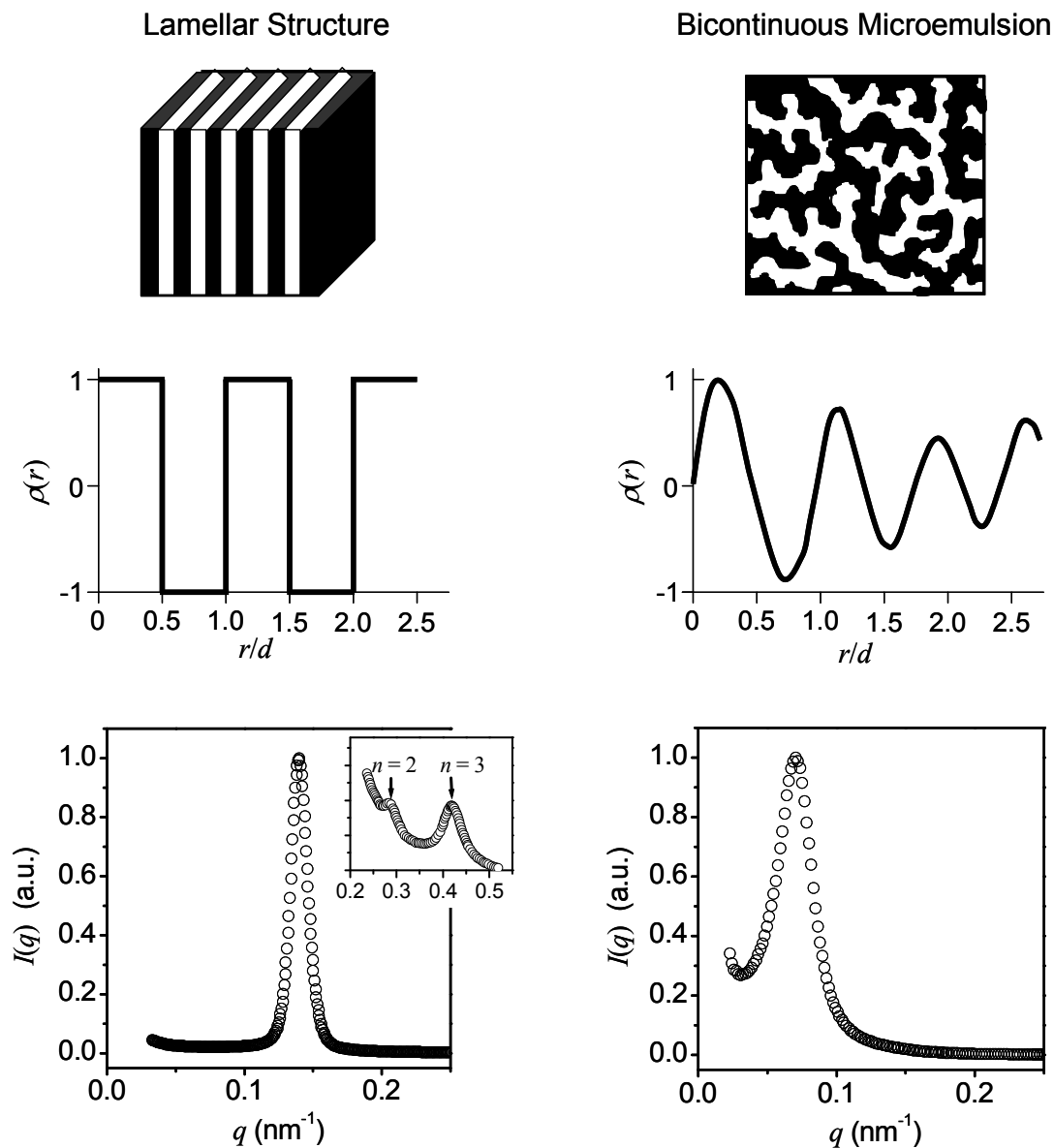


Figure 2.3. Illustrations of structure in real space (top), electron density profiles (middle), and intensity profiles (bottom) for highly segregated lamellae and a bicontinuous microemulsion. Intensity is given in arbitrary units. The inset for the intensity profile of the lamellar structure shows the second and third order peaks.

correlated, the peaks broaden and weaken; these imperfections lead to an eventual loss of all higher order peaks.

The blends used in our studies all lack long range structural order and, therefore, do not exhibit higher order peaks. In addition, these blends are essentially isotropic under equilibrium conditions and, thus, exhibit nearly isotropic scattering in the absence of flow. As an example, consider a bicontinuous microemulsion (B μ E), which also has alternating domains of A and B, but the domains are cocontinuous and slightly miscible. This structure in real space, in comparison to lamellae, is represented by the illustrations and the plots of $\rho(r)$ in Figure 2.3. The one-dimensional plot of the intensity as a function of q in Figure 2.3 shows that the B μ E exhibits a broad primary peak associated with the domain spacing and no observable higher order peaks. Since the equilibrium structure of a bicontinuous microemulsion is isotropic, the primary peak appears as an isotropic ring in a 2-D scattering pattern as shown in Figure 2.4(a). When subjected to certain shear flow conditions, the microstructure deforms, partially aligning along the flow direction. As in the lamellar system, the alignment of the scattering (as shown in Figure 2.4(b) by vector $\mathbf{M}$) is parallel to the interface normal. Therefore, the actual B μ E structure is oriented perpendicular to this direction (along vector $\mathbf{N}$). In this scattering pattern, the peak is quite diffuse along the azimuthal direction, indicating that the distribution of the structural orientation is fairly broad. Also, the intensity of the peak along $\mathbf{M}$ has increased as a result of shear, corresponding to an increase in the amount of interface aligned perpendicular to $\mathbf{M}$.

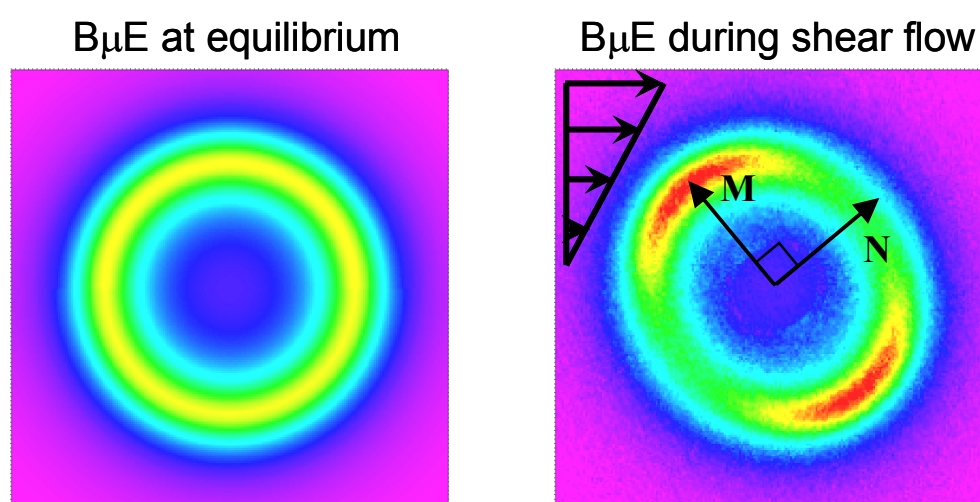


Figure 2.4. Representative scattering patterns of a bicontinuous microemulsion.

The discussion presented here provides a qualitative overview of the scattering behavior of two-phase systems, such as the polymer blends employed in our studies. More detailed scattering models relevant to the different blends systems are introduced as appropriate in the subsequent chapters.

2.4. *In Situ* Shear Flow Experiments

In situ scattering techniques provide the capability to probe structural dynamics in a material during shear flow. A significant advantage of these techniques over *ex situ* methods is the ability to observe structural changes in real time. Therefore, if the behavior of the sample is not well-understood, experimental conditions can be adjusted on-site to ensure that the important features of the structural response are captured. Also in contrast to *ex situ* methods, multiple experiments may be performed using a single sample, providing economies of time and sample quantity. We have used *in situ* small-angle x-ray scattering techniques to investigate the effects of applied shear flow on blends having droplet/matrix, bicontinuous microemulsion, and sponge phase morphologies.

2.4.1. Facility

In situ SAXS experiments were conducted using beamline 5ID-D in the DuPont-Northwestern-Dow (DND-CAT) synchrotron research facility at the Advanced Photon Source at the Argonne National Laboratory. The incident radiation is generated using an

undulator, from which energies as high as 18 keV can be selected. Our experiments use energies in the upper range limit to minimize absorption by the sample, which is quite thick (~ 1 cm). The undulator radiation available at beamline 5ID produces a high flux, highly collimated beam that enables collection of time-resolved scattering measurements from thick samples in the small-angle regime. Three two-dimensional charge-coupled device (CCD) detectors are available at the beamline, providing a range of possible data collection rates. The MarCCD collects at ~ 0.3 frame/sec, the RoperCCD at ~ 1.25 frame/sec, and the GemstarCCD at ~ 7 frame/sec. However, the image quality is compromised with increasing detector speed. For accessing the small-angle regime, the beamline allows for a maximum sample-to-detector distance of approximately 10.5 meters. In traveling these long distances, the transmitted incident and scattered waves can scatter from density fluctuations in the surrounding air. To minimize any parasitic air scattering, the distance between the sample and the detector must be placed under vacuum. Further precaution can be taken by also placing the sample under vacuum. The 5ID facility has a large vacuum chamber, shown in Figure 2.5, which can accommodate our shear cell with the loaded sample. Use of the vacuum chambers places the entire experiment, with the exception of the detector, under vacuum.

2.4.2. Shear Cell

The polymer blends were subjected to a homogeneous shear field using an annular cone and plate device developed by Caputo and Burghardt (2001) specifically for use with synchrotron radiation. Since homogeneous shear fields are often employed in rheometry,

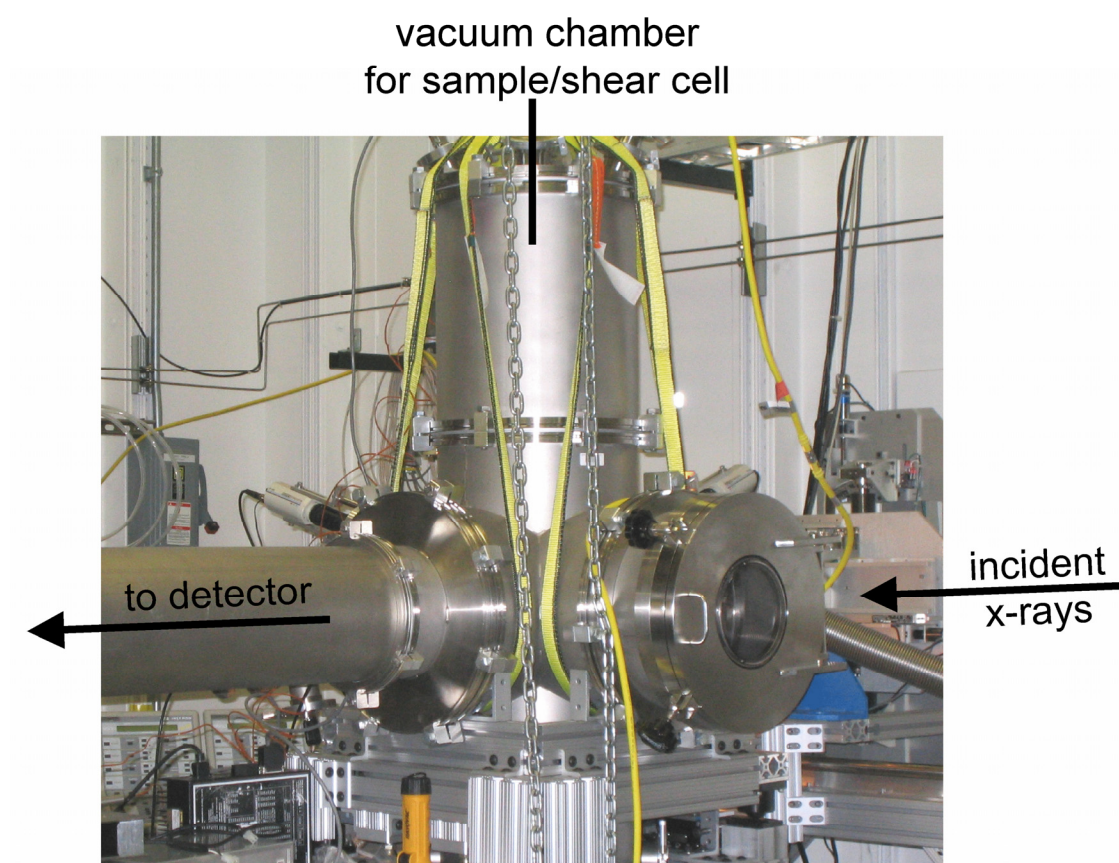


Figure 2.5. Vacuum chamber at beamline 5ID-D of the DND-CAT facilities.

scattering measurements collected under equivalent conditions allow for connections to be made between the structural and rheological responses of a material. Two important quantities of interest measured in rheometry, the shear stress (σ_{xy}) and first normal stress difference ($N_1 = \sigma_{xx} - \sigma_{yy}$), result from deformation of microstructure in the flow-gradient (x - y) plane of the shear flow field (shown in Figure 2.6). The annular cone and plate shear cell is unique in that it provides the ability to observe scattering associated with material deformation within the flow-gradient plane during shear.

A schematic of the shear cell is provided in Figure 2.7. The angle of the cone is 5° . The shear cell is mounted on a platform at a 2.5° angle so that the horizontal incident x-ray beam passes through a small aperture in the front side of the fixed bottom plate, through the virtual tip of the cone, and then through the sample on the opposite side of the cone and plate. The total sample thickness through which the beam passes is 1 cm. On the outer edge of the annulus, the sample is exposed to a free surface. On the inner edge of the annulus, the bottom plate is designed with a thin aluminum barrier, which prevents the sample from flowing towards the center of the shear cell due to normal forces that may be generated during shear.

The bottom plate of the shear cell is fixed while the upper cone is rotated by a stepper motor. Unidirectional shear flow or oscillatory shear can be applied using a programmable motor controller. Due to the limited resolution of the motor, its motion control becomes unreliable for shear rates less than 0.1 s^{-1} . For experiments involving lower shear rates, a 50:1 gear reducer was used to improve the accuracy of the motor.

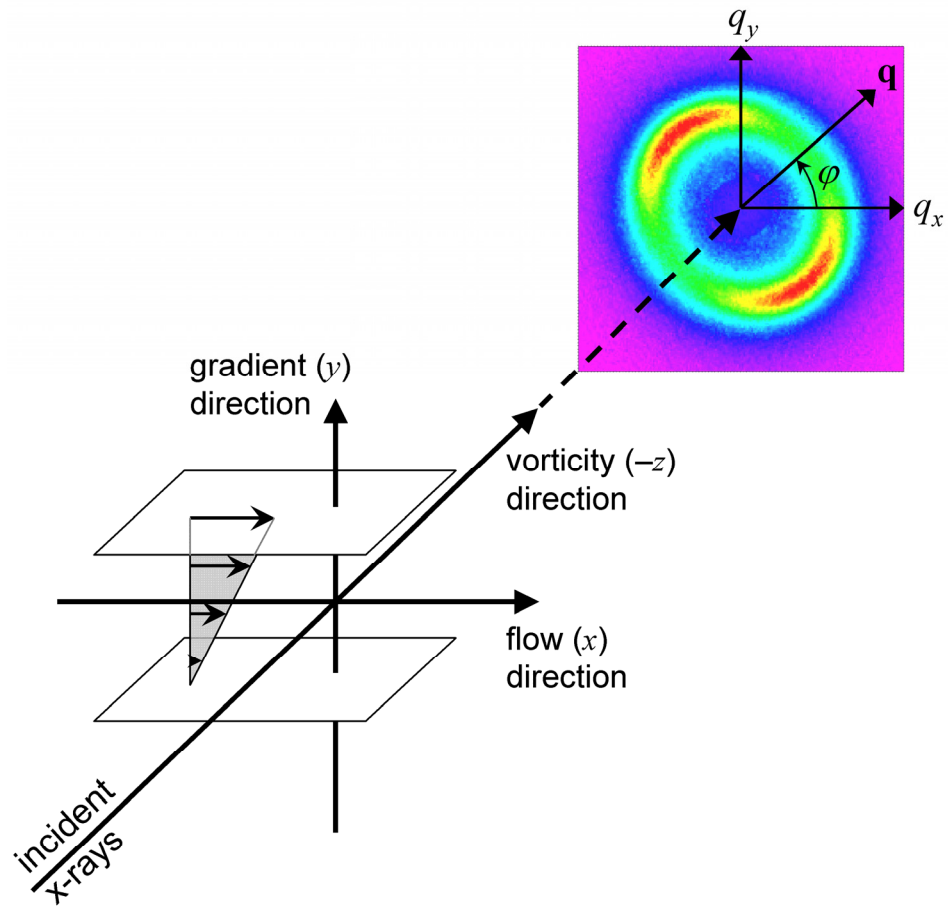


Figure 2.6. Geometry of a simple shear field. The incident beam in our flow experiments travels along the vorticity direction. ϕ is the azimuthal angle.

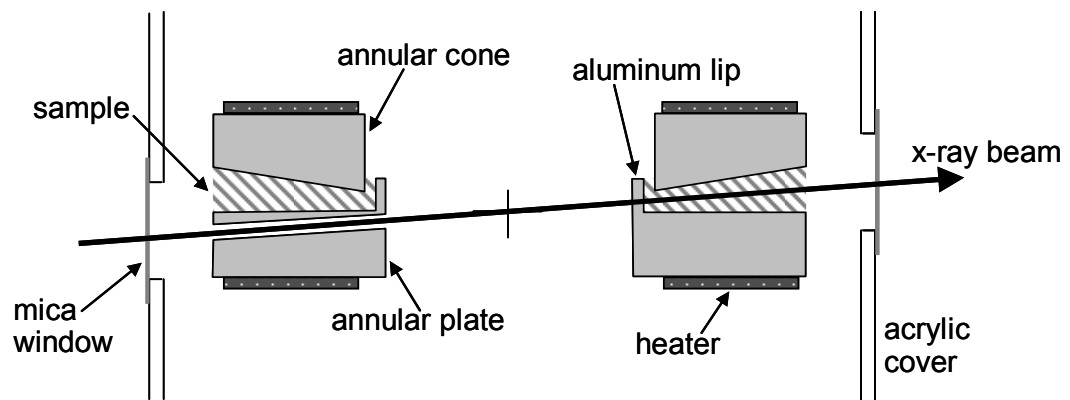


Figure 2.7. Representative schematic of the annular cone and plate shear cell [adapted from Caputo and Burghardt (2001)]. Dimensions are not to scale.

The cone and plate fixtures have been machined from aluminum, which provides good heat conduction. Flexible heaters are positioned on the surfaces of the upper and lower fixtures opposite the sample. The flux to each heater is provided by independent controllers that monitor temperature via thermocouples embedded in each fixture. The temperature control is within approximately $\pm 1^\circ\text{C}$. A more detailed description of the shear cell design and accessories are provided by Caputo (2002a).

A typical setup of the shear cell at the synchrotron facility is shown in Figure 2.8. The shear cell is mounted on an open translation table, and a vacuum chamber is placed between the shear cell and the detector. With this layout, the beam path immediately upstream and immediately downstream from the shear cell is exposed to air, which may result in some parasitic scattering at small angles. An inert environment can be provided to the sample by sealing the open sides of the flow device with acrylic plates and purging the sample area with helium. The plates contain mica windows positioned in the path of the x-ray beam to avoid parasitic scattering from the acrylic (see Figure 2.7).

Alternatively, an inert sample environment can be achieved by placing the shear cell in the vacuum chamber shown in Figure 2.5. We have modified the electrical connections from the shear cell to the temperature and motor control devices, which are positioned outside the vacuum chamber, so that the connections could be made using sealed feed-through ports located at the top of the chamber.

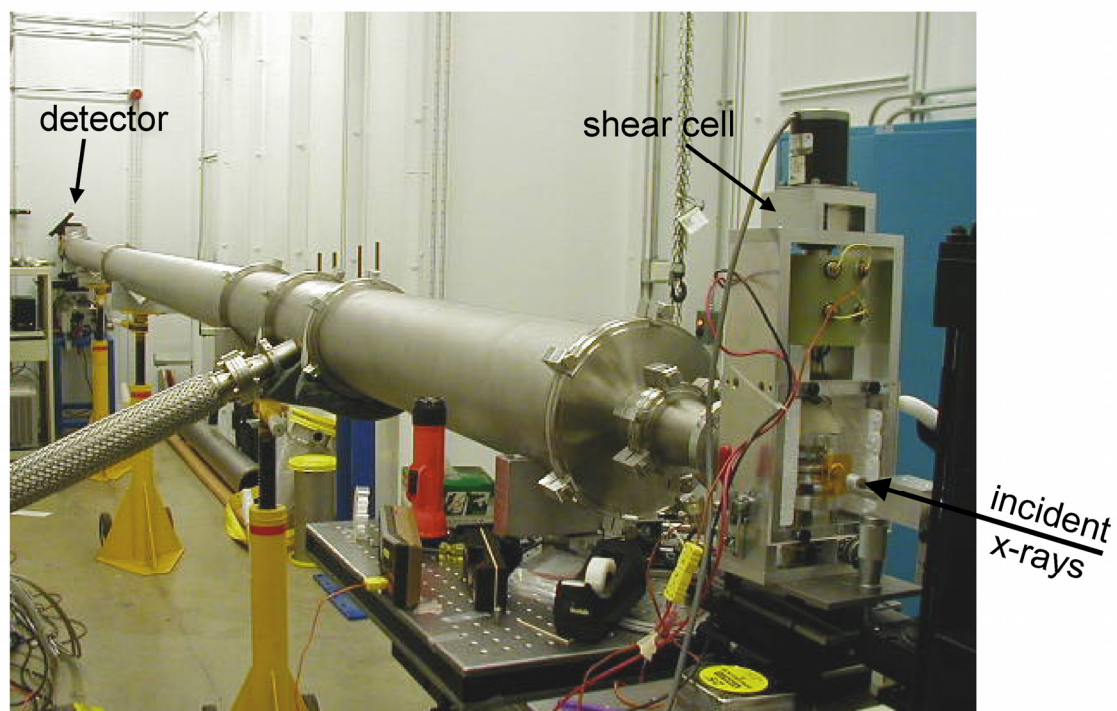


Figure 2.8. Typical setup of *in situ* SAXS experiment at beamline 5ID-D of the DND-CAT facilities.

2.4.3. Installation of Mica Window

The general setup in Figure 2.8 was used in a previous experiment with a poly(ethyl ethylene) (PEE)/poly(dimethyl siloxane) (PDMS) bicontinuous microemulsion by Caputo *et al.* (2002b) to access the small-angle regime. In these experiments, significant parasitic scattering was observed around the beam stop that extended to $q = 0.06 \text{ nm}^{-1}$ along the horizontal direction of the scattering pattern (see Figure 2.9). Scattering from our blend systems persists to even smaller scattering vectors. Therefore, this parasitic scattering must be significantly reduced or eliminated to ensure the success of our experiments.

The “lozenge-shaped” parasitic scattering feature in the PEE-PDMS experiment was initially attributed to air scattering from around the shear cell or a misalignment of the beam through the aperture in the bottom plate [Caputo *et al.* (2002b)]. If the source of this feature is air scattering, placing the shear cell in the large vacuum chamber shown in Figure 2.5 should nearly eliminate the lozenge-shaped feature. We have taken this approach in an experiment with a polystyrene (PS)/polyisoprene (PI) bicontinuous microemulsion. The sample-to-detector distance for this experiment was 10.5 m and completely under vacuum. Despite these changes, the lozenge-shaped feature, although significantly less intense in comparison to the microemulsion scattering peak, was still present in our experiment (Figure 2.9). Therefore, the parasitic feature does not arise from air scattering. We attribute the weaker parasitic scattering in our experiment, relative to the B μ E peak, to stronger scattering from the PS-PI B μ E. That is, the electron

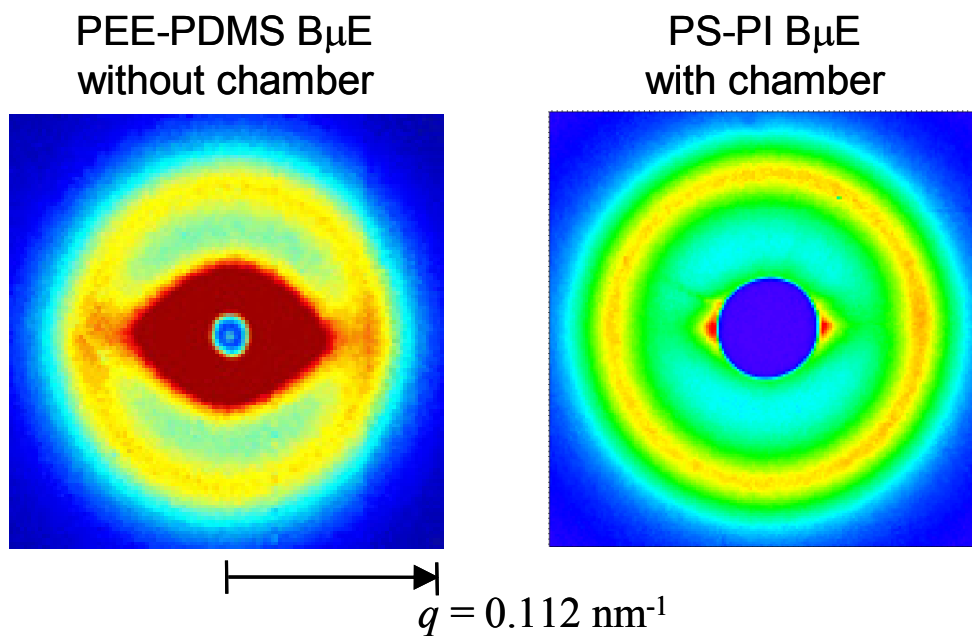


Figure 2.9. Representative images of the lozenge-shaped parasitic scattering observed (surrounding the beam stop) in SAXS experiments with the shear cell. The isotropic ring in each image is the scattering peak from a bicontinuous microemulsion. The circular feature at the center of each image is a beam stop. The q scale bar applies to both images. The image for the PEE-PDMS B μ E is from Caputo *et al.* (2002b).

density contrast between homopolymers in the PS-PI system is larger than the contrast in the PEE-PDMS system.

Following the experiment with the vacuum chamber, it became apparent that the aluminum barrier on the inner annulus of the bottom plate was the probable source of the parasitic scattering. To investigate this possibility, a small section of the barrier intersecting the path of the incident beam was removed and replaced with a thin sheet of mica (SPI supplies; West Chester, PA; Grade V-1) to prevent sample leakage. The mica “window” in the bottom plate is shown in Figure 2.10. Experiments conducted with the mica window for a sponge phase and an immiscible blend showed no sign of the lozenge-shaped parasitic scattering (see Figure 2.11), confirming that, indeed, the aluminum barrier had caused the parasitic scattering in past experiments. With the use of the mica window and a 2.4 mm diameter beam stop, we are able to reach a low- q limit of 0.015 nm^{-1} , which is sufficient for achieving our research goals.

2.4.4. Analysis

The two-dimensional scattering patterns, collected during experiments with the annular cone and plate shear device, provide information about shear-induced structural changes in the sample occurring within the flow-gradient (x - y) plane (Figure 2.6). We have characterized the deformation of the microstructure within this plane by computing, for each time-resolved scattering pattern, a second moment tensor of the scattering vector weighted by the scattered intensity:

$$\langle \mathbf{q}\mathbf{q} \rangle = \begin{pmatrix} \langle q_x q_x \rangle & \langle q_x q_y \rangle \\ \langle q_x q_y \rangle & \langle q_y q_y \rangle \end{pmatrix} = \iint \mathbf{q}\mathbf{q} I(\mathbf{q}) dq_x dq_y . \quad (2.14)$$



Figure 2.10. Mica window viewed from the front side (top) and back side (bottom) of the bottom plate of the shear cell. The narrow pin through the center of the plate represents the path of the x-ray beam.

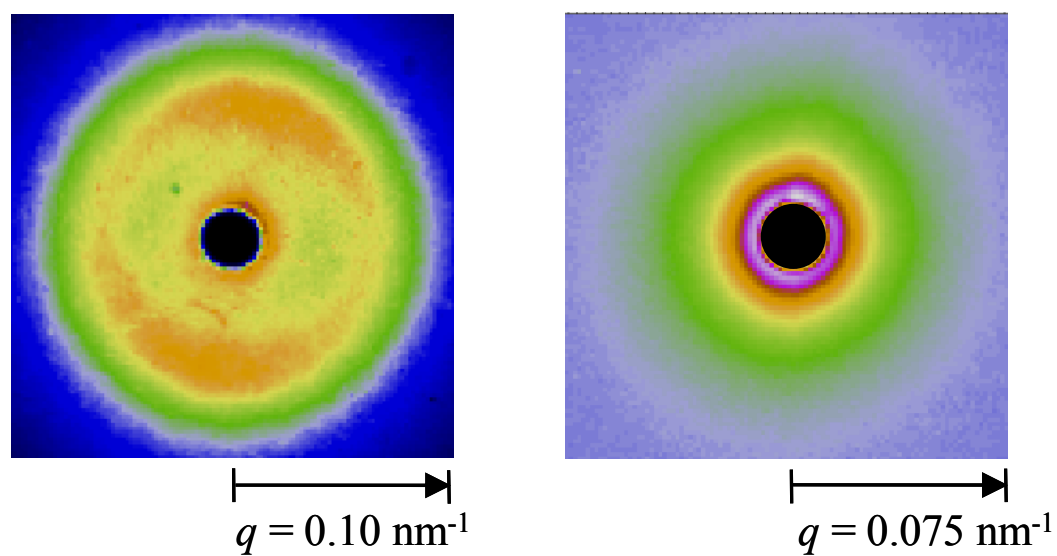


Figure 2.11. Representative scattering patterns collected using the mica window installed in the shear cell. Left: Polystyrene/poly(styrene-ethylene/butylene-styrene) sponge phase. Right: 80/20 weight% polystyrene/poly(methyl methacrylate) blend.

This tensor is similar to the stress tensor measured in rheometry, where $\langle q_x q_y \rangle$ and $[\langle q_x q_x \rangle - \langle q_y q_y \rangle]$ are the scattering analogs of the shear stress and first normal stress difference, respectively.

Under quiescent conditions, where the scattering is isotropic, the diagonal components are given by

$$\langle q_x q_x \rangle = \langle q_y q_y \rangle = \frac{1}{2} \langle qq \rangle_0 = \frac{1}{2} \iint q^2 I(q) dq_x dq_y . \quad (2.15)$$

When $\langle \mathbf{qq} \rangle$ is normalized by $\frac{1}{2} \langle qq \rangle_0$, the sample in its isotropic state yields diagonal components equal to 1 and off-diagonal components equal to 0. Alternatively, $\langle \mathbf{qq} \rangle$ for each scattering pattern may be “self”-normalized by its corresponding value of

$\frac{1}{2} [\langle q_x q_x \rangle + \langle q_y q_y \rangle]$. It should be noted that the total scattering (within the plane projected onto the detector) from the sample is contained in the sum $\langle q_x q_x \rangle + \langle q_y q_y \rangle$.

Therefore, any change in the total scattered intensity associated with deformation of microstructure will be lost using self-normalization. Also in the case of self-normalization, an isotropic sample will yield the diagonal components of $\langle \mathbf{qq} \rangle$ equal to 1.

The selection of which of these two normalization procedures should be applied to $\langle \mathbf{qq} \rangle$ requires consideration of the nature of the sample and experimental factors.

The degree of anisotropy in the microstructure can be characterized by computing the difference in the eigenvalues of $\langle \mathbf{qq} \rangle$, which yields

$$AF = \sqrt{(\langle q_x q_x \rangle - \langle q_y q_y \rangle)^2 + 4\langle q_x q_y \rangle^2} . \quad (2.16)$$

This relationship is often referred to as the “principal anisotropy factor”. When AF has been self-normalized, an isotropic sample gives $AF = 0$, and perfect orientation of the microstructure (in any single direction) gives $AF = 1$. (For data that has been normalized by the quiescent state, AF can exceed 1 if structural arrangements during shear lead to an increase in total scattered intensity within the x-y plane.) The orientation of the principal axes of $\langle \mathbf{q}\mathbf{q} \rangle$, and thus the microstructure, with respect to the flow direction is given by the angle, χ :

$$\chi = \frac{1}{2} \tan^{-1} \left(\frac{2\langle q_x q_y \rangle}{\langle q_x q_x \rangle - \langle q_y q_y \rangle} \right). \quad (2.17)$$

Depending on the detector used, the experimental setup, and the nature of the sample, some corrections and/or normalization procedures are applied to the scattering patterns prior to computing the second moment tensor. These procedures, which we perform using Fit2D x-ray analysis package [Hammersley], are addressed in the experimental sections for each of the blend systems.

2.5. X-Ray Photon Correlation Spectroscopy

2.5.1. Introduction

Experimental measurement of relaxation in complex fluids at thermal equilibrium is critical to developing an understanding of the underlying physics associated with the fluid structure. Light photon correlation spectroscopy (LPCS), also known as dynamic light scattering (DLS), has long been used to probe thermally-induced dynamics in complex

fluids occurring on micrometer length scales [Berne (1976)]. Neutron spin-echo (NSE) spectroscopy has been used to investigate dynamics at smaller length scales [Komura *et al.* (2001); Schleger *et al.* (1998)], but the technique is limited to time scales less than several nanoseconds. The recent development of x-ray photon correlation spectroscopy (XPCS) also provides the opportunity for measuring dynamics at smaller length scales (5 – 300 nm), but at slower time scales (0.1 – 100 seconds) that are more relevant to polymer systems [Falus *et al.* (2004); Sandy *et al.* (1999)]. XPCS is, therefore, a very useful technique for probing the dynamics of our bicontinuous microemulsion system.

The XPCS technique involves illuminating a sample with a coherent x-ray beam, which produces a “speckled” intensity pattern that varies in time as the sample undergoes thermally-induced concentration fluctuations. The rise and decay of these concentration fluctuations is described by the dynamic structure factor, $S(\mathbf{q}, t)$, which is the spatial Fourier transform of the density-density autocorrelation function $\langle \rho(\mathbf{r}', t) \rho(\mathbf{r}, 0) \rangle$ (as can be inferred from eqn. 2.13). For a two-component system, $\rho(\mathbf{r}, t)$ represents the concentration of one of the components at position $\mathbf{r}$ and time t . $S(\mathbf{q}, t)$ is related to the time-autocorrelation function, $g_2(\mathbf{q}, t)$, of the speckle intensity, which is defined as

$$g_2(\mathbf{q}, t) \equiv \frac{\langle I(\mathbf{q}, t') I(\mathbf{q}, t' + t) \rangle}{\langle I(\mathbf{q}, t') \rangle^2} \quad (2.18)$$

where $I(\mathbf{q}, t')$ is the scattered intensity at wvector $\mathbf{q}$ and time t' , t is the delay time between measurements, and the brackets $\langle \dots \rangle$ denote an average over the number of time points in the ensemble. In the case of isotropic samples, such as a bicontinuous

microemulsion, g_2 depends only on the magnitude of the scattering vector. A speckle pattern of our bicontinuous microemulsion is provided in Figure 2.12.

Once the autocorrelation function is computed, the dynamic structure factor can be determined using the relationship:

$$g_2(q, t) = 1 + C|f(q, t)|^2 \quad (2.19)$$

where C is an experimental parameter, and $f(q, t) [= S(q, t)/S(q)]$ is the *normalized* dynamic structure factor. For a simple diffusion process, $f(q, t)$ is given by a single-exponential function:

$$f(q, t) = \exp[-t / \tau_q] \quad (2.20)$$

where $\tau_q [= (Dq^2)^{-1}]$ is the q -dependent relaxation time, and D is the diffusion coefficient.

For a sample exhibiting a distribution of relaxation processes, the normalized dynamic structure factor can be written as a *stretched*-exponential function:

$$f(q, t) = \exp[-(t / \tau_q)^\nu] \quad (2.21)$$

where ν is the stretching exponent. ν equals unity for a single-mode relaxation and decreases as the distribution of the relaxation spectrum broadens. The average relaxation time, $\langle \tau_q \rangle$, can then be computed using the relationship:

$$\langle \tau_q \rangle = \left(\frac{\tau_q}{\nu} \right) \Gamma\left(\frac{1}{\nu} \right) \quad (2.22)$$

where $\Gamma(x)$ is the Gamma function [Lee *et al.* (1980)].

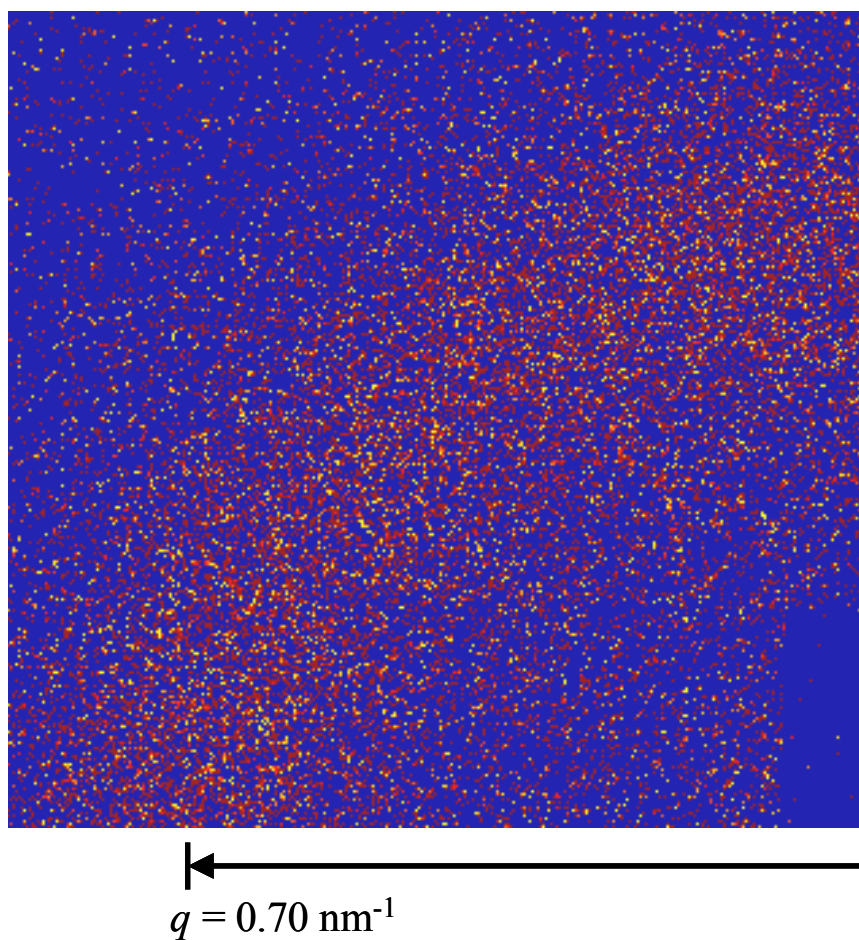


Figure 2.12. Representative “speckle” pattern of a PS-PI bicontinuous microemulsion collected with an exposure time of 17 ms. The image only shows the second quadrant of the 2-D scattering. A full 2-D image collected with a much longer exposure time will appear as the left-hand scattering image in Figure 2.4.

2.5.2. Experiment and Analysis

XPCS experiments were performed at beamline 8ID-I (IMMY/XOR-CAT facility) at the Advanced Photon Source using undulator radiation with a selected energy of 7.5 keV and an average flux that is several orders of magnitude greater than the flux generated at beamline 5ID. The higher fluxes and lower energy used in XPCS experiments, in comparison to *in situ* SAXS experiments, are required for achieving a high level of beam coherence. The sample-to-detector distance was 3.5 meters, and the sample thickness was ~ 2 mm. Additional details regarding XPCS setup and procedures at 8ID are provided elsewhere [Falus *et al.* (2004); Sandy *et al.* (1999)].

At each measurement temperature, multiple sequences of at least 850 time-resolved images were collected at rates of 5, 59, and 333 frames/sec using a two-dimensional CCD detector. To minimize the risk of sample degradation, due to the high flux and low energy of the beam, a fresh region of the sample was exposed for each new sequence collected. For each sequence, the scattering intensity autocorrelation function $g_2(q, t)$ is computed for each pixel using the definition in eqn. 2.18. To increase the signal-to-noise ratio, the pixels were averaged azimuthally and to a radial resolution of $\Delta q = 0.0032 \text{ nm}^{-1}$. For each temperature and frame rate, the g_2 values from multiple sequences were averaged together to further optimize the signal-to-noise ratio. Finally, the averaged g_2 values for each of the frame rates at a given temperature were merged together using a linear least-squares procedure described elsewhere [Lumma *et al.* (2000)]. Eqn. 2.19 was then fit to the experimentally determined $g_2(q, t)$ using the

appropriate form of $f(q,t)$. These fits thus yield the relaxation times and diffusion coefficients as a function of length scale within the sample.

CHAPTER 3.

CHARACTERIZATION OF STRUCTURAL DYNAMICS IN IMMISCIBLE HOMOPOLYMER BLENDS VIA SAXS TECHNIQUES

3.1. Introduction

Many commercially important blends are composed of two immiscible homopolymers, where the minor phase is dispersed as micron-sized droplets in the matrix phase. To predict the effects of processing or compatibilization on the size and shape of the dispersed phase, four mechanisms must be considered: droplet deformation, breakup, coalescence, and relaxation. Several experimental techniques have been developed for investigating these processes in blends. The selection of an appropriate technique requires consideration of many factors, including concentration of dispersed phase, optical and thermal properties of the blend constituents, characteristic length scale of the microstructure, and the type of information desired from the experiment (*e.g.*, single droplet dynamics, interactions between droplets, final droplet size/shape, relaxation time of the blend, *etc.*).

Morphology evolution during flow is fairly well-understood for dilute blends consisting of Newtonian components. However, the majority of commercial blends are

highly concentrated and composed of non-Newtonian phases. The flow behavior of these systems is considerably more complex and remains an important area of research today. Progress in this field has been significantly hampered by the difficulties and limitations associated with *in situ* experimental studies of opaque, concentrated blends. We have investigated *in situ* x-ray scattering as a potential new route for studying structural dynamics in these systems.

Although the micron-sized droplets in immiscible blends cannot be directly probed using x-rays, scattering theory suggests that scattering of x-rays from the phase *interface* should be accessible in the small-angle regime. This scattering, known as Porod scattering, should thus enable measurement of changes in the orientation and quantity of interface with time, which can be related (using appropriate assumptions) to the size and shape of the droplets. To establish the feasibility of this technique for immiscible polymer blends, we have conducted two separate sets of experiments.

The first set of experiments is a simple coarsening study of isotropic immiscible blends under quiescent conditions, where the growth in droplet size is measured *ex situ* for samples quenched at various times during high-temperature annealing. This study demonstrates that Porod scattering measurements can be used for determination of an average droplet size in isotropic immiscible blends and provides support for the possibility of performing *in situ* SAXS measurements during flow. Thus, in the second set of experiments, real-time scattering measurements were collected of an immiscible blend in response to applied shear flow, allowing for observation of shear-induced deformation of interface. Using these measurements, we examined the validity of a

simple model, which describes the scattering from an ellipsoid, for determination of the deformed droplet shape in these blend systems.

This chapter is organized as follows. First, the existing characterization techniques for immiscible fluids having droplet/matrix morphologies are briefly reviewed, and the advantages and limitations of each technique are addressed. The concept of x-ray scattering from interface is then discussed in regards to isotropic and anisotropic systems. Finally, the two experimental studies are individually presented.

3.2. Background

3.2.1. Experimental Methods for Probing Dynamics in Immiscible Blends

The first fundamental studies of droplet/matrix morphologies under flow began with a single Newtonian droplet suspended in a Newtonian matrix viewed *in situ* by optical microscopy [Taylor (1934)]. From hydrodynamic equations at low Reynolds number, Taylor determined the maximum stable size of a single droplet in simple shear flow and verified this result experimentally using a parallel band shearing apparatus. He characterized the degree of deformation and stability of the droplet size using two dimensionless values: (1) a viscosity ratio, $p = \eta_d/\eta_m$, and (2) a capillary number,

$$Ca = \frac{\dot{\gamma}\eta_m R}{\Gamma} \quad (3.1)$$

where η_d is the droplet viscosity, η_m is the matrix viscosity, $\dot{\gamma}$ is the shear rate, R is the droplet radius, and Γ is the interfacial tension. If Ca^* represents the capillary number (ratio of viscous forces to interfacial forces) at which the droplet is stable, droplet

breakup will occur for $Ca > Ca^*$. Several groups have since employed optical microscopy to investigate the effects of viscosity ratio and flow type on the capillary number, breakup mechanism, and steady-state droplet shape/orientation [Bartok and Mason (1959); Bentley and Leal (1986); Grace (1982); Tsakalos *et al.* (1998)].

A schematic representation of an isolated droplet undergoing shear flow is shown in Figure 3.1. Many of the early shear studies of droplet deformation/breakup involved visualization along a single principal axis of the shear field, assuming that the cross-section of the oriented droplet remains circular due to interfacial tension. More recently, Guido and coworkers (1998, 2001) have measured the three-dimensional droplet shape at moderate deformations using an optical parallel plate device that allows separate visualization along two perpendicular directions (vorticity and velocity gradient directions). In their measurements, the minor axes (R_2 and R_3 , shown in Figure 3.1) of the oriented droplet became asymmetric with increasing capillary number, thus demonstrating the importance of considering the three-dimensional structure even under moderate flow conditions. These data were shown to closely match theoretical predictions from second-order fluid dynamics equations that were derived using a perturbation procedure for small deformation around the spherical shape [Frankel and Acrivos (1970); Rallison (1984)].

In real two-phase systems, prediction of droplet size and shape is further complicated by the presence of neighboring droplets. During shear, the morphology is dictated by a competition between breakup and coalescence, which reach a dynamic equilibrium at steady-state. Several groups have used optical microscopy to investigate

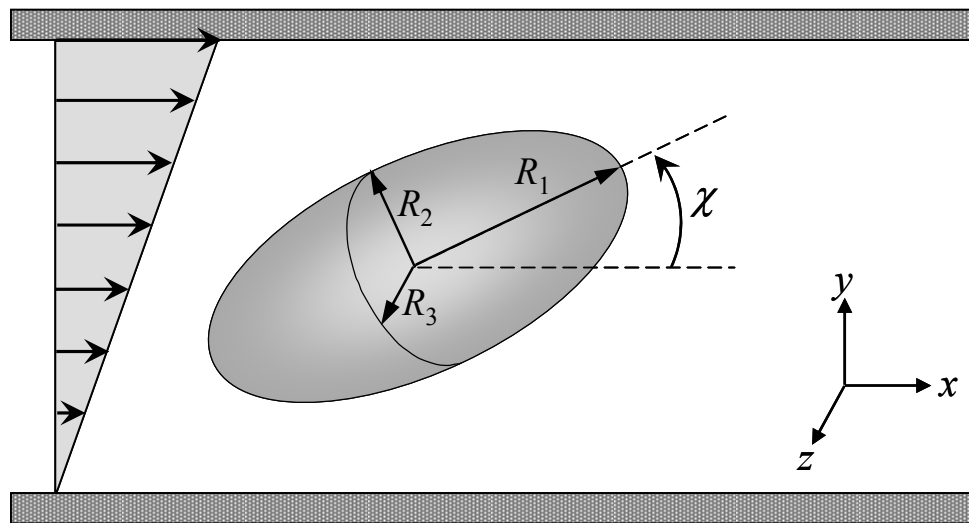


Figure 3.1. Schematic representation of an isolated droplet undergoing shear flow between two parallel plates.

these dynamics [Burkhart *et al.* (2001); Grizzuti and Bifulco (1997); Guido and Simeone (1998); Vinckier *et al.* (1998)]. Although optical microscopy is advantageous in that it allows for direct visualization of droplet dynamics *in situ*, this technique is limited to low concentrations (<10% dispersed phase) and translucent materials (*i.e.*, closely index-matched) in which the droplets are large (tens of microns).

For slightly more concentrated systems with smaller droplet sizes, small-angle light scattering (SALS) [Mewis *et al.* (1998); Rusu and Peuvrel-Disdier (1999); Sondergaard and Lyngaae-Jorgensen (1996)] and linear conservative dichroism [Oosterlinck *et al.* (2005); Van Puyvelde *et al.* (2000); Yang *et al.* (1998)] are typically employed. For example, Mewis *et al.* (1998) used SALS to study the response of droplets to large step-ups in shear rate and the relaxation mechanism following cessation of flow. As a result of the sudden shear rate increase, the droplet stretches into a long filament, as indicated by the streak in the SALS image in Figure 3.2(a). If the droplet returned to a single spherical shape upon flow cessation, the streak pattern would return to a near isotropic pattern as observed before the step increase. The appearance of the additional peaks during relaxation suggests the filament breaks into a series of daughter droplets during relaxation due to Rayleigh's instability. Scattering models for filaments with sinusoidal surfaces and for a series of aligned spheres were derived to verify these results. In addition, the average size of the spherical droplets (*i.e.*, in a relaxed state before inception of shear) was determined using Debye-Beuche theory [Debye *et al.* (1957)].

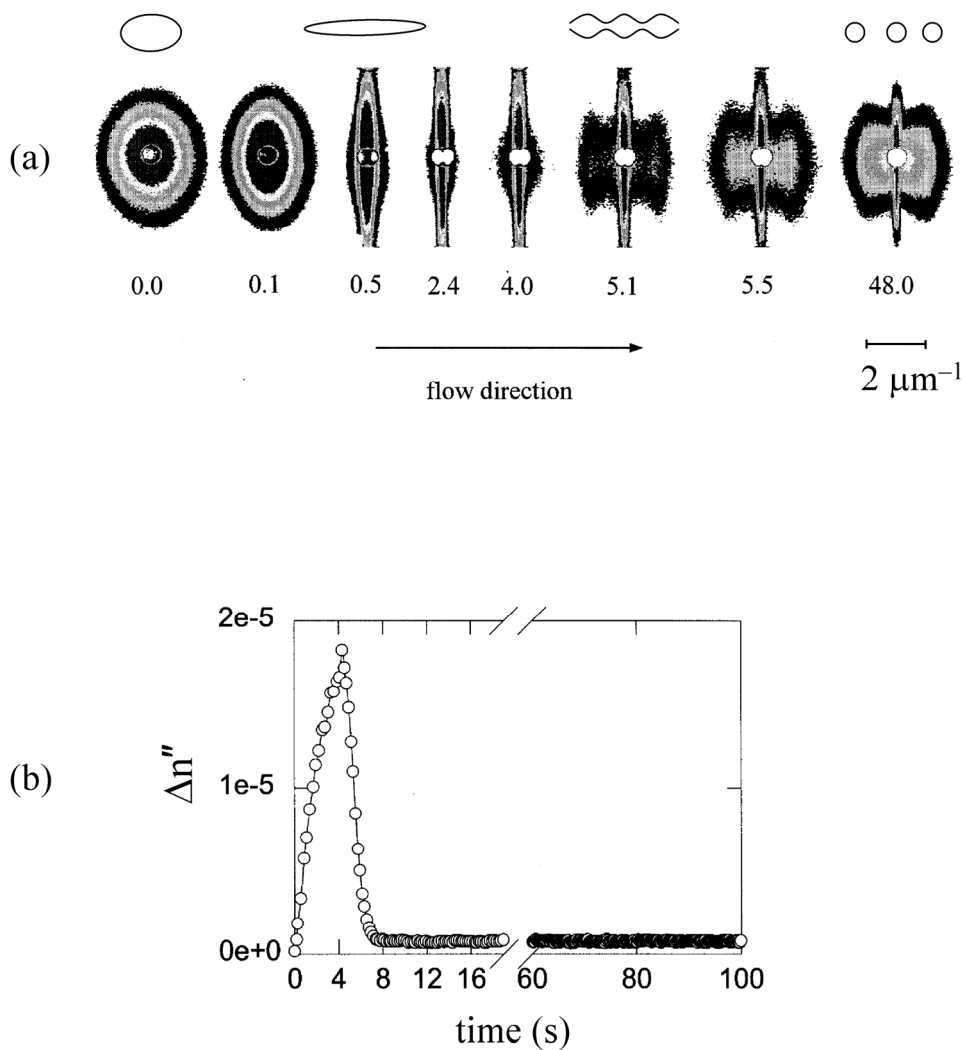


Figure 3.2. (a) Time evolution of SALS patterns and (b) the corresponding dichroism for 1% poly(dimethyl siloxane) in polyisobutene in an interrupted step-up from 2 to 30 s^{-1} at 23°C . Numbers under the SALS patterns and on the abscissa of the dichroism plot refer to time elapsed since the increase in shear rate. The flow was interrupted at 4 seconds after the increase in shear rate [from Yang *et al.* (1998)].

Yang *et al.* (1998) complimented these SALS studies with linear conservative dichroism ($\Delta n''$), which measures polarization-dependent attenuation of light. If the sample is anisotropic, the transmitted light intensity in perpendicular polarization directions will be different. This technique is, thus, very sensitive to structural changes, and can be used to determine the time scales at which these changes occur. As shown in Figure 3.2(b), the dichroism responds quickly to the step-up in shear rate, and then quickly responds again as the filament breaks into relaxed spherical droplets upon flow cessation. Interestingly, additional studies have shown evidence for the existence of a stress-optical relation involving linear conservative dichroism for strongly deformed drops [Van Puyvelde *et al.* (2000)]. SALS and linear conservative dichroism techniques provide a very useful approach for fundamental investigations of droplet dynamics in immiscible blends; however, the low energies of visible light waves limit the use of these techniques to semi-concentrated, nearly index-matched systems. More concentrated, turbid blends, which more closely resemble commercial systems, are generally studied using rheology and/or *ex situ* electron microscopy techniques.

In rheological studies, one is interested in connecting changes in measured stress with deformation of microstructure during flow. In two-phase systems, the phase interface resists deformation during flow to maintain a lower interfacial energy. This resistance produces stress that exists in addition to stress resulting from the individual blend components. The “excess” stress associated with interface deformation is given by $\sigma_{\text{excess}} = -\Gamma \mathbf{s}$ where $\mathbf{s}$ is the interface tensor, which describes the shape and orientation of

the interfaces in the blend [Batchelor (1970); Onuki (1987)]. According to Doi and Ohta (1991), the interface tensor can be written as

$$\mathbf{s} = \frac{1}{V} \int \left(\mathbf{nn} - \frac{1}{3} \mathbf{I} \right) dS. \quad (3.2)$$

where V is the total volume of the system, $\mathbf{n}$ is the unit vector normal to the interface, $\mathbf{I}$ is the unit tensor, and dS is the area of an interfacial element. Interface tensors for ellipsoidal [Wetzel and Tucker (1999)] and cylindrical [Vinckier *et al.* (1997)] droplets are provided in the literature.

If the stress contributions from the individual blend components are known, the excess stress can be determined from the total stress measured in rheological experiments. For blends composed of Newtonian phases with similar viscosities, the blend deforms affinely and separation of stresses is straightforward [Jansseune *et al.* (2000, 2001)]. Models have been developed for determining a volume-average droplet diameter from linear viscoelastic stress measurements of these types of blends [Graebling and Muller (1990); Palierne (1990)]. These models have since been used to study coalescence [Vinckier *et al.* (1998)] and the effects of compatibilizer on droplet breakup [Velankar *et al.* (2001)]. In these studies, the droplet size was determined as a function of time by interrupting flow periodically to collect linear viscoelastic measurements. For typical blend systems, however, in which the phases are non-Newtonian and exhibit a large viscosity contrast, the interfacial and component stress contributions are difficult to discern. Models that relate stress to microstructure in these more complex systems are not yet available.

Ex situ electron microscopy techniques are also common for characterizing morphological changes in concentrated blends [Lebovitz *et al.* (2002a); Martin *et al.* (2000); Sundararaj and Macosko (1995); Wu (1987)]. The general procedure involves interrupting flow at selected time points, quenching the sample to preserve the microstructure, and viewing a two-dimensional fractured surface of the sample under a microscope. Since instantaneous stopping of flow and quenching of the sample is not experimentally realizable, *ex situ* electron microscopy techniques are useful for experiments where the relaxed structure of the blend following flow cessation is of interest. However, the microstructure is typically altered to some degree in the quenching process. Furthermore, in contrast to *in situ* experiments, fresh sample is needed for each time point and experimental condition. Additional disadvantages of *ex situ* studies are associated with analysis of the electron micrographs. Once a sufficient number of micrographs are obtained, additional steps are often required to “clean up” undesirable topographical characteristics (such as fracture lines on the surface of the sample) in the images before the particle size distribution is measured. For even a small number of samples, these methods can be very time-consuming, and often require subjective judgments about whether a given morphological feature is a droplet to be included in the measured distribution. Clearly, *in situ* measurements, allowing structural changes to be monitored in real time, are preferred, but *ex situ* microscopy methods can compliment *in situ* studies by providing direct measurement of the average structural length scale in a sample.

Each of the experimental methods discussed above provide unique advantages for probing shear-induced structure in polymer blends. However, *in situ* methods have not yet been developed for investigating morphological changes in concentrated blends that bear greater resemblance to commercial systems. One objective of this dissertation is to establish the feasibility of such experiments using *in situ* small-angle x-ray scattering techniques.

3.2.2. Porod's Law

All scattering techniques rely upon interference among waves scattered from regions of varying scattering power within the sample. For systems of discrete particles, (whose positions are uncorrelated), destructive interference leads to suppression of intensity at $qR \sim O(1)$, where R is the particle radius. This concept is illustrated in Figure 3.3, which shows the scattering from a single spherical particle. Classical scattering methods for measuring particle sizes (*e.g.*, light scattering measurements of radius of gyration in dilute polymer solutions) generally rely on these interference phenomena at $qR \sim O(1)$. Applying this criterion of $qR \sim O(1)$ to x-ray scattering from typical immiscible polymer blends (in which $R \sim 1 \mu\text{m}$), these interference effects occur at very small scattering angles that are difficult to access experimentally ($q < 0.001 \text{ nm}^{-1}$).

In two-phase systems, however, scattering also persists to $qR \gg 1$ and is related to the electron density contrast at the interface in the system. This scattering is described by Porod's law [Porod (1982)]:

$$I(q \rightarrow \infty) = \frac{2\pi(\Delta\rho)^2 S}{q^4} \quad (3.3)$$

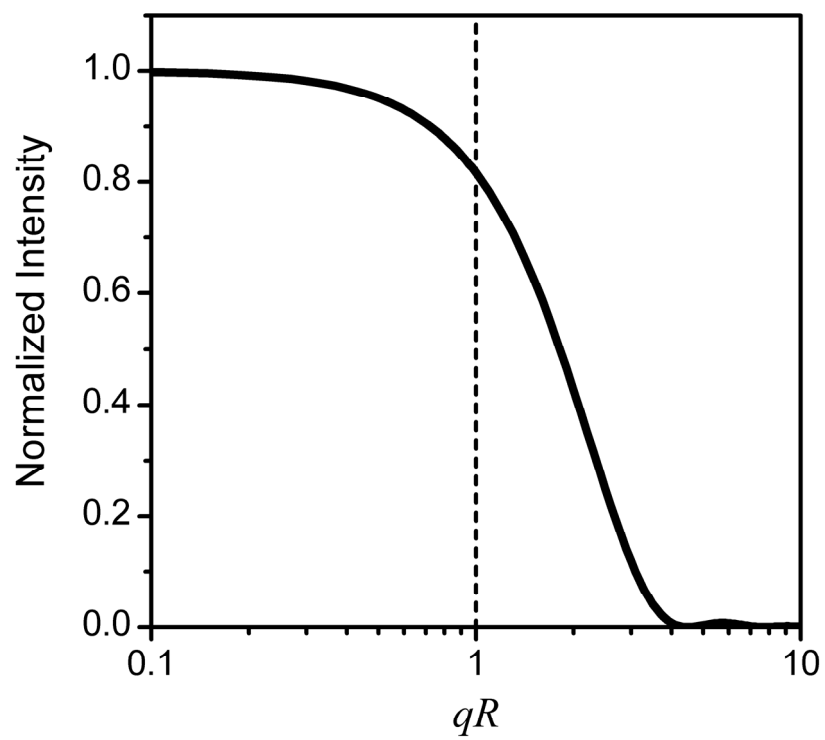


Figure 3.3. Scattering from a single spherical particle [eqn. 3.5 normalized by $\rho_1^2(4\pi R^3/3)^2$].

where $\Delta\rho [= \rho_1 - \rho_2]$ is the scattering length density contrast between the two phases, and S is the total amount of interfacial area in the scattering volume V . This relationship is valid under the following assumptions: (1) the system is composed of two phases, each of constant scattering length density (ρ_1 and ρ_2), (2) the interfacial boundaries are sharp, and (3) the system is isotropic. Although Porod's law can be derived in a general sense, we will demonstrate the derivation by appropriately considering the scattering from a system of spheres suspended in a matrix [Roe (2000)].

The normalized scattering amplitude, $A(q)$, for a single sphere of radius R and uniform scattering length density ρ_1 can be written as (from eqn. 2.11)

$$A(q) = \int_0^\infty \rho(r) \exp[-iqr] dr \quad \text{where} \quad \rho(r) = \begin{cases} \rho_1, & r \leq R \\ 0, & r > R \end{cases} \quad (3.4)$$

Due to the spherical symmetry, the scattering depends only on the magnitude of the scattering vector. Evaluation of eqn. 3.4, and multiplying by its complex conjugate yields the scattered intensity:

$$I(q) = \rho_1^2 \left(\frac{4}{3} \pi R^3 \right)^2 \frac{9(\sin qR - qR \cos qR)^2}{(qR)^6}. \quad (3.5)$$

Eqn. 3.5 (which is the expression plotted in Figure 3.3) can then be rewritten for a system of N spheres dispersed in a matrix of scattering length density ρ_2 :

$$\begin{aligned} I(q) &= \sum_{k=1}^N (\Delta\rho)^2 \left(\frac{4}{3} \pi R_k^3 \right)^2 \frac{9(\sin qR_k - qR_k \cos qR_k)^2}{(qR_k)^6} \\ &= \sum_{k=1}^N (\Delta\rho)^2 8\pi^2 \left[\frac{R_k^2 (1 + \cos 2qR_k)}{q^4} - \frac{2R_k \sin 2qR_k}{q^5} + \frac{1 - \cos 2qR_k}{q^6} \right] \end{aligned} \quad (3.6)$$

As $q \rightarrow \infty$, the second and third terms within the brackets in eqn. 3.6 become negligible. In the first term, $\sum \cos 2qR_k$ averages to zero for a system of spheres with a distribution of radii. With these simplifications, eqn. 3.6 reduces to eqn. 3.3 where $S = \sum 4\pi R_k^2 = 4\pi N \langle R^2 \rangle$. It should be noted that eqn. 3.6 is valid only for a dilute system in which the positions of the spheres are uncorrelated, so that waves scattered from different spheres do not result in interference effects. The derivation for concentrated systems is more involved and is given by Roe (2000). However, the effects of concentration on the scattered intensity profile are only observed for $qR \leq 1$. That is, the form of the asymptotic result for $q \rightarrow \infty$ (as given by eqn. 3.3) is independent of concentration, and indeed applies to *any* isotropic two-phase structure and not just a dispersion of spherical droplets.

Scattered intensity measured in absolute units is normalized by the total scattering volume V . The absolute form of Porod's law is thus given by

$$I(q \rightarrow \infty) = \frac{2\pi(\Delta\rho)^2(S/V)}{q^4} = \frac{K_P}{q^4} \quad (3.7)$$

where $K_P [= 2\pi(\Delta\rho)^2(S/V)]$ is the Porod coefficient. If the scattered intensity of a two-phase system is measured in absolute units, and the electron densities of the two phases are known, the specific surface area (S/V) in the sample can be determined. For a system such as an isotropic immiscible polymer blend, in which the dispersed phase is a distribution of spheres,

$$\frac{S}{V} = \frac{6\Phi}{\langle D \rangle_{vs}} \quad (3.8)$$

where

$$\langle D \rangle_{vs} = \frac{\sum_k n_k D_k^3}{\sum_k n_k D_k^2}. \quad (3.9)$$

In the above equations, $\langle D \rangle_{vs}$ is the surface-area-average diameter, Φ is the volume fraction of the dispersed phase, and n_k is the number of spheres of diameter D_k . Therefore, if the volume fraction of the dispersed phase is known, an average droplet size can be obtained from a single scattering measurement from a single sample.

Whereas eqn. 3.7 is valid for isotropic systems only, several groups have considered generalizations of Porod's law to anisotropic two-phase systems [Ciccariello *et al.* (2002); Guinier and Fournet (1955); Hamzeh and Bragg (1974); Wu (1980)]. These analyses show that an oriented system of particles yields a Porod coefficient that strongly depends on the orientation of $\mathbf{q}$. Furthermore, the scattered intensity may deviate from q^{-4} , depending on the particle shape. Oriented ellipsoids, for example, maintain q^{-4} dependence in the limit of $q \rightarrow \infty$ [Hamzeh and Bragg (1974); Wu (1980)]. The scattered intensity for parallelepipeds or cylinders, on the other hand, decreases as q^{-2} along the directions perpendicular to the plane faces of the particles [Guinier and Fournet (1955)]. Schneider *et al.* (2002) recently showed that deviation from q^{-4} dependence is associated with vanishing Gaussian curvature of the interface.

For immiscible blends subjected to shear, where the deformation is not too large, the oriented droplets are often represented as ellipsoids with principal radii R_1 , R_2 , and R_3 as shown in Figure 3.1. When the incident beam is aligned parallel with the minor axis

along R_3 , as illustrated in Figure 3.4, the high- q scattering from a single ellipsoid (projected onto the detector) is given by

$$I(q, \varphi) = \frac{2\pi(\Delta\rho)^2}{q^4} \frac{(S/V)}{[\varepsilon_1^2 \cos^2 \varphi + \varepsilon_2^2 \sin^2 \varphi]^2} = \frac{K_P(\varphi)}{q^4} \quad (3.10)$$

where φ is the azimuthal angle with respect to the principal axis along R_1 , S is the surface area of the equivalent volume sphere of radius R , and $K_P(\varphi) [= K_P/(\varepsilon_1^2 \cos^2 \varphi + \varepsilon_2^2 \sin^2 \varphi)^2]$ is the anisotropic Porod coefficient [Wu (1980)]. $\varepsilon_1 [= R_1/R]$ and $\varepsilon_2 [= R_2/R]$ are the stretch ratios along the principal axes 1 and 2, respectively.

Eqn. 3.10 gives two special cases:

$$I(q, \varphi = 0) = \frac{K_P}{q^4} \frac{1}{\varepsilon_1^4} \quad (3.11)$$

$$I(q, \varphi = \pi/2) = \frac{K_P}{q^4} \frac{1}{\varepsilon_2^4}. \quad (3.12)$$

where K_P is the isotropic Porod coefficient defined in eqn. 3.7. Therefore, if K_P has been determined for the spherical droplet prior to deformation, then ε_1 and ε_2 can be independently determined from fits to the scattering data at $\varphi = 0$ and $\varphi = \pi/2$, respectively. The expression given by eqn. 3.10 is valid for a system of many ellipsoids if the ellipsoids are assumed to be of equal shape and orientation; expressions for the scattered intensity profile become significantly more complex for systems with a distribution of shapes and/or orientation [Hamzeh and Bragg (1974)].

Porod scattering is commonly applied to study morphology in various isotropic two-phase systems, including foams [Axelos and Boué (2003)], aerogels [Wang *et al.* (1991)], porous solids [Spalla *et al.* (2003)], and particulate systems [Beaucage *et al.*

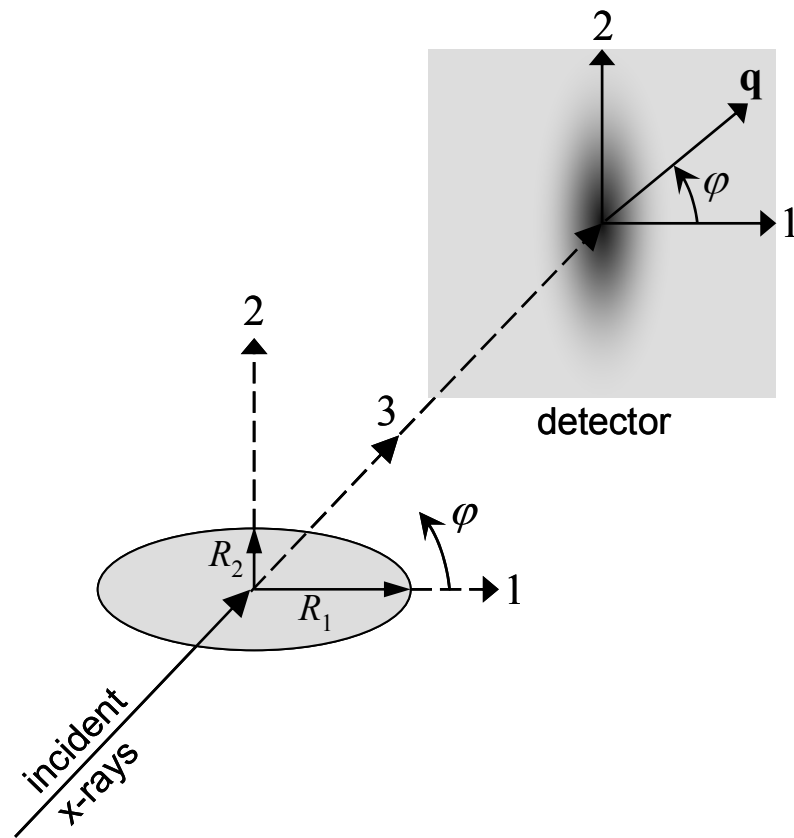


Figure 3.4. Illustration of the scattering from a single ellipsoid, where the incident x-ray beam is parallel with the principal axis along R_3 .

(2004); Kammler *et al.* (2004)]. In addition, anisotropic Porod models have been employed to characterize surface area and void shape in foams [Olivier *et al.* (1996)] and plasma-sprayed ceramic deposits [Boukari *et al.* (2003); Ilavsky *et al.* (1997)]. For immiscible polymer blends, Porod theory has been used to probe specific surface area and interfacial thickness under static conditions [Gemeinhardt and Moore (2005); Perrin and Prud'homme (1994)]. However, this theory has not yet been applied for characterization of droplet size, shape, or orientation in polymer blends. The ability to obtain this information via SAXS measurements provides a valuable approach for studying droplet dynamics in these systems. We have investigated the possibility of this technique in two independent experiments: (1) a coarsening study under isotropic, quiescent conditions, and (2) an *in situ* shear flow experiment.

3.3. Coarsening Study at Quiescent Conditions

In this experiment, droplet growth was characterized *ex situ* as a function of time for two immiscible polymer blend systems subjected to high-temperature annealing. The annealing was conducted under quiescent conditions, which produces morphologies with relaxed, spherical droplets. Therefore, SAXS measurements could be interpreted using isotropic Porod theory (eqns. 3.7 – 3.9) to determine droplet sizes. This SAXS technique was then verified using scanning electron microscopy.

3.3.1. Experiment

3.3.1.1. *Materials*

Two types of blends of polystyrene (PS) ($M_n = 101,000$, $M_w/M_n = 2.70$, Aldrich) and poly(methyl methacrylate) (PMMA) ($M_w \sim 120,000$, Aldrich) were prepared as documented by Lebovitz *et al.* (2002a) with a composition of 70/30 weight% PS/PMMA. The first blend was prepared via melt-extrusion, and the extrudate was pelletized. The second blend was prepared using solid-state shear pulverization [Furguele *et al.* (2000); Lebovitz *et al.* (2002a, 2002b)], where the product was collected in powder/flake form.

3.3.1.2. *Sample Preparation and Annealing*

The blends were dried under vacuum at 80°C for several hours and then molded into 1/16" thick disks at 190°C and ~300 psi using a brass mold and a hydraulic press with heated platens (PHI-Tulip). Melt blended samples were prepared by first pre-heating pellets at 190°C for 2 minutes and then applying pressure for 6 minutes to consolidate the polymer in the disk-shaped mold. The pulverized blend samples were prepared by heating the powder at 190°C for 5 minutes (during which additional powder was added to the melting sample to provide enough polymer to fill the mold), followed by 4 additional minutes under pressure to consolidate the sample. The above protocols define the 'zero' time points in this coarsening study; for each blend, samples were prepared with additional annealing times of 10, 30, 60, 120, or 240 minutes at 190°C in the hot press. Samples were quenched by removing the sample from the hot press and allowing the sample cool at room temperature and atmospheric pressure to minimize deformation of

the dispersed phase during the quench. For selected time points, two samples of a given blend type were annealed simultaneously. Results from these duplicate samples provided a rough measure of the consistency of the SAXS technique for determination of droplet size.

3.3.1.3. X-Ray Scattering

Small-angle x-ray scattering measurements of each blend were collected *ex situ* using beamline 5ID-D at the Advanced Photon Source. The sample disks were mounted on a sample changer within a vacuum chamber such that the incident beam (17 keV) passed through the 1/16"-thickness of the disk. Scattering patterns of the samples at room temperature were collected on a two-dimensional MarCCD detector using pin hole collimation and a sample-to-detector distance of 10.2 meters, which was completely under vacuum. One-dimensional scans of $I(q)$ were extracted from the two-dimensional scattering patterns using the analysis package Fit2D [Hammersley].

Scattering data were corrected by performing a background subtraction (due to electronic noise from the detector), and calibrated to absolute intensity [Russell *et al.* (1988)] using a glassy carbon standard [Ilavsky], accounting for sample absorbance and thickness. Detectors positioned upstream and downstream (removable) from the sample allowed for absorbance measurement, from which attenuation coefficients were obtained. The experimental attenuation coefficients of the homopolymers, $\mu_{PS} = 0.640 \text{ cm}^{-1}$ and $\mu_{PMMA} = 0.980 \text{ cm}^{-1}$, obtained from absorbance measurements are comparable to tabulated values, $\mu_{PS} = 0.671 \text{ cm}^{-1}$ and $\mu_{PMMA} = 0.993 \text{ cm}^{-1}$ [NIST]. Furthermore,

scattering measurements were collected for disks of each of the pure homopolymers (prepared under the same molding conditions described above) to obtain an approximate measure of “frozen” thermal density fluctuations within the polymer samples. After accounting for the proportions of each of the homopolymers in the blends, this scattering was subtracted from the total measured scattering of the blend samples. However, scattering resulting from density fluctuations was found to be small compared to the Porod scattering (< 5% even at the high- q end of the measurable Porod region). The electron densities, n , of the homopolymers were estimated using their respective bulk densities in the glassy state (1.05 g/cm³ for PS and 1.19 g/cm³ for PMMA) [Brandrup *et al.* (1999)]: $n_{\text{PS}} = 340.0 \text{ e}^-/\text{nm}^3$, $n_{\text{PMMA}} = 386.3 \text{ e}^-/\text{nm}^3$.

3.3.1.4. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to verify the SAXS technique for determining an average droplet size in the blends. Blend samples were fractured to expose a two-dimensional cross-section of the morphology, which was coated with a 5 nm layer of gold using a Cressington 208HR sputter coater (located at the Biological Imaging Facility (BIF) of Northwestern University). The coated surfaces were viewed using a Hitachi S-3500N scanning electron microscope (located at the Electron Probe Instrumentation Center (EPIC) at Northwestern University) with a 8.5 kV accelerating voltage. For each annealing condition, 100 – 700 (usually 300 – 700) droplets were characterized for melt-blended samples, while 500 – 1000 droplets were characterized for pulverized samples.

Edge detection analysis could not be performed on the raw SEM micrographs due to the presence of fracture lines on the sample surface. Therefore, droplets were hand-traced onto a transparency, which was scanned into a computer, and the droplet areas were measured using Scion Image Beta 4.0.2 analysis software. Equivalent sphere diameters, D_k , were then obtained from the area measurements. Since the SEM micrographs are two-dimensional slices through the sample, the measured diameters are profiles of the three-dimensional droplets rather than the actual diameters of the droplets, leading to an under-estimated D_k . However, some smaller droplets are missed as a result of the two-dimensional slicing, and this tends to counterbalance the former effect [DeHoff and Rhines (1968)]; additional (unknown) biases may further be introduced by nonideal sectioning of the sample due to complicated fracture mechanics near droplet inclusions. Stereological corrections performed in polymer blend studies by Macosko and coworkers (1995, 1996, 2002) typically showed $< 10\%$ error in the number-average diameter, $\langle D \rangle_n$, and in $\langle D \rangle_{vs}$. For the majority of their measurements, corrections were not performed because the errors were considered small, and the overall trends were unaffected. Based on these findings, we assume that the errors are also likely to be small in our droplet measurements, and, therefore, we did not make stereological corrections.

3.3.2. Results

3.3.2.1. Melt-Extruded Blend

The SEM images in Figure 3.5 show the droplet/matrix morphology of the melt-extruded blends after annealing at 190°C for set periods of time. Coarsening of the droplets during

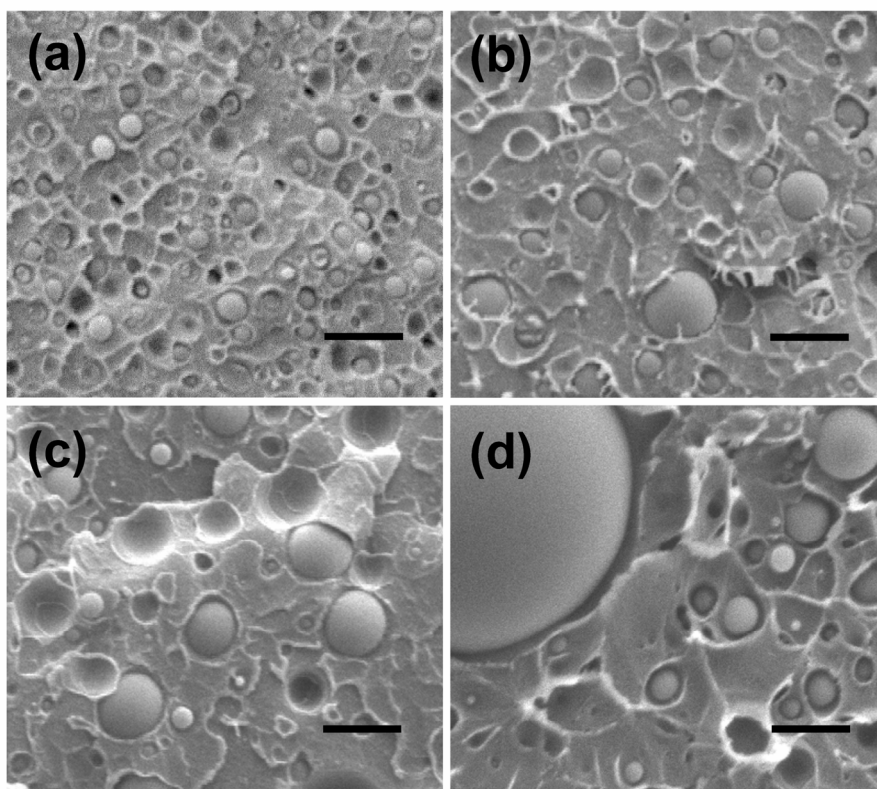


Figure 3.5. SEM micrographs of a 70/30 weight% PS/PMMA blend prepared via melt-extrusion and annealed at 190°C for (a) 10 min, (b) 30 min, (c) 60 min, (d) 240 min. Scale bar = 5 μm .

annealing is apparent in these micrographs. For the zero-time point, a significant amount of anisotropy is present in most micrographs (not shown), indicating that the droplets had not yet fully relaxed from the applied pressure during compression molding. A few regions in this sample appeared isotropic, and the droplets in these regions were characterized. However, the size distribution for this time point may be biased, at least to a small extent, since the sampling for droplet measurement was not completely random. No anisotropy was observed for the remaining time points. The growth of $\langle D \rangle_n$ with annealing time is plotted in Figure 3.6. The abscissa is defined with anneal time to the $1/3^{\text{rd}}$ power since droplet size is expected to grow as $[\text{time}]^{1/3}$ for coarsening and/or Ostwald ripening during the late stages of growth [Siggia (1979); Song and Torkelson (1994)]. The data approximately follow this behavior.

As shown in Figure 3.7, the experimental scattered intensity for the melt-extruded blend closely follows $I \sim q^{-4}$ behavior predicted by Porod's law. In addition, the Porod scattering intensity decreases with annealing time as the droplets increase in size because of coarsening. A surface-area-average diameter was determined for each annealing time point by fitting Porod's law (eqn. 3.7) to the experimental data. For each of the 30, 60, and 120 min annealing times, duplicate samples were measured, and the mean $\langle D \rangle_{vs}$ values were computed. These results are plotted in Figure 3.8 along with $\langle D \rangle_{vs}$ values calculated from the droplet size distribution as measured by SEM. For the 30 min annealing time, the upper and lower error bars on the SAXS data represent the larger and smaller measured values, respectively, of the two samples. The "error bars" for the 60 and 120 min annealing times are too small ($\pm 0.04 \mu\text{m}$) to be represented in Figure 3.8.

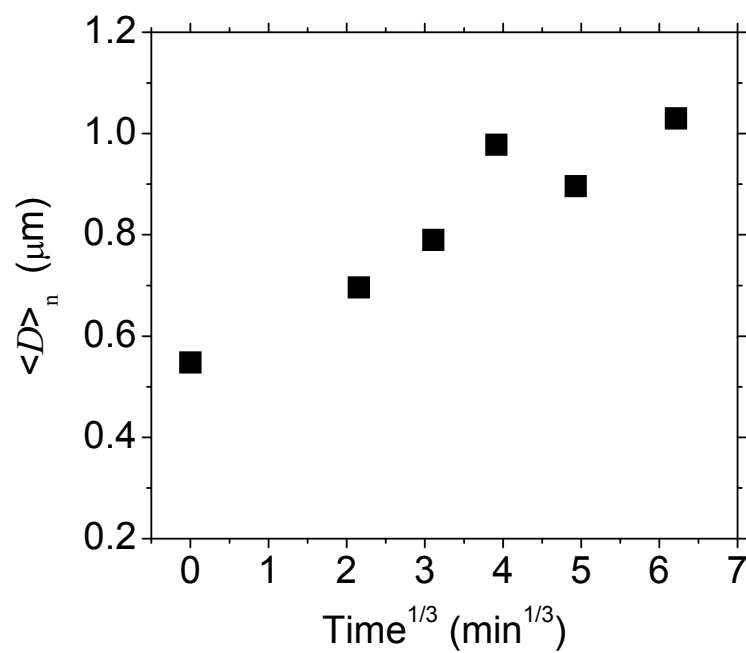


Figure 3.6. Growth of number-average droplet diameter with annealing time at 190°C, as measured by SEM, in a 70/30 weight% PS/PMMA blend prepared via melt-extrusion.

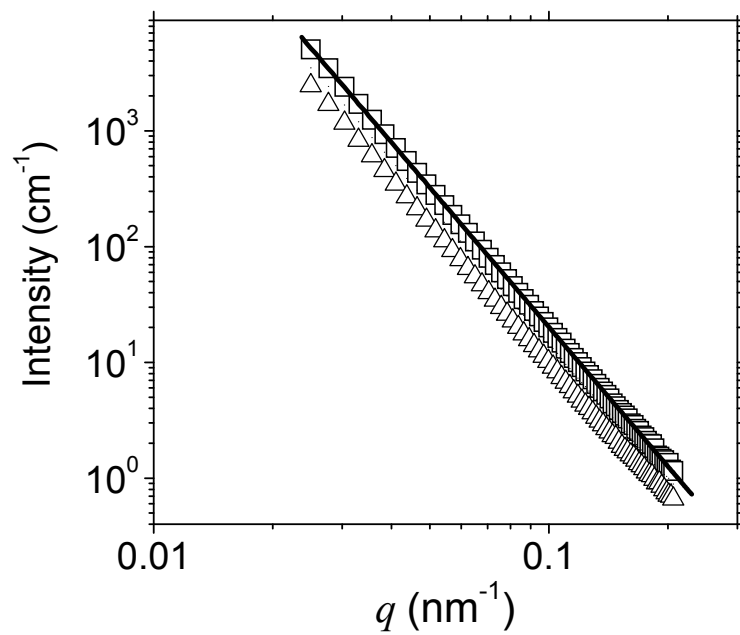


Figure 3.7. Scattered intensity of a 70/30 weight% PS/PMMA blend prepared via melt-extrusion and annealed at 190°C for ($\square$) 0 min and (Δ) 240 min. The solid line is Porod's law (eqn. 3.7) fit to experimental data at 0 min.

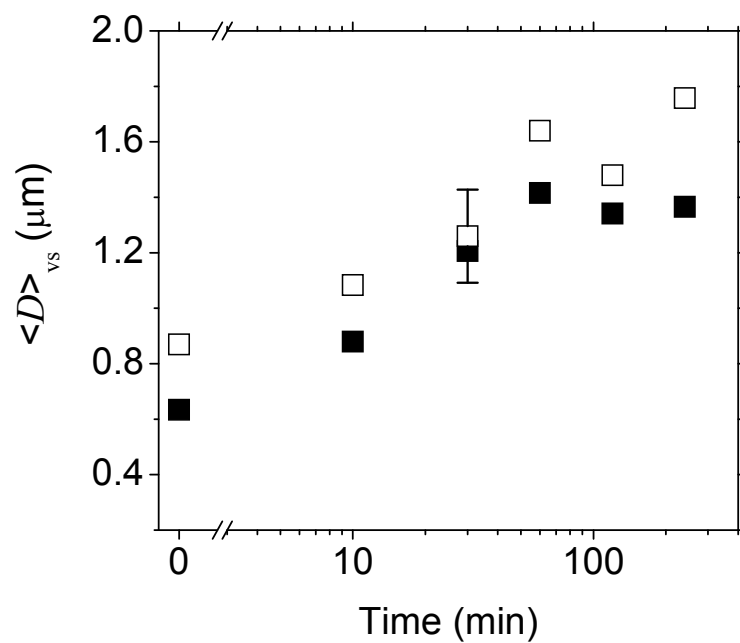


Figure 3.8. Behavior of $\langle D_{vs} \rangle$ during annealing at 190°C as measured by SEM (■) and SAXS (□) for a 70/30 weight% PS/PMMA blend prepared via melt-extrusion.

In the case where two SAXS measurements (*i.e.*, from duplicate samples) were averaged, the SEM data for the two samples were treated as a single distribution. Hence, only a single $\langle D \rangle_{vs}$ value was obtained from SEM for each annealing time.

In the case of the melt-extruded blends, measurement by SAXS is approximately 10 – 20% greater than measurement by SEM. Stereological corrections may bring the data into closer agreement. However, SEM methods are, in general, fairly subjective and can result in significant errors. Selection of surface regions can be investigator-dependent, leading to a bias in the size distribution. For example, if the distribution is very broad, it becomes difficult to obtain images that accurately represent the distribution. So, if micrographs are collected at higher magnifications to access the smaller droplets, the larger droplets may be excluded. Despite the moderate discrepancy between the absolute measured values from SAXS and SEM, the coarsening behavior during annealing is captured by both methods.

3.3.2.2. *Pulverized Blend*

As shown in the SEM images of Figure 3.9, some coarsening also occurs in the pulverized blend. The growth of the number-average diameter with annealing time is plotted in Figure 3.10. Comparison of the behavior of $\langle D \rangle_n$ in both blends reveals a larger growth rate in the melt-extruded blend (~91% growth) than in the pulverized blend (~48% growth). This result is consistent with a previous study by Lebovitz *et al.* (2002a), who showed that, during long-term, high temperature annealing, certain pulverized blends are stable to static coarsening relative to blends melt-processed by

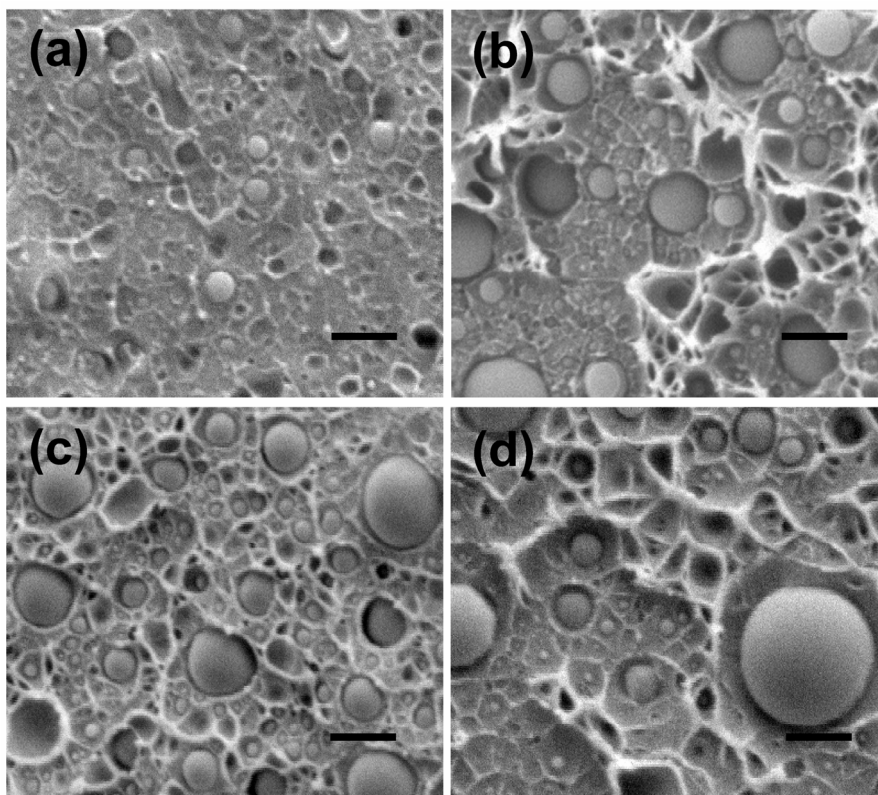


Figure 3.9. SEM micrographs of a 70/30 weight% PS/PMMA blend prepared via solid-state shear pulverization and annealed at 190°C for (a) 0 min, (b) 30 min, (c) 60 min, (d) 240 min. Scale bar = 3 μm.

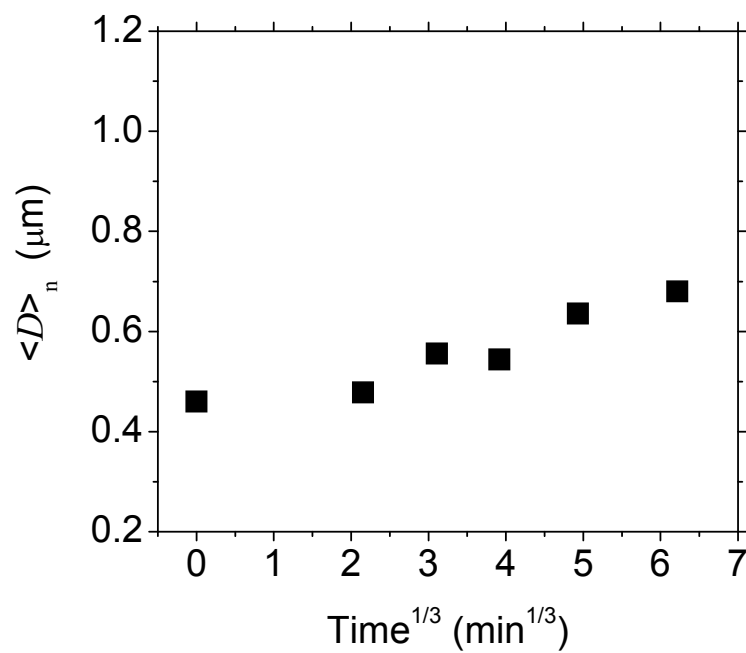


Figure 3.10. Growth of number-average droplet diameter with annealing time at 190°C, as measured by SEM, in a 70/30 weight% PS/PMMA blend prepared via pulverization.

twin-screw extrusion. The higher stability of the pulverized blends is attributed to the occurrence of chain scission during the pulverization process, which can result in recombination of the radicals at the interface of the two phases and, thus, block copolymer formation [Lebovitz *et al.* (2002b)].

Experimental SAXS data, shown in Figure 3.11, follow $I \sim q^{-3.8}$ behavior rather than $I \sim q^{-4}$ as predicted by Porod's law. Negative deviation from Porod's law (*i.e.*, $I \sim q^{-\alpha}$, where $\alpha > 4$) has been observed in compatibilized blends, where addition of block copolymer increases the interfacial thickness in the two-phase system [Perrin and Prud'homme (1994)]. Positive deviations ($3 < \alpha < 4$) have been observed in various systems, and have frequently been associated with fractally rough surfaces (surface fractal scattering) [Bale and Schmidt (1984); Hurd *et al.* (1989); Schmidt (1991)]. This seems an unlikely explanation in the current case, where annealing in the melt should lead to smooth interfaces, even in the pulverized sample. However, as demonstrated by Beaucage and coworkers (1999), a broad droplet size can lead to power-law scattering with $\alpha < 4$. For a monodisperse set of droplets, the onset of the Porod regime shifts to higher q for smaller droplets. Therefore, if a sample contains a sufficiently heterogeneous mixture of small and large droplets, sub-Porod scattering from the smaller droplets could be superimposed onto the Porod scattering from the larger droplets within a given q range. This would cause the slope of the experimental $I(q)$ to be less than that predicted by eqn. 3.7.

During pulverization, the polymers are processed below the glass transition and/or melting temperature(s). Since the material does not "flow" during processing, some

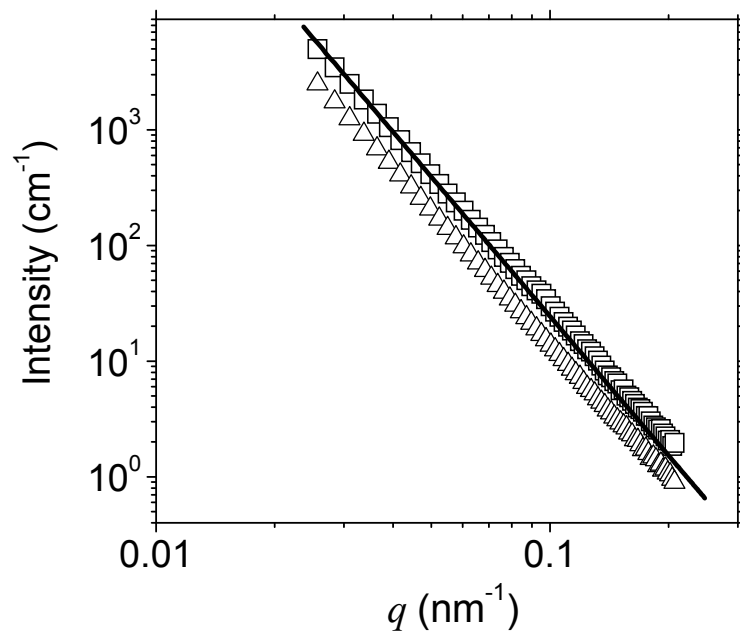


Figure 3.11. Scattered intensity of a 70/30 weight% PS/PMMA blend prepared via pulverization and annealed at 190°C for ($\square$) 0 min and ($\triangle$) 240 min. The solid line is Porod's law (eqn. 3.7) fit to experimental data at 0 min.

regions are subjected to much higher shear stresses and, thus, higher deformation than other regions. In these higher deformation regions, a much finer morphology is expected. Thus, if pulverization of the PS/PMMA blend in the present study resulted in this type of morphological inhomogeneity, perhaps it would cause the positive deviation from the scattering theory as described above. Indeed, significant variation in droplet size from region to region was evident in SEM micrographs of the pulverized samples (Figure 3.12). In fact, some regions of the sample (not shown) contain mostly small droplets that fall below the resolution of the SEM ($< 0.1 \mu\text{m}$). Because of these unfavorable factors, obtaining an unbiased droplet size distribution via SEM is difficult. The melt-extruded blend morphology is, in general, more uniform throughout the sample.

Since the slope of the scattered intensity deviates from Porod's law, a range of $\langle D \rangle_{\text{vs}}$ values was determined for each sample by fitting eqn. 3.7 to the low- q and high- q regions of the experimental data. The mean of these $\langle D \rangle_{\text{vs}}$ was taken to be characteristic of a given sample, while the breadth of this range is typically $\pm 0.03 - 0.05 \mu\text{m}$. Two separate samples per anneal time were measured by SAXS, and the two $\langle D \rangle_{\text{vs}}$ values at a given anneal time agreed within $\sim 0.05 \mu\text{m}$. The averaged values from duplicate samples are plotted in Figure 3.13. Despite the above-stated complications in data collection using either characterization method, the SAXS and SEM measurements of $\langle D \rangle_{\text{vs}}$ agree very well.

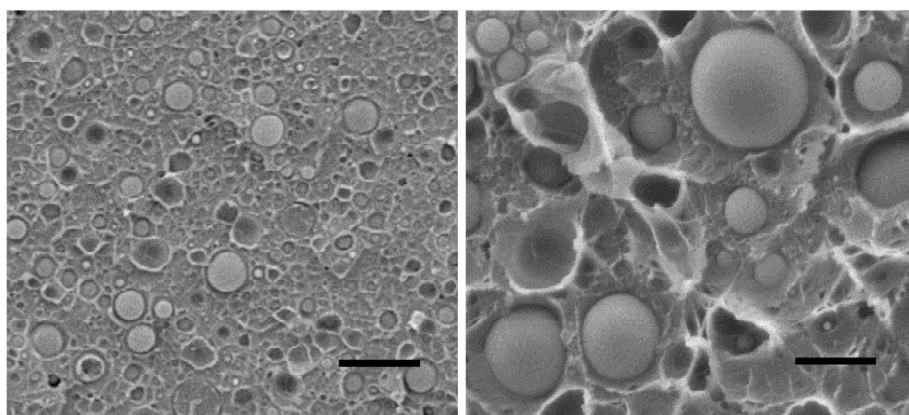


Figure 3.12. SEM micrographs comparing two different regions of a 70/30 weight% PS/PMMA blend prepared via pulverization and annealed for 30 min at 190°C. Scale bar = 5 μm in both images.

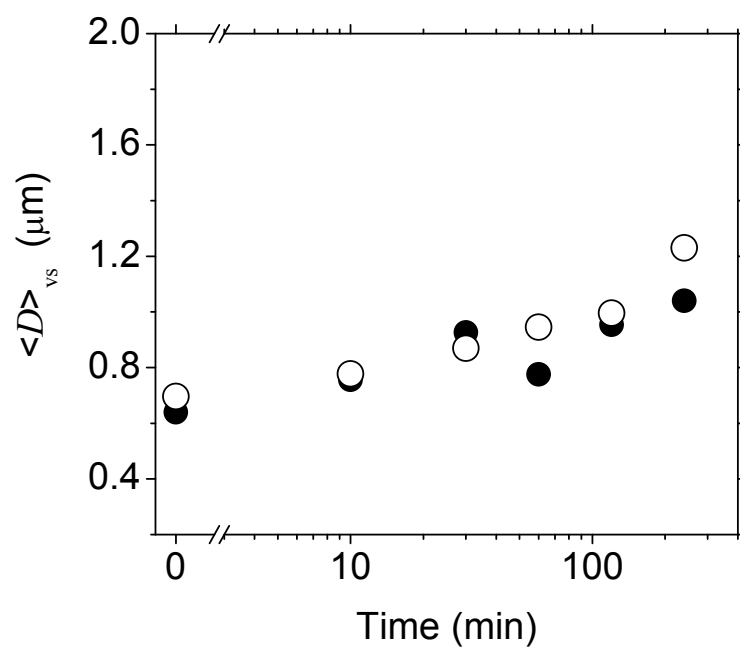


Figure 3.13. Behavior of $\langle D_{vs} \rangle$ during annealing at 190°C as measured by SEM ($\bullet$) and SAXS ($\circ$) for a 70/30 weight% PS/PMMA blend prepared via pulverization.

3.3.3. Summary

The coarsening behavior of the dispersed phase in concentrated immiscible blends of PS/PMMA prepared by either melt-extrusion or pulverization was characterized using SAXS and Porod theory, which is based on the existence of interfacial area rather than of the spherical droplets themselves. For both blends, the surface-area-average droplet diameters determined by SAXS agree well with those measured by SEM. Furthermore, a difference between the overall morphologies in the two blends that is apparent in the SEM micrographs also appears to be reflected in the scattering behavior. From this study, we conclude that SAXS is a useful alternative or complementary technique to laborious and time-consuming microscopy techniques for characterizing changes in droplet size in immiscible polymer blends. Although SAXS measurements were collected *ex situ* for samples quenched at various times during annealing, the success of this experiment suggests the possibility of collecting SAXS measurements *in situ* during coarsening or flow experiments.

3.4. *In Situ* Shear Flow Study

We have conducted the first time-resolved SAXS measurements of shear-induced structural dynamics in an immiscible binary homopolymer blend exhibiting a droplet/matrix morphology. The experiments were performed using an annular cone and plate device, which allowed for observation of scattering from the sample in the flow-gradient (x - y) plane of a simple shear field. Deformation of the interface was

characterized by computing second moment tensor of the scattering vector, weighted by the scattered intensity. By assuming the deformed droplets to be ellipsoidal, we also considered the validity of the ellipsoid scattering model by Wu (1980) (eqn. 3.10) for characterizing the morphology of our blend system.

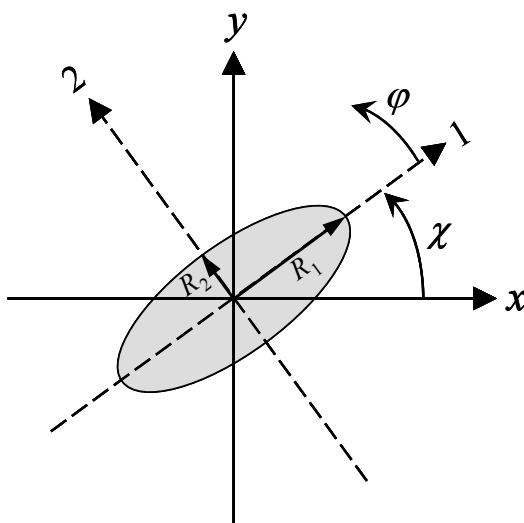
3.4.1. Anisotropic Porod Model

This experiment probes shear-induced deformation of interface in an 80/20 wt% PS/PMMA blend via two-dimensional scattering measurements in the Porod regime. Although the deformation and orientation of interface can be generally characterized using a second moment tensor analysis, an appropriate model must be employed to extract information regarding the specific deformation of the microstructure. As a potential model for our blend system, we investigate the simple expression by Wu (1980), which describes the scattering from an ellipsoid.

The analysis of Wu is presented in the coordinate frame of the principal droplet deformation (Figure 3.4). In shear, however, droplets are rotated relative to the lab coordinate frame defining the shear flow axes. An oriented ellipsoid as viewed in the flow-gradient plane during shear flow is illustrated in Figure 3.14. Within this illustration, the experimental coordinate frame is defined by (x,y) , and the principal coordinate frame by $(1,2)$. The second moment tensor associated with each coordinate frame can be written as

$$\langle \mathbf{q}\mathbf{q} \rangle = \iint \mathbf{q}\mathbf{q} I(q) d\mathbf{q} \quad (3.13)$$

(a) real space



(b) reciprocal space

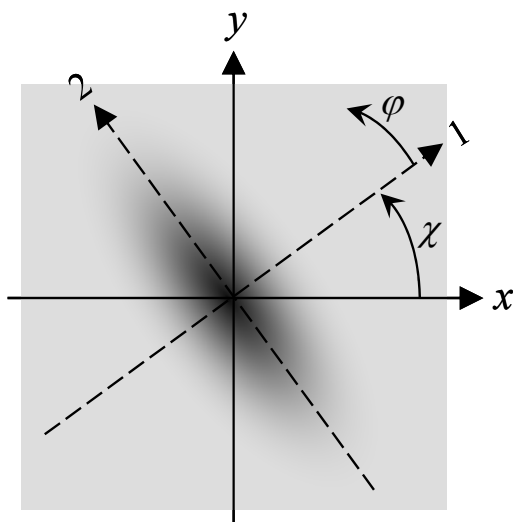


Figure 3.14. Illustration of (a) an oriented droplet undergoing shear flow (in real space) and (b) the associated scattering from the droplet. (x,y) defines the experimental coordinate frame, and $(1,2)$ defines the principal coordinate frame. χ is the orientation of the principal frame with respect to the experimental frame. φ is the azimuthal angle with respect to the 1-axis of the principal frame.

$$= \begin{pmatrix} \langle q_x q_x \rangle & \langle q_x q_y \rangle \\ \langle q_x q_y \rangle & \langle q_y q_y \rangle \end{pmatrix} \quad (\text{experimental frame}) \quad (3.14)$$

$$= \begin{pmatrix} \langle q_1 q_1 \rangle & 0 \\ 0 & \langle q_2 q_2 \rangle \end{pmatrix} \equiv \begin{pmatrix} Q_1 & 0 \\ 0 & Q_2 \end{pmatrix} \quad (\text{principal frame}) \quad (3.15)$$

where Q_1 and Q_2 are the principal values of $\langle \mathbf{q}\mathbf{q} \rangle$.

The principal values can be solved analytically in terms of the ellipsoid model by substituting the expression for the intensity (eqn. 3.10) into eqn. 3.13. We begin this brief derivation by writing the definition of $\langle \mathbf{q}\mathbf{q} \rangle$ (eqn. 3.13) for the principal frame in polar coordinates:

$$\begin{aligned} \langle \mathbf{q}\mathbf{q} \rangle &= \int_0^{2\pi} \int_{q_{\min}}^{\infty} \mathbf{q}\mathbf{q} I(q, \varphi) dq d\varphi \\ &= \int_0^{2\pi} \int_{q_{\min}}^{\infty} q^2 \begin{pmatrix} \cos^2 \varphi & 0 \\ 0 & \sin^2 \varphi \end{pmatrix} I(q, \varphi) dq d\varphi \end{aligned} \quad (3.16)$$

where $q_1 = q \cos \varphi$ and $q_2 = q \sin \varphi$. For convenience, the lower limit in the integral over q is constrained by $q_{\min}$, which defines the minimum q -value accessible in the scattering experiment. Substitution of eqn. 3.10 into 3.16 and evaluation of the integral over q yields

$$\langle \mathbf{q}\mathbf{q} \rangle = \frac{K_P}{q_{\min}} \int_0^{2\pi} \begin{pmatrix} \cos^2 \varphi & 0 \\ 0 & \sin^2 \varphi \end{pmatrix} \frac{d\varphi}{[\varepsilon_1^2 \cos^2 \varphi + \varepsilon_2^2 \sin^2 \varphi]^2} \quad (3.17)$$

where K_P is the isotropic Porod coefficient. Evaluation of eqn. 3.17 for each of the diagonal components then gives the principal values:

$$\langle q_1 q_1 \rangle = Q_1 = \frac{K_P \pi}{q_{\min}} \frac{1}{\varepsilon_1^3 \varepsilon_2} \quad (3.18)$$

$$\langle q_2 q_2 \rangle = Q_2 = \frac{K_P \pi}{q_{\min}} \frac{1}{\varepsilon_1 \varepsilon_2^3}. \quad (3.19)$$

At isotropic, quiescent conditions, where the droplet is spherical ($\varepsilon_1 = \varepsilon_2 = 1$),

$$Q_1 = Q_2 = Q_0 = \frac{K_P \pi}{q_{\min}}. \quad (3.20)$$

The components of $\langle \mathbf{q}\mathbf{q} \rangle$ in the principal and experimental coordinate frames are related by the invariants, Z_I and Z_{II} , of $\langle \mathbf{q}\mathbf{q} \rangle$:[§]

$$Z_I = \text{tr}\langle \mathbf{q}\mathbf{q} \rangle = Q_1 + Q_2 = \langle q_x q_x \rangle + \langle q_y q_y \rangle \quad (3.21)$$

$$Z_{II} = \frac{1}{2} [Z_I^2 - \text{tr}\langle \mathbf{q}\mathbf{q} \rangle^2] = Q_1 Q_2 = \langle q_x q_x \rangle \langle q_y q_y \rangle - \langle q_x q_y \rangle^2. \quad (3.22)$$

Another convenient relationship between the two coordinate frames is given by the difference in the principal values (*i.e.*, the principal anisotropy factor):

$$AF \equiv Q_2 - Q_1 = \sqrt{(\langle q_x q_x \rangle - \langle q_y q_y \rangle)^2 - 4\langle q_x q_y \rangle^2}, \quad (3.23)$$

which provides a measure of the degree of alignment of interface in the blend. By computing $\langle \mathbf{q}\mathbf{q} \rangle$ from the scattering data in the experimental frame, the principal values are easily determined using eqns. 3.21 and 3.23. If the ellipsoid model by Wu is valid, K_P and the droplet stretch ratios can then be directly obtained from the principal values using eqns. 3.18 – 3.20.

While the model presented here has been derived for the case of a single ellipsoid, it also applies to a system of ellipsoids monodisperse in shape and orientation. We note

[§] For a more detailed discussion regarding principal values and invariants, refer to Macosko (1994).

that the dispersed phase in our blend is concentrated and exhibits some polydispersity in size, which likely results in some variation in the shape and orientation of the droplets when subjected to shear. Accounting for these effects in the anisotropic scattering behavior is non-trivial and outside the scope of this study. However, if the polydispersity in a particular system is sufficiently low, the single ellipsoid model provides a simple and straightforward approach for determination of an average droplet size and shape from SAXS measurements. Application of this model to the present experimental study should provide some insight into its validity for concentrated immiscible blend systems.

3.4.2. Experiment

3.4.2.1. Materials

For *in situ* SAXS studies, a single blend of polystyrene ($M_n = 91,900$, $M_w/M_n = 2.3$, Dow Styron 615APR) and poly(methyl methacrylate) ($M_n = 18,700$, $M_w/M_n = 1.9$, Scientific Polymer Products, Inc.) was prepared with a composition of 80/20 weight% PS/PMMA. The homopolymers were selected for their similar viscosities ($\eta_{PS} = 8,200$ Pa.s, $\eta_{PMMA} = 12,400$ Pa.s at 190°C), a condition that results in optimal mixing of the two phases with fairly low polydispersity in droplet size. Furthermore, a viscosity-matched system is expected to yield ellipsoidal-shaped droplets under moderate shear flow conditions ($Ca < 1$), allowing for investigation of the aforementioned scattering model.

3.4.2.2. *Sample Preparation*

Prior to blending, the PS pellets and PMMA powder were vacuum dried for 12 hours at 60°C. Even after vacuum drying at 60°C, the PMMA powder foamed when heated above the glass transition temperature (~100°C). Therefore, PMMA was annealed under vacuum at 190°C for an additional 3 hours to remove any remaining low molecular weight volatiles.

The homopolymers were blended in a helicone mixer (Design Integrated Technology, Inc., Warrenton, VA) at 195°C, and the extrudate was collected in ~0.5 gram portions. Using a hydraulic press (PHI-Tulip) and a brass mold with heated platens, these portions were then molded at 190°C into the form of a ring for convenient loading onto the annular cone and plate shear cell used in the x-ray experiment. One of the blend samples was prepared for SEM (as described in Section 3.3.1.4) to verify good dispersion of the minor phase in the blend. A representative micrograph of the blend morphology in Figure 3.15 shows good dispersion with an average droplet size less than 1 μm .

3.4.2.3. *Rheology*

Linear viscoelastic measurements of the blend and the individual homopolymers at 190°C were conducted using a Rheometric Scientific ARES rheometer with parallel plate fixtures. The complex viscosities and complex moduli as a function of angular frequency are presented in Figures 3.16. The viscosity and moduli of the blend lie between the values of the individual homopolymers at intermediate and high frequency, and enhanced

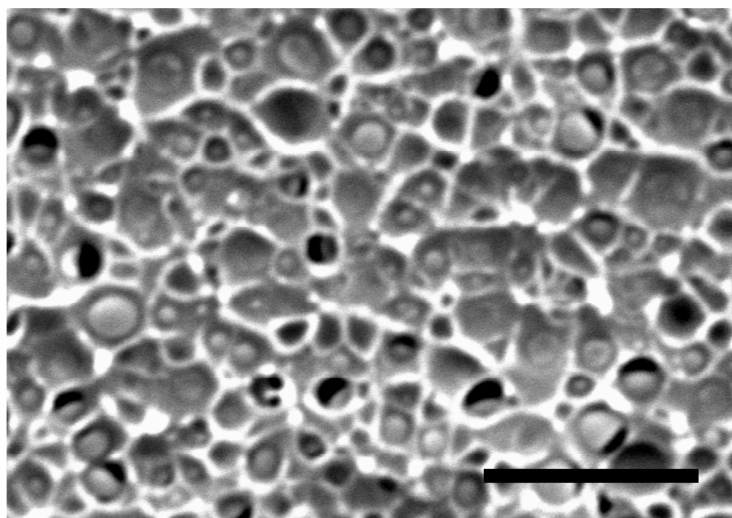


Figure 3.15. Representative SEM micrograph of the 80/20 weight% PS/PMMA blend used in the *in situ* SAXS experiment. Scale bar = 3 μm .

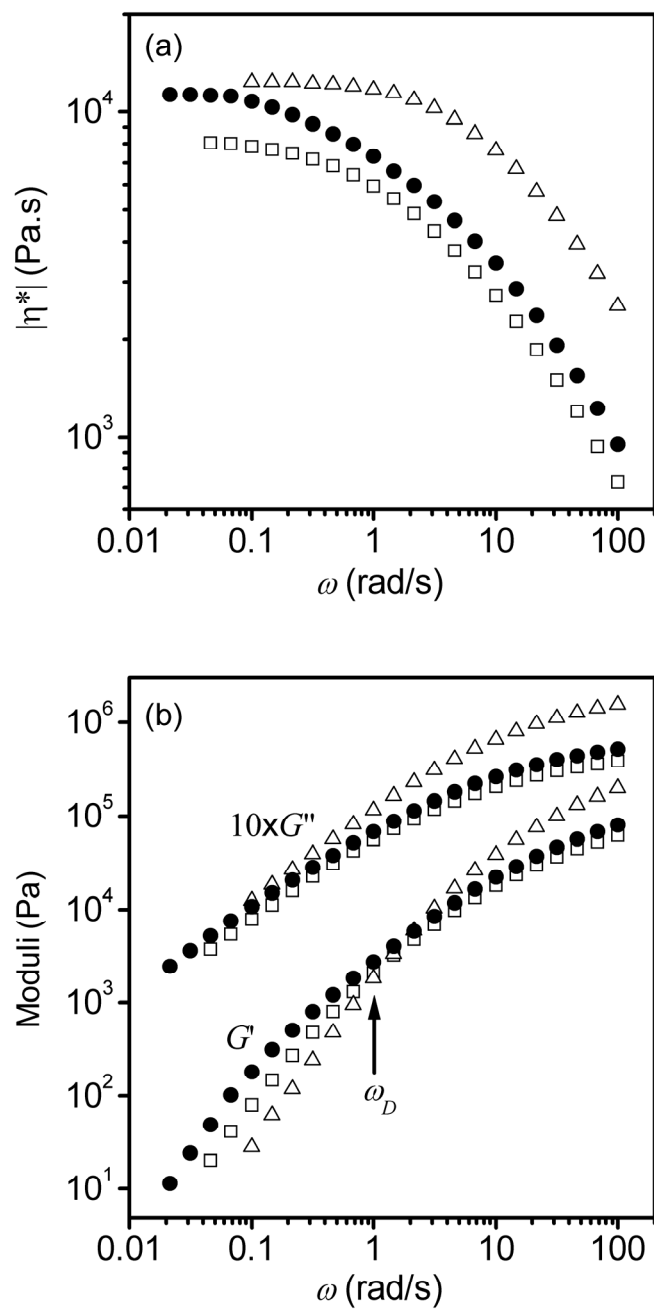


Figure 3.16. (a) Complex viscosities and (b) complex moduli of the 80/20 wt% PS/PMMA blend (●), PS homopolymer (□), and PMMA homopolymer (Δ) used in *in situ* SAXS experiments. Data were collected at 190°C.

viscoelasticity is observed at low frequency due to the presence of microstructure. The storage modulus, G' , of the blend exhibits a small shoulder at $\omega_D \sim 1$ rad/s, which is associated with the average relaxation time of the droplets ($\bar{\lambda}_D \sim 1/\omega_D$) [Graebling *et al.* (1993)]. A dynamic strain sweep conducted at 10 rad/s showed the blend to be linear for strains less than 15%.

3.4.2.4. *In Situ X-Ray Scattering*

In situ SAXS experiments were conducted at beamline 5ID-D at the Advanced Photon Source using 15 keV radiation and 8.04 meter sample-to-detector distance. The annular cone and plate shear cell, with the mica window installed in the bottom plate, was mounted on a translation table using the general setup shown in Figure 2.8. The sample area was enclosed using the acrylic plates (as shown in Figure 2.7) and purged with helium gas to provide an inert environment. Step strain deformation was applied to the 80/20 wt% PS/PMMA blend, which was maintained at a temperature of 190°C. Time-resolved two-dimensional scattering patterns were collected using a GemstarCCD detector with a frame rate of ~ 7 frames/sec. To determine the electronic background noise from the detector, “dark” images were periodically collected with the beam shutter closed. These “dark” images were subtracted from all scattering patterns prior to analysis of the data. In addition, several scattering patterns of the blend in its quiescent state were collected before each experiment.

Of the three detectors available at beamline 5ID, the Gemstar detector provides the fastest data collection rates. Use of this detector was necessary to capture the rapid

dynamics of the PS/PMMA blend system in response to shear. The current software for driving this detector, however, does not provide the capability to coordinate measurement of the incident and transmitted beam intensities with measurement of the scattering pattern. Without this capability, the scattering data cannot be calibrated to absolute values, and thus the absolute droplet size in the blend cannot be determined. We also note that since the sample is exposed on the outer edge of the annular shear cell, the sample thickness (between the inner and outer edges of the annulus) may not be perfectly uniform along the angular direction between the shear cell plates. Therefore, the sample thickness exposed to the incident beam may vary with shear cell position. We do not have a feasible method for monitoring these variations and their impact on the absolute scattered intensity. Although the scattering could not be measured in absolute units, *relative* changes in the scattering *profile* during shear can be characterized to extract useful information regarding deformation of the microstructure.

3.4.3. Results

3.4.3.1. Representative Scattering Data

Figure 3.17 shows representative scattering patterns of the blend under quiescent conditions and immediately following a step strain (at 30%, 70% and 300% strain). Comparison of these images clearly show changes in the scattered intensity distribution associated with shear-induced deformation of the two-phase structure. The anisotropy in the scattering resulting from interface deformation is further illustrated in Figure 3.18, which shows one-dimensional intensity scans extracted from 2-D patterns collected at

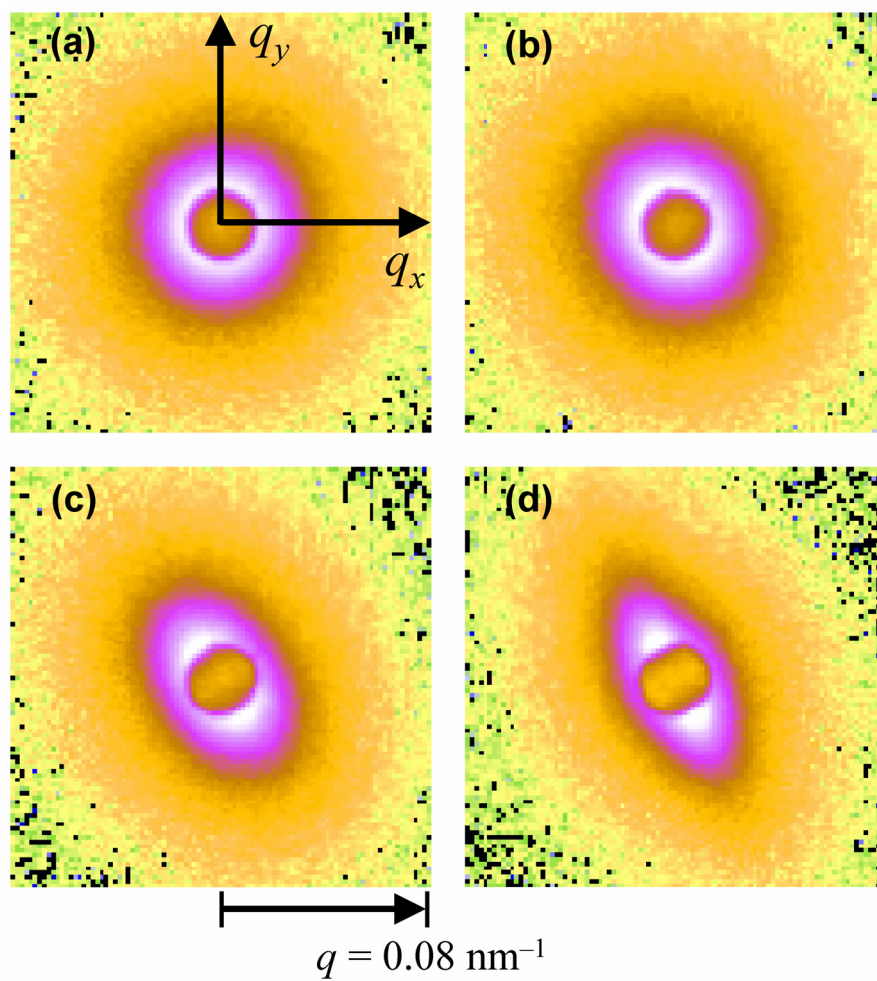


Figure 3.17. Representative scattering patterns of an 80/20 weight% PS/PMMA blend: (a) quiescent (isotropic) conditions and immediately following a step strain at (b) 30%, (c) 70%, and (d) 300% strain.

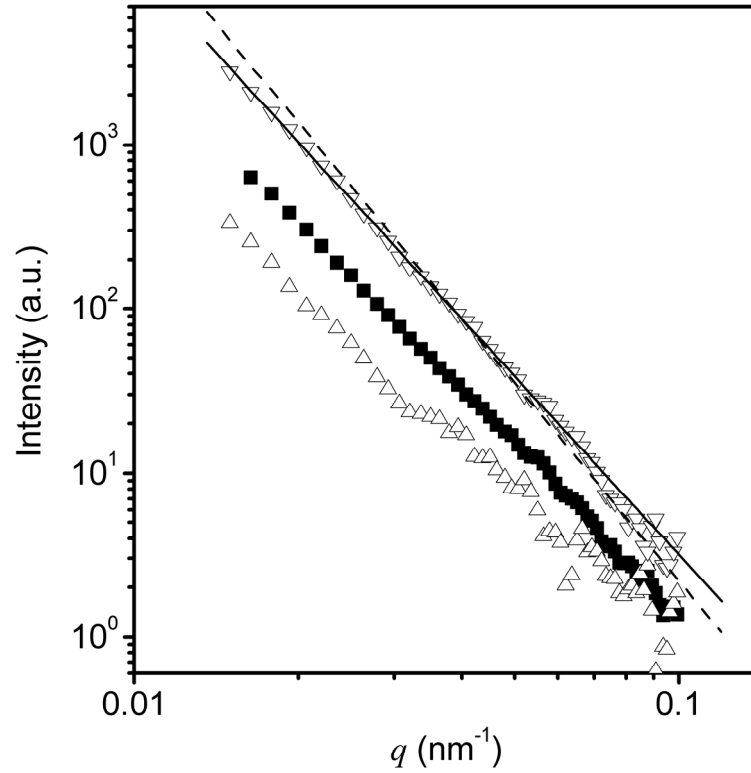


Figure 3.18. One-dimensional intensity scans extracted from 2-D patterns of an 80/20 wt% PS/PMMA blend at quiescent conditions (■) and immediately following a 300% step strain (Δ, ∇). (Δ) and (∇) represent data along the principal axes at $\varphi = 0$ and $\varphi = \pi/2$, respectively. The dashed line represents Porod's law ($I \sim q^{-4}$), and the solid line represents $I \sim q^{-3.6}$.

quiescent conditions and immediately following a 300% step strain. The data corresponding to the 300% step strain were extracted along the principal directions (at $\varphi = 0$ and $\varphi = \pi/2$). At $\varphi = \pi/2$, for example, the increase in intensity from the quiescent state reflects an increase in the amount of interface whose normal is parallel with that direction. The 300% step data at $\varphi = 0$ exhibits a shoulder at $q \sim 0.03 \text{ nm}^{-1}$, which is evident in most of the data that scatter within this lower intensity range. This feature may be associated with some residual background noise and/or parasitic scattering due to imperfect collimation of the beam.

The 1-D scattering data in Figure 3.18 show $I \sim q^{-3.6}$ rather than the expected $I \sim q^{-4}$. This q -dependence is consistent for all scattering data, under quiescent and shear conditions. SEM micrographs collected from several regions within the blend sample show a fairly low polydispersity in droplet sizes (Figure 3.15) in comparison to the pulverized sample presented in the coarsening study (Figure 3.12). The positive deviation from Porod's law observed in this set of scattering data is, therefore, unlikely to be related to the droplet size distribution. Even after subtraction of the detector background noise, the intensity across the detector area protected by the beam stop is significant ($\sim 10\%$ of the highest measured intensity from the blend at low q) and may be related to some flare from the incident beam. If some of this parasitic scattering persists beyond the beam stop to wider scattering angles, it could cause the deviation from the expected q -dependence in our data. Regardless of the source of the deviation, we consider the deviation to be fairly small and proceed with our analysis of the data.

As discussed earlier, we cannot determine an average droplet size from the SAXS data due to our inability to calibrate the data to absolute units. If we assume the fluctuations in the beam intensity and sample thickness to be negligible over the duration of a single experiment, the measured intensity, $I_m(q)$, differs from the absolute intensity for all time points by a multiplication factor, C_{abs} :

$$I(q) = C_{abs} I_m(q). \quad (3.24)$$

This multiplication factor can be conveniently lumped into the isotropic Porod coefficient [$K_P = C_{abs} \cdot 2\pi(\Delta\rho)^2(S/V)$], which can be determined from scattering data collected at quiescent conditions prior to each experiment. According to the ellipsoid model, $K_P(\varphi)$ determined from anisotropic scattering data can be normalized by K_P to give

$$\frac{K_P(\varphi)}{K_P} = \frac{1}{[\varepsilon_1^2 \cos^2 \varphi + \varepsilon_2^2 \sin^2 \varphi]^2}, \quad (3.25)$$

which shows the effect of the droplet stretch ratios on the scattered intensity profile along the azimuthal direction. ε_1 and ε_2 can then be independently computed from values of $K_P(\varphi)/K_P$ at $\varphi = 0$ and $\varphi = \pi/2$, respectively. Therefore, although the size of the droplets cannot be obtained from K_P in our experiments, changes in the droplet shape (as described by the ellipsoid scattering model) can still be determined.

To compute $K_P(\varphi)/K_P$, the 2-D scattering patterns (for quiescent and anisotropic data) were first divided azimuthally into 10° sections. The pixels within each section were then averaged azimuthally and radially to obtain a single average intensity value, $I_{avg}(\varphi)$, for that section. Lastly, dividing $I_{avg}(\varphi)$ from an anisotropic scattering pattern by $I_{avg}(\varphi)$ from quiescent data yields $K_P(\varphi)/K_P$. Figure 3.19 shows $K_P(\varphi)/K_P$ for the 300%

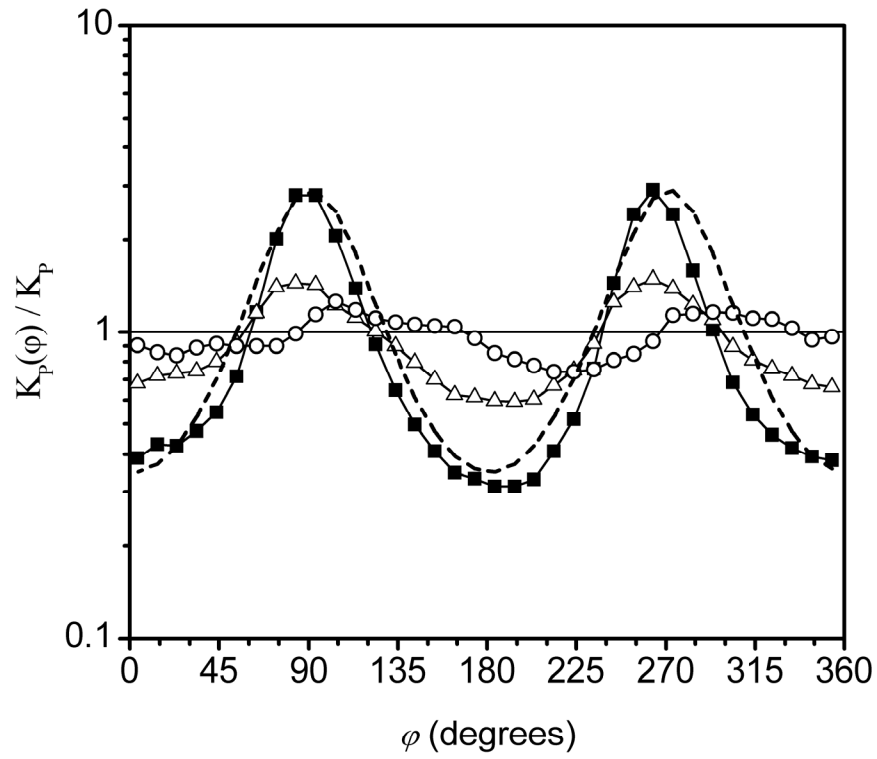


Figure 3.19. Normalized anisotropic Porod coefficient as a function of φ for an 80/20 wt% PS/PMMA blend immediately following a 300% step strain: (■) $t = 0$, (Δ) $t = 1$ second, and (○) $t = 2$ seconds. The dashed line represents $K_P(\varphi)/K_P$ according to the ellipsoid model (eqn. 3.25) using ε values extracted along principal directions $\varphi = 0$ and $\varphi = \pi/2$.

step strain experiment. These data clearly show anisotropy immediately after the step strain, followed by relaxation back towards an isotropic state ($K_P(\varphi)/K_P \rightarrow 1$).

Extracting $K_P(\varphi)/K_P$ values at $\varphi = 0$ and $\varphi = \pi/2$ from the data set at $t = 0$ gives $\varepsilon_1 = 1.301$ and $\varepsilon_2 = 0.821$ as the droplet stretch ratios resulting from a 300% step strain. The degree of deformation described by these values is fairly small, especially considering the closely matched homopolymer viscosities ($\eta_{\text{PMMA}}/\eta_{\text{PS}} \sim 1.5$) and the large magnitude of the applied strain. Substitution of ε_1 and ε_2 back into the full expression for $K_P(\varphi)/K_P$ given by eqn. 3.25 shows that the scattering model does not fully capture the intensity profile observed in experiment (Figure 3.19).

To obtain a rough estimate of the “expected” deformation, we consider the case of affine deformation of an ellipsoid where the major stretch ratio is related to the applied shear strain, γ_0 , by [Elemans *et al.* (1993)]

$$\varepsilon_1 = \sqrt{1 + \frac{\gamma_0^2}{2} + \frac{\gamma_0}{2} \sqrt{\gamma_0^2 + 4}} \quad (3.26)$$

and $\varepsilon_2 = 1/\varepsilon_1$. In blends consisting of Newtonian phases with nearly matched viscosities, droplets tend to deform affinely immediately following inception of flow at high deformation rates [Almusallam *et al.* (2000); Yamane *et al.* (1998)]. According to eqn. 3.26, 300% strain yields $\varepsilon_1 = 3.3$ and $\varepsilon_2 = 0.30$, showing much greater deformation than the ε values obtained from applying $K_P(\varphi)/K_P$ (eqn. 3.25) to the experimental data. The ellipsoid scattering model gives the following expression for the anisotropy factor in terms of the stretch ratios:

$$AF = \frac{Q_2 - Q_1}{Q_0} = \frac{1}{\varepsilon_1 \varepsilon_2^3} - \frac{1}{\varepsilon_1^3 \varepsilon_2} \quad (3.27)$$

where the principal values have been normalized by the quiescent state. For an ellipsoid that deforms affinely in response to a 300% step strain, we expect $AF = 11$. Therefore, the ellipsoid model describes extremely large amounts of scattering anisotropy associated with only moderate amounts of droplet deformation. This initial glance at the single ellipsoid model for determination of droplet shape suggests that the model may not apply to our blend system. To further characterize the shear-induced deformation in the blend and investigate the applicability of the model in this case, we employ a second moment tensor analysis.

3.4.3.2. Second Moment Tensor Analysis

Before calculating the second moment tensor, a mask was placed over the beam stop and over the outer regions of the 2-D scattering patterns, as shown in Figure 3.20. This mask fixes the range of q -values to be included in the analysis such that the q -range is the same along all radial directions ($q = 0.015 - 0.102 \text{ nm}^{-1}$). For all masked, time-resolved scattering patterns, $\langle \mathbf{q}\mathbf{q} \rangle$ was computed as given by eqn. 2.14. The principal anisotropy factor and orientation angle were then calculated using eqns. 2.16 and 2.17, respectively.

To allow for convenient interpretation of the data, the second moment tensor was normalized by the quiescent condition. This was accomplished by first computing $\langle \mathbf{q}\mathbf{q} \rangle$ for several quiescent patterns collected prior to each shear experiment, and then computing the average of each quiescent $\langle \mathbf{q}\mathbf{q} \rangle$ component. For a true isotropic sample,

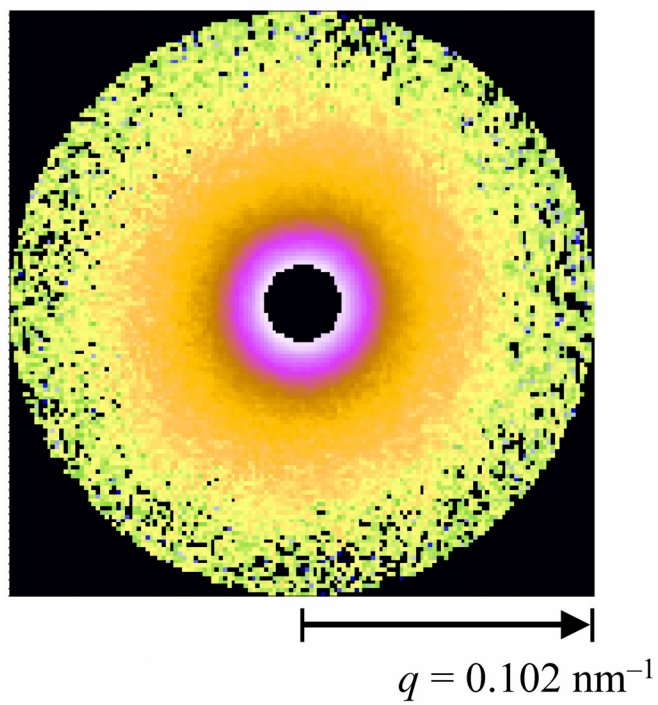


Figure 3.20. Two-dimensional quiescent scattering pattern with the mask applied prior to calculation of the second moment tensor for *in situ* SAXS studies of an 80/20 wt% PS/PMMA blend.

the diagonal components are equal [$\langle q_x q_x \rangle = \langle q_y q_y \rangle$], and the off-diagonal components, $\langle q_x q_y \rangle$, are zero. However, a small difference (5 – 10%) between the experimental $\langle q_x q_x \rangle$ and $\langle q_y q_y \rangle$ was observed, and $\langle q_x q_y \rangle$ exhibited non-zero values. We proceeded by defining the quiescent state as the average of the quiescent diagonal components:

$$\frac{1}{2} \langle qq \rangle_0 = \frac{1}{2} [\langle q_x q_x \rangle + \langle q_y q_y \rangle]_0.$$

Then, $\langle \mathbf{q}\mathbf{q} \rangle$ for each shear experiment was normalized by $\frac{1}{2} \langle qq \rangle_0$. At this time, we cannot provide a definitive explanation for the slight anisotropy observed at quiescent conditions. Some possibilities include slight anisotropy in the sample, non-uniform sensitivity of the detector pixels, and/or some asymmetric stray scattering associated with imperfect collimation of the beam.

In Figure 3.21(a), the “quiescent”-normalized $\langle \mathbf{q}\mathbf{q} \rangle$ components are plotted as a function of time for the 300% step strain experiment. The diagonal components show significant noise that is largely associated with fluctuations in the incident beam intensity with time (which we could not measure). Because of these fluctuations and the difference between $\langle q_x q_x \rangle$ and $\langle q_y q_y \rangle$ observed at quiescent conditions ($t < 0$), it is difficult to distinguish changes in these individual components resulting from the step strain. To more easily observe changes in $\langle q_x q_x \rangle$ and $\langle q_y q_y \rangle$, the baselines of these components were shifted to unity. This was performed by subtracting the average quiescent value of $\langle q_x q_x \rangle$ (or $\langle q_y q_y \rangle$) from $\langle q_x q_x \rangle$ (or $\langle q_y q_y \rangle$) for all time points. Similarly, the baseline for $-\langle q_x q_y \rangle$ was shifted to zero. Adjusting the baselines in this

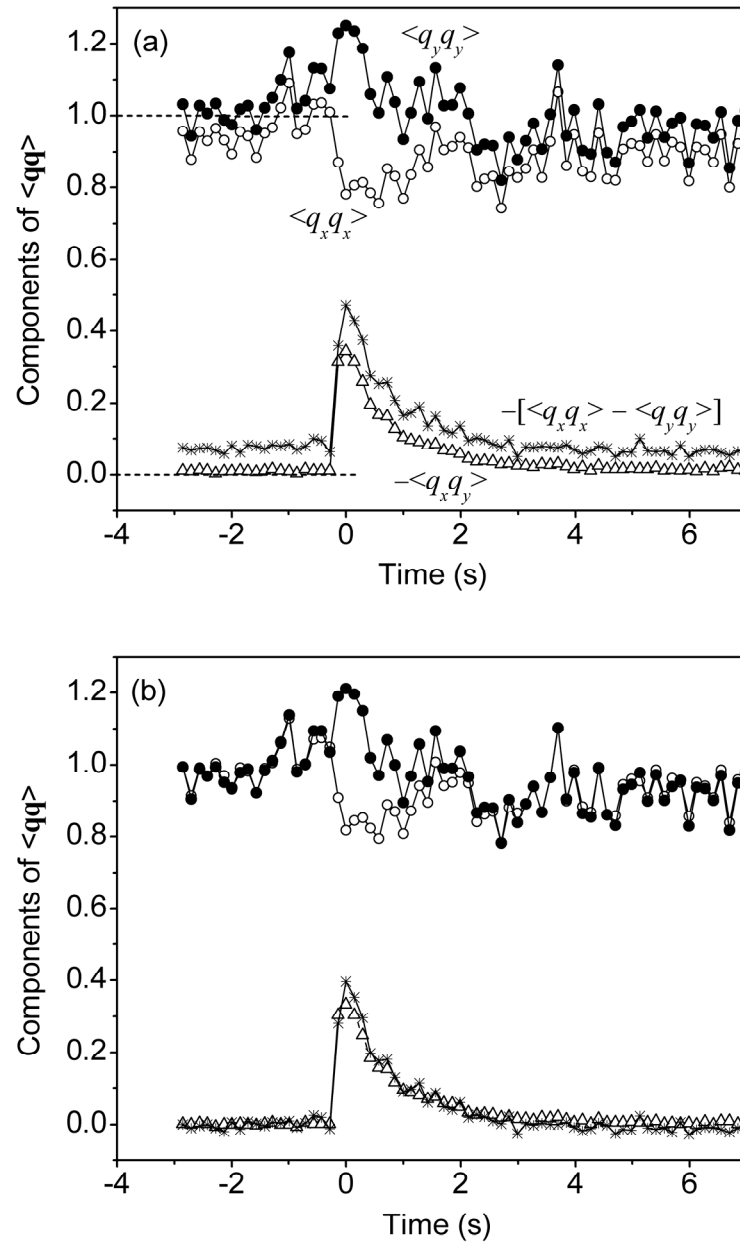


Figure 3.21. Components of $\langle qq \rangle$ for an 80/20 wt% PS/PMMA blend subjected to a 300% step strain: (a) normalized by the quiescent state, $\frac{1}{2}\langle qq \rangle_0$, (b) quiescent-normalized and baseline-adjusted. The zero time point ($t = 0$) is defined as the time at which application of the step strain has been completed.

way (*i.e.*, to the definition of an isotropic state) also produces more realistic values of the principal anisotropy factor and orientation angle.

The quiescent-normalized, baseline-adjusted $\langle \mathbf{q}\mathbf{q} \rangle$ components for the 300% step strain experiment are shown in Figure 3.21(b). Upon application of the step strain, $\langle q_x q_y \rangle$ grows in magnitude due to the increased scattering within the second and fourth quadrants of the 2-D pattern, which produces a negative value. Simultaneously, $\langle q_x q_x \rangle$ decreases and $\langle q_y q_y \rangle$ increases, resulting in anisotropy between the diagonal components $[\langle q_x q_x \rangle - \langle q_y q_y \rangle]$. The quantities $\langle q_x q_y \rangle$ and $[\langle q_x q_x \rangle - \langle q_y q_y \rangle]$ relax at the same rate, indicating that the droplets relax at equal rates along both principal axes. The anisotropy in the scattering relaxes over ~ 2 seconds, which is comparable to the droplet relaxation time observed in rheological measurements.

The principal values of $\langle \mathbf{q}\mathbf{q} \rangle$, the orientation angle, and the principal anisotropy factor for the 300% step strain are shown in Figure 3.22. The orientation angle remains nearly constant during relaxation, which is a consequence of equal relaxation rates of $\langle q_x q_y \rangle$ and $[\langle q_x q_x \rangle - \langle q_y q_y \rangle]$. The random fluctuations in χ at long times are due to the fact that the formula for χ (eqn. 2.17) becomes ill-defined as anisotropy relaxes. Also, the normalized anisotropy factor shows significant degree of alignment of the interface in the blend resulting from the applied deformation. However, the value for AF immediately following the step strain ($AF = 0.76$) is only a small fraction of the anisotropy predicted by the ellipsoid scattering model for the case of affine deformation ($AF = 11$) as discussed earlier.

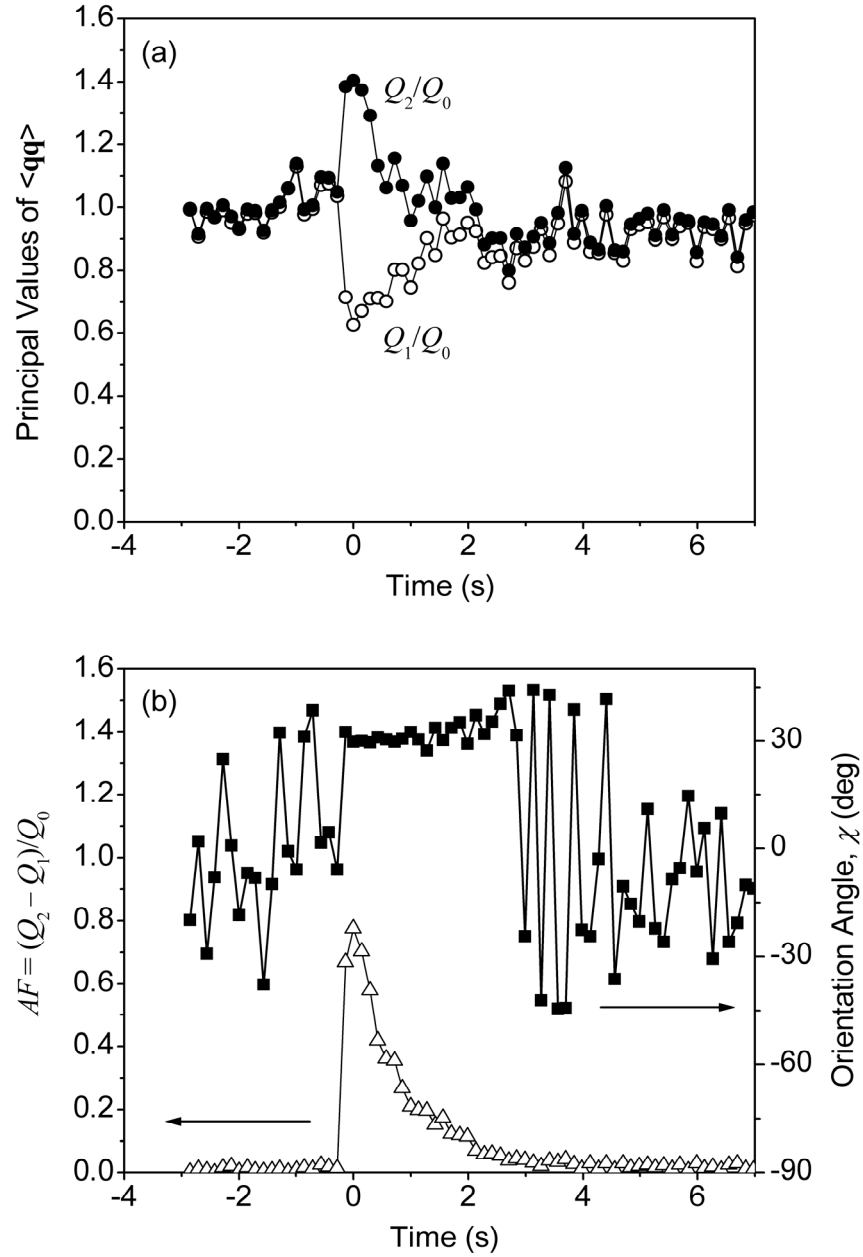


Figure 3.22. (a) Principal values of $\langle \mathbf{qq} \rangle$ for an 80/20 wt% PS/PMMA blend subjected to a 300% step strain. (b) The corresponding principal anisotropy factor and orientation angle. The data have been computed from quiescent-normalized, baseline-adjusted $\langle \mathbf{qq} \rangle$.

The principal stretch ratios of the droplets, determined from the second moment tensor analysis (using eqns. 3.18 – 3.20), are plotted as a function of time in Figure 3.23. The values of ε_1 and ε_2 immediately following the step strain are similar to those obtained from one-dimensional scattering data extracted at $\varphi = 0$ and $\varphi = \pi/2$. Again, the droplet deformation is less severe than we would expect for such a large strain. These results underline the fact that the ellipsoid model shows a very strong dependence of scattering anisotropy on the anisotropy of the droplet.

At small strains, the fluctuations in the beam intensity overwhelm the changes occurring in the diagonal components of $\langle \mathbf{q}\mathbf{q} \rangle$ upon application of step strain. This is illustrated in Figure 3.24 for the case of a 30% step strain. In the computation of $\langle q_x q_y \rangle$ and $[\langle q_x q_x \rangle - \langle q_y q_y \rangle]$, on the other hand, information related to the magnitude of the beam intensity naturally cancels out, producing much smoother results for these quantities. Consequently, the fluctuations in the beam intensity are also not reflected in the principal anisotropy factor and orientation angle. The principal values and stretch ratios, however, strongly depend on the values of the individual $\langle q_x q_x \rangle$ and $\langle q_y q_y \rangle$ components. Thus, the absolute values of ε_1 and ε_2 are unreliable at low strains, as shown in Figure 3.25, due to the large fluctuations in the beam intensity.

In order to improve the quality of the data at low strains, normalization by some quantity related to the beam intensity is required. To obtain this information, we consider the sum of the diagonal components $\langle q_x q_x \rangle + \langle q_y q_y \rangle$, which represents the total amount of scattering from the sample that is projected onto the 2-D detector. Note that this

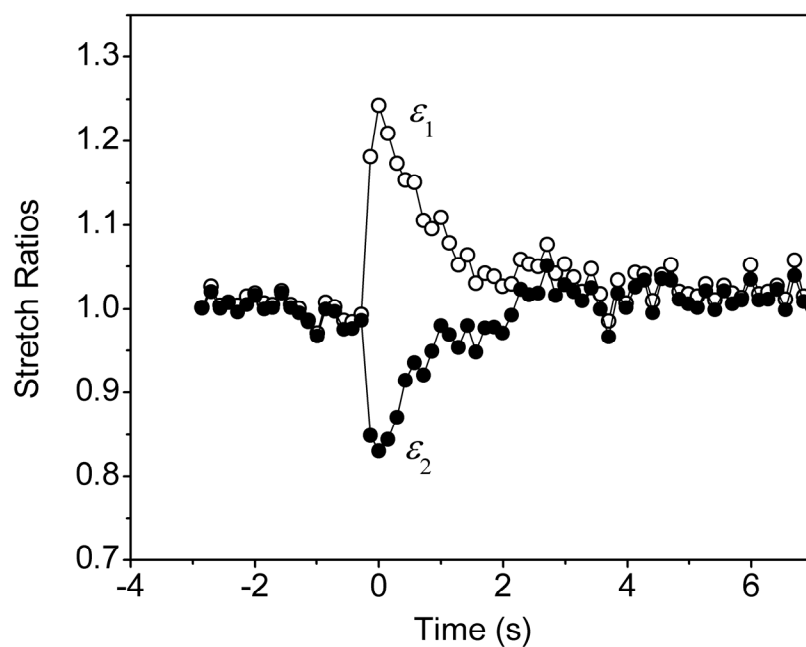


Figure 3.23. Principal stretch ratios of the deformed droplets in an 80/20 wt% PS/PMMA blend subjected to a 300% step strain. Values were determined from quiescent-normalized, baseline-adjusted $\langle \mathbf{qq} \rangle$.

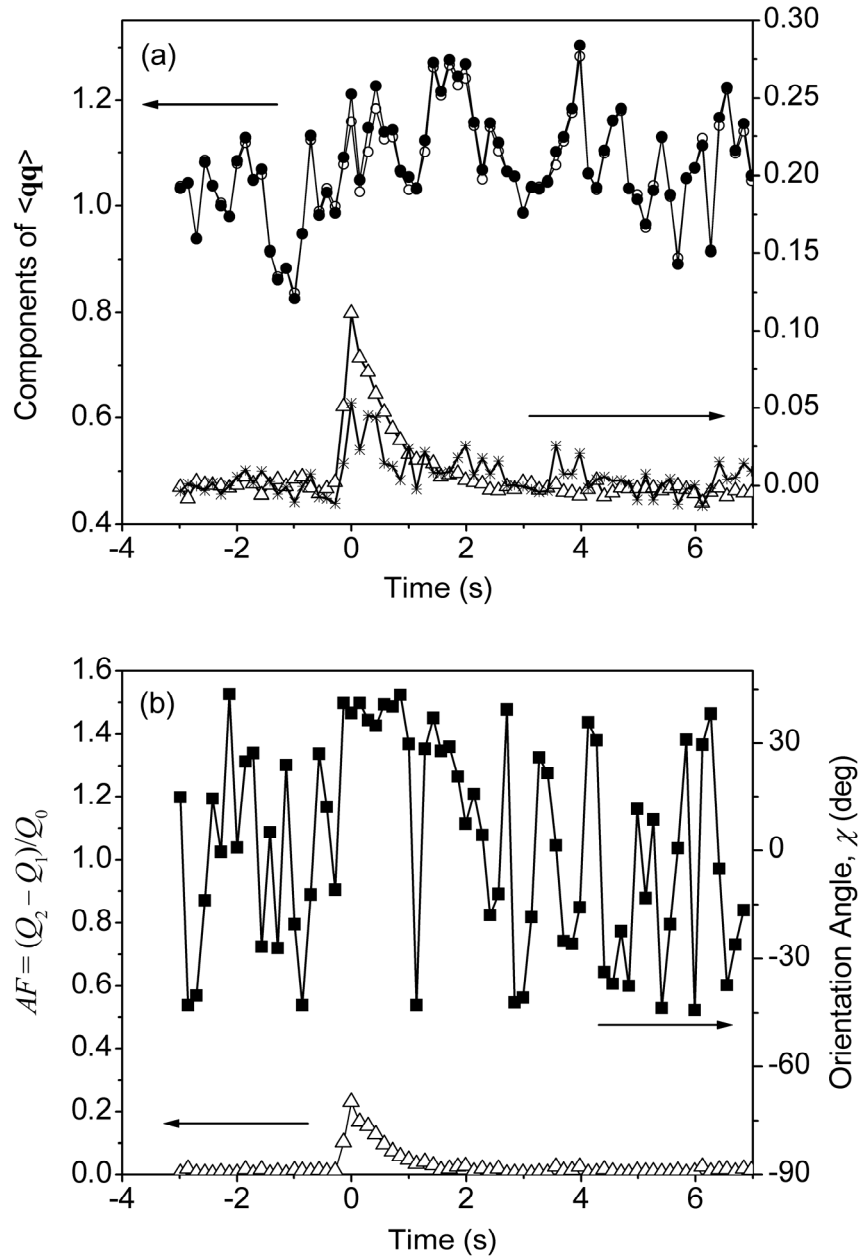


Figure 3.24. (a) Components of $\langle \mathbf{q}\mathbf{q} \rangle$ for an 80/20 wt% PS/PMMA blend subjected to a 30% step strain: ($\circ$) $\langle q_x q_x \rangle$, ($\bullet$) $\langle q_y q_y \rangle$, (Δ) $-\langle q_x q_y \rangle$, ($*$) $-\langle [q_x q_x] - [q_y q_y] \rangle$. (b) The corresponding principal anisotropy factor and orientation angle. $\langle \mathbf{q}\mathbf{q} \rangle$ has been normalized by the quiescent state and baseline-adjusted.

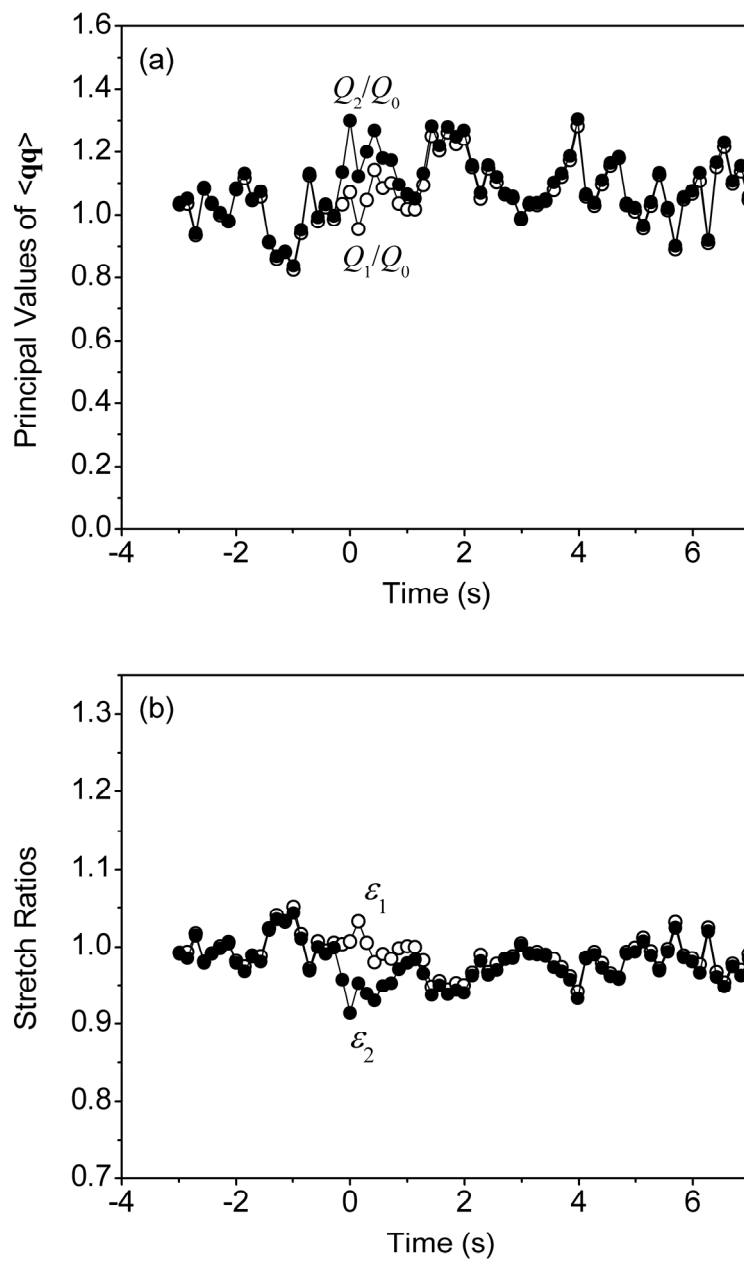


Figure 3.25. (a) Principal values of $\langle \mathbf{qq} \rangle$ and (b) principal stretch ratios for an 80/20 wt% PS/PMMA blend subjected to a 30% step strain. The data have been computed from quiescent-normalized, baseline-adjusted $\langle \mathbf{qq} \rangle$.

equals the sum of the principal values, $Q_1 + Q_2$. Any change in the incident beam intensity with time will yield a proportional change in $\langle q_x q_x \rangle + \langle q_y q_y \rangle$. Additional changes in $\langle q_x q_x \rangle + \langle q_y q_y \rangle$ may occur due to rotation or creation of interface upon application of step strain, as implied by eqns. 3.10 and 3.16 (since the quantity of interface is contained within $K_P(\phi)$). In our data, however, any changes in $\langle q_x q_x \rangle + \langle q_y q_y \rangle$ that occur due to deformation of microstructure, even for the case of 300% step strain, are overwhelmed by fluctuations in the beam intensity (Figure 3.26). Since any changes associated with microstructure deformation are indistinguishable, we have “self”-normalized $\langle \mathbf{q}\mathbf{q} \rangle$ for each time point by its corresponding $\frac{1}{2}[\langle q_x q_x \rangle + \langle q_y q_y \rangle]$ to remove the dependence on the beam intensity.

The self-normalized, baseline-adjusted $\langle \mathbf{q}\mathbf{q} \rangle$ components for the 300% and 30% step strain are shown in Figures 3.27 and 3.28, respectively. The noise in the diagonal components has been nearly eliminated by the self-normalization procedure. As a result, small changes in these components associated with a 30% step strain are much more apparent. In the 300% step strain, the magnitudes of $\langle q_x q_x \rangle$ and $\langle q_y q_y \rangle$ immediately following the step strain ($t = 0$) do not differ significantly from the values in the quiescent-normalized case. In addition, for both the 30% and 300% step strains, self-normalization has minimally affected the magnitudes of $\langle q_x q_y \rangle$ and $[\langle q_x q_x \rangle - \langle q_y q_y \rangle]$ (and thus AF and χ). The consistency in the behavior of these quantities supports the validity of applying self-normalization to our data.

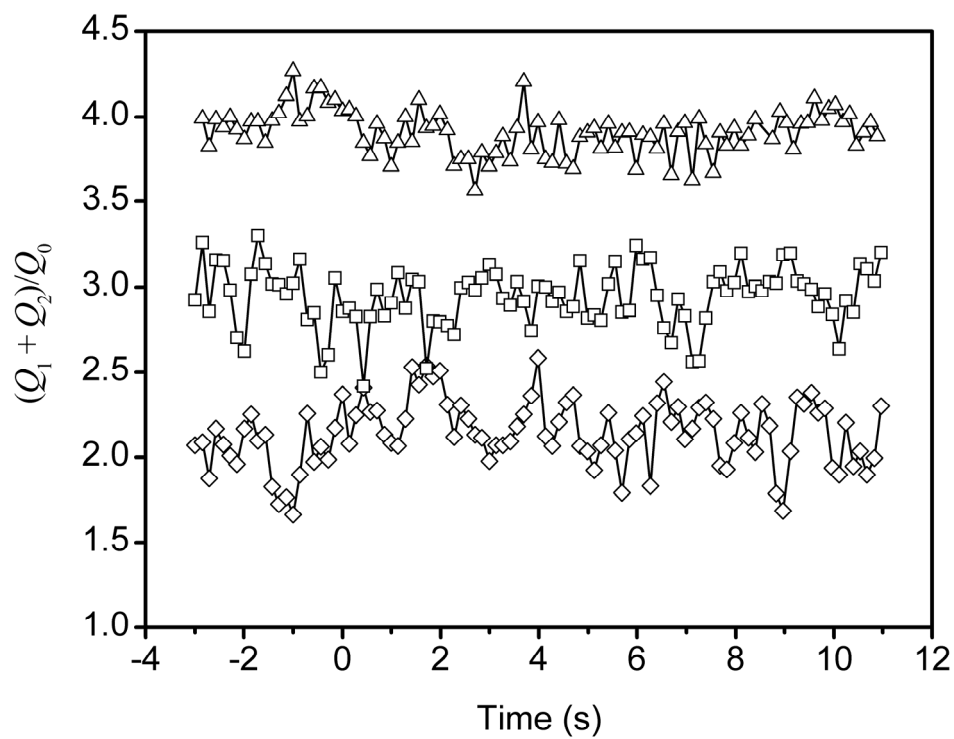


Figure 3.26. “Total” scattered intensity, normalized by the quiescent state $\frac{1}{2}\langle qq \rangle_0$, as a function time during a step strain experiment at ($\diamond$) 30%, ($\square$) 70%, and (Δ) 300% strain. The 70% and 300% data have been shifted using multiplication factors of 1.5 and 2, respectively.

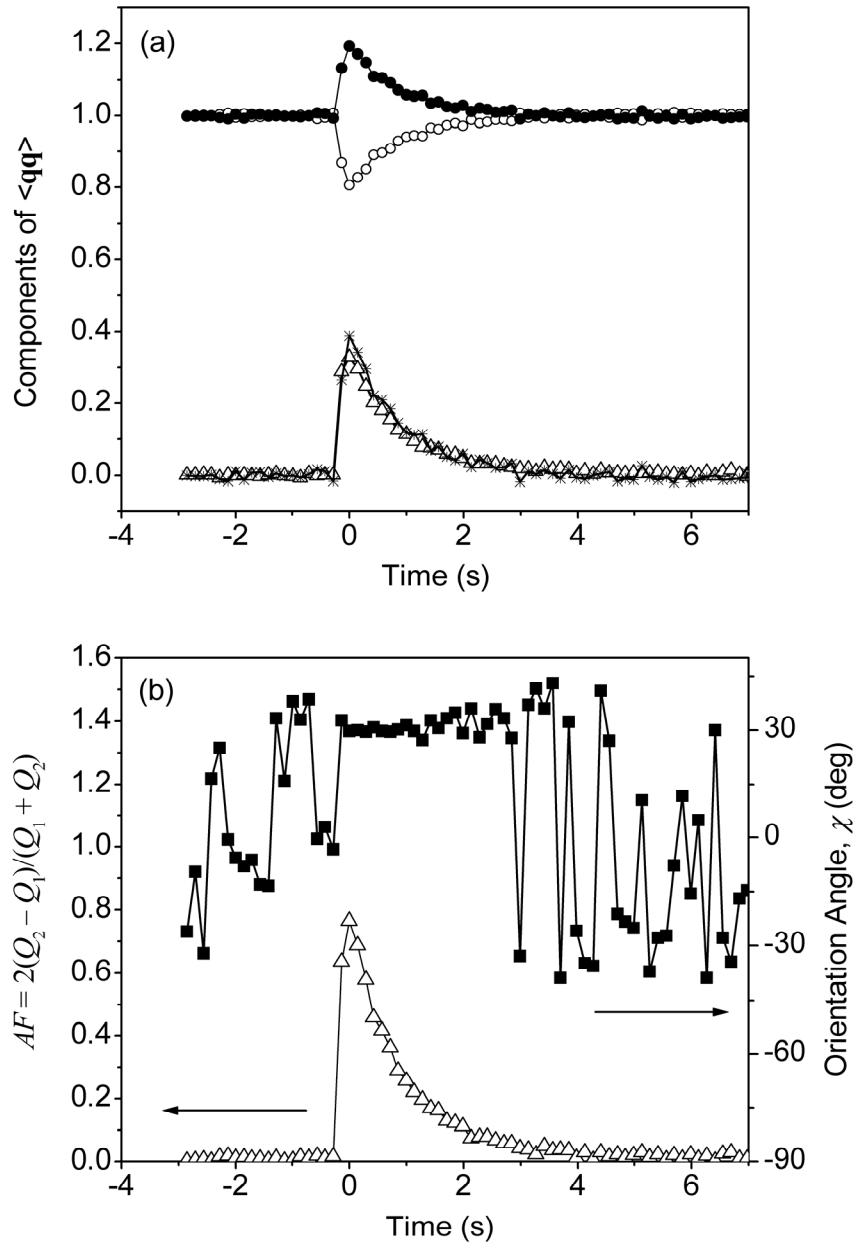


Figure 3.27. (a) Components of $\langle \mathbf{q}\mathbf{q} \rangle$ for an 80/20 wt% PS/PMMA blend subjected to a 300% step strain: (○) $\langle q_x q_x \rangle$, (●) $\langle q_y q_y \rangle$, (Δ) $-\langle q_x q_y \rangle$, (*) $-\langle q_y q_x \rangle$. (b) The corresponding principal anisotropy factor and orientation angle. $\langle \mathbf{q}\mathbf{q} \rangle$ has been self-normalized by $\frac{1}{2}[\langle q_x q_x \rangle + \langle q_y q_y \rangle]$ and baseline-adjusted.

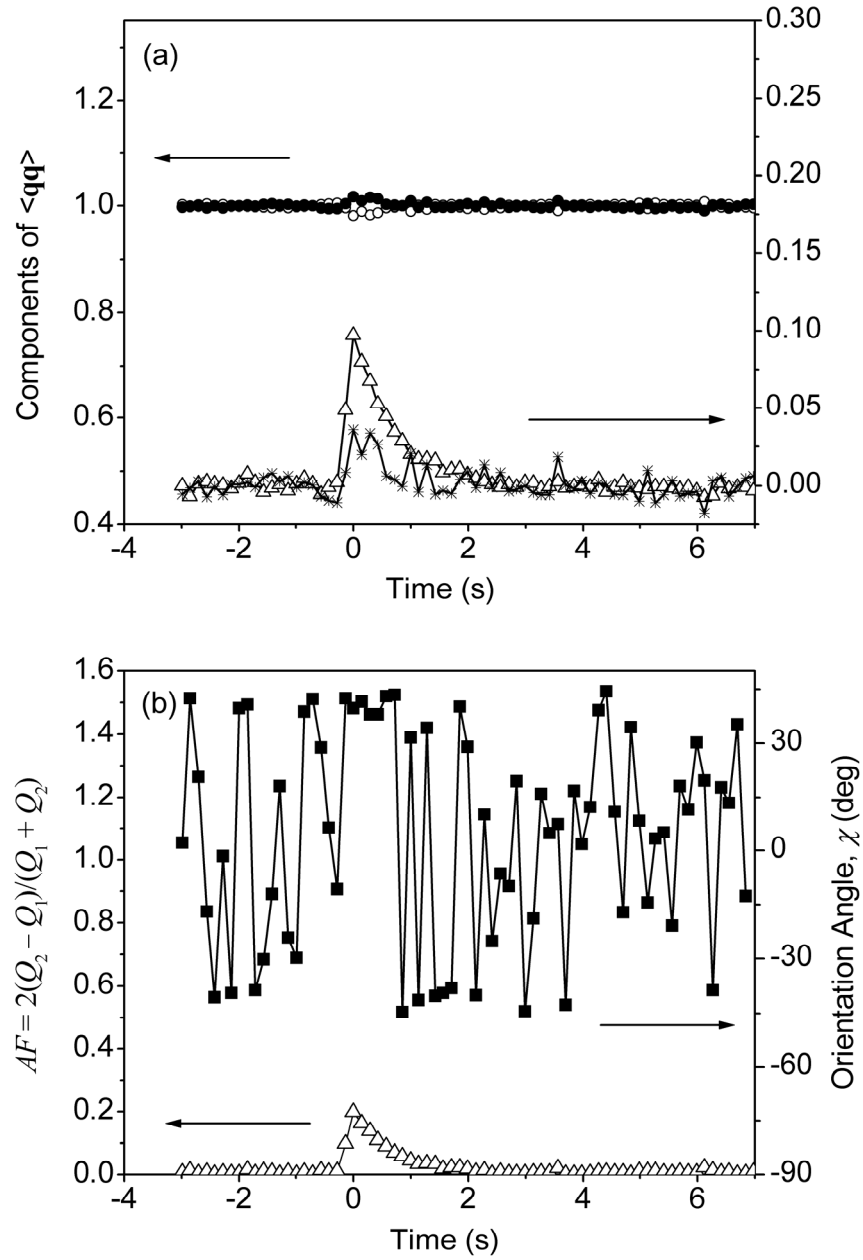


Figure 3.28. (a) Components of $\langle \mathbf{q}\mathbf{q} \rangle$ for an 80/20 wt% PS/PMMA blend subjected to a 30% step strain: ($\circ$) $\langle q_x q_x \rangle$, ($\bullet$) $\langle q_y q_y \rangle$, (Δ) $-\langle q_x q_y \rangle$, ($*$) $-\langle q_x q_y \rangle$. (b) The corresponding principal anisotropy factor and orientation angle. The data have been self-normalized and baseline-adjusted.

Information regarding the microstructure (in the x - y plane) is contained within two quantities: (1) the first invariant of $\langle \mathbf{q}\mathbf{q} \rangle$ (eqn. 3.21) and (2) the principal anisotropy factor (eqn. 3.23), which are both obtained from $\langle \mathbf{q}\mathbf{q} \rangle$ determined within the experimental coordinate frame. With self-normalization of the data, the information contained in the invariant is lost. Thus, the principal values cannot be independently determined and, consequently, neither can the principal stretch ratios. However, using appropriate assumptions, some information may be extracted from the principal anisotropy factor.

For the case of self-normalization, the principal anisotropy factor is given by

$$AF = \frac{Q_2 - Q_1}{\frac{1}{2}(Q_1 + Q_2)}. \quad (3.28)$$

Substituting the expressions for Q_1 and Q_2 as defined by the ellipsoid model (eqns. 3.18 – 3.19) then gives AF in terms of the stretch ratios:

$$AF = \frac{\varepsilon_1^2 - \varepsilon_2^2}{\varepsilon_1^2 + \varepsilon_2^2}. \quad (3.29)$$

Since AF is the only known quantity related to the stretch ratios, additional assumptions about the relationship between ε_1 and ε_2 must be employed to solve for these quantities independently.

We examine two extreme cases of deformation which provide simple relationships between the stretch ratios. For uniaxial deformation of droplets, the cross-section of the droplet remains symmetric:

$$\varepsilon_2 = \varepsilon_3 = \frac{1}{\sqrt{\varepsilon_1}} \quad (3.30)$$

where conservation of volume imposes the constraint $\varepsilon_1 \varepsilon_2 \varepsilon_3 = 1$. In the case of planar deformation, the droplet radius along the vorticity direction remains unaffected by shear flow:

$$\varepsilon_2 = \frac{1}{\varepsilon_1}, \quad \varepsilon_3 = 1. \quad (3.31)$$

Affine deformation of droplets in shear flow would lead to the planar deformation case. As mentioned earlier, this type of deformation might be expected in a system with roughly matched viscosities and rapid deformation during the step strain. On the other hand, direct droplet visualization has shown rapid “transverse” relaxation towards a uniaxially symmetric ellipsoidal shape under the influence of surface tension [Almusallam *et al.* (2000); Jansseune *et al.* (2001)]; on longer times, droplets relax back to spherical shape while retaining uniaxial symmetry. For our purposes, these two limiting cases serve to bracket the range of droplet shape expected in these experiments.

Solving for ε_1 in terms of the self-normalized principal anisotropy factor yields

$$\varepsilon_1 = \left[-\frac{AF + 1}{AF - 1} \right]^{1/3} \quad (\text{uniaxial deformation}) \quad (3.32)$$

$$\varepsilon_1 = \left[-\frac{AF + 1}{AF - 1} \right]^{1/4}. \quad (\text{planar deformation}) \quad (3.33)$$

We emphasize again that these assumed deformation types are implemented under the restriction of a fixed invariant, a consequence of self-normalization. Figure 3.29 shows the principal stretch ratios, based on the assumptions of uniaxial and planar deformation, resulting from 300% and 30% step strain. Using these assumed deformation types produces similar values of ε_1 and ε_2 as obtained in the case of normalization by the

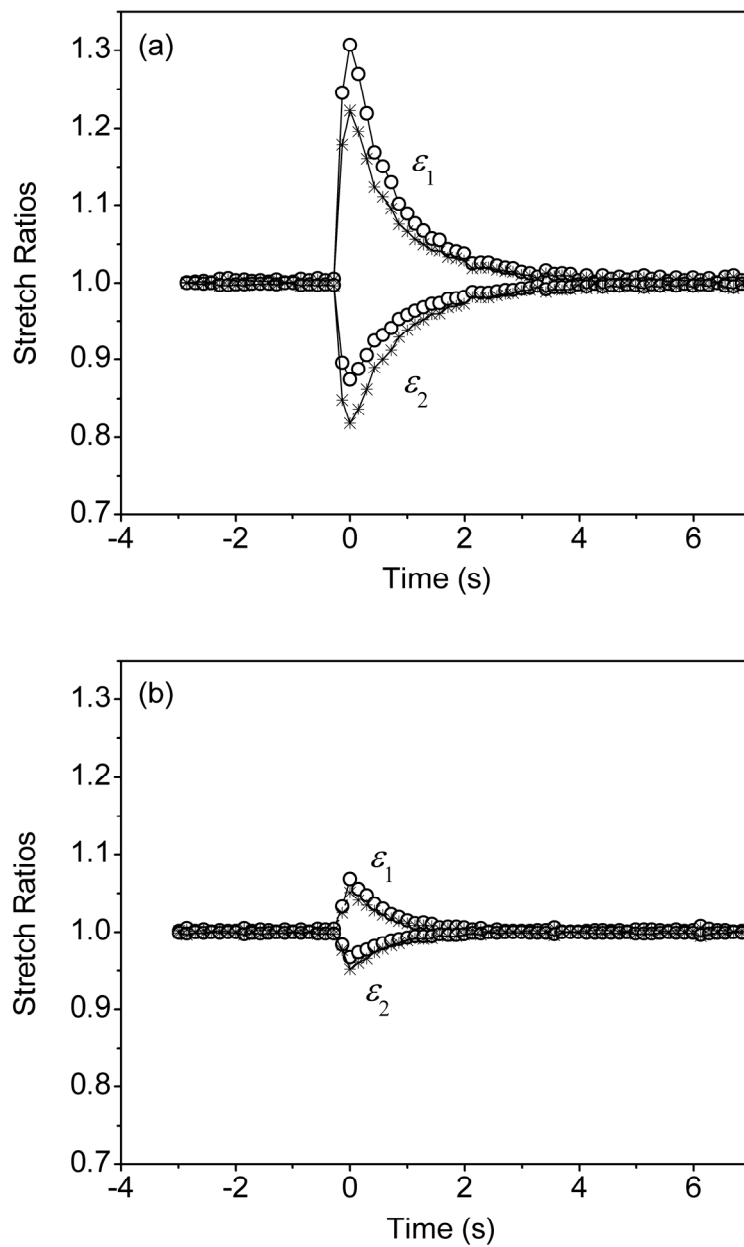


Figure 3.29. Principal stretch ratios of the deformed droplets in an 80/20 wt% PS/PMMA blend subjected to (a) 300% and (b) 30% step strain. Values were determined from self-normalized, baseline-adjusted $\langle \mathbf{qq} \rangle$ and assuming either uniaxial ($\circ$) or planar ($*$) deformation.

quiescent state (*i.e.*, no imposed deformation type), but the noise associated with beam fluctuations has been eliminated.

The stretch ratios determined via the different analytical approaches for $t = 0$ are summarized in Table 3.1. For the higher strains (70% and 300%), ε values computed using the quiescent-normalization approach fall in between the values computed using self-normalization with the assumed deformation types, as we might have expected. In the case of the lower strain (30%), quiescent normalization gives stretch ratios outside the values obtained using self-normalization. Presumably, the values computed using the self-normalization approaches are more reliable for the lower strain data since self-normalization eliminates effects of fluctuations in beam intensity. For comparison, stretch ratios expected for affine deformation in response to a specified strain (given by eqn. 3.26) are provided in the bottom row of Table 3.1.

As discussed earlier, analysis of the x-ray data using the single ellipsoid scattering model yields fairly low droplet deformation when compared to the values expected for affine deformation. One possible explanation for the much lower than “expected” stretch ratios is that the dispersed and matrix phases both exhibit viscoelastic character (Figure 3.16). The effects of viscoelasticity of the individual phases on the deformation and relaxation of the dispersed phase is not well-understood; however, elasticity of the droplet phase has been reported in some cases to stabilize the droplets to deformation [Lerdwijitjarud *et al.* (2002) and references therein]. We also note that the viscosity of the dispersed phase in our experiment is slightly greater than the matrix viscosity, which results in smaller deformation than would occur in a more matched system [Grace

Table 3.1. Principal Droplet Stretch Ratios as Given by the Single Ellipsoid Model for an 80/20 wt% PS/PMMA Blend Subjected to Step Strain.

	30% Strain		70% Strain		300% Strain	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
1D	1.018	0.899	1.230	0.857	1.301	0.821
2D-QN	1.032	0.952	1.193	0.888	1.242	0.831
2D-SN(u)	1.069	0.951	1.217	0.906	1.307	0.875
2D-SN(p)	1.051	0.967	1.159	0.863	1.223	0.818
Affine	1.161	0.861	1.409	0.710	3.303	0.303

1D: values determined from one-dimensional scattering data at $\varphi = 0$ and $\pi/2$.

2D-QN: values determined from quiescent-normalized $\langle \mathbf{q}\mathbf{q} \rangle$ data.

2D-SN(u): values determined from self-normalized $\langle \mathbf{q}\mathbf{q} \rangle$ data and assuming uniaxial deformation.

2D-SN(p): values determined from self-normalized $\langle \mathbf{q}\mathbf{q} \rangle$ data and assuming planar deformation.

Affine: values expected for affine deformation according to eqn. 3.26.

(1982)]. An alternative explanation for the lower than expected deformation is that the ellipsoid scattering model is not applicable to the blend system.

According to the single ellipsoid model, the ellipsoid scatters the least intensity along its major principal axis. Furthermore, the magnitude of the scattering along this direction depends strongly on the major principal stretch ratio ($I \sim \varepsilon_1^{-4}$). In considering a two-phase system with a distribution of droplet sizes, the smaller droplets will deform less than larger droplets under shear. Due to the ε_1^{-4} dependence, these less deformed, smaller droplets will dominate the scattering along the major principal axis. In addition, interactions between droplets in concentrated systems under shear may lead to a distribution in droplet orientation and/or non-ellipsoidal droplet shapes. Thus, the minimum intensity along the azimuthal direction in this case does not solely represent the major principal axis of a single deformed droplet. Also, elasticity in one or both of the blend phases can lead to non-ellipsoidal shapes. Examination of the single ellipsoid model in these contexts suggests how the model may become invalid for even a narrow distribution in droplet shape and/or orientation, leading to smaller than expected deformation for a polydisperse system when used to quantitatively analyze the data.

The SEM micrograph of the blend in Figure 3.15 shows a highly concentrated morphology with moderate polydispersity in droplet size. The small degree of droplet deformation for this system, as depicted by the ellipsoid model, underscores the significant impact of polydispersity on the anisotropic scattering behavior. Hamzeh and Bragg (1974) have considered the effects of polydispersity in size and orientation of

ellipsoids on the scattered intensity. However, their analysis provides a complex set of expressions that are difficult to implement for interpretation of experimental data.

Although we are unable, at this point, to make explicit connections between the scattering and droplet shape in an immiscible polymer blend in response to flow, we have successfully demonstrated that deformation and alignment of interface in these systems can be generally characterized using a second moment tensor analysis. The results from this study are summarized in Figure 3.30 and 3.31, which show the orientation angle and principal anisotropy factor, respectively, a function of applied step strain. Here, we again compare the data to expectations for affine deformation of microstructure, which gives the following prediction for the orientation angle [Elemans *et al.* (1993)]:

$$\chi = \frac{1}{2} \tan^{-1} \left(\frac{2}{\gamma_0} \right). \quad (3.34)$$

This relationship approximately holds for strains up to 100%. At higher strains, the behavior strongly deviates from the affine prediction, possibly due to interactions between droplets and/or elastic effects in the matrix and dispersed phases. Figure 3.31 shows that, as expected, the degree of alignment increases with increasing applied strain. In addition, we were able to observe the relaxation of the anisotropy with time as a result of our ability to collect measurements *in situ*.

3.4.4. Summary

Time-resolved small-angle x-ray scattering measurements were collected *in situ* for an immiscible binary homopolymer blend subjected to step strain deformation. This experiment accessed scattering from the blend in the Porod regime, allowing for

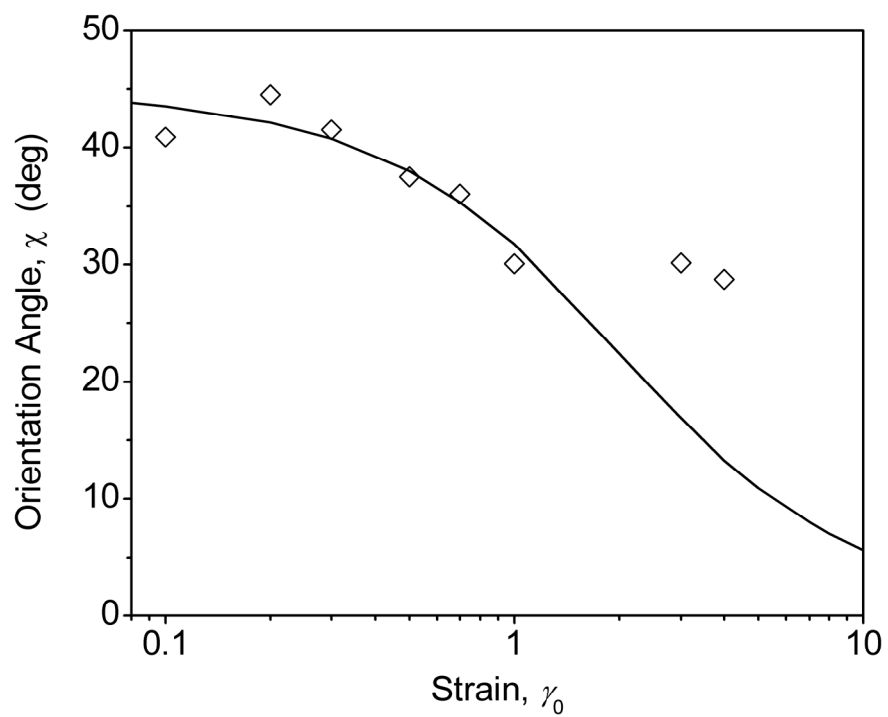


Figure 3.30. Initial orientation angle as a function of applied step strain for an 80/20 wt% PS/PMMA blend. The solid line represents predictions for affine deformation (eqn. 3.34).

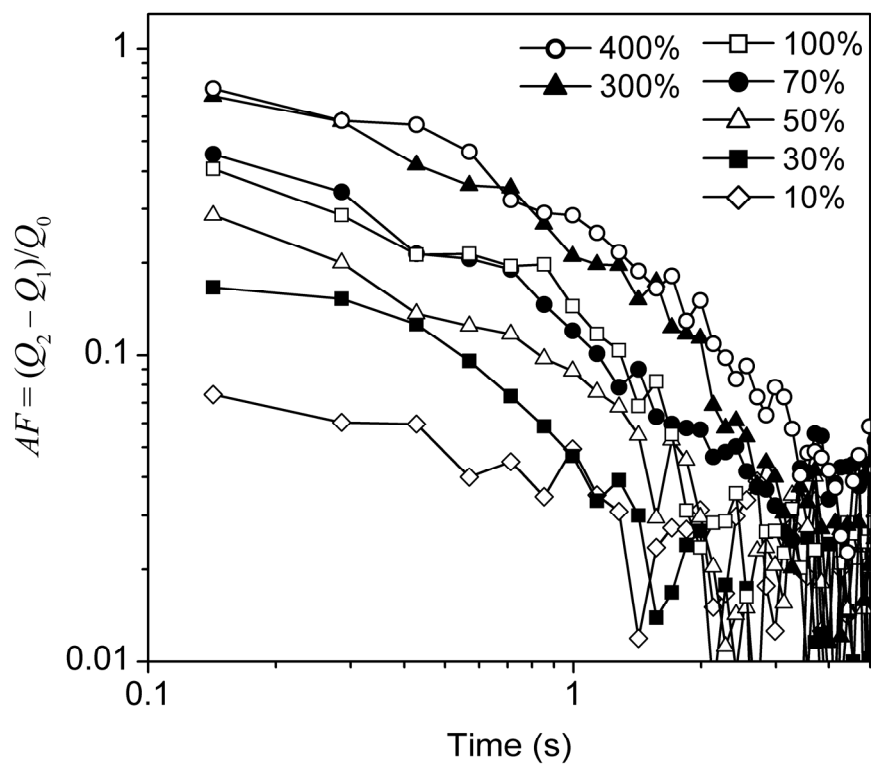


Figure 3.31. Principal anisotropy factor (computed from quiescent-normalized, baseline-adjusted $\langle \mathbf{qq} \rangle$) as a function of time for an 80/20 wt% PS/PMMA blend subjected to a step strain at various strains.

observation of shear-induced deformation of interface. The orientation and degree of alignment of interface was quantified by applying a second moment tensor analysis to the two-dimensional scattering patterns. In addition, the scattering from a single ellipsoid, as presented by Wu (1980), was examined as a potential model for determination of droplet shape from the SAXS measurements. Analyses using the ellipsoid model yielded extremely low levels of droplet deformation in response to applied step strain, despite the fact that the x-ray patterns themselves are highly anisotropic. The applicability of the model to these data may possibly be compromised by (1) non-ellipsoidal shapes of the dispersed droplets due to elastic effects or interactions between droplets in this concentrated dispersion, and/or (2) polydispersity in droplet shape arising from unequal deformation of different sized droplets.

This study marks the first experimental investigation of shear-induced structural dynamics in immiscible polymer blends via *in situ* SAXS. While quantitative analysis of changes in droplet shape would require more sophisticated models, these results demonstrate that the deformation of interface can be readily characterized using a second moment tensor analysis of the scattered intensity in the Porod regime. Furthermore, these results show that *in situ* SAXS techniques may serve as a valuable tool for studying structural dynamics in concentrated immiscible blends for which *in situ* techniques were not previously available. The experiments presented here were conducted using a single blend sample and a simple flow condition with moderate levels of deformation (*i.e.*, finite amounts of strain that did not result in droplet breakup). Additional studies are obviously

needed to fully define both the potential and limitations of *in situ* SAXS techniques for probing these systems.

CHAPTER 4.

EQUILIBRIUM AND SHEAR-INDUCED STRUCTURAL DYNAMICS OF A POLYMER BICONTINUOUS MICROEMULSION

4.1. Introduction

Polymer bicontinuous microemulsions (B μ E) are blends of two immiscible homopolymers (A and B) in equal volumes compatibilized by a symmetric diblock copolymer (A-B), resulting in an isotropic, cocontinuous morphology with a characteristic length scale of tens of nanometers. In contrast to typical cocontinuous immiscible blends, in which the micron-sized domains coarsen with time at high temperatures, bicontinuous microemulsions are a special case of a highly compatibilized system where the nanoscale microstructure exists at equilibrium. Interest in B μ Es originates from the technological significance of oil/water/surfactant (o/w/s) systems, which have many current industrial and biological applications [Paul and Moulik (2001); Schwuger *et al.* (1995); Tricoli *et al.* (2006)]. Recently, much focus has been directed towards polymer B μ Es; these systems possess significant potential for the development of new materials, such as a new class of nanoporous materials [Zhou *et al.* (2006a)].

Additionally, owing to the long chain polymer molecules, polymer bicontinuous microemulsions exhibit much slower dynamics than o/w/s systems, and, thus, may serve as model systems for studying the dynamics of the B μ E morphology.

While several polymer bicontinuous microemulsions have been formulated [Corvazier *et al.* (2001); Hillmyer *et al.* (1999); Lee *et al.* (2003); Pipich *et al.* (2004); Washburn *et al.* (2000); Zhou *et al.* (2006b)], the equilibrium and flow behavior has been extensively characterized for only a single polymer B μ E system [Burghardt *et al.* (2002); Caputo *et al.* (2002b); Krishnan *et al.* (2002a, 2002b); Morkved *et al.* (1999, 2000)]. This system, composed of poly(ethyl ethylene) (PEE), poly(dimethyl siloxane) (PDMS), and PEE-*b*-PDMS copolymer, revealed rich, complex dynamics associated with the interconnected morphology. Significant viscoelastic behavior was reported for equilibrium conditions and low shear rates; however, strong shear conditions eventually resulted in a structural transformation from the nanoscale B μ E to a microscale phase-separated morphology [Krishnan *et al.* (2001a)].

The slow (*i.e.*, experimentally accessible) dynamics of the PEE-PDMS B μ E enabled Burghardt and coworkers [Burghardt *et al.* (2002); Caputo *et al.* (2002b)] to perform the first test of predictions by Pätzold and Dawson (1996a, 1996b) for B μ E rheology and shear-induced structural behavior. This theoretical description, which is based on a time-dependent Landau-Ginzburg model, captured many of the qualitative features of the linear viscoelastic behavior and of the structural response at low shear rates. However, the model failed to predict the absolute values of the rheological parameters. Nor does the model predict phase-separation at high shear rates. The results

from the PEE-PDMS studies highlight some of the significant deficiencies in the Pätzold and Dawson theory. Accounting for these deficiencies presents a significant challenge, particularly since the underlying physics associated with the complex B μ E behavior are not well-understood.

In attempt to achieve a better understanding of bicontinuous microemulsions and to provide further insight for the development of theory, we have characterized the equilibrium and shear-induced dynamics of another B μ E composed of polystyrene (PS), polyisoprene (PI), and PS-*b*-PI. In our studies, the universality of the rheology and shear-induced structural dynamics of B μ Es was investigated by drawing direct comparisons to the previously documented PEE-PDMS B μ E. We have conducted *in situ* SAXS experiments that allowed for simultaneous observation of the shear-induced orientation of the B μ E structure and the evolution of phase-separated structures at high shear rates. In previous *in situ* SAXS experiments with the PEE-PDMS B μ E, only deformation of the B μ E structure was observable [Caputo *et al.* (2002b)]; thus, the structural changes during phase separation could not be fully characterized. Also, we have performed x-ray photon correlation spectroscopy experiments to probe equilibrium dynamics at length scales comparable to the B μ E domain size. These measurements were then employed to reevaluate the performance of the Pätzold and Dawson predictions for the linear viscoelastic behavior of bicontinuous microemulsions.

In this Chapter, we first discuss the phase behavior of ternary mixtures consisting of two immiscible fluids and a surfactant. The current theory for the static behavior and equilibrium dynamics of bicontinuous microemulsions is then presented. This discussion

is followed by a brief review of the documented experimental studies of B μ E systems and their significant contributions to this field of research. We then present our experimental investigation of a PS/PI/PS-*b*-PI bicontinuous microemulsion.

4.2. Background

4.2.1. Phase Behavior of Ternary Systems

For mixtures of two immiscible fluids, addition of an appropriate surfactant alters the interfacial properties in the system, allowing for a variety of microstructures to be achieved. In the case of an immiscible blend of homopolymers (A and B), diblock copolymer (A-B) can serve as such a surfactant. The equilibrium phase behavior of ternary systems is quite complex and may be represented in the form of a prism. As shown in Figure 4.1(a), slicing the prism horizontally yields an isothermal phase diagram. This view of the phase prism shows the existence of ordered phases (*e.g.*, lamellae, hexagonally packed cylinders, cubic spherical and gyroid phases) at high concentrations of surfactant [Kunieda and Shinoda, (1982); Washburn *et al.* (2000)]. At low concentrations of surfactant, the interface is unstable, leading to the formation of macroscopic phase separated structures. The bicontinuous microemulsion phase found within a small window between the lamellar and phase-separated regions.

Slicing the phase prism vertically along equal volume fractions of immiscible fluid components ($\Phi_A = \Phi_B$) yields an isopleth diagram (Figure 4.1(b)).

Oil/water/surfactant systems exhibit “fish-cut” isopleths, which result from the highly

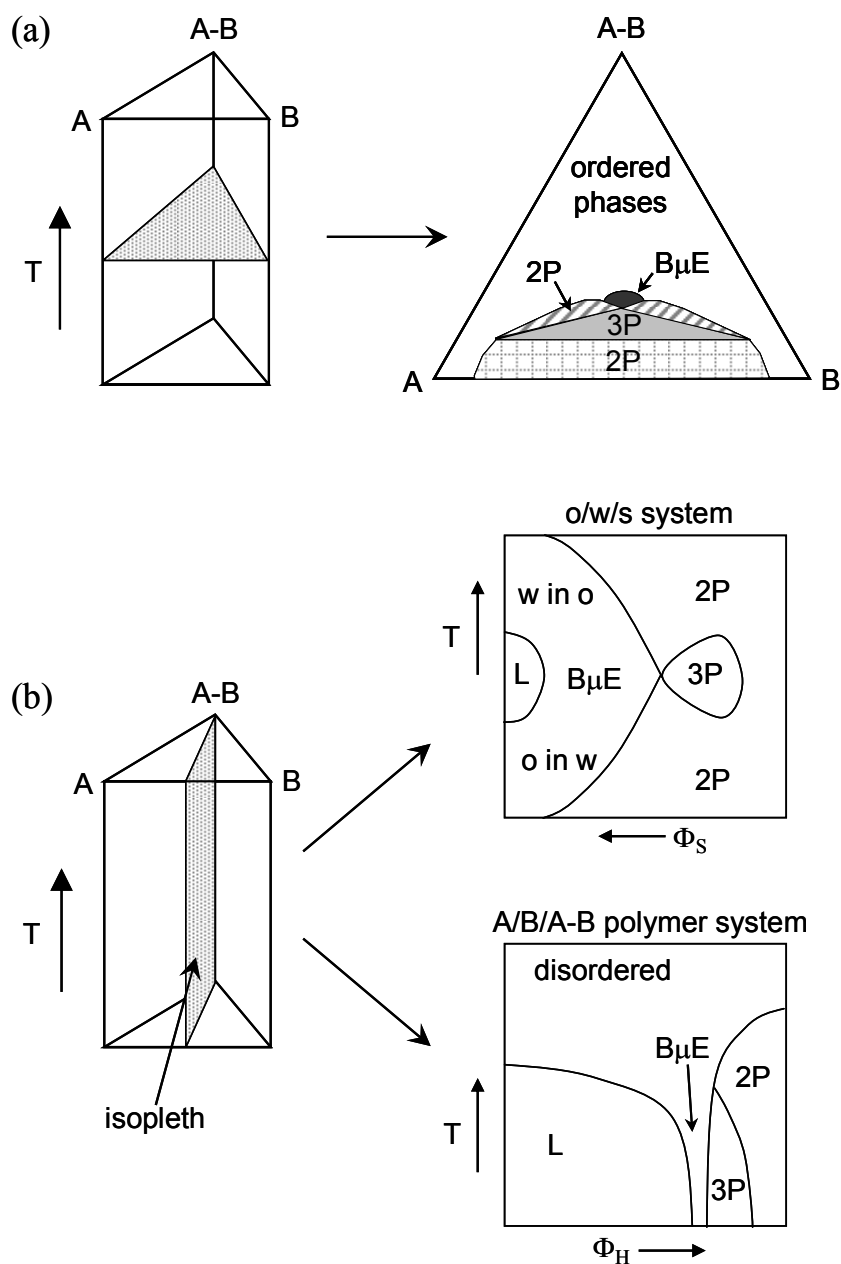


Figure 4.1. Schematic phase diagram for ternary systems: (a) isothermal phase diagram, (b) isopleth phase diagrams for oil/water/surfactant systems (top) and A/B/A-B polymer systems (bottom). 2P = two-phase, 3P = three-phase, L = lamellae [adapted from Krishnan *et al.* (2002a)].

temperature-dependent interactions between the hydrophobic and hydrophilic groups in the system [Kahlweit *et al.* (1987)]. For a narrow temperature range, a lamellar structure exists at high concentration of surfactant (Φ_S), which transitions to a B μ E phase at $\Phi_S \sim 10 - 30\%$ (depending on the nature of the surfactant). Low concentrations of surfactant yield phase-separated morphologies at all temperatures. The “fish-cut” isopleth has recently been produced in an A/B/A-C polymer blend, where the highly temperature-dependent interactions between homopolymer B and the C-component of the copolymer give the isopleth its “fish-cut” shape [Lee *et al.* (2003)].

A typical isopleth diagram for an A/B/A-B polymer blend, which represents the systems of focus in this Chapter, is also shown in Figure 4.1(b). Within the isopleth for these systems, the blend is disordered at high temperature for all blend compositions. At low temperatures, the progression of morphology with copolymer concentration is similar to the o/w/s systems. Low concentrations of copolymer yield a lamellar phase, in which the domains swell with increasing homopolymer concentration. At sufficiently high total homopolymer concentration ($\Phi_H = \Phi_A + \Phi_B$), the swollen lamellar structure is overwhelmed by thermal fluctuations, resulting in a bicontinuous microemulsion. Further increase in homopolymer concentration results in a macrophase separated morphology. One of the most notable differences between the o/w/s and A/B/A-B systems is the size of the temperature window over which the B μ E phase exists. Due to the simpler thermodynamics of A/B/A-B systems, the B μ E phase is stable over a much larger range of temperatures in these cases, providing an experimental advantage.

The creation of an A/B/A-B isopleth diagram, as shown in Figure 4.1(b), requires symmetry in the chain lengths of the two homopolymers ($N_A \approx N_B$) and in the block copolymer composition ($f_A \approx 0.5$). Furthermore, the condition $N_{A-B} \approx 5N_A$ assures that the order-disorder transition temperature of the block copolymer is similar to the critical temperature of the binary blend of homopolymers; this results in preferential placement of the block copolymer at the phase interface at low temperatures [Hillmyer *et al.* (1999)]. For A/B/A-B blends with $N_{A-B} \approx 5N_A$, the B μ E phase is located at $\Phi_H \approx 0.90$ [Hillmyer *et al.* (1999); Corvazier *et al.* (2001)]. Messé *et al.* (2003) have shown that the condition $N_{A-B} < 5N_A$ results in more weakly structured B μ E phases existing for $\Phi_H < 0.90$. Recently, Zhou *et al.* (2006) demonstrated that the conformational symmetry of the A and B species should also be considered in the design of ternary systems. Conformational asymmetry leads to “interruption” of the B μ E channel at low temperatures by ordered phases.

4.2.2. Shear-Induced Structural Transitions in Complex Fluids

As illustrated in the previous section for polymer blends and o/w/s mixtures, multi-component fluids form a wide array of interesting morphologies. The equilibrium structures of these fluids are dictated by a delicate balance between energetic interactions and entropic packing constraints of the constituent molecules. When a complex fluid is slightly perturbed, either by thermally-induced motion (at equilibrium) or an external force, the fluid relaxes over time scales that are characteristic of its microstructure. If the time scale of an applied external force, such as shear flow, is comparable to or exceeds

the characteristic times of the fluid, the thermodynamic balance is disrupted, leading to deformation of the microstructure or even a complete structural transformation.

Flow-induced structural transformations have been observed in a large number of complex fluids. Many of these reported structural transitions are interpreted as resulting from apparent shifts in phase boundaries caused by flow. For example, in binary homopolymer blends near the critical point, flow can induce either mixing [Hashimoto *et al.* (1990); Hobbie *et al.* (1992); Nakatani *et al.* (1990)] or demixing [Gerard *et al.* (1999); Mani *et al.* (1992)]. In neat A-B block copolymer just above the order-disorder transition, shear has been found to suppress concentration fluctuations, resulting in formation of lamellae [Koppi *et al.* (1993)]. Mahjoub *et al.* (1998), Porcar *et al.* (2003), and Yamamoto and Tanaka (1996) have reported shear-induced transition of sponge phases to lamellae. Sponge phases are isotropic structures similar to bicontinuous microemulsions, except the two domains in a sponge phase are composed of the same fluid (usually, either water or an oil) and separated by a continuous, multiply connected bilayer membrane (rather than a monolayer of surfactant). Isotropic-to-lamellar transitions under shear, such as those observed in disordered diblock copolymers and sponge phases, have been predicted by Cates and Milner (1989).

As mentioned earlier, Krishnan *et al.* (2002a) have observed a shear-induced structural transformation in a polymer B μ E. Considering the narrow channel over which the B μ E phase exists within the A/B/A-B isopleth (Figure 4.1(b)), one might expect flow to cause the system to shift into one of the neighboring phase regions (*i.e.*, lamellar, phase-separated, or disordered). Indeed, the polymer B μ E was found to “enter” the

phase-separated regime. However, this response seems to be in contrast with the behavior of the similarly structured o/w/s sponge phase, which forms lamellae at high shear rates. The evolution of shear-induced structural changes in the previously documented polymer B μ E [Krishnan *et al.* (2002a)] is presented in greater detail later on in this Chapter. Possible explanations (based on a study by Narayanan *et al.* (2006)) for the apparent discrepancy in the behavior of the two bicontinuous morphologies are also briefly discussed.

4.2.3. Landau-Ginzburg Model

4.2.3.1. Static Behavior

Much of the current theoretical descriptions for the static and dynamic behavior of bicontinuous microemulsions is based on the phenomenological Landau-Ginzburg free energy expansion F of the scalar order parameter ϕ [Gompper and Hennes (1994, 1996); Granek and Cates (1992); Nonomura and Ohta (1999); Pätzold and Dawson (1996a, 1996b); Teubner and Strey (1987)]:

$$F = a_0 + a_1\phi + a_2\phi^2 + \dots + c_1(\nabla\phi)^2 + c_2(\nabla^2\phi)^2 + \dots \quad (4.1)$$

where ϕ represents the local deviation from the average concentration of component A or B. Teubner and Strey (1987) found that only three terms of the free energy expansion are required to describe the static structure factor, $S(q)$, of B μ E systems:

$$S(q) = \frac{kT}{a_2 + c_1q^2 + c_2q^4} \quad (4.2)$$

where k is the Boltzmann constant, and T is temperature. Coefficients a_2 and c_2 are positive values describing fluctuations in the average composition and curvature elasticity of the interface, respectively. For BμEs, c_1 is negative, which drives the system to form interface and yields the characteristic scattering peak at $q = q_{\max} = \sqrt{-c_1 / 2c_2}$. As the temperature is increased, c_1 becomes positive, and the system enters a more usual disordered phase. Note that the structure factor decays as q^{-4} at large q , which is consistent with Porod's law (eqn. 3.7).

The autocorrelation function $P(q)$ yielding eqn. 4.2 is given by

$$P(r) = \frac{d}{2\pi r} \exp[-r / \xi] \sin\left(\frac{2\pi r}{d}\right). \quad (4.3)$$

This form of the autocorrelation function accounts for the two essential structural features in bicontinuous microemulsions: (1) the alternating domains of A and B, and (2) the loss of long-range order of the domains. These structural features in terms of the free energy coefficients are written as

$$d = 2\pi \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} - \frac{1}{4} \left(\frac{c_1}{c_2} \right) \right]^{-1/2} \quad (4.4)$$

$$\xi = \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} + \frac{1}{4} \left(\frac{c_1}{c_2} \right) \right]^{-1/2} \quad (4.5)$$

where d is the domain periodicity, and ξ is the correlation length of the periodic structure and provides a measure of the degree of “rigidity” of the interface. For typical BμEs, $\xi < d$ reflecting the lack of long-range order.

Schubert *et al.* (1994) defined an amphiphilicity factor, $f_a \equiv c_1 / \sqrt{4a_2c_2}$, to characterize the “strength” of the B μ E structure. Negative c_1 values lead to negative f_a values, which thus correspond to a tendency to form interfaces due to vanishingly small interfacial tension. Strong amphiphilicity, with $f_a < -1$, leads to the formation of a lamellar phase. Slightly lower amphiphilicity, with $-1 < f_a < 0$, yields a strongly structured or “good” B μ E phase. As c_1 becomes positive, with $0 < f_a < 1$, the microemulsion structure is weak. Further decrease in amphiphilicity, with $f_a > 1$, results in a disordered blend that lacks structure.

4.2.3.2. *Equilibrium Dynamics*

Using a Landau-Ginzburg free energy description, several groups have developed expressions for the dynamics of bicontinuous microemulsions in thermal equilibrium. Some of these analyses include a second order parameter, ψ , to account for the local amphiphile concentration in the system. The simplest case uses a Langevin equation that neglects (1) the presence of amphiphile and (2) the coupling of the hydrodynamic flow field to ϕ [Gompper and Hennes (1994)]. This description predicts single-exponential relaxation of the normalized dynamic structure factor, $f(q,t)$:

$$f(q,t) = \frac{S(q,t)}{S(q)} = \exp[-t / \tau_q] \quad (2.20)$$

where $\tau_q [= (D(q)q^2)^{-1}]$ is the characteristic relaxation time of the structure of length scale $\sim 1/q$. The dynamic structure factor, $S(q,t)$, is the autocorrelation function of ϕ (*i.e.*,

$\langle \phi(q,t)\phi(-q,0) \rangle$) and, therefore, describes the rise and decay of concentration fluctuations of component A (or B) in the microemulsion.

More sophisticated analyses of BμE equilibrium dynamics include coupling between the order parameters (ϕ and ψ) as well as coupling of the hydrodynamic flow field to the order parameters. Using a mean-field theory approach, Granek and Cates (1992) account for these couplings relationships in their treatment of a time-dependent Landau-Ginzburg model for sponge phases. In this case, their analysis for a symmetric sponge with a conserved order parameter, ϕ , may also apply to bicontinuous microemulsions [Komura *et al.* (2001)]. The predicted form of $f(q,t)$ is a complicated, non-exponential expression and is, therefore, excluded here for brevity. Hennes and Gompper (1996) treat the same time-dependent Landau-Ginzburg model used by Granek and Cates with a field-theoretic approach, which yields $f(q,t) = t^{-5/2} \exp[-t/\tau_q]$. Nonomura and Ohta (1999) evaluate BμE dynamics by applying a general Brownian motion theory to derive equations of motion for ϕ , ψ , and the velocity field. This treatment is limited to the low- q range and predicts single-exponential relaxation of $f(q,t)$ (eqn. 2.20).

Zilman and Granek (1996) have derived expressions for membrane dynamics that are *not* based on a Landau-Ginzburg model. Rather, the undulations of non-interacting membrane plaquettes are described using the Helfrich-bending free energy:

$$F = \frac{\kappa}{2} (\varepsilon_1 + \varepsilon_2 - 2\varepsilon_0)^2 + \bar{\kappa} \varepsilon_1 \varepsilon_2 \quad (4.6)$$

where ε_1 and ε_2 are the principle curvatures at each point on the membrane, ε_0 is its spontaneous curvature, and κ is the bending modulus. This description is only valid for large q and predicts stretched-exponential relaxation:

$$f(q, t) = \exp[-(t / \tau_q)^\nu] \quad (2.21)$$

with $\nu = 2/3$.

The expressions for the normalized dynamic structure factor resulting from these more sophisticated theories indicate that relaxation in bicontinuous microemulsions occurs due to multiple processes. In general, these processes are predicted to be diffusive ($\tau_q \sim q^{-2}$) at small q and non-diffusive at large q with $\tau_q \sim q^{-3}$.

4.2.3.3. Rheology

Pätzold and Dawson (1996a, 1996b) have also considered the dynamics of bicontinuous microemulsions, deriving predictions for the linear viscoelastic properties based on a time-dependent Landau-Ginzburg model. Following established procedures, they began their derivation by writing Langevin equations for the order parameter ϕ and velocity field $\mathbf{v}$ using mode coupling terms:

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \mathbf{v}) = \Lambda \nabla^2 \frac{\delta}{\delta \phi} \int_V F(\phi) d\mathbf{r} + \boldsymbol{\eta}_\phi \quad (4.7)$$

$$\frac{\partial \mathbf{v}}{\partial t} + \nabla \cdot (\mathbf{v} \mathbf{v}) = \eta_0 \nabla^2 \mathbf{v} + \sigma_0 \nabla (\nabla \cdot \mathbf{v}) - \phi \nabla \frac{\delta}{\delta \phi} \int_V F(\phi) d\mathbf{r} + \boldsymbol{\eta}_\mathbf{v} \quad (4.8)$$

where Λ is the mobility coefficient (Onsager coefficient), the free energy $F(\phi)$ is defined by eqn. 4.1, and $\boldsymbol{\eta}_\phi$ and $\boldsymbol{\eta}_\mathbf{v}$ are noise terms. The analysis was then simplified by imposing

a linear velocity profile ($\mathbf{v} = \dot{\gamma}(t)y\mathbf{e}_x$), thereby neglecting the effects of hydrodynamic interactions in the system (thus, eqn. 4.7 may be solved without consideration of eqn. 4.8). It should be noted that the analysis also neglects the presence of amphiphile in the system, which is restricted to the interface and may affect the flow field. Despite these simplifications, the resulting rheological predictions show how significant viscoelastic character results from the deformation and relaxation of the interconnected morphology in B μ E systems.

The viscoelastic response associated with the B μ E structure is produced in addition to stress resulting from the blend constituents. The following rheological expressions by Pätzold and Dawson are provided in terms of the “excess” viscoelasticity associated with the B μ E structure only, and, therefore, contributions from the pure components are not included. In the case of $\dot{\gamma} \rightarrow 0$, Pätzold and Dawson showed that the excess zero-shear viscosity, $\Delta\eta_0$, associated with the B μ E structure is given by

$$\Delta\eta_0 = \frac{kT\xi^3}{240\pi\Lambda c_2} f_1(\alpha) \quad (4.9)$$

where $\alpha = d/\xi$, $f_1(\alpha) = (\pi^2 + \alpha^2)/(4\pi^2 + \alpha^2)$. The complex viscosity components, η' and η'' , were then derived by applying a time-dependent perturbation to the system and computing the resulting shear stress. Burghardt *et al.* (2002) have provided these expressions in dimensionless form:

$$\frac{\Delta\eta'}{\Delta\eta_0} = \frac{32\beta^3}{\pi\xi^3 q_{\max}^3 f_1(\alpha)} \int_0^\infty \frac{\hat{q}^8 (1 - \hat{q}^2)^2}{[W^2 + \hat{q}^4 (\beta\hat{q}^4 - 2\beta\hat{q}^2 + 1)^2][\beta\hat{q}^4 - 2\beta\hat{q}^2 + 1]} d\hat{q} \quad (4.10)$$

$$\frac{\eta''}{\Delta\eta_0} = \frac{32\beta^3}{\pi\xi^3 q_{\max}^3 f_1(\alpha)} \int_0^\infty \frac{W\hat{q}^6(1-\hat{q}^2)^2}{[W^2 + \hat{q}^4(\beta\hat{q}^4 - 2\beta\hat{q}^2 + 1)^2][\beta\hat{q}^4 - 2\beta\hat{q}^2 + 1]^2} d\hat{q} \quad (4.11)$$

where $\hat{q} = q/q_{\max}$, $\beta = c_1^2/(4a_2c_2)$ (square of the amphiphilicity factor), and $W [= \omega c_2/(\Lambda a_2|c_1|)]$ is a dimensionless frequency. Finally, the average relaxation time of the microemulsion is defined as

$$\bar{\lambda} \equiv \lim_{\omega \rightarrow 0} \frac{\eta''/\omega}{\eta'} = \frac{d^4 \xi^2}{32\Lambda c_2} \frac{f_2(\alpha)}{f_1(\alpha)} \quad (4.12)$$

where $f_2(\alpha) = (32\pi^6 + 32\pi^4\alpha^2 + 2\pi^2\alpha^4 + 7\alpha^6)/(4\pi^2 + \alpha^2)^5$. In order to conveniently compare the predictions to experimental measurements, we use the dimensionless frequency, $\omega\bar{\lambda}$ (rather than W), as provided by Burghardt *et al.* (2002):

$$\omega\bar{\lambda} = W \frac{q_{\max}^6 d^4 \xi^2}{16\beta} \frac{f_2(\alpha)}{f_1(\alpha)}. \quad (4.13)$$

The general predicted response by eqns. 4.10 and 4.11 is Rouse-like, characterized by terminal (liquid-like) response at low frequency changing to $\Delta\eta' \approx \eta'' \sim \omega^{-1/2}$ at high frequency. These expressions (*i.e.*, the complex viscosity components in *reduced* form) can be evaluated using structural parameters extracted from static x-ray or neutron scattering data. Evaluation of the *absolute* values of the rheological parameters, however, also requires knowledge of the Onsager coefficient Λ . This quantity is related to $f(q,t)$, which can be measured using photon correlation spectroscopy (PCS) techniques. As a result of neglecting the presence of amphiphile and the coupling between the flow field and the order parameter, the Pätzold and Dawson model predicts single-exponential relaxation of $f(q,t)$ (eqn. 2.20). In the case of single-exponential relaxation where $\tau_q \sim q^{-2}$, the Onsager coefficient can be obtained using the relationship

$$D(q) = [\tau_q q^2]^{-1} = \frac{kT}{S(q)} \Lambda. \quad (4.14)$$

Pätzold and Dawson (1996a, 1996b) also considered shear-induced structural changes and the associated rheology of B μ Es under steady shear conditions. As mentioned earlier, their analysis does not predict phase-separation at high shear rates. Rather, the model describes a general loss of connectivity in the B μ E structure along the velocity gradient direction with increasing shear rate. However, the details of this structure at local length scales are unclear. Caputo *et al.* (2002b) have investigated the accuracy of the model in predicting the behavior of a PEE-PDMS microemulsion at low to intermediate shear rates (prior to the onset of phase-separation). We restrict ourselves to evaluating the performance of the predictions for the linear viscoelastic behavior.

4.2.4. Dynamics of Oil/Water/Surfactant Microemulsions

Documentation of the dynamics of oil/water/surfactant bicontinuous microemulsions has been quite limited up to this point due to the experimental difficulties associated with accessing the fast relaxation times of these systems. The development of neutron spin-echo (NSE) spectroscopy, which probes nanosecond time scales, has enabled measurement of the dynamics of o/w/s B μ Es in thermal equilibrium [Komura *et al.* (2001); Mihailescu *et al.* (2001)]. At length scales comparable to and smaller than the B μ E domain size ($q \geq q_{\max}$), the reported behavior is similar to the theoretical description by Zilman and Granek (1996) for fluctuating membrane plaquettes (*i.e.*, stretched-exponential relaxation with $\nu \sim 2/3$ and $\tau_q \sim q^{-3}$). At much larger length scales ($q < q_{\max}$),

the dynamics are diffusive ($\tau_q \sim q^{-2}$) [Mihailescu *et al.* (2001)]. The mechanisms governing this behavior are still not well-understood, and the behavior of the Onsager coefficient has not been examined.

Warr and coworkers (1992, 1995) and Bolzinger-Thevenin *et al.* (1999) have measured the rheology of o/w/s B μ Es and found that very high shear rates ($>10^3 \text{ s}^{-1}$) were required to perturb the microstructure. The observed mechanical response was shear-thinning, which Anklam *et al.* (1995) attributed to the breaking of interconnections in the B μ E structure along the shear gradient direction. However, the microstructure itself was not confirmed experimentally. Extreme shear rates are also needed to induce deformation in the similarly structured o/w/s sponge phases [Mahjoub *et al.* (1998); Porcar *et al.* (2003); Yamamoto and Tanaka (1996)]. As mentioned earlier, sufficiently high shear rates lead to transformation to a lamellar phase. The fast dynamics of these small molecule systems prevent detailed investigation of the mechanisms (or time-evolution) of the shear-induced structural changes. The slower dynamics of polymer systems, which we employ in the present study, provide new experimental capabilities for resolving the behavior of self-assembling fluids.

4.2.5. Dynamics of a PEE-PDMS Microemulsion

4.2.5.1. *Equilibrium Behavior*

Using rheology and light photon correlation spectroscopy (LPCS), Bates, Lodge, and coworkers have characterized the equilibrium dynamics of a bicontinuous microemulsion composed of PEE, PDMS, and PEE-PDMS [Burghardt *et al.* (2002); Morkved *et al.*

(1999, 2001)]. The homopolymers used in this blend were reported as Newtonian so that the B μ E viscoelasticity was dominated by the blend microstructure. LPCS measurements showed that the dynamic structure factor contained three exponential modes: a single dominating mode associated with collective diffusion of the B μ E domains, and two unidentified smaller modes that may be associated with copolymer dynamics or undulation of the interfaces [Morkved *et al.* (1999)]. The Onsager coefficient was determined from the dominant (single-exponential) B μ E mode, and this information along with static scattering data were used to compute the rheological predictions of Pätzold and Dawson [Burghardt *et al.* (2002)]. Although the model describes the general shape of the viscoelastic spectrum very well, it significantly under-predicts the magnitude of the viscosity and relaxation time of the PEE-PDMS microemulsion, as shown in Figure 4.2.

As discussed by Burghardt *et al.* (2002), discrepancies between experiment and the Pätzold and Dawson predictions may result from deficiencies in the model, such as its imposed linear velocity profile, which neglects coupling between the structure and the flow field, including possible effects of viscosity contrast between the blend constituents. Furthermore, the model does not account for the presence of amphiphile, which is restricted to the interface and may also affect the flow field. In addition, Burghardt *et al.* noted that the Onsager coefficient may serve as a source of discrepancy. In the PEE-PDMS studies, Λ was measured using LPCS, which probes length scales (~ 500 nm) much larger than the characteristic length scale of the microemulsion (~ 80 nm). However, the Onsager coefficient is expected to be q -dependent at smaller length scales

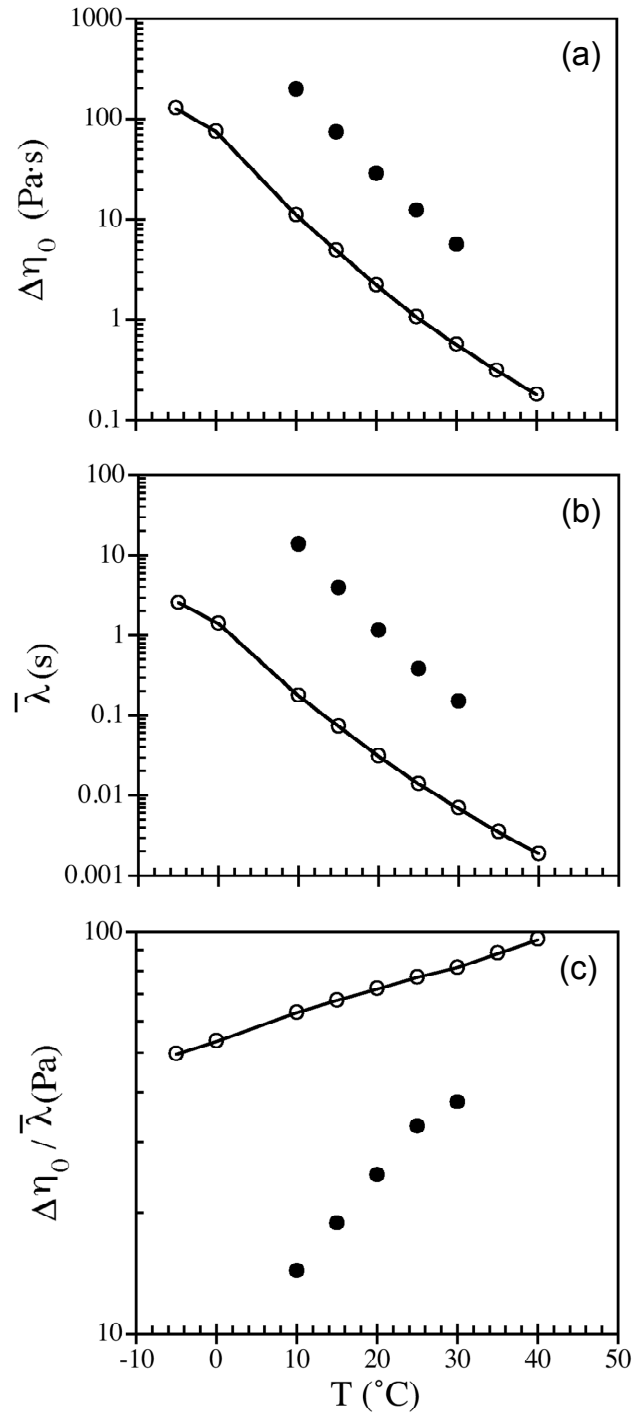


Figure 4.2. Absolute tests of Pätzold-Dawson predictions for the PEE-PDMS B μ E: (a) excess zero-shear viscosity, (b) average relaxation time, and (c) ratio of excess viscosity to relaxation time. (●) experimental data. (○) predictions of eqns. 4.9 and 4.12 [from Burghardt *et al.* (2002)].

due to the hydrodynamic interactions between patches of interface [Granek and Cates (1992)]. Although Pätzold and Dawson do not provide any description of a q -dependent Onsager coefficient, perhaps the performance of the model could be improved by measuring $\Lambda(q)$ at length scales comparable to the B μ E domain size. One objective of our study is to investigate this possibility by measuring $\Lambda(q)$ at the dominant length scale of a PS-PI bicontinuous microemulsion using x-ray photon correlation spectroscopy. By measuring the dynamics of the PS-PI B μ E via XPCS and rheology, we also examine the universality of the equilibrium behavior of the B μ E morphology.

4.2.5.2. *Shear-Induced Dynamics*

Bates, Lodge, and coworkers also investigated the shear-induced structural response of the PEE-PDMS microemulsion [Caputo *et al.* (2002b); Krishnan *et al.* (2002a, 2002b)]. Rheology and small-angle neutron scattering (SANS) measurements collected during steady shear conditions revealed four behavioral regimes, each corresponding to a different morphological state [Krishnan *et al.* (2002a)]. These regimes, shown in Figure 4.3, are characterized as follows.

The B μ E structure is unperturbed at low shear rates (regime I), as indicated by the Newtonian mechanical response and the isotropic neutron scattering. Shear thinning and anisotropic scattering at intermediate rates (regime II) are associated with deformation and alignment of the microemulsion structure under flow. At higher shear rates (regime III), the shear stress is nearly independent of shear rate. In addition, the corresponding SANS patterns show a weakened B μ E peak accompanied by the appearance of scattered

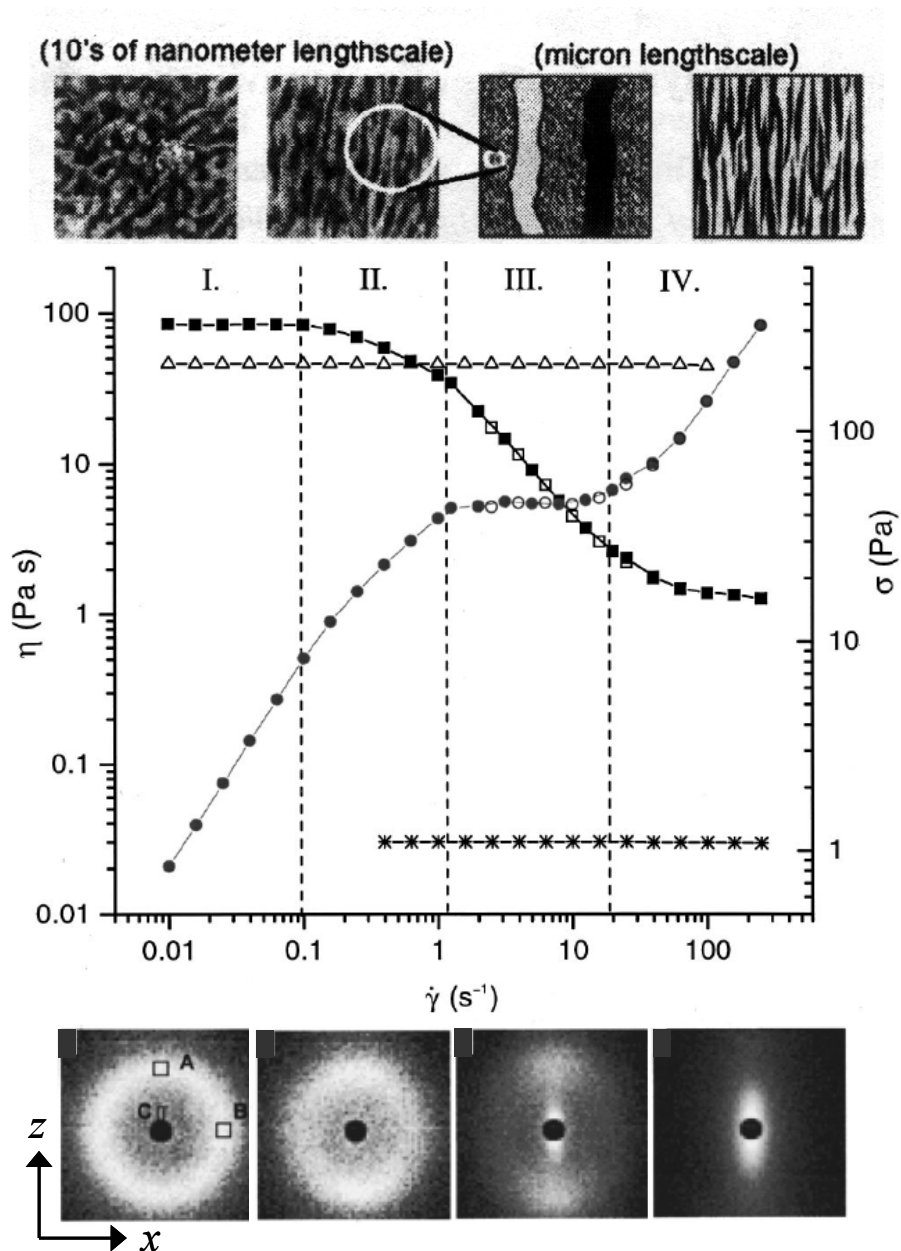


Figure 4.3. Steady shear data of the PEE-PDMS BμE showing the four behavioral regimes as a function of shear rate. Top: schematic representation of the morphologies. Middle: mechanical measurements. (■) BμE viscosity, (●) BμE shear stress, (Δ) PEE viscosity, and (*) PDMS viscosity. Bottom: SANS patterns at 0, 0.316, 10, and 316 s^{-1} [from Krishnan *et al.* (2002a)].

intensity at lower scattering angles. This behavior was attributed to the microemulsion undergoing partial phase separation, where the degree of phase separation increases with increasing shear rate. Thus, within regime III, the steady-state morphology is hypothesized to be a three-phase coexistence of the nano-scale B μ E with two micro-scale homopolymer-rich phases. At even higher shear rates (regime IV), the microemulsion peak in the SANS pattern is no longer existent at steady-state, indicating that the B μ E has completely transformed to a micron-scale phase-separated morphology.

Krishnan *et al.* (2002b) conducted a more detailed investigation of structural evolution with time in the four behavioral regimes via transient rheological measurements of the PEE-PDMS B μ E. The viscosity as a function of time is presented in Figure 4.4 for start-up of shear at various shear rates. The different behavioral regimes are clearly reflected in the different evolutionary responses of the viscosity with time. At low shear rates in regime I, the response is linear as indicated by the steady, monotonic growth in viscosity toward its steady-state value. Upon entering regime II, the viscosity exhibits an overshoot associated with orientation of the B μ E structure under flow. In regime III, the behavior is more complex. Following the overshoot, the viscosity reaches a distinct plateau and then slowly decreases to the final steady-state value.

To provide insight into the structural changes yielding the complex rheological response in regime III, Krishnan *et al.* (2002b) performed *in situ* small-angle light scattering and optical microscopy experiments, which allow for tracking of the evolution of phase-separated structures in the system. (The length scale of the B μ E structure is too small to be probed by these techniques.) These measurements showed (1) the onset of

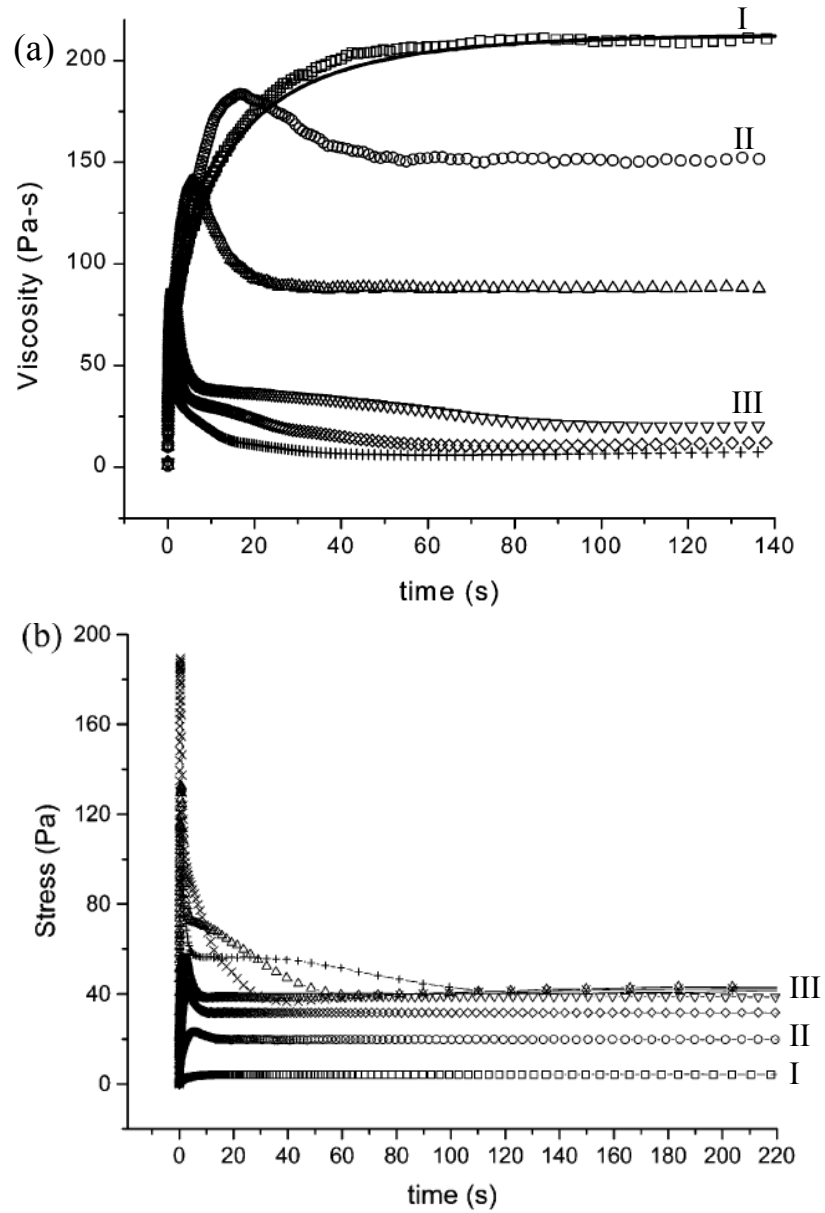


Figure 4.4. (a) Viscosity as a function of time in a PEE-PDMS BμE during start-up of shear flow: Regime I, ($\square$) 0.01 s^{-1} ; Regime II, ($\circ$) 0.1 , (Δ) 0.316 s^{-1} ; Regime III, (∇) 2 , ($\diamond$) 3.16 , ($+$) 5 s^{-1} .
 (b) Shear stress as a function of time: Regime I, ($\square$) 0.05 s^{-1} ; Regime II, ($\circ$) 0.316 , ($\diamond$) 0.7 , (∇) 1.0 s^{-1} ; Regime III, ($+$) 2 , (Δ) 3.16 , ($\times$) 5 s^{-1} .
 [from Krishnan *et al.* (2002b)].

phase-separation immediately following the viscosity overshoot, and (2) a gradual increase in the degree of phase-separation over the duration of the viscosity plateau before reaching the steady-state three-phase structure. In addition, the breadth of the plateau was found to shorten with increasing shear rate, indicating that the steady-state three-phase morphology is established more quickly at higher rates.

Caputo *et al.* (2002b) complemented these studies with *in situ* small-angle x-ray scattering experiments in which they collected time-resolved measurements of the PEE-PDMS B μ E within the flow-gradient plane during shear. These measurements enabled more detailed characterization of shear-induced deformation of the B μ E structure. In addition, Caputo *et al.* examined potential relationships between the scattering and the rheological behavior of the microemulsion. Significant parasitic scattering at smaller angles (refer to Figure 2.9 and the discussion in Section 2.4.3) overwhelmed any scattering that may be associated with large scale phase-separated structures at high shear rates. Consequently, experiments were restricted to low to moderate shear conditions for which phase-separation does not occur (*i.e.*, regime II).

In regards to the occurrence of phase-separation, Krishnan *et al.* (2002a) originally suggested that this transition is potentially associated with the significant viscosity-contrast between the homopolymers, which is about three orders of magnitude (Figure 4.3). That is, beyond a critical shear rate, the lower viscosity homopolymer (PEE) “ejects” itself from the B μ E structure to serve as a slip layer and limit the stress in the system. Considering that the viscosity-contrast in o/w/s systems is fairly small, this hypothesis serves as a feasible explanation for the very different phase transition

observed in sponge phases (which transition to a lamellar phase) than in the polymer B μ E.

Recent simulations of shear-induced phase transitions in low molecular weight ternary polymer blends by Narayanan *et al.* (2006) (using a Brownian dynamics approach) contradict the viscosity-contrast hypothesis. In fact, their results indicate that phase-separation will occur in polymer bicontinuous microemulsions even when the homopolymer viscosities are matched. In these simulations, very high shear rates were required to cause phase-separation in the matched system, and the critical shear rate at which this transition occurs was found to shift to lower values with increasing viscosity contrast. This suggests that while viscosity contrast may not be necessary for shear-induced phase separation, it might render the system more susceptible to this transformation.

The simulations also showed contraction of the block copolymer chains along the velocity gradient direction at high shear rates that coincides with the onset of phase-separation. The copolymer chains were specified as 5 times larger than the homopolymer chains and are therefore more susceptible to deformation. This observation indicates strong coupling between the polymer chain conformations during flow and the system thermodynamics. Contraction of the copolymer chains at the interface leads to an increased number of contacts between the A (or B) component of the block copolymer with the A (or B) species of homopolymer. These increased contacts raise the interfacial tension between the two phases, and the resulting effect is for the B μ E to decrease the amount of interfacial area by undergoing phase-separation. The study by Narayanan *et*

al. (2006) demonstrates that the “interplay” between chain conformation and their flow deformation in polymer blends can lead to flow-induced phase behavior that is vastly different than the behavior of small molecule mixtures (for which these coupling effects are negligible). These insights also highlight the limitations of the much coarser order parameter models which lack any molecular-level detail. The polymers used in the simulations consist of only a few monomeric units in length, indicating that chain effects are significant even in low molecular weight polymer systems.

Since only a single polymer B μ E has been investigated experimentally, it is not certain that the observed shear-induced behavior is general to all polymer B μ E systems. The simulations by Narayanan *et al.* show a gradual increase in the degree of phase-separation with increasing shear rate and are, therefore, consistent with the behavior of the PEE-PDMS microemulsion. Expanding on this previous work, we have employed rheology and *in situ* SAXS to investigate the shear-induced behavior of a second polymer B μ E (the same PS-PI system used in our equilibrium experiments). In the previous *in situ* SAXS experiment with the PEE-PDMS B μ E, scattering associated with phase-separated structures was not observed due to large amounts of parasitic scattering at small angles. This parasitic scattering has been substantially reduced in our experiments, allowing for simultaneous observation of the B μ E deformation and the formation of phase-separated structures during shear.

4.3. Phase Behavior of PS/PI/PS-*b*-PI Blends

We began our studies of the PS-PI bicontinuous microemulsion by characterizing the isopleth phase behavior of the model ternary blend system and determining the compositions at which the B μ E phase exists. The equilibrium microstructure of the B μ E sample was then characterized in greater detail as a function of temperature using SAXS and the Teubner-Strey model (eqn. 4.2).

4.3.1. Materials

The B μ E system used in the present study is composed of polystyrene, polyisoprene, and poly(styrene-*block*-isoprene). PS and PI(cis-1,4-addition) homopolymers, both having a molecular weight of $M_n = 3000$ with low polydispersity ($M_w/M_n \leq 1.08$), were obtained from Polymer Source, Inc (Dorval, QC, Canada). PS-*b*-PI copolymer, having a molecular weight of $M_n = 20,850$ ($M_w/M_n = 1.01$) and a weight fraction of PS $w_{PS} = 0.520$, was obtained from the University of Minnesota Polymer Synthesis Facility (Minneapolis, MN).

To determine the blend compositions at which the B μ E phase exists, an isopleth diagram was created by characterizing several blends of varying composition. Each blend was prepared using equal volumes of polystyrene and polyisoprene with 5, 10, 20, 25, or 50 volume% block copolymer. Specific volumes of the polymers were determined at 160°C using temperature-dependent expressions provided in the literature [Han *et al.* (1989)]. A thermal stabilizer (Irganox 1010, Ciba Specialty Chemicals) was added to the blends at 0.2 weight%, and dissolution in toluene was used to facilitate mixing of the

blend components (90/10 weight% solvent/polymer). Most of the solvent was evaporated in a vacuum oven at room temperature over 8 hours, and the remaining solvent was evaporated at 60°C for one week. The blends were annealed for a minimum of 6-8 hours at 150°C immediately prior to experiments.

4.3.2. Construction of Isopleth Diagram

Birefringence measurements were performed to determine the order-disorder transition temperatures, T_{ODT} , of the pure diblock and of the copolymer-rich samples ($\Phi_H = \Phi_{PS} + \Phi_{PI} = 0.50, 0.75, 0.80, 0.90$). Similarly, cloud point measurements were performed to determine the critical temperature, T_c , of the binary homopolymer blend and of the homopolymer-rich samples ($\Phi_H = 0.90, 0.95$). These measurements were carried out using an optical microscope (Nikon OPTIPHOT2-POL) equipped with a hot stage (Mettler FP82HT). Copolymer-rich samples were heated at rate of 1°C/min under a nitrogen atmosphere, and the disappearance of birefringence was observed as the T_{ODT} was reached. Homopolymer-rich samples were cooled at a rate of 1°C/min, and the T_c was marked by a transition from translucence to turbidity of the sample.

The T_{ODT} 's of the copolymer-rich samples were also measured using a Rheometric Scientific ARES strain-controlled rheometer with 50 mm diameter parallel plate fixtures. Isochronal temperature scans were carried out at 5 rad/s and 0.3% strain (within the determined linear regime of the samples) with a heating rate of 0.3°C/min. As the temperature was increased, a sharp decrease in the dynamic storage modulus was

observed at the temperature at which the sample transitions from a lamellar to disordered phase [Rosedale and Bates (1990)].

The morphologies of the copolymer-rich blends were verified via SAXS measurements collected at beamline 5ID-D of the Advanced Photon Source. SAXS data were collected at room temperature using a 17 keV x-ray beam, 10.1 meter sample-to-detector distance (under vacuum), and a two-dimensional MarCCD detector. Additional SAXS measurements of the $\Phi_H = 0.90$ blend at various temperatures were performed under vacuum at beamline 8ID-I using 7.5 keV radiation.

4.3.3. Results

The PS-PI bicontinuous microemulsion was designed using a formulation developed by Bates, Lodge, and coworkers for A/B/A-B blends, which requires that $\Phi_A = \Phi_B$, $f_A = 0.5$, $N_A \approx N_B$, and $N_{A-B} \approx 5N_A$ [Hillmyer *et al.* (1999)]. Φ_A and Φ_B are the volume fractions of homopolymers A and B, respectively, and f_A is the volume fraction of A in the diblock copolymer. N_A , N_B , and N_{A-B} are the degrees of polymerization for homopolymer A, homopolymer B, and diblock copolymer A-B, respectively. The PS/PI/PS-*b*-PI blends employed in this study yield an isopleth diagram, presented in Figure 4.5, that closely resembles the behavior of previously documented systems.

Birefringence and rheology measurements for the pure diblock ($\Phi_H = 0$) and copolymer-rich samples ($\Phi_H = 0.50, 0.75, 0.80$) reveal distinct order-disorder transition temperatures, which are plotted in Figure 4.5. Room temperature SAXS profiles of the copolymer-rich samples show sharp, Gaussian first-order peaks and smaller second- and

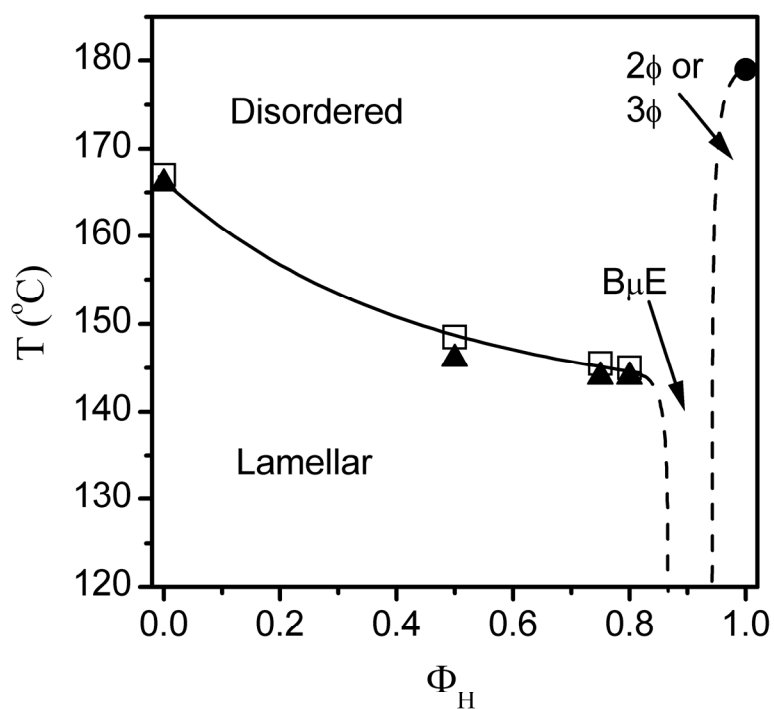


Figure 4.5. Isopleth phase diagram of PS/PI/PS-*b*-PI blends at equal volumes of PS and PI homopolymer. The abscissa represents total homopolymer concentration, $\Phi_H = \Phi_A + \Phi_B$. The order-disorder temperatures of the lamellar blends were measured by rheology (□) and birefringence (▲). The critical temperature of the binary homopolymer blend was determined via cloud point measurement (●).

third-order peaks, as expected for lamellar morphology (Figure 4.6) [Mai *et al.* (1996)]. In symmetric lamellae, the second-order peak is suppressed, and, thus, our lamellar structures appear to be slightly asymmetric. We prepared our blends such that the PS and PI domains have equal volumes at 160°C, whereas these SAXS measurements were collected near 25°C. Since density is a temperature-dependent quantity, the domains are anticipated to have greater symmetry at higher temperatures in the melt, where most of the experiments described in this paper were performed. As the homopolymer concentration is increased, the primary scattering peak shifts to smaller scattering vector, reflecting a swelling of the lamellar domains ($d = 2\pi/q_{\text{max}}$).

On the other side of the isopleth, the binary homopolymer blend ($\Phi_H = 1$) exhibits a distinct critical point at 179°C in cloud point measurement. The $\Phi_H = 0.95$ sample is very turbid, characteristic of macrophase separation, but a distinct critical point was not observed. It should be noted, however, that blends containing small amount of block copolymer often require long equilibration times of several hours or days [Washburn *et al.* (2000)]. We did not allow for such long equilibration times in our measurements. The $\Phi_H = 0.90$ sample also exhibited some turbidity up to 195°C, well above the critical temperature of the binary blend. This sample did not exhibit any birefringence, even at low temperatures, and a sharp drop in the storage modulus during mechanical rheometry was not observed. Therefore, neither a distinguishable order-disorder transition nor a critical point can be reported. For the $\Phi_H = 0.90$ blend, the x-ray scattering peak is much broader than the primary peaks in the copolymer-rich samples (Figure 4.6), and no higher order peaks are observed. In addition, the scattering peak is well-described by the

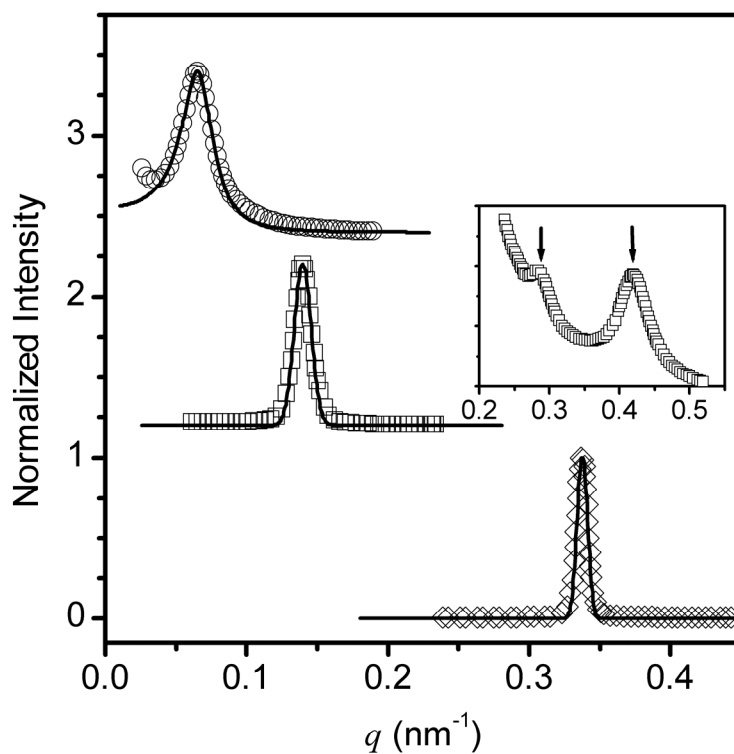


Figure 4.6. SAXS profiles of pure PS-PI diblock copolymer ($\diamond$) and ternary blends (PS/PI/PS-*b*-PI), $\Phi_H = 0.80$ ($\square$) and $\Phi_H = 0.90$ ($\circ$), at room temperature. Gaussian curves were fit to data for the pure copolymer and $\Phi_H = 0.80$ blend, and the Teubner-Strey model (eqn. 4.2) was fit to the $\Phi_H = 0.90$ data. The fits are represented by solid lines. SAXS data are normalized by the peak intensity and shifted vertically for visual clarity. The inset features the second- and third-order peaks due to scattering from lamellar structure in the $\Phi_H = 0.80$ blend.

Teubner-Strey structure factor (eqn. 4.2) for bicontinuous microemulsions. Based on these observations, we conclude the $\Phi_H = 0.90$ blend to be a bicontinuous microemulsion phase.

As shown in Figure 4.7, the microemulsion scattering peak persists to temperatures of at least 150°C, beyond the disorder line of the swollen lamellar phase in the isopleth diagram. The Teubner-Strey model was fit to the scattering data collected at various temperatures, and the fitting coefficients are listed in Table 4.1. Some discrepancy between the microemulsion sample ($\Phi_H = 0.90$) and the model is evident at small and large scattering vectors (*i.e.*, outside the peak region). The lack of agreement at large q has been reported for other B μ E systems and is potentially associated with Gaussian coil scattering from the polymer chains, which predicts $I(q) \sim q^{-2}$ [Hillmyer *et al.* (1999)]. Alternatively, local structural details in the microemulsion may not be accounted for by the Teubner-Strey model since higher order terms in the Landau-Ginzburg expansion are neglected. The discrepancy at small scattering vector may result from the coexistence of larger length scale structures with the B μ E phase [Lee *et al.* (1998)]. However, the Teubner-Strey structure factor accurately represents the scattering profile in the vicinity of the peak and is, therefore, a suitable model for extracting information regarding the B μ E structure from the experimental data.

The Teubner-Strey model defines two structural length scales in terms of the fitting coefficients. These quantities, the domain periodicity and the domain correlation length, are given by eqns. 4.4 and 4.5. The domain periodicity, plotted in Figure 4.8, is fairly stable within the measured temperature region, indicating stability of the

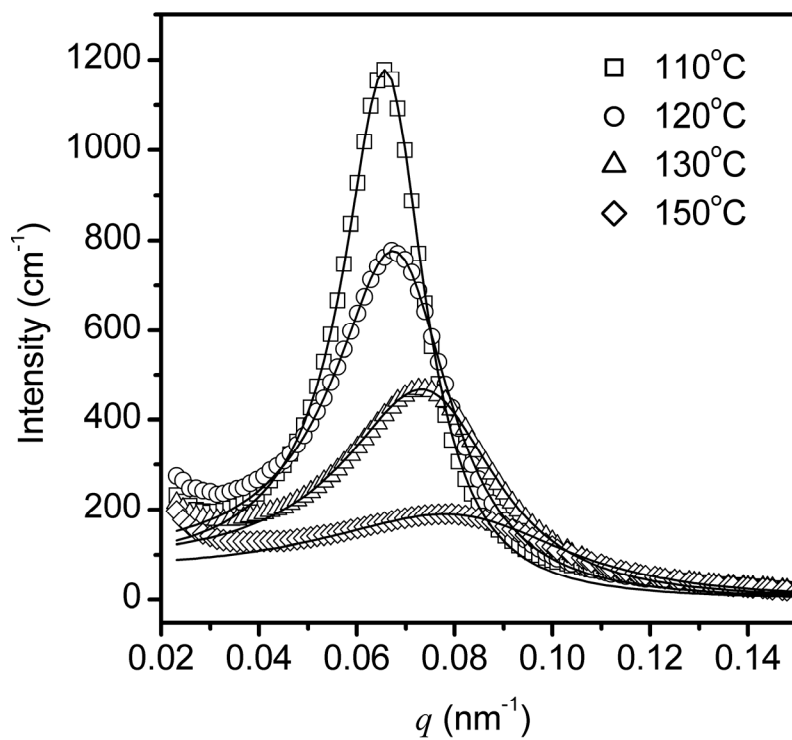


Figure 4.7. SAXS profiles of the PS-PI B μ E sample ($\Phi_H = 0.90$) as a function of temperature. Solid lines represent fits of the Teubner-Strey model (eqn. 4.2) to the data.

Table 4.1. Parameters of the Teubner-Strey Structure Factor fit to SAXS Data for the PS-PI B μ E.

T	$q_{\max}$	a_2	c_1	c_2
(°C)	(nm ⁻¹)	(cm)	(cm.nm ²)	(cm.nm ⁴)
110	0.0657	0.00967	-4.09	474
115	0.0671	0.00917	-3.62	402
120	0.0674	0.00803	-2.97	327
125	0.0701	0.00896	-2.99	304
130	0.0732	0.00951	-2.75	257
135	0.0754	0.0105	-2.72	239
140	0.0773	0.0113	-2.62	219
150	0.0780	0.0124	-2.36	194

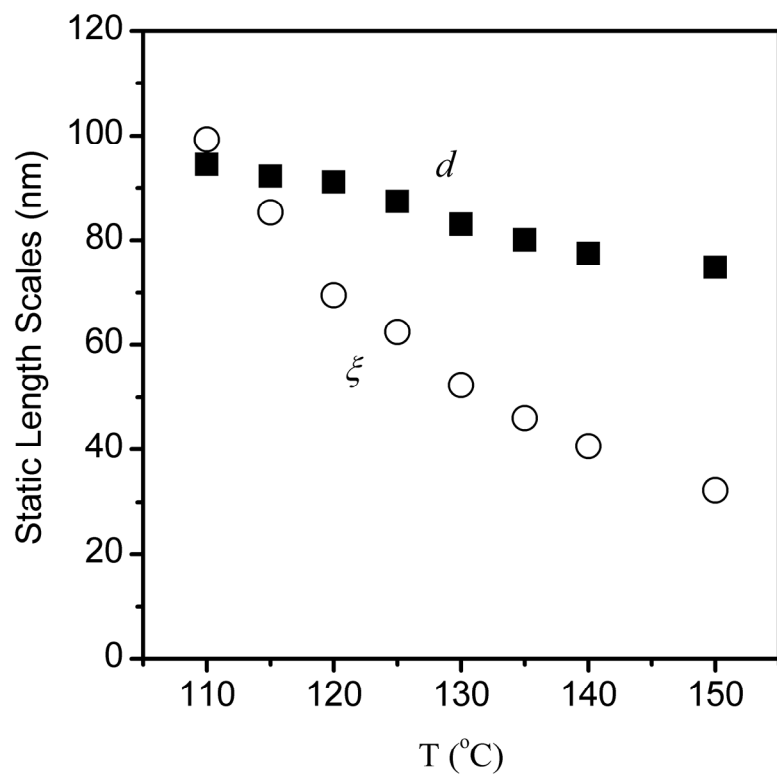


Figure 4.8. Temperature dependence of the PS-PI B μ E domain periodicity (■) and correlation length (○) computed from Teubner-Strey fitting coefficients.

microemulsion structure. The correlation length, however, decreases significantly with increasing temperature, suggesting a softening of the interface due to thermal fluctuations [Corvazier *et al.* (2001)].

For typical bicontinuous microemulsions, $\xi < d$ reflecting their lack of long-range order. As $\xi/d \rightarrow 1$ at lower temperatures (near 110°C in our sample), the microemulsion domains become more correlated. Indeed, Ryan and coworkers studied a different PS-PI B μ E system for which they report $\xi/d > 1$ at sufficiently low temperatures [Messé *et al.* (2003)]. This behavior was associated with a transition from a single-phase B μ E to a biphasic B μ E + lamellae as the temperature was decreased. Washburn *et al.* (2000) also reported a transition from a single-phase B μ E to a lamellar + B μ E coexistence phase in a blend of poly(ethylene oxide), squalane, and poly(ethylene oxide-*b*-ethylenepropylene). In the latter case, SAXS profiles support their claim of a coexistence phase; at lower temperatures, the microemulsion scattering peak is accompanied by a second prominent peak, which is associated with the coexisting lamellar structures. For our sample, the SAXS profile at 110°C shows no evidence of additional peaks to suggest a concomitant lamellar phase. Although the trend of $\xi/d \rightarrow 1$ in Figure 4.8 suggests the possibility of a B μ E + lamellar coexistence phase at lower temperatures, we cannot provide definitive conclusions at this time regarding the microstructure in this region. Additional measurements at these lower temperatures and for other blend compositions in or near the microemulsion channel are required.

As discussed in Section 4.2.3.1, the PS-PI microemulsion structure can also be characterized by computing the amphiphilicity factor, $f_a \equiv c_1 / \sqrt{4a_2c_2}$. This quantity is

plotted in Figure 4.9 as a function of temperature. Within the measured range of temperatures, values are within the range $0 < f_a < 1$, which describes a strongly structured B μ E phase. A fresh batch of microemulsion sample was prepared for each experiment performed in the following equilibrium and shear studies.

4.4. Equilibrium Dynamics of a PS-PI B μ E

We now discuss the equilibrium dynamics of the PS-PI microemulsion sample ($\Phi_H = 0.90$), which was characterized using rheology and x-ray photon correlation spectroscopy. The similarities and differences in the linear viscoelastic behavior of the PS-PI B μ E and the PEE-PDMS B μ E [Burghardt *et al.* (2002); Krishnan *et al.* (2002a)] were investigated. XPCS measurements were employed to test the linear viscoelastic predictions by Pätzold and Dawson for bicontinuous microemulsions.

4.4.1. Experiment

Rheological measurements of the microemulsion sample and each of the constituent homopolymers were conducted with the ARES rheometer using cone and plate fixtures (50 mm diameter, 0.04 rad cone angle). Dynamic frequency sweeps were performed in the linear regime with frequencies between 0.01 and 100 rad/s. All measurements were collected under a nitrogen atmosphere and with a temperature control of $\pm 0.1^\circ\text{C}$. XPCS measurements of the microemulsion sample were conducted at beamline 8ID-I of the Advanced Photon Source as described in Section 2.5.2.

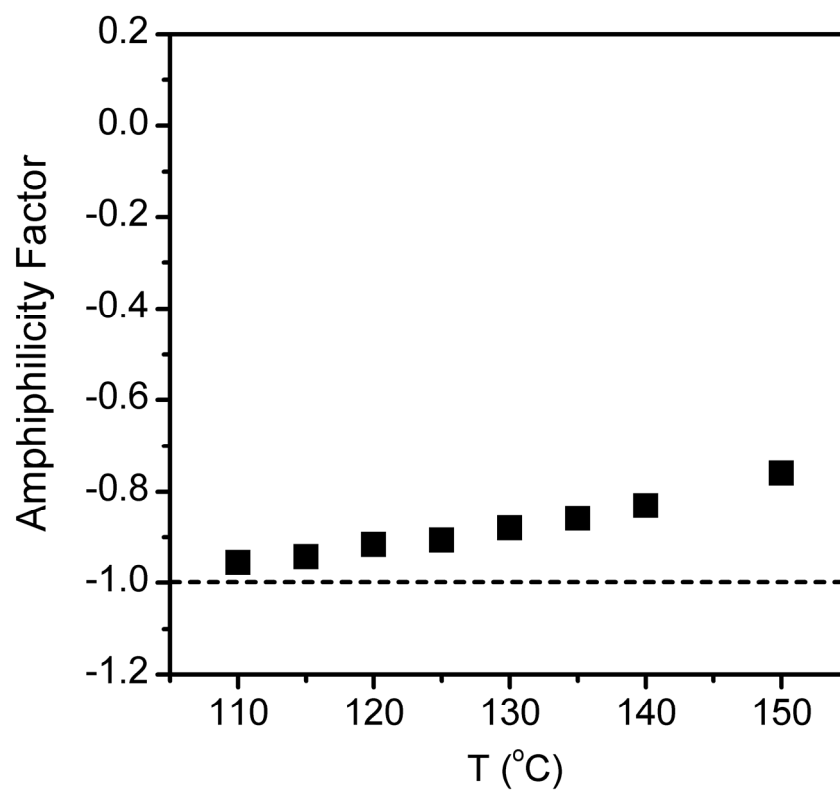


Figure 4.9. Amphiphilicity factor of the PS-PI bicontinuous microemulsion as a function of temperature.

4.4.2. Results

4.4.2.1. Rheology

The microemulsion sample was subjected to dynamic frequency sweeps within the linear viscoelastic regime at several temperatures between 125°C and 145°C. Dynamic strain sweeps at 10 rad/s revealed the linear regime to exist for <5% strain at 125°C and <15% strain at 145°C. High frequency measurements (10 to 100 rad/s) were conducted at lower strains (e.g., 1% strain at 125°C, 10% strain at 145°C). The measured complex viscosity, $|\eta^*|$, and phase angle, δ , are plotted in Figure 4.10 as a function of angular frequency, ω . At low frequencies, $|\eta^*|$ exhibits a Newtonian plateau, and $\delta \rightarrow 90^\circ$, indicating terminal (liquid-like) behavior. At higher frequencies, $|\eta^*|$ is shear-thinning, and δ decreases, which suggest perturbation of the B μ E structure at these time scales. The shift in phase angle towards lower frequency with decreasing temperature is associated with a slowing down of the microemulsion dynamics. Additionally, the phase angle features a shoulder at high temperatures, which becomes a minimum followed by a downturn as the temperature decreases. The lack of self-similarity in the phase angle data indicates that the sample is not thermorheologically simple and does not obey time-temperature superposition. The increasing elasticity with decreasing temperature corresponds to an increase in the degree of segregation between the B μ E domains.

Rheological measurements were also collected for each of the homopolymers. The viscosities of PS and PI, which are constant over the experimental range of frequencies, differ by more than three orders of magnitude (Figure 4.11). This large viscosity contrast reflects the large difference in glass transition temperatures of PS ($T_g \approx$

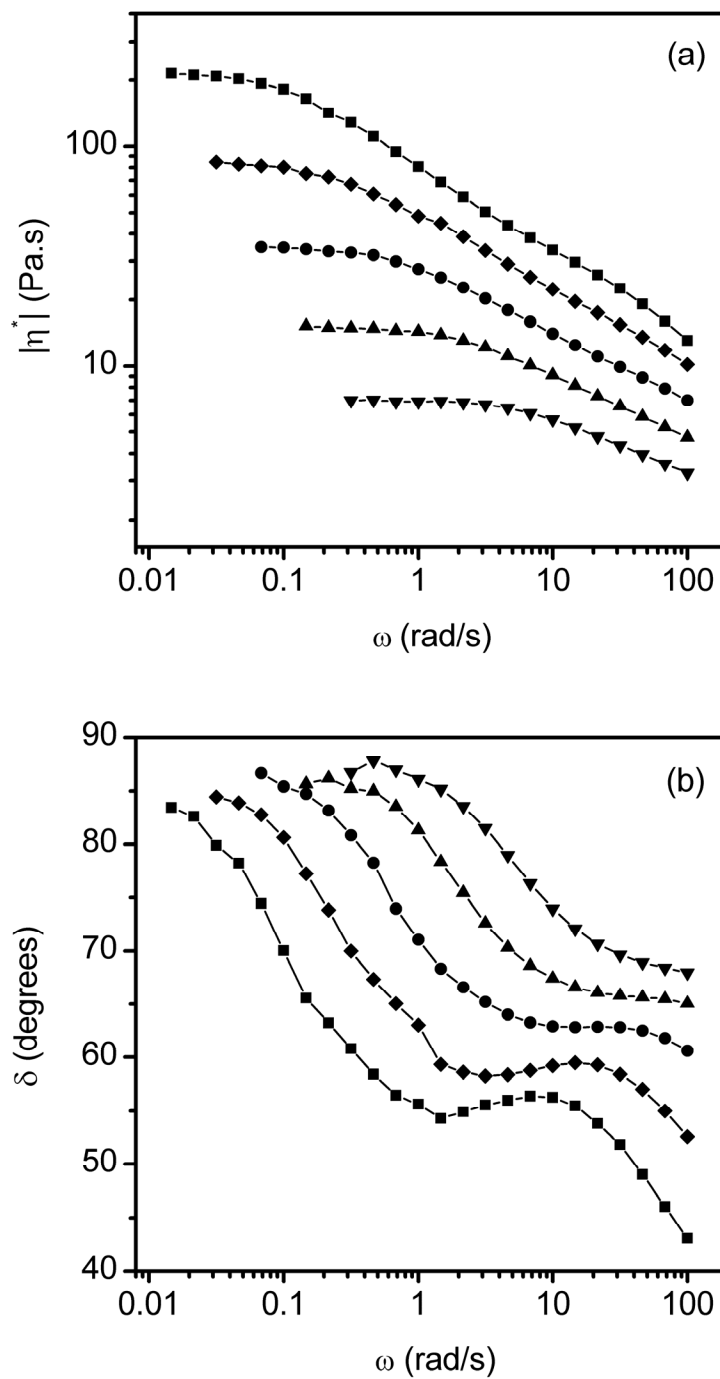


Figure 4.10. (a) Complex viscosity and (b) Phase angle of the PS-PI B μ E as a function of angular frequency measured at temperatures of (■) 125, (♦) 130, (●) 135, (▲) 140, (▼) 145°C. The solid lines serve as aids to the eye.

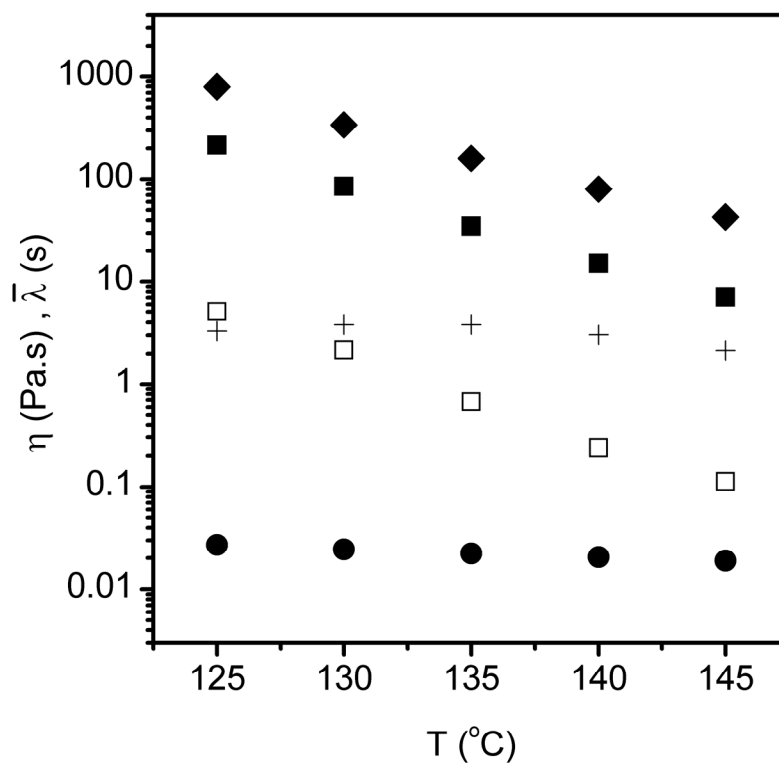


Figure 4.11. Zero-shear viscosities of the PS homopolymer (♦), PI homopolymer (●), and PS-PI B μ E (■) as a function of temperature. The “background” viscosity (+) and average relaxation time of the B μ E (□), determined by fitting a Generalized Maxwell model to the experimental data, are also plotted.

82°C) and PI ($T_g \approx -70^\circ\text{C}$). The rheological data were collected closer to the glass transition of PS, and, therefore, PS exhibits a stronger temperature dependence than PI. Since the molecular weights of the homopolymers are low, they are not expected to contribute significantly to the pronounced viscoelasticity of the blend shown in Figure 4.10. However, the polystyrene homopolymer exhibits measurable viscoelasticity at high frequencies ($\omega > 1$ rad/s) and low temperatures ($T < 135^\circ\text{C}$). For example, its terminal relaxation time is 0.0015 sec at 125°C. The polyisoprene homopolymer, on the other hand, does not exhibit measurable viscoelasticity within the experimental range of frequencies.

In general, the linear viscoelastic behavior of our PS-PI B μ E is very similar to the PEE-PDMS B μ E studied by Krishnan *et al.* (2002a). Both microemulsions are liquid-like at low frequency and transition to a more elastic character at higher frequency. Additionally, within the temperature ranges studied in each sample, the absolute values and temperature-dependence of the zero-shear viscosities and relaxation times of the two microemulsion systems are remarkably similar. The rheological similarities are not, perhaps, entirely surprising considering the similarities in the thermodynamics (*i.e.*, location of the B μ E phase in the isopleth) as well as in the rheological properties of the constituent homopolymers.

A significant difference between the two microemulsion systems is evident at the highest experimental frequencies. Following the minimum in δ at high frequency (Figure 4.10(b)), the PS-PI system exhibits a downturn in the phase angle, thus becoming more elastic. Conversely, the PEE-PDMS system exhibits an *upturn* in the phase angle and

returns to a more liquid-like state. This difference in behavior is likely related to the dynamics of the polymer chains, which may contribute to the measured viscoelasticity of the bicontinuous microemulsion at high frequencies. The homopolymers used in the PEE-PDMS microemulsion were reported to be Newtonian, whereas we report measurable viscoelasticity in our polystyrene homopolymer. Since the PS-*b*-PI copolymer is greater than five times the length of the homopolymers, we also expect the PS block to exhibit viscoelasticity; however, the elastic character of the PS block cannot be independently measured because the copolymer microphase separates at temperatures within the microemulsion channel. Based on these observations, we speculate that the elastic character of the polystyrene components in our microemulsion results in the enhanced elastic response relative to the PEE-PDMS B μ E at high frequency.

The two B μ E systems also show a notable difference in the “composite” zero-shear viscosity relative to the respective constituent viscosities. As shown in Figure 4.11, the zero-shear viscosity of the PS-PI microemulsion lies between the viscosities of the two homopolymers, and exhibits a slightly stronger temperature-dependence than PS due to the changing degree of segregation between the domains. If both homopolymer domains in the B μ E deform equally during shear, the microemulsion viscosity should approximately equal the sum of the homopolymer viscosities weighted by the corresponding volume fractions. Using this approach, the expected viscosity of the PS-PI B μ E is ~50% of the PS homopolymer viscosity. Additional contributions from the PS-PI copolymer and its confinement to the interface could further increase the viscosity of the microemulsion. However, the zero-shear viscosity of our PS-PI microemulsion is only

17–27% of the PS viscosity. This result is in contrast to the PEE-PDMS B μ E investigated by Krishnan *et al.* (2002a), who reported the B μ E zero-shear viscosity to be *larger* than the high-viscosity PEE component (which also is more than three orders of magnitude greater than the low-viscosity component, PDMS). The lower viscosity of the PS-PI B μ E (relative to the constituent viscosities) may be partially explained in terms of the degree of segregation between the domains. Structural information obtained from static scattering data show that the PS-PI microemulsion has a larger correlation length than the PEE-PDMS system. Larger correlation lengths imply an increased degree of segregation with perhaps a lesser degree of connectivity between similar domains, possibly resulting in a lower viscosity. Furthermore, the B μ E viscosity may also be influenced by the degree of viscosity contrast between the homopolymers. The lower-viscosity domains deform at a greater rate than the high-viscosity domains under applied shear, yielding a lower effective “composite” viscosity. This effect may be greater in the PS-PI B μ E, which has a greater viscosity contrast than the PEE-PDMS B μ E.

The rheological data for the PS-PI microemulsion were fit with a generalized Maxwell model using two relaxation modes per decade. As in the PEE-PDMS B μ E [Krishnan *et al.* (2002a)], a purely viscous mode at zero relaxation time is necessary to accurately describe the data. This purely viscous mode is presumably dominated by the viscous dissipation of the pure components in the blend, and, therefore, we refer to this viscous mode as “background” viscosity, η_b . If η_b originates from the pure components, the temperature-dependence is expected to follow that of polystyrene. For the PEE-PDMS B μ E, η_b does in fact closely follow the temperature-dependence of the high T_g

PEE component [Krishnan *et al.* (2002a)]. However, as shown in Figure 4.11, η_b is insensitive to changes in temperature for the PS-PI B μ E. The cause of this result is unclear and may be influenced by partial miscibility and/or high viscosity-contrast between the homopolymers. Also, the microemulsion may have additional viscoelastic modes at high frequencies that are experimentally inaccessible, and the viscous contributions of these modes may be inadvertently lumped into this “background” viscosity. Estimation of η_b solely from contributions of the homopolymers is non-trivial since their large viscosity-contrast results in unequal deformation rates in the domains under applied shear; in addition, the possible role of the PS-*b*-PI copolymer cannot be estimated since the pure copolymer is microphase separated at these temperatures. Finally, estimation of η_b in the PS-PI B μ E is further complicated, relative to the PEE-PDMS microemulsion, by the elasticity of the PS components at high frequency.

Although the “background” viscosity may be an imperfect representation of the pure component contributions to the measured rheology, subtraction of η_b from the total measured response of the B μ E provides the best approximation of the “excess” viscoelasticity resulting exclusively from the bicontinuous microstructure. Excluding the viscous “background” mode, the average relaxation time, $\bar{\lambda}$, of the microemulsion can be computed from the relaxation spectrum:

$$\bar{\lambda} = \frac{\sum \eta_k \lambda_k}{\sum \eta_k} \quad (4.15)$$

where η_k and λ_k are the viscosity and relaxation time, respectively, corresponding to each viscoelastic mode k fit to the experimental data. The decrease in the average relaxation

time with increasing temperature, shown in Figure 4.11, largely reflects an acceleration of the B μ E dynamics as the constituent viscosities decrease. Also, close inspection of Figure 4.11 shows that $\bar{\lambda}$ exhibits a slightly stronger temperature-dependence than the PS homopolymer viscosity. This enhanced temperature-dependence in the relaxation time is associated with the changing degree of segregation between the homopolymer domains with temperature.

The “excess” complex viscosity components are plotted in Figure 4.12, where $\Delta\eta'$ ($= \eta' - \eta_b$) and η'' are the viscous and elastic components, respectively. These quantities have been normalized by the “background”-subtracted zero-shear viscosity, $\Delta\eta_0$ ($= \eta_0 - \eta_b$), and presented as a function of the reduced frequency, $\omega\bar{\lambda}$. In this reduced form, the data collapse well into a single master curve. Some variation between data sets exists at high frequency, which may result from imperfect determination of the “background” contributions from the pure components. Despite this variation, $\Delta\eta'$ and η'' appear to merge together at high frequency.

As discussed earlier, Pätzold and Dawson have derived predictions for the excess linear viscoelastic behavior of bicontinuous microemulsions (1996a, 1996b). The predictions for the reduced form of the complex viscosity components (eqns. 4.10 and 4.11) were computed for the PS-PI B μ E using the SAXS data collected at 135°C. These predictions are presented in Figure 4.12 along with the experimental mechanical data (in reduced form, the predictions are only slightly temperature-dependent over the range considered here). As in the case of the PEE-PDMS B μ E [Burghardt *et al.* (2002)], the model describes the qualitative behavior quite well with the exception at high frequency,

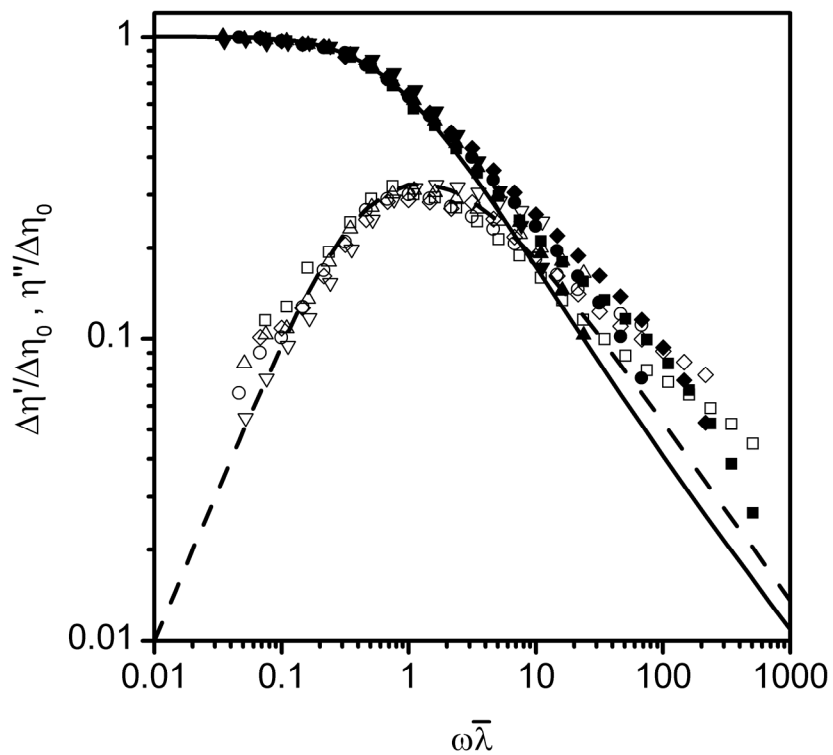


Figure 4.12. Components of the “excess” complex viscosity of the PS-PI BμE plotted in reduced form. The elastic and viscous components are represented by open and closed symbols, respectively. The solid and dashed lines are predictions (eqns. 4.9 and 4.10) based on a time-dependent Landau-Ginzburg model by Patzold and Dawson.

where the predicted slope of the viscosity components (*i.e.*, $-1/2$) is steeper than the experimentally observed slope. Burghardt *et al.* (2002) noted that the discrepancy at high frequency does not likely result from errors in lumping some of the excess properties into the viscous “background” subtraction, since increasing the viscous contribution of the B μ E causes even greater deviation from the predicted behavior. The PS-PI system is also complicated by possible *elastic* contributions from PS homopolymer, which enhance the measured response of the microemulsion at high frequency. Accounting for the viscoelastic contributions from polystyrene would bring the experimental data in closer agreement with theory. Despite these discrepancies, the Pätzold-Dawson model qualitatively describes the shape of the relaxation spectrum very well.

To test the ability of the Pätzold-Dawson model to predict *absolute* values of rheological parameters, measurement of the Onsager coefficient is required. We have measured the q -dependent Onsager coefficient at the length scale of the microemulsion structure using XPCS. These XPCS measurements along with the quantitative performance of the model for the PS-PI B μ E are discussed in the following sections.

4.4.2.2. X-Ray Photon Correlation Spectroscopy

XPCS is a useful tool for studying the dynamics of materials, such as polymer systems, which exhibit relaxation on time scales of 0.1 – 100 seconds and length scales of 5 – 300 nm. Therefore, considering the static scattering and rheological results presented above, XPCS is a very suitable technique for probing the dynamics of our PS-PI microemulsion

system. From XPCS measurements, the scattering intensity autocorrelation function, $g_2(q, t)$, was computed using the definition (as described in Section 2.5):

$$g_2(q, t) \equiv \frac{\langle I(q, t') I(q, t' + t) \rangle}{\langle I(q, t') \rangle^2}. \quad (2.18)$$

This quantity is related to the normalized dynamic structure factor by

$$g_2(q, t) = 1 + C |f(q, t)|^2 \quad (2.19)$$

where C is an experimental parameter. For the PS-PI BμE, $g_2(q, t)$ does not decay as a single-exponential function (see Figure 4.13), indicating that the structure relaxes via multiple processes. We have chosen to fit eqn. 2.19 to our experimental data using a stretched-exponential form of $f(q, t)$ (eqn. 2.21). The stretching exponent ν and average relaxation time $\langle \tau_q \rangle$ obtained from these fits are plotted in Figure 4.14.

The stretching exponent at higher temperatures (125°C and 130°C) is nearly independent of q and ranges between $0.5 \leq \nu \leq 0.65$. At lower temperatures, ν lies within this range at small q , but appears to become a decreasing function of q for $q > q_{\max}$ of the static structure factor. Furthermore, this decrease in ν at large q becomes steeper with decreasing temperature. As suggested by our rheological measurements, chain dynamics appear to become significant on experimental time scales (≥ 10 ms) for temperatures lower than 130°C. Therefore, at large q , where structures comparable to the length scale of polymer chains are probed, relaxation of the polymer chains occurs on similar time scales as microemulsion relaxation. These additional relaxation processes that are associated with chain dynamics may contribute to the broadening of the relaxation spectrum, particularly at the lowest temperatures. Although this observation

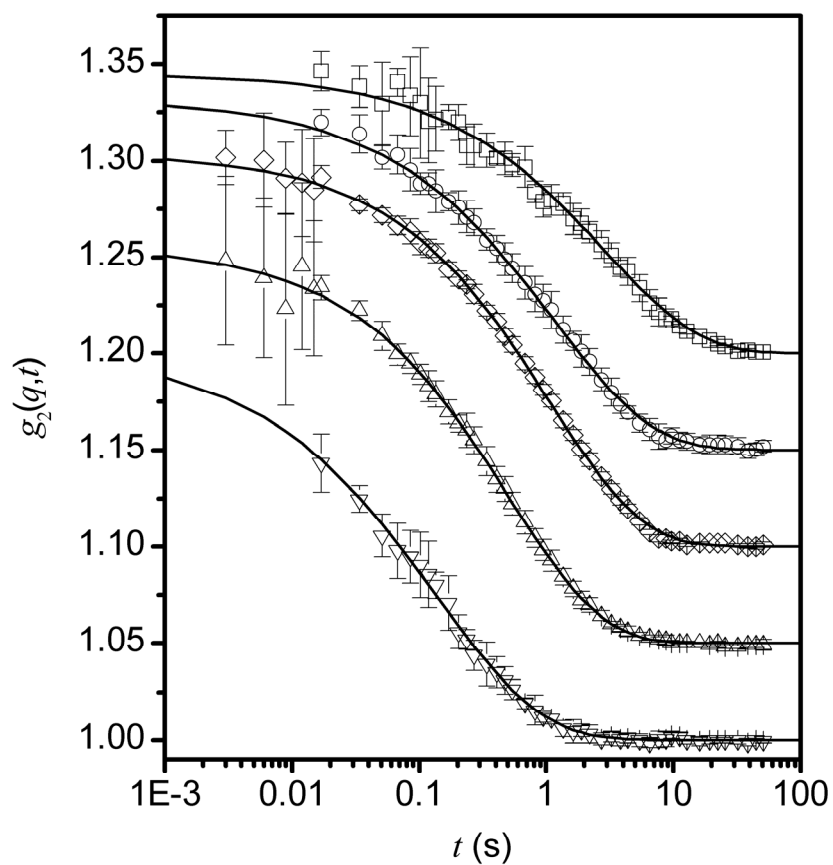


Figure 4.13. Intensity autocorrelation function as a function of delay time for the PS-PI BμE at 120°C and various wavevectors: ($\square$) 0.036, ($\circ$) 0.055, ($\diamond$) 0.067, (Δ) 0.080, (∇) 0.09 nm⁻¹. For clarity, the data sets are shifted vertically from each other by 0.05. The solid lines are stretched-exponential fits.

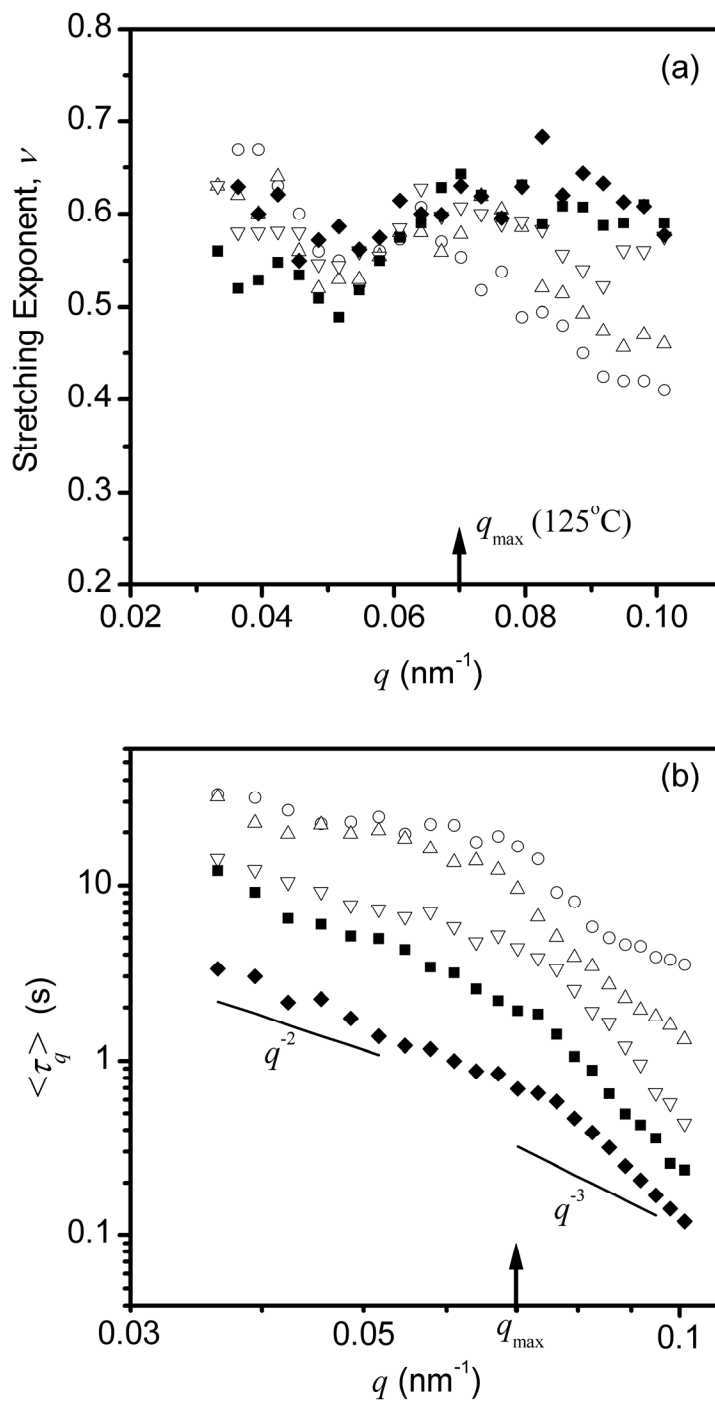


Figure 4.14. (a) Stretching exponent and (b) Average relaxation time of the PS-PI B μ E as a function of q for various temperatures: ($\circ$) 110°C, (Δ) 115°C, (∇) 120°C, ($\blacksquare$) 125°C, and ($\blacklozenge$) 130°C. The arrows indicate q_{max} of the static structure factor at 125°C.

complicates our interpretation of these data, it promises deeper insights into the dynamics of polymer systems.

In general, the stretching exponents determined from fits to the experimental data are close to $\nu = 2/3$ as predicted by the membrane theory by Zilman and Granek (1996) for $q \gg q_{\max}$. Stretched-exponential relaxation with similar values of ν have been experimentally observed in other systems containing fluctuating membranes and interfaces, including polymer vesicles [Falus *et al.* (2005)] and o/w/s sponge phases [Freyssingeas *et al.* (1997); Maguey and Bellocq (2001)], lamellae [Komura *et al.* (2001); Mihailescu *et al.* (2002)], and bicontinuous microemulsions [Komura *et al.* (2001); Mihailescu *et al.* (2001)]. Interestingly, Ruegg *et al.* (2006) have also recently reported stretched-exponential relaxation in a PS-PI B μ E at high temperatures that transitions to *compressed*-exponential ($\nu > 1$) relaxation at low temperatures. The compressed-exponential behavior, which was observed within 5 – 15°C of the glass transition temperature (T_g) of the polystyrene homopolymer, was suggested to perhaps be related to the spontaneous breakup of microstructure. Our lowest temperature measurements are somewhat farther from the T_g of the polystyrene used in the present study, and we do not observe any evidence to suggest an increase in ν or an eventual crossover to $\nu > 1$ at even lower temperatures. As indicated by the Teubner-Strey fitting coefficients, the PS-PI B μ E in the present study is a more strongly structured B μ E, presumably due to the larger ratio of N_{A-B}/N_A in our case. These differences in formulation and testing conditions may explain the differences found in these two studies.

The average relaxation time, presented in Figure 4.14(b), decreases monotonically with increasing q . As the temperature decreases, however, a shoulder appears to develop in the vicinity of $q = q_{\max}$ of the static structure factor, which suggests the formation of a peak at even lower temperatures. A peak in $\langle \tau_q \rangle$ occurring at $q_{\max}$ of the structure factor is known as “de Gennes narrowing” [deGennes (1959)]. This behavior is often observed in systems which exhibit a peak in the structure factor resulting from a structure that is favored by low free energy. Hennes and Gompper (1996) predict a peak in $\langle \tau_q \rangle$ at $q = q_{\max}$ for the condition $(2\xi/d) > 3.5$, but that $\langle \tau_q \rangle$ is a monotonically decreasing function of q for $(2\xi/d) \leq 3.5$. For the PS-PI B μ E, $(2\xi/d) = 2.1$ at 110°C. Therefore, the growth of the shoulder in $\langle \tau_q \rangle$ with decreasing temperature seems to be consistent with the Hennes-Gompper predictions.

For diffusive motion in systems at large length scales, the scaling relationship $\tau_q \sim q^{-2}$ is generally observed. The PS-PI B μ E appears to follow this scaling for $q < q_{\max}$. This behavior is perhaps more clear in a plot of $[\langle \tau_q \rangle q^2]^{-1}$ as a function of q , as shown in Figure 4.15(a). For $q < q_{\max}$, $[\langle \tau_q \rangle q^2]^{-1}$ is nearly independent of q , with the exception of the data at 110°C. Even in the case of 110°C, $[\langle \tau_q \rangle q^2]^{-1}$ seems to approach a constant value at the smallest measured scattering vectors. For $q > q_{\max}$ at all temperatures, $\langle \tau_q \rangle$ is more strongly dependent on q . At the highest scattering vectors and lowest temperatures, however, $\langle \tau_q \rangle$ seems to return to the q^{-2} scaling relationship. These observations are generally consistent with the behavior of the PS-PI B μ E by Ruegg *et al.* (2006) for high temperatures (*i.e.*, in the stretched-exponential regime).

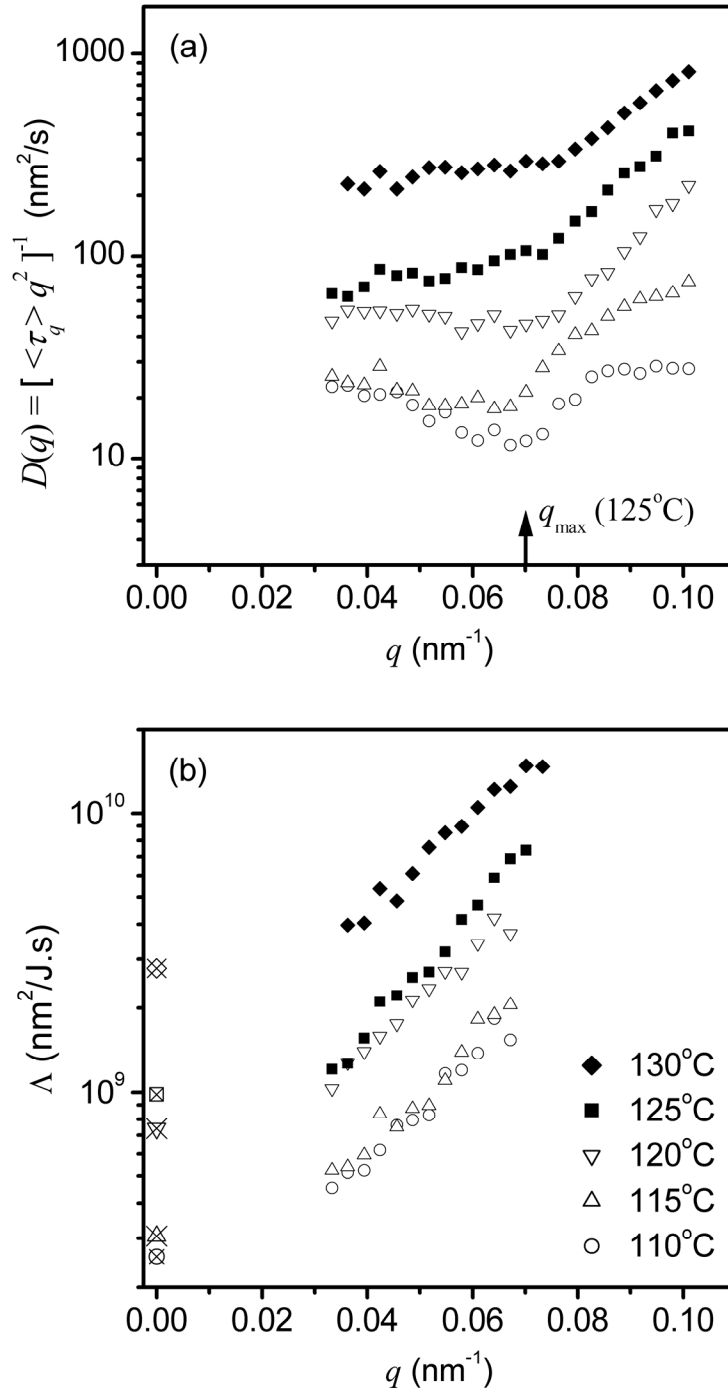


Figure 4.15. (a) $[\langle \tau_q \rangle q^2]^{-1}$ and (b) Onsager coefficient of the PS-PI BμE as a function of q for various temperatures. Symbols with an “X” represent $\Lambda(q \rightarrow 0)$ computed using $D(q \rightarrow 0)$ from (a) and $S(q = 0)$ from eqn. 4.2.

The Landau-Ginzburg models for bicontinuous microemulsions predict $\tau_q \sim q^{-2}$ for $q \ll q_{\max}$ [Granek and Cates (1992); Hennes and Gompper (1996); Nonomura and Ohta (1999)]. For $q \gg q_{\max}$, the Landau-Ginzburg theory by Granek and Cates (1992) predicts $\tau_q \sim q^{-3}$ as a result of hydrodynamic effects at smaller length scales. The membrane theory by Zilman and Granek (1996) also predicts $\tau_q \sim q^{-3}$ for large q . Although our experimental results agree with theoretical scaling at small q , the experimental relaxation time at large q scales more strongly than q^{-3} , particularly at low temperatures. Since measurements in the high q region may be confounded by chain dynamics, it is difficult at this time to assess this discrepancy between experiment and theory.

The Pätzold-Dawson model, which neglects the presence of amphiphile and coupling between the flow field and the order parameter, predicts single-exponential relaxation of $f(q,t)$. Although the PS-PI BμE exhibits *stretched*-exponential relaxation, we approximate the Onsager coefficient by assuming eqn. 4.14 to valid for $q \leq q_{\max}$ (where $\tau_q \sim q^{-2}$) and using the average relaxation time $\langle \tau_q \rangle$. The Onsager coefficient computed in this manner is presented in Figure 4.15(b). In general, the Onsager coefficient increases with increasing temperature, but the strength of the temperature-dependence is somewhat variable. The sample was annealed for 45 minutes at each temperature prior to collecting XPCS measurements. However, measurements were collected in non-sequential order with respect to temperature, and it is possible that the variability in the temperature-dependence results from the sample morphology not having reached equilibrium prior to each set of measurements.

The measured Onsager coefficient is an increasing function of q . However, since $S(q)$ and $D(q)$ are expected to approach a constant value as $q \rightarrow 0$, $\Lambda(q \rightarrow 0)$ should also become constant. Although $D(q \rightarrow 0)$ (from Figure 4.15(a)) appears to approach a constant value at the smallest measured scattering vector, $S(q)$ (Figure 4.7) is still changing. To estimate $\Lambda(q \rightarrow 0)$, we have taken the experimentally determined $D(q \rightarrow 0)$ and the theoretical $S(q)$ (eqn. 4.2 using the fitting coefficients from Table 4.1) computed at $q = 0$. The values for $\Lambda(q \rightarrow 0)$ are plotted in Figure 4.15(b). For $q > q_{\max}$, both theory and experiment indicate that the relaxation time scales more strongly than $\tau_q \sim q^{-2}$. Since the exact scaling is unknown, we do not have an appropriate method for estimating $\Lambda(q)$ in this q -range. For the purpose of testing the rheological predictions by Pätzold and Dawson, we are only interested in $\Lambda(q)$ on length scales comparable to and larger than the B μ E domain size ($q \leq q_{\max}$).

4.4.2.3. Pätzold-Dawson Rheological Predictions

The XPCS results above already highlight significant limitations of the single-order parameter theory underlying the analysis of bicontinuous microemulsion rheology of Pätzold and Dawson, which accounts for neither a q -dependent Onsager coefficient nor non-exponential relaxation of $f(q, t)$. At the same time, Figure 4.12 demonstrates surprisingly robust qualitative predictions of the shape of the viscoelasticity. Despite the shortcomings of the model, we return here to a brief consideration of its absolute predictions of viscosity and relaxation time (eqns. 4.9 and 4.12) in order to complete the comparison with the previously studied PEE-PDMS system [Burghardt *et al.* (2002)].

The evaluation of the absolute predictions requires knowledge of structural parameters obtained from static SAXS measurements (presented in Table 4.1 and Figure 4.7) as well as the Onsager coefficient. Since Pätzold and Dawson do not account for the possibility of a q -dependent Onsager coefficient, we consider here only an ad hoc procedure of using $\Lambda(q)$ determined at $q \rightarrow 0$ and at the peak ($q = q_{\max}$) of the static structure factor in evaluating the predictions. The former should be analogous to the use of an Onsager coefficient determined from LPCS in the PEE-PDMS study, while the latter provides a crude means of considering whether measuring dynamics on more relevant length scales impacts the quality of the predictions. The resulting two sets of predictions are plotted in Figure 4.16 along with the experimental data.

The model, evaluated for both cases $\Lambda(q \rightarrow 0)$ and $\Lambda(q_{\max})$, underpredicts both the excess zero-shear viscosity and average relaxation time. However, predictions using $\Lambda(q \rightarrow 0)$ perform significantly better than those using $\Lambda(q_{\max})$. The failure of the model to predict the absolute values of the rheological properties is consistent with the study by Burghardt *et al.* (2002) for the PEE-PDMS B μ E (see Figure 4.2). When using $\Lambda(q \rightarrow 0)$, the discrepancy between experiment and theory is much smaller in the PS-PI system compared to the PEE-PDMS B μ E and, somewhat surprisingly, attempts to “improve” upon this by employing an Onsager coefficient measured at relevant length scales actually worsens the predictions considerably. Additionally, regardless of which Onsager coefficient is used, the predictions closely parallel the temperature-dependence of the viscosity and relaxation time, which was not the case in PEE-PDMS (Figure 4.2) [Burghardt *et al.* (2002)].

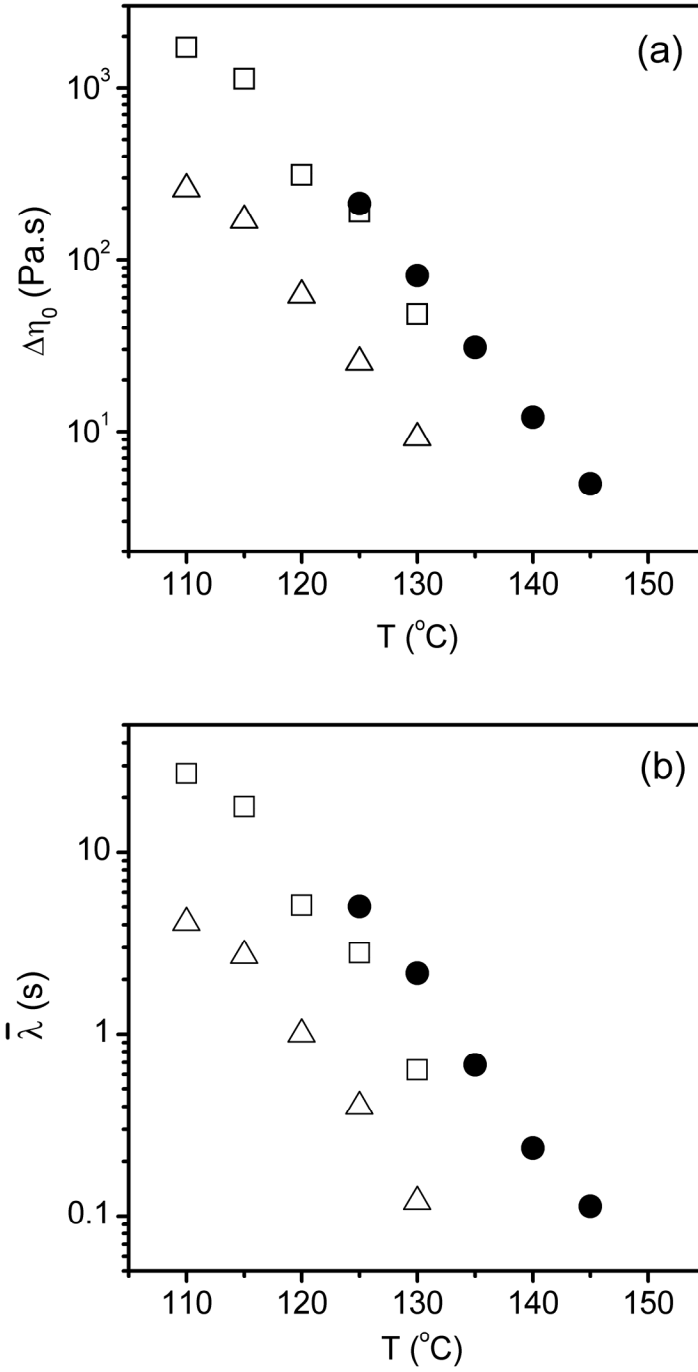


Figure 4.16. Absolute tests of the Pätzold-Dawson predictions for linear viscoelastic properties of the PS-PI BμE: (a) excess zero-shear viscosity, (b) average relaxation time. (●) Experimental data. Predictions of eqns. 4.9 and 4.12 using $\Lambda(q)$ determined at (□) $q \rightarrow 0$ and (Δ) $q = q_{\text{max}}$ of the static structure factor.

Burghardt *et al.* noted that computing the ratio $\Delta\eta_0 / \bar{\lambda}$ (an effective “modulus”) provides an additional quantitative test of the model. In this quantity all predicted dependence on the Onsager coefficient is removed. As shown in Figure 4.17, the model fails to quantitatively predict this “modulus”, which is consistent with the findings in the PEE-PDMS B μ E (Figure 4.2(c)). However, the model again performs somewhat better for the PS-PI B μ E, relative to the PEE-PDMS B μ E, in predicting both the absolute values and temperature-dependence of $\Delta\eta_0 / \bar{\lambda}$. The discrepancy between the experimental and theoretical “modulus” for the two microemulsion systems indicates that the failure of the model is related to issues other than (or in addition to) uncertainties in the measurement of Λ .

Recognizing the inherent deficiencies in the Pätzold-Dawson model revealed by the XPCS measurements of the PS-PI B μ E, it is hardly surprising that its rheological predictions should fail, and perhaps somewhat remarkable that it performs as well as it does in Figure 4.12. The results of this study underscore the need to account for more accurate physics, such as a description of hydrodynamic interactions and the presence of amphiphile, in the development of theory. Snabre and Porte (1990) have performed viscosity measurements of an o/w/s sponge phase that also underline the importance of accounting for coupling between the microstructure and the flow field in bicontinuous types of morphologies. The sponge phase exhibited Newtonian behavior over a wide range of shear rates, which suggests that the membrane is (more or less) preserved during shear. Also, the measured zero-shear viscosity as $\Phi_S \rightarrow 0$ (where Φ_S is the surfactant concentration) was much larger than the viscosity of the pure solvent. An interpretation

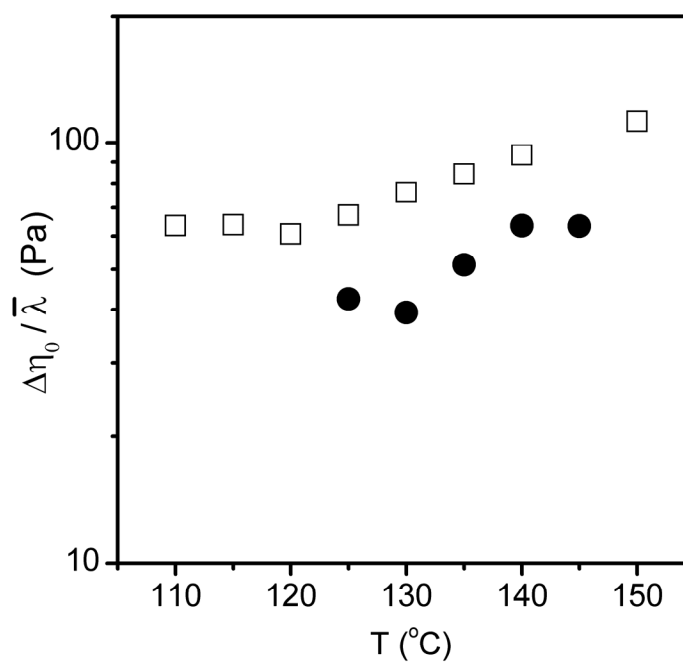


Figure 4.17. Absolute test of the Pätzold-Dawson predictions for linear viscoelastic properties of the PS-PI B μ E: ratio of excess viscosity to relaxation time as a function of temperature. (●) Experimental data. (□) Pätzold-Dawson prediction.

of the results was provided indicating that the deformation of the solvent in the sponge domains (or “cells”) is much greater than that of the pure solvent subjected to the same effective shear rate. As demonstrated by the Granek and Cates (1992) and Hennes and Gompper (1996) theories describing bicontinuous microemulsions in thermal equilibrium, accounting for hydrodynamic effects and the presence of amphiphile is non-trivial. Due to these complexities, it is difficult to speculate how the predictions of rheological properties would be impacted.

4.4.3. Summary

The equilibrium dynamics of a polystyrene-polyisoprene bicontinuous microemulsion have been characterized using rheology and x-ray photon correlation spectroscopy. Direct comparison of the PS-PI B μ E to the previously documented PEE-PDMS B μ E [Burghardt *et al.* (2002); Krishnan *et al.* (2002a)] shows many similarities in the linear viscoelastic behavior of the two systems. Subtle differences in the overall behavior of the two microemulsions are attributed to differences in the degree of viscosity contrast and degree of segregation between the B μ E domains in each system. The higher elasticity in the PS-PI B μ E, relative to the PEE-PDMS B μ E, at high frequency may be partially due to elastic contributions from the polystyrene components in the blend.

XPCS measurements of the PS-PI B μ E show non-exponential relaxation of the dynamic structure factor and a q -dependent Onsager coefficient. Although the Pätzold-Dawson model predicts a *single*-exponential form of $f(q,t)$ and assumes a q -independent Onsager coefficient, we proceeded with an *ad hoc* test of its rheological predictions using

Λ determined at $q \rightarrow 0$ and $q = q_{\max}$ of the static structure factor. The model generally performs better for the PS-PI B μ E than for the PEE-PDMS B μ E, but still fails to predict the absolute values of the viscosity and average relaxation time. Furthermore, using Λ measured at the dominant length scale of the microemulsion provides no improvement over using $\Lambda(q \rightarrow 0)$. The results of this study show the need for the development of more sophisticated theory, which account for hydrodynamic effects and the presence of amphiphile, to describe the rheological properties of bicontinuous microemulsions. XPCS and rheology data collected at lower temperatures further demonstrate that, in the specific case of polymer microemulsions, the effects of the polymer chains should also be considered.

4.5. Shear-Induced Dynamics of a PS-PI B μ E

Our final experiments of the PS-PI microemulsion ($\Phi_H = 0.90$) involve the use of rheology and *in situ* small-angle x-ray scattering to interrogate the effects of shear flow on the B μ E structure. Additional (limited) experiments were performed using optical microscopy to complement the rheology and SAXS data. Comparisons were again made to the PEE-PDMS B μ E [Caputo *et al.* (2002b); Krishnan *et al.* (2002b)] to determine characteristics that are potentially general to polymer bicontinuous microemulsions.

4.5.1. Experiment

4.5.1.1. Rheology

Rheological data were collected for start-up and cessation of steady shear flow at 130°C. Measurements were performed with the ARES rheometer using cone and plate fixtures (50 mm diameter, 0.04 radian cone angle) and a nitrogen atmosphere.

4.5.1.2. *In Situ X-Ray Scattering*

In situ SAXS experiments were conducted at beamline 5ID-D of the Advanced Photon Source using 17 keV undulator radiation. The annular cone and plate shear cell was mounted in a large vacuum chamber, shown in Figure 2.5. This setup placed the sample/shear cell and the paths of the incident, transmitted, and scattering x-rays entirely under vacuum. The microemulsion sample was subjected to oscillatory shear, step strain, and start-up/cessation of steady shear flow at 125°C or 130°C. Time-resolved scattering patterns of the flow-gradient (x - y) plane were collected at a rate of ~ 1.25 frames/s using a two-dimensional CCD detector (Roper) positioned 10.2 meters downstream from the shear cell. Changes in the incident beam flux with time were monitored using an ion chamber positioned upstream from the shear cell.

4.5.1.3. *Correction Procedures and Analysis of X-Ray Data*

A representative scattering pattern of the PS-PI B μ E at equilibrium is shown in Figure 4.18(a). As in the SAXS experiments probing the PEE-PDMS microemulsion [Caputo *et al.* (2002b)], the scattering patterns show two main features. The first feature is an

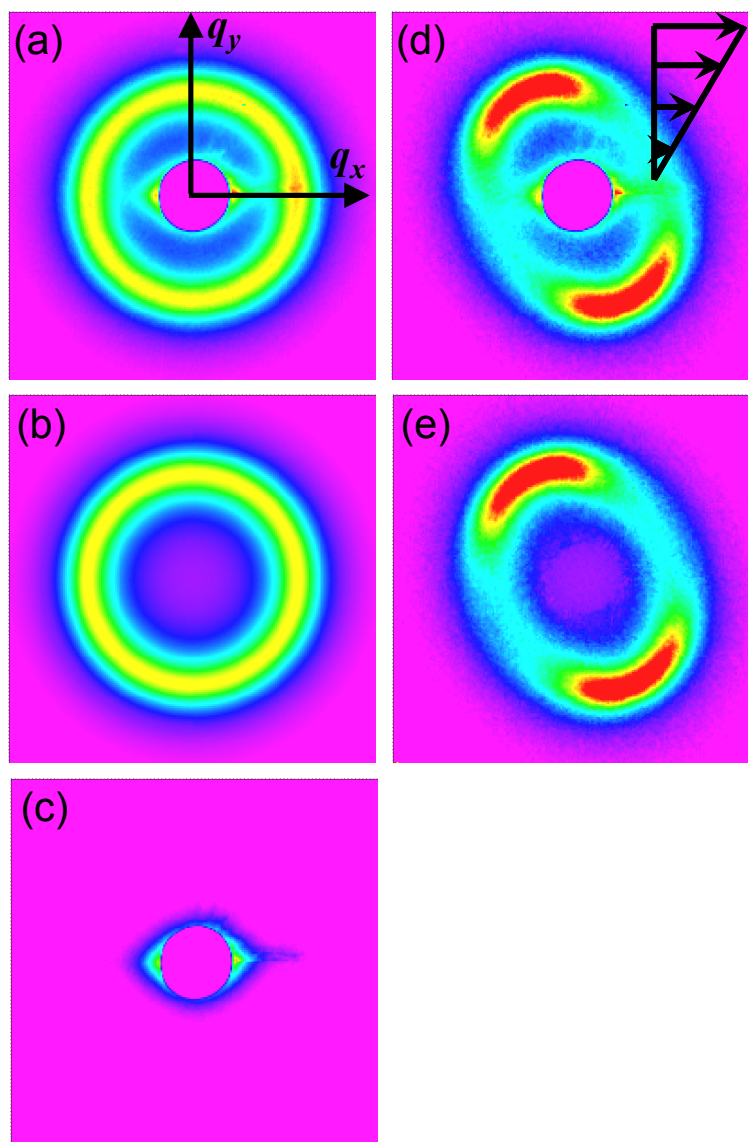


Figure 4.18. Illustration of the correction procedures applied to scattering patterns of the PS-PI B μ E. (a) Normalized quiescent pattern prior to subtraction of the parasitic feature. (b) “Ideal” quiescent pattern generated from 1-D data extracted along q_y in image (a) and replacing the low- q region with the fit from the Teubner-Strey structure factor. Subtraction of image (b) from image (a) yields (c) an image of the parasitic feature. The parasitic image (c) subtracted from (d) a normalized shear pattern gives (e) the final corrected shear image. The intensity scale is the same in all images. The q -range in these images is $|q_x, q_y| \leq 0.136 \text{ nm}^{-1}$ and $q_{\text{max}} = 0.078 \text{ nm}^{-1}$ at 125°C .

isotropic ring associated with scattering from B μ E structure. The second, “lozenge-shaped” feature at lower scattering angles is attributed to scattering from the aluminum barrier in the bottom plate of the shear cell. This parasitic scattering could not be eliminated because our experiments were performed prior to installation of the mica window in the barrier (refer to Section 2.4.3). However, the level of parasitic scattering relative to the intensity of the microemulsion peak is significantly lower than in the SAXS experiments conducted with the PEE-PDMS B μ E (see Figure 2.9) [Caputo *et al.* (2002b)]. The reduced degree of parasitic scattering in our experiments showed promise for observation of scattering from phase-separated structures at high shear rates.

Before subjecting the scattering patterns to a quantitative analysis, we have applied a series of normalization and correction procedures, which are very similar to those used by Caputo *et al.* (2002b). These procedures were performed as a set for each independent shear experiment. First, to account for fluctuations in the incident beam intensity with time, each scattering pattern was normalized by the incident beam flux, which was measured for each time point using the ion chamber. Next, a number of quiescent patterns collected prior to a particular shear experiment were averaged together, and the intensity of the microemulsion peak along the q_y direction (*i.e.*, the direction least impacted by the parasitic scattering) was determined. All scattering images collected during the shear experiment were then normalized by this value, giving a scaled intensity at the peak of the microemulsion ring equal to 1 at quiescent conditions.

The final correction applied to the patterns involves subtraction of the parasitic scattering feature, which was carried out as follows. One-dimensional scattering data

was extracted from normalized, quiescent scattering patterns along the q_y direction, where the microemulsion scattering is least affected by the parasitic scattering. The Teubner-Strey structure factor (eqn. 4.2) was fit to the 1-D data, and the experimental data for $q < 0.06 \text{ nm}^{-1}$ was then replaced with the Teubner-Strey fit. The modified 1-D data was then used to generate a two-dimensional “ideal” quiescent pattern, shown in Figure 4.18(b). Subtracting the generated 2-D image from the original, normalized quiescent pattern yields an image of the parasitic feature, shown in Figure 4.18(c). This parasitic image was then subtracted from all scattering patterns obtained during a shear experiment. An example of a normalized and corrected scattering pattern of the B μ E during shear flow is shown in Figure 4.18(d).

We note at this point that the parasitic feature removed from the patterns does not solely represent the scattering from the aluminum barrier. Recall from Figure 4.7 that the PS-PI microemulsion exhibits an upturn in intensity at low q that is not described by the Teubner-Strey structure factor. In our shear experiments, this “extra” low- q scattering from the sample cannot be distinguished from the scattering from the shear cell barrier. As a result, scattering from both sources are lumped into the parasitic feature that is subtracted from all patterns. However, this consequence is not a concern for experiments of oscillatory shear, step strain, or shear inception at low shear rates, where we are mainly interested in the dynamics associated with the B μ E scattering peak. For shear inception experiments at high shear rates, we should still be able to observe any additional low- q scattering that appears if the B μ E structure undergoes phase separation.

To quantify shear-induced deformation of the microstructure, we have performed a second moment tensor analysis of the corrected 2-D scattering patterns. For all scattering patterns, $\langle \mathbf{q}\mathbf{q} \rangle$ was computed as given by eqn. 2.14 over the range $|q_x, q_y| \leq 0.136 \text{ nm}^{-1}$. As mentioned earlier, several quiescent patterns were collected prior to each shear experiment, and $\langle \mathbf{q}\mathbf{q} \rangle$ was calculated for the corrected average quiescent pattern.

The diagonal components for an isotropic, quiescent pattern are given by

$$\langle q_x q_x \rangle = \langle q_y q_y \rangle = \frac{1}{2} \langle qq \rangle_0 = \frac{1}{2} \iint q^2 I(q) dq_x dq_y . \quad (2.15)$$

For all scattering patterns within a shear experiment, $\langle \mathbf{q}\mathbf{q} \rangle$ was normalized by $\frac{1}{2} \langle qq \rangle_0$, which gives the diagonal components equal to 1 and the off-diagonal components equal to 0 when the scattering is isotropic. The principal anisotropy factor, AF , and the orientation angle, χ , were then computed from the quiescent-normalized $\langle \mathbf{q}\mathbf{q} \rangle$ using eqns. 2.16 and 2.17, respectively.

4.5.1.4. *In Situ Optical Microscopy*

In situ optical microscopy experiments were performed using a Linkam CSS-450 shear cell mounted onto the stage (specific to the shear cell) of a Nikon microscope (OPTIPHOT2-POL). The shear cell was equipped with transparent glass plates, allowing visualization of the flow-vorticity (x - z) plane. Due to the fairly high turbidity of the microemulsion sample, a very small gap (150 μm) was required to allow sufficient amounts of light to pass through the sample. Time-resolved, two-dimensional images of the microstructure were collected during start-up of shear flow and cessation from steady

shear at 130°C. The images were obtained using a Hitachi CCD camera (KP-M22) driven by a DT3155 frame grabber card (Data Translation, Inc., Marlboro, MA) installed in a lab computer.

4.5.2. Results

4.5.2.1. Oscillatory Shear and Step Strain Deformation

Here, we report the behavior of a PS-PI bicontinuous microemulsion in response to oscillatory shear and step strain deformation, which was probed using *in situ* SAXS. Caputo *et al.* (2002b) have performed nearly identical (and more extensive) experiments in which possible connections between x-ray anisotropy and rheology were investigated for the PEE-PDMS B μ E. These previous studies were inspired by a Landau-Ginzburg model by Pätzold and Dawson (1996b) that strongly suggests the existence of such connections for microemulsions. However, experimental results showed some significant discrepancies between the scattering and rheological behavior, particularly during relaxation upon flow cessation. Our analysis is less concerned with investigation of rheo-x-ray relationships; instead, we examine the extent to which the behavior of the two polymer B μ E systems, under low to moderate shear deformation, is universal. In order to make comparisons to the PEE-PDMS B μ E, the presentation of our data is very similar to the documentation by Caputo *et al.* (2002b).

Figure 4.19 shows the scattering analogs of the shear stress and first normal stress difference of the PS-PI B μ E during oscillatory shear at 50% strain. The shear stress analog oscillates at the frequency of the applied strain, but is shifted by a phase that

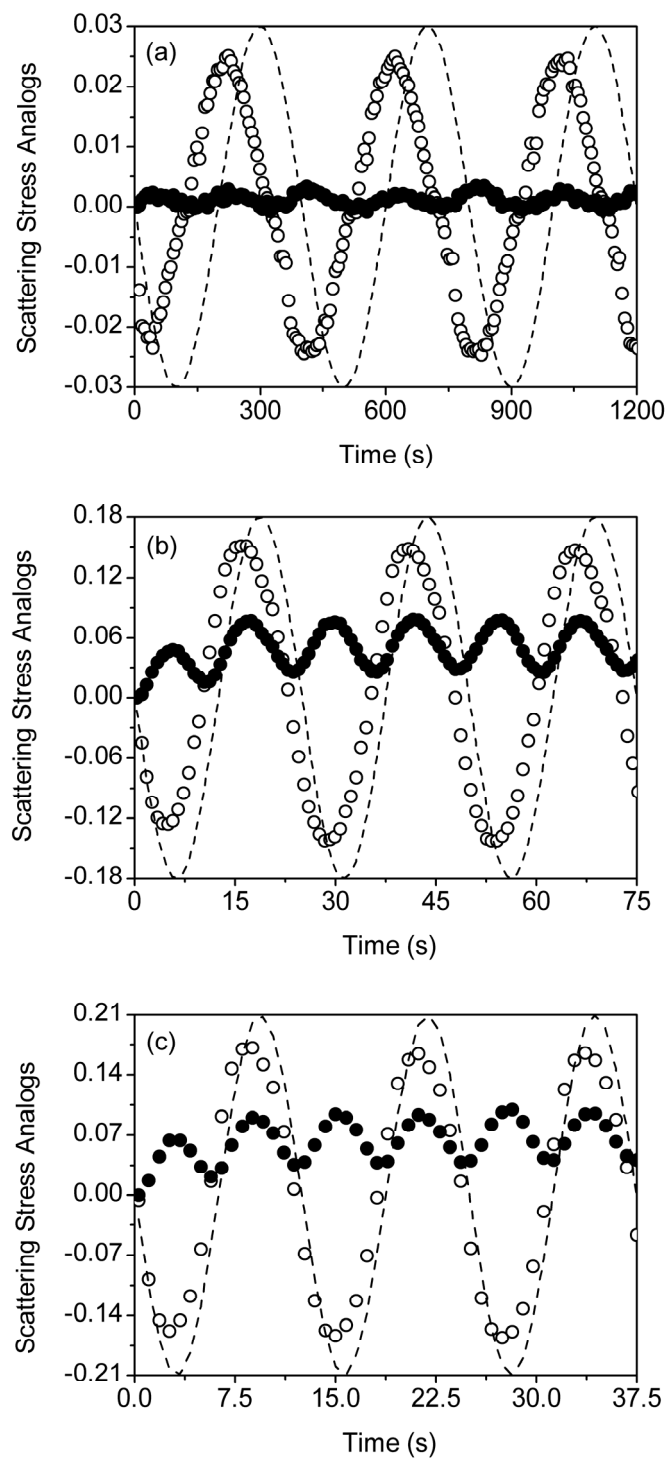


Figure 4.19. Scattering behavior of the PS-PI BμE during oscillatory shear at 125°C and 50% strain: $-\langle q_x q_y \rangle$ (○), $-\langle q_x q_x \rangle - \langle q_y q_y \rangle$ (●). The dashed line represents the applied strain wave. (a) $f = 0.0025$ Hz. (b) $f = 0.04$ Hz. (c) $f = 0.08$ Hz.

depends on the applied frequency. The phase difference is greatest at low frequencies, indicative of a liquid-like response. With increasing frequency, the phase difference becomes smaller, reflecting more elastic-like behavior. The analog of the first normal stress difference oscillates with respect to a nonzero value at twice the applied frequency. These results parallel those for the PEE-PDMS system.

If the response of a fluid is linear, we can consider a treatment analogous to the shear stress measured in conventional rheology, writing the x-ray anisotropy in terms of components that are in-phase and out-of-phase with the applied strain:

$$-\frac{\langle q_x q_y \rangle}{\frac{1}{2} \langle q q \rangle_0} = \gamma_0 [G'(\omega) \sin \omega t + G''(\omega) \cos \omega t] \quad (4.16)$$

where the applied strain is given by $\chi(t) = \gamma_0 \sin \omega t$. For fluids exhibiting single-exponential stress relaxation (eqn. 4.19), the x-ray analogs of the storage and loss moduli are given by

$$G'(\omega) = \frac{G(\omega\lambda)^2}{1 + (\omega\lambda)^2} \quad \text{and} \quad G''(\omega) = \frac{G\omega\lambda}{1 + (\omega\lambda)^2}, \quad (4.17)$$

respectively, where G is the modulus and λ is the relaxation time. G' and G'' determined from oscillatory data at 50% strain (assuming eqn. 4.16 to be valid) are plotted in Figure 4.20. Over this frequency range, these data are described fairly well by the predictions of eqn. 4.17 using $\lambda = 8.4$ sec and an “x-ray anisotropy modulus” of $G = 0.35$.

The fact that G' and G'' from oscillatory data are in fairly close agreement with the predictions of eqn. 4.17 suggests that the scattering of the PS-PI B μ E obeys nearly single-exponential relaxation. The agreement between eqn. 4.17 and the data in Figure

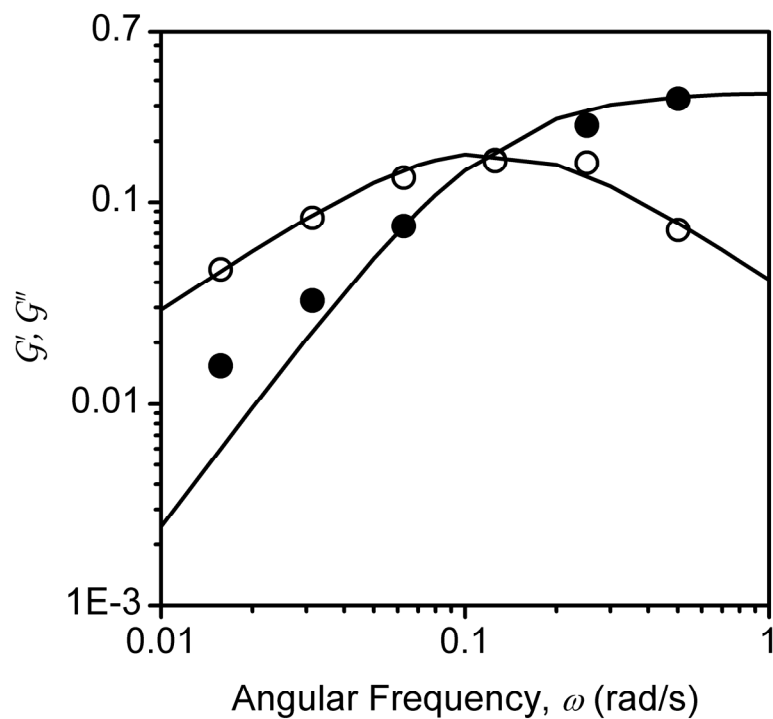


Figure 4.20. Scattering analogs of the storage and loss moduli, G' ($\bullet$) and G'' ($\circ$), of the PS-PI B μ E measured during oscillatory shear at 125°C and 50% strain. The solid curves represent predictions of eqns. 4.17 using $G = 0.35$ and $\lambda = 8.4$ sec.

4.20, together with the smooth sinusoidal shape of the shear stress analog data in Figure 4.21, also suggests that the microemulsion response is nearly linear up to 50% strain. G' and G'' values extracted from oscillatory data at 25% strain (not shown) nearly overlap with results from oscillation at 50% strain, further indicating that the scattering behavior is approximately linear over this range of strain values.

Figure 4.21(a) shows the scattering anisotropy and orientation angle following step strain deformation of the PS-PI BμE. As might be expected, AF increases and χ decreases with increasing applied strain. In addition, the orientation angle remains constant during relaxation, indicating that the scattering analogs of the shear stress, $\langle q_x q_y \rangle$, and the first normal stress difference, $[\langle q_x q_x \rangle - \langle q_y q_y \rangle]$, relax at the same rate.

As shown in Figure 4.21(b), the microemulsion scattering nearly follows expectations for the orientation angle in the case of affine deformation, which is given by [Elemans *et al.* (1993)]

$$\chi = \frac{1}{2} \tan^{-1} \left(\frac{2}{\gamma_0} \right) \quad (4.18)$$

where γ_0 is the applied strain.

The relaxation of the scattering shear stress analog following step strain deformation is shown in Figure 4.22(a). The data exhibit faster relaxation at short times ($t < 5$ seconds), and then relax at a slower rate over intermediate to longer times. This response is in disagreement with oscillatory results, which suggest single-exponential relaxation. It is also in contrast to the PEE-PDMS BμE, which exhibits robust single-exponential relaxation of $-\langle q_x q_y \rangle$ following a step strain and cessation of steady shear

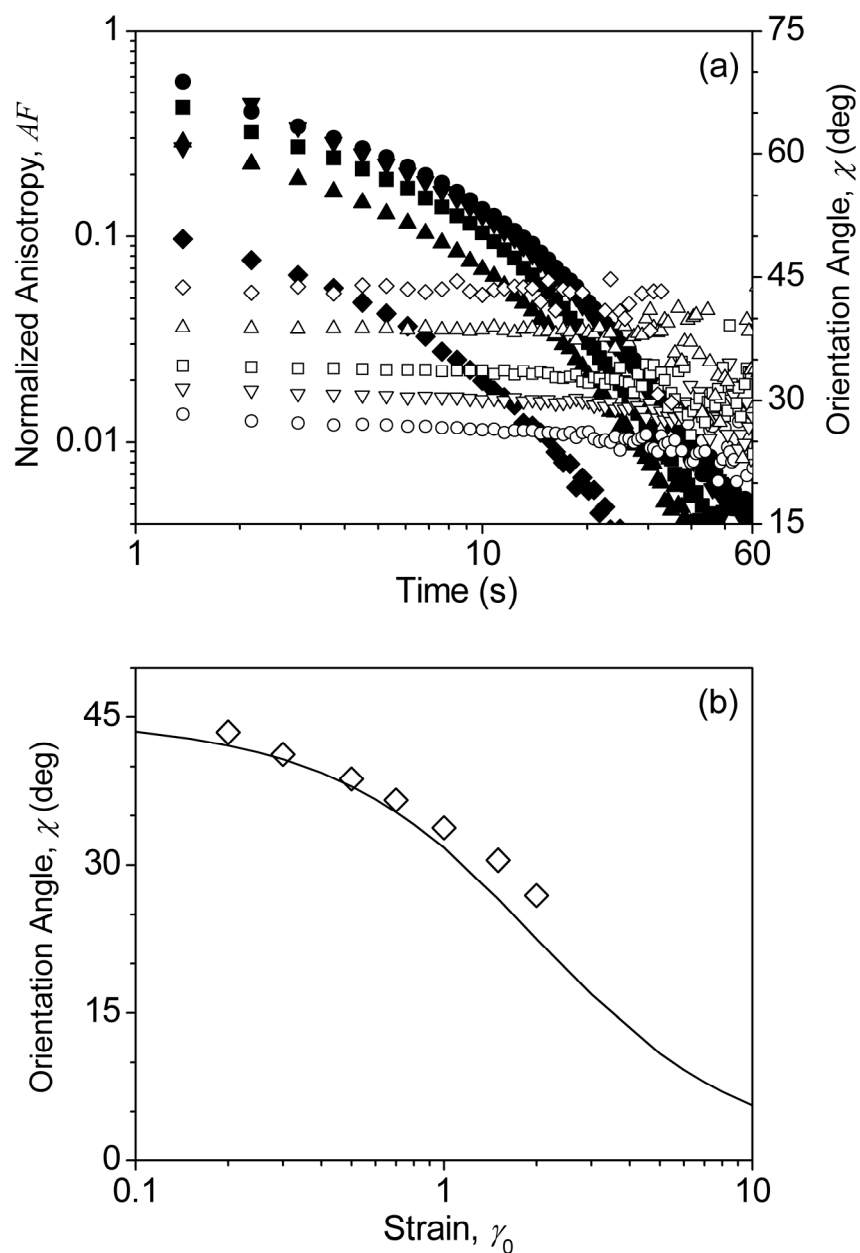


Figure 4.21. (a) Relaxation of the normalized anisotropy factor (closed symbols) and orientation angle (open symbols) following step strain deformation of the PS-PI B μ E at 125°C: ($\blacklozenge, \lozenge$) 20%, ($\blacktriangle, \triangle$) 50%, ($\blacksquare, \square$) 100%, ($\blacktriangledown, \triangledown$) 150%, and ($\bullet, \circ$) 200% strain. (b) Initial orientation angle as a function of applied strain; the solid curve represents predictions for affine deformation (eqn. 4.18).

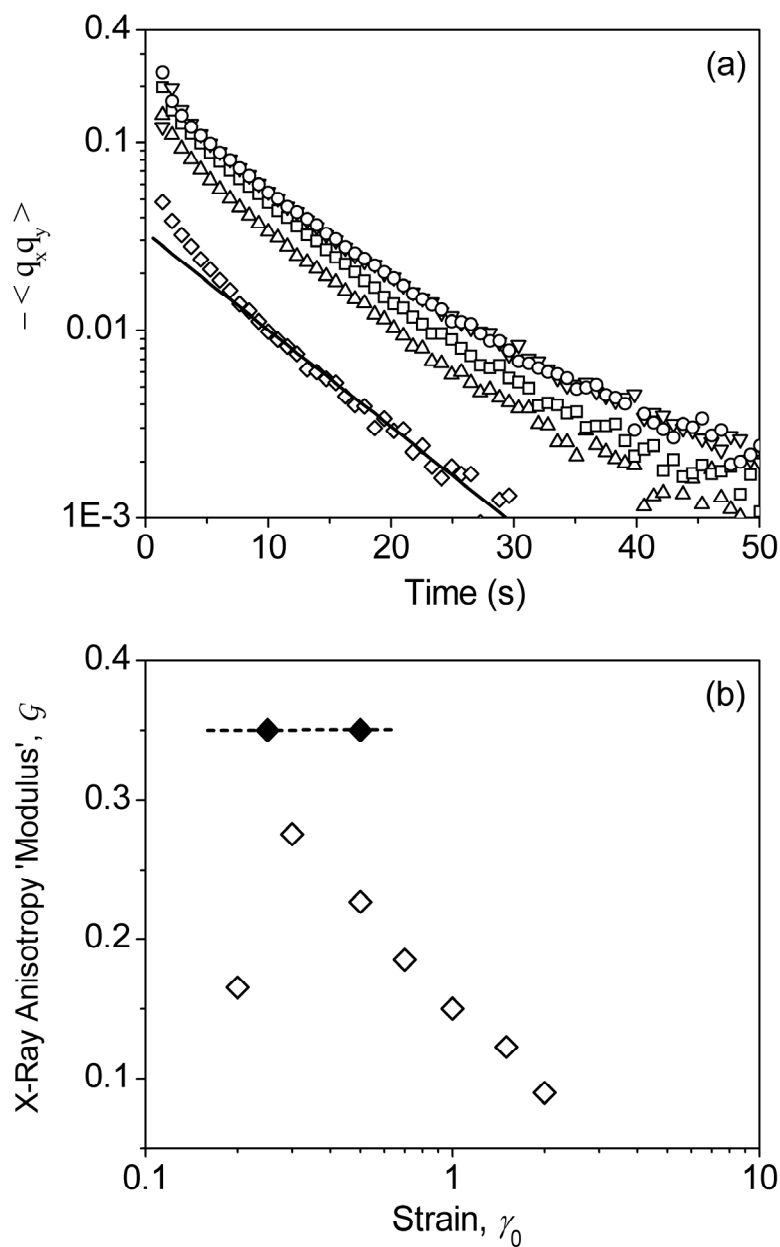


Figure 4.22. (a) Relaxation of the scattering shear stress analog following step strain deformation of the PS-PI B μ E at 125°C: ($\diamond$) 20%, (Δ) 50%, ($\square$) 100%, (∇) 150%, and ($\circ$) 200% strain. The solid line represents the single-exponential prediction (eqn. 4.19) with $\lambda = 8.4$ sec and $G = 0.165$. (b) Strain-dependence of the scattering “modulus” obtained from fits of eqn. 4.19 to data in step strain data in (a) (open symbols). The closed symbols represent G obtained from fits of eqn. 4.17 to oscillatory data.

flow. The source of the faster relaxation process observed in the PS-PI system at short times is unclear at the present time. However, beyond this initial faster relaxation, the data appear to follow single-exponential relaxation.

By analogy with mechanical shear stress from rheometry, for single-exponential relaxation we can write

$$-\frac{\langle q_x q_y \rangle}{\frac{1}{2} \langle qq \rangle_0} = \gamma_0 G \exp[-t / \lambda]. \quad (4.19)$$

For $t > 5$ sec, this relationship represents the scattering shear stress analog of the PS-PI BμE fairly well using $\lambda = 8.4$ sec, which is consistent with the value of λ obtained using single-mode predictions of the oscillatory response (eqn. 4.17). This agreement suggests that the PS-PI BμE is indeed dominated by a single relaxation process. By fitting eqn. 4.19 (with $\lambda = 8.4$) to the step strain data in Figure 4.22(a), the scattering “modulus” G was determined as a function of strain. These values are plotted in Figure 4.22(b).

In conventional rheology of complex fluids, the relaxation modulus becomes independent of strain as the linear regime is approached at sufficiently low strains. Since the scattering modulus is not constant within the range of applied strains during SAXS experiments, we cannot determine solely on the basis of these step strain experiments whether a linear regime exists. The “modulus” increases from 20% to 30% strain and then exhibits strain-softening with increasing strain. We note that the measured anisotropy at 20% strain is quite small, and thus the determined “modulus” for this low strain level may be susceptible to errors. (In fact, results from oscillatory data for strains $< 25\%$ were found to be fairly noisy and unreliable.) The potential strain-hardening from

20% to 30% and the strain-softening from 30% to 50% are inconsistent with oscillatory results that indicate the scattering response should be linear for $\leq 50\%$ strain. At this time, we are unable to provide an explanation for this discrepancy between oscillatory and step strain results.

An additional discrepancy in the PS-PI B μ E response to oscillatory and step strain deformation is observed in the *magnitudes* of the “modulus” G . The values of G obtained from step strain data at $\leq 50\%$ strain are much smaller than G values obtained from oscillatory data (Figure 4.22(b)). The smaller G values from step strain may possibly result from a non-instantaneously applied step strain. Prior to *in situ* SAXS experiments with the PS-PI B μ E, a gear reducer was attached to the shear cell motor to provide improved motion control of the upper rotating plate at low shear rates (see Section 2.4.2). However, a drawback of using the gear reducer is that it lengthens the time over which a step strain is applied (~ 1 sec). A slow step imposition would reduce the “stress” level achieved since some relaxation would occur during the deformation. Thus, a faster applied step strain would likely bring the G values into closer agreement with those obtained for oscillatory shear. The gear reducer was not employed in SAXS experiments of the PEE-PDMS B μ E, and much better agreement between G values was observed in this case [Caputo *et al.* (2002b)].

The scattering behavior of the PS-PI B μ E in response to step strain and oscillatory shear is remarkably similar to the reported behavior of the PEE-PDMS B μ E [Caputo *et al.* (2002b)]. One interesting similarity in the two microemulsions is the possible existence of strain-hardening in the scattering “modulus” at moderate strains.

Mechanical step strain experiments were not conducted for the PS-PI B μ E, but mechanical data for the PEE-PDMS B μ E did *not* show strain-hardening over any measured strains [Krishnan *et al.* (2002b)]. Strain-softening was observed in the PEE-PDMS mechanical response for strains greater than 50%. Caputo *et al.* (2002b) could not offer an explanation for the discrepancy between the scattering and mechanical response. We again note that the strain-hardening behavior may be partially associated with errors in the computed data, due to the fairly low anisotropy in the B μ E scattering at lower strain levels.

Possibly the only significant difference between the two B μ E systems (for the range of shear experiments covered) is that the PEE-PDMS microemulsion exhibited robust single-exponential relaxation of the scattering anisotropy with no signs of a faster relaxation mode at short times. Given the possible artifacts caused by slow step application, we place greater weight on the oscillatory data that suggest the PS-PI system also follows single-exponential structural relaxation. As in studies of the PEE-PDMS B μ E, the single-exponential decay of the scattering is in direct contrast with XPCS measurements (Figure 4.13) and linear viscoelastic rheological data (Figure 4.12), which show a spectrum of relaxation times. This discrepancy indicates that SAXS and rheology probe different processes in the microemulsion during relaxation.

The numerous similarities in the two polymer B μ E systems reported in our studies, thus far, suggest that the behavior of bicontinuous microemulsions is fairly universal under equilibrium and moderately non-linear conditions. However, some subtle differences between the PS-PI and PEE-PDMS microemulsions were observed,

particularly in linear viscoelastic measurements (Section 4.4.2.1). These differences were attributed to varying degrees of (1) elasticity in one or more of the blend constituents, (2) viscosity contrast between the B μ E domains, and/or (3) segregation between the B μ E domains. One might expect that these factors play stronger roles in the response of bicontinuous microemulsions under more severely non-linear conditions.

4.5.2.2. *Shear Flow Inception and Relaxation*

Rheology

Transient rheological measurements of the PS-PI B μ E during start-up of shear flow revealed interesting behavior that strongly depends on shear rate (Figure 4.23). As mentioned previously in the discussion of the B μ E equilibrium dynamics, since the homopolymers exhibit very low levels of elasticity, we expect that the observed behavior is dominated by the B μ E microstructure. At very low shear rates, the time-evolution of the viscosity/shear stress is nearly linear and agrees well with the prediction computed using the independently measured linear viscoelastic spectrum (Section 4.4.2.1). This relationship is given by

$$\eta(t) = \sum \eta_k (1 - \exp[-t / \lambda_k]). \quad (4.20)$$

(Agreement between the data and the linear viscoelastic prediction is more apparent in Figure 4.25 below, which emphasizes short-time behavior.) Slightly higher shear rates ($> 0.05 \text{ s}^{-1}$) begin to show more complex behavior. Upon shear inception at these rates, the viscosity/stress initially exhibits an overshoot, followed by an undershoot, and then slowly plateaus at the steady-state value. As the shear rate is increased, the overshoot

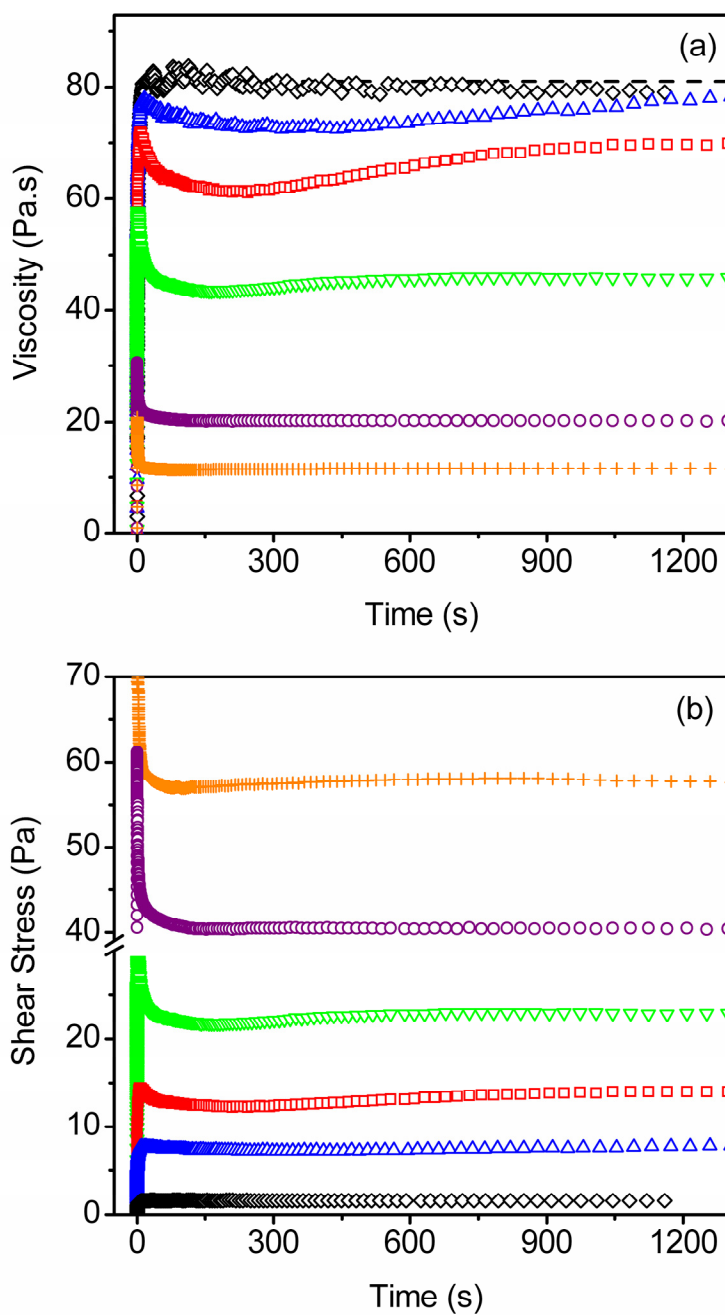


Figure 4.23. (a) Transient viscosity and (b) transient shear stress of a PS-PI BμE ($T = 130^\circ\text{C}$) during start-up of shear flow at ($\diamond$) 0.02, (Δ) 0.1, ($\square$) 0.2, (∇) 0.5, ($\circ$) 2, and ($+$) 5 s^{-1} . The dashed line in (a) represents the prediction for the transient viscosity based on independent measurements of the linear viscoelastic spectrum (Section 4.4.2.1)

and undershoot become more pronounced. Further increase in shear rate, however, leads to a diminishing of the plateau growth and a shift in the minimum to shorter times. The minimum becomes nearly indistinguishable at the highest measured shear rates. Mechanical measurements were restricted to $\leq 5 \text{ s}^{-1}$ due to the occurrence of edge fracture at higher shear rates.

After conducting a few experiments at the “higher” accessible shear rates, it became apparent that the rheological data were not entirely reproducible. Figure 4.24 shows measurements of the transient viscosity at 0.02 s^{-1} and 130°C , collected before and after shearing at a higher shear rate of 0.2 s^{-1} . As a result of shearing at a higher rate, the steady-state viscosity within the linear regime (0.02 s^{-1}) had increased significantly. Even after allowing the sample to relax for 1.5 hours, only partial recovery of the original steady-state viscosity was achieved. This change in the measured response suggests that shearing at higher rates induces a structural change in the sample that is long-lived. In order to facilitate recovery of the initial, equilibrium morphology, the sample was annealed for 1.5 hours at a higher temperature of 150°C and then cooled back down to 130°C . Repeating the shear experiment at 0.02 s^{-1} gives a response very similar to data collected prior to shearing at higher rates. Therefore, the equilibrium B μ E structure appears to be recoverable by annealing at higher temperatures. For all rheological data presented in this section (including Figure 4.23), the sample was annealed prior to each shear experiment for 1.5 hours at 150°C to establish an equilibrated initial condition.

Some of the features exhibited by the PS-PI microemulsion during shear inception are common to many types of complex fluids, whereas other features are more unique.

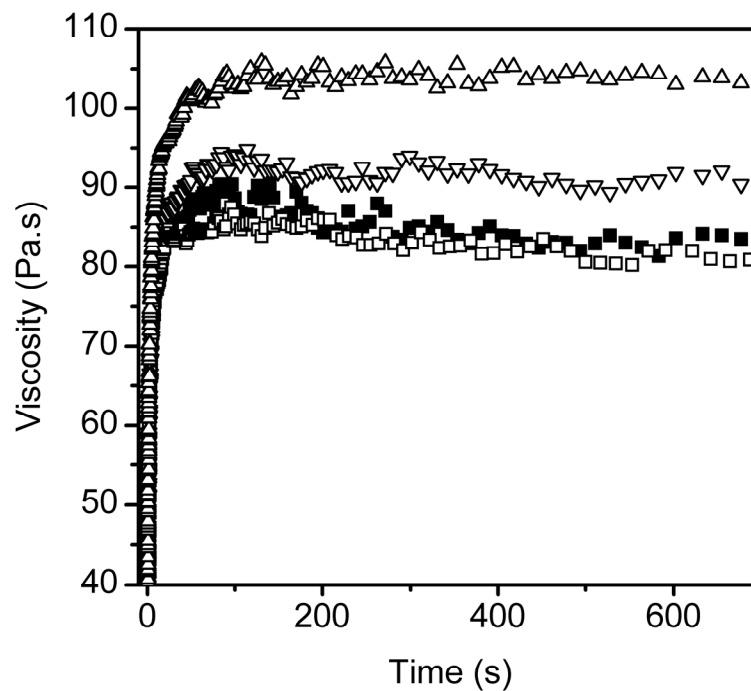


Figure 4.24. Transient viscosity of a PS-PI B μ E during start-up of shear flow at 0.02 s^{-1} and 130°C . Data were collected:
 (■) prior to performing any experiments at higher shear rates,
 (Δ) after shear at 0.2 s^{-1} and 5 minutes of relaxation,
 (∇) after shear at 0.2 s^{-1} and then annealing for 1.5 hours at 130°C ,
 ($\square$) after shear at 0.2 s^{-1} , annealing at 150°C for 1.5 hours, and then cooling back down to 130°C .

The monotonic growth in viscosity/stress observed at the lowest shear rate (0.02 s^{-1}) is characteristic of a linear viscoelastic response often reported for complex fluids. This response implies that the B μ E structure is essentially unperturbed by flow at these shear rates. The overshoot observed upon shear inception at higher shear rates is a typical *non-linear* response of complex fluids, and is generally associated with shear-induced orientation of the microstructure. We, therefore, expect at this point that the overshoot in the present case corresponds to stretching and aligning of the B μ E domains along the flow direction. Alignment of the B μ E domains leads to a reduction in the amount of interface oriented perpendicular to the flow direction, and, consequently, a reduction in the measured viscosity/stress with time during shear. The response following the overshoot in the PS-PI microemulsion at these higher rates is more unusual and suggests the occurrence of a more complex structural change (as also indicated by Figure 4.24); further discussion regarding this behavior is provided below.

The progression in the behavior of the PS-PI B μ E with increasing shear rate shows some general similarities to the PEE-PDMS B μ E documented by Krishnan *et al.* (2002b) (compare Figures 4.4 and 4.23). At very low shear rates, both microemulsions exhibit a linear response, referred to by Krishnan *et al.* as regime I for the PEE-PDMS B μ E. An overshoot immediately following start-up of shear at higher shear rates is also observed in both systems. At sufficiently high shear rates in the PS-PI and PEE-PDMS B μ Es, the initial overshoot is followed by an additional (different) feature that progresses slowly toward steady-state. This behavior is classified by Krishnan *et al.* as regime III.

For both B μ Es within their respective regime III, the steady-state viscosity as a function of shear rate shows a greater extent of shear-thinning than the complex viscosity.

The differences between the two microemulsions in response to shear inception are very distinctive. First, the overshoots observed in the PEE-PDMS B μ E reach above the curve predicted by linear viscoelasticity, whereas the overshoots in the PS-PI B μ E are contained below the linear curve (Figure 4.25). The shear strain value corresponding to the overshoot decreases with higher shear rates in the PS-PI system. This is in contrast to the PEE-PDMS B μ E for which the overshoot occurs at larger strains for higher shear rates. Second, in the lower range of shear rates for which the overshoot occurs in the PEE-PDMS system (regime II), the overshoot is *not* followed by any additional features (an undershoot or shoulder) with time; this regime does not exist for the PS-PI microemulsion. Rather, at the shear rate for which the PS-PI B μ E begins to exhibit an overshoot, the additional feature also becomes apparent. Therefore, this system seems to jump from regime I to regime III at a critical shear rate. Third, the steady-state shear stress of the PEE-PDMS B μ E is nearly independent of shear rate within regime III, whereas this is not the case for the PS-PI B μ E over any range of measured shear rates.

Another significant difference between the microemulsions is the *shape* of the feature occurring after the initial overshoot at higher shear rates. The PEE-PDMS system shows a broad shoulder and then slowly *decreases* to the steady-state value. On the other hand, the PS-PI B μ E exhibits a minimum and then slowly *increases* toward steady-state. In both B μ E systems, the time-period over which these features occur decreases with increasing shear rate, eventually becoming almost indistinguishable in the data. *In situ*

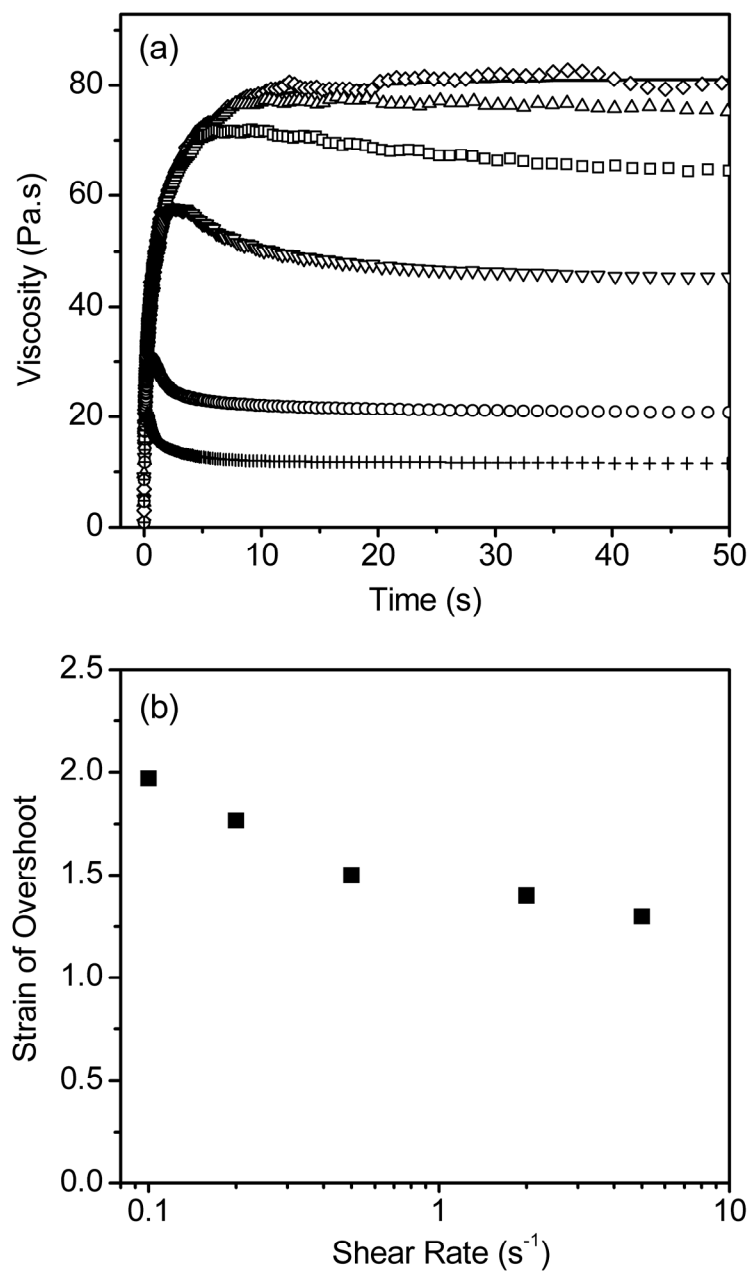


Figure 4.25. (a) Viscosity evolution of a PS-PI B μ E ($T = 130^\circ\text{C}$) at short times during start-up of shear flow: ($\diamond$) 0.02, (Δ) 0.1, ($\square$) 0.2, (∇) 0.5, ($\circ$) 2, and ($+$) 5 s⁻¹. (b) Shear rate dependence of the strain corresponding to the initial overshoot.

SALS and optical microscopy experiments by Krishnan *et al.* (2002b) indicate that the broad shoulder in the PEE-PDMS B μ E is associated with the onset of phase-separation. Recent simulations by Narayanan *et al.* (2006) also show the occurrence of shear-induced phase separation of a polymer B μ E at high shear rates. Considering the results of these previously documented studies, we anticipate that the complex response following the overshoot in the PS-PI microemulsion is related to phase-separation. However, differences in the evolution of viscosity/shear stress, in comparison to the PEE-PDMS B μ E, suggest that some differences exist in the phase-separation process.

For the PEE-PDMS B μ E, measurements of the first normal stress difference, N_1 , were qualitatively similar to the shear stress during shear inception at all shear rates. Due to the limited resolution of the ARES rheometer transducer, reliable normal force measurements of the PS-PI B μ E could only be obtained for the largest accessible shear rates of $0.5 - 5 \text{ s}^{-1}$, which show only small signs of an undershoot in the viscosity/shear stress. For these shear rates, N_1 exhibits an initial overshoot before declining to the steady-state value (Figure 4.26).

As a final comparison between the rheology of the two microemulsion systems, we consider the shear stress response upon cessation of steady shear. Figure 4.27 shows relaxation of shear stress in the PS-PI B μ E. At the lowest applied shear rate (0.02 s^{-1}), the relaxation follows the prediction using the independently measured linear viscoelastic data. Relaxation from slightly higher shear rates ($0.1 - 0.5 \text{ s}^{-1}$) occur over similar time scales, but starting from higher stress values. Following shear at the highest rates (2 and 5 s^{-1}), relaxation appears to exhibit two modes. A faster relaxation at short times, and a

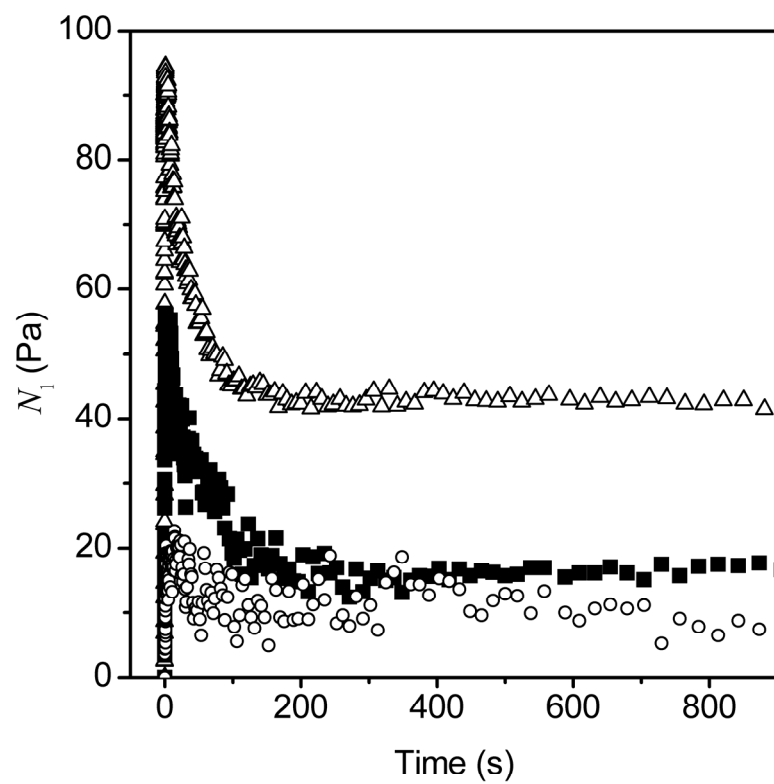


Figure 4.26. Evolution of first normal stress difference in a PS-PI B μ E during start-up of shear flow at 130°C: ($\circ$) 0.5 , ($\blacksquare$) 2 s^{-1} and ($\triangle$) 5 s^{-1} .

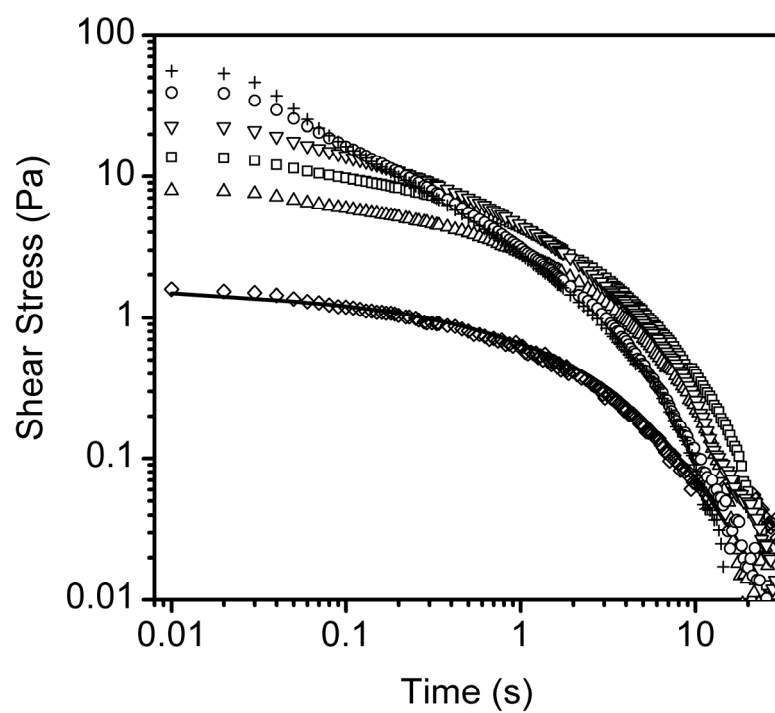


Figure 4.27. Shear stress relaxation of a PS-PI B μ E ($T = 130^\circ\text{C}$) following cessation of steady shear flow at ($\diamond$) 0.02, (Δ) 0.1, ($\square$) 0.2, (∇) 0.5, ($\circ$) 2, and ($+$) 5 s $^{-1}$. The solid line represents the prediction using the independently measured linear viscoelastic spectrum.

slower relaxation at longer times that is similar to the relaxation from lower shear rates. The relaxation behavior as a function of shear rate is very similar to the relaxation of the PEE-PDMS microemulsion [Krishnan *et al.* (2002b)], which exhibits two-mode relaxation following steady shear within regime III. The faster mode at short times in this case was attributed to retraction of elongated phase-separated domains into spherical droplets, which was observed in optical microscopy experiments. The similarities in the relaxation of the two microemulsions further suggest that the complex response in the PS-PI B μ E at higher shear rates is related to phase-separation. We have performed *in situ* SAXS and optical microscopy experiments to help resolve the shear-induced structural changes occurring in this system.

In Situ X-Ray Scattering

Figure 4.28 presents representative SAXS patterns of the PS-PI microemulsion during shear inception at various shear rates. The pattern collected during shear at 0.02 s^{-1} (pattern (a)) shows very little anisotropy in the B μ E peak, which is consistent with the linear response in the transient rheological data (Figure 4.23). At higher shear rates (patterns (b) – (d)), the B μ E peak is fairly anisotropic and a streak of intensity is apparent at lower scattering angles that is aligned closer to the velocity gradient direction. This low- q scattering reflects the existence of larger length structures in the B μ E sample more closely aligned with the flow direction, which appear to be produced during shear. The increasing strength of the low- q feature with increasing shear rate corresponds to a greater concentration of the larger structures. We note at this point that the patterns in

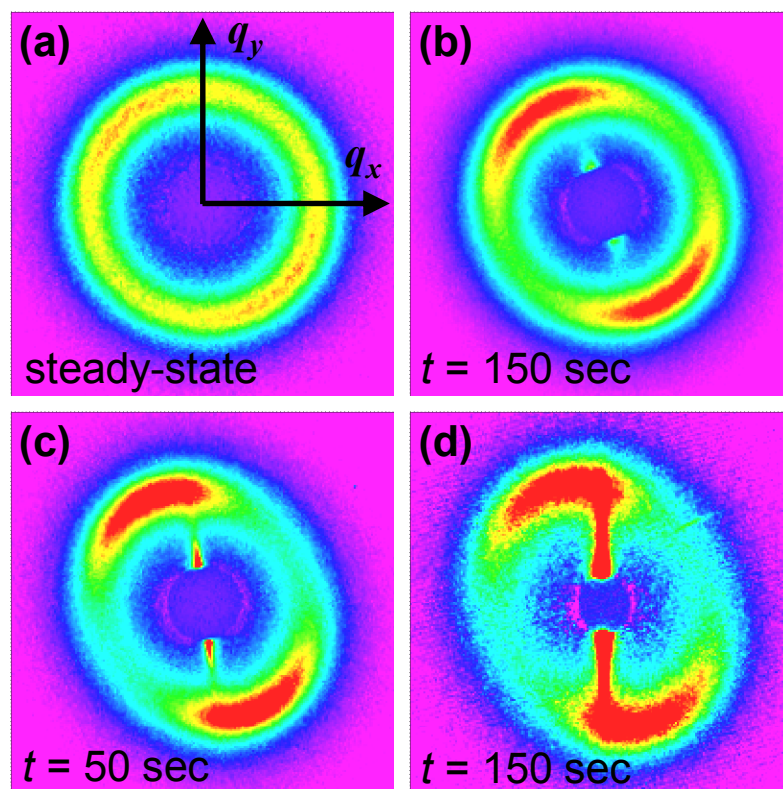


Figure 4.28. Representative scattering patterns of a PS-PI BμE during start-up of shear flow at 130°C and (a) 0.02 , (b) 0.07, (c) 0.20, and (d) 2.0 s⁻¹. Patterns correspond to the time-point at which the low- q scattering is the strongest during shear; this does not necessarily correspond to steady-state. The intensity scale is the same in all images. The q -range in these images is $|q_x, q_y| \leq 0.136 \text{ nm}^{-1}$.

Figure 4.28 exhibiting low- q scattering do not represent steady-state, but rather the time point at which the low- q scattering is most intense. The time-evolution of these processes will be examined in detail below.

One-dimensional intensity scans, obtained from quiescent data before and after shear at the higher rates ($> 0.04 \text{ s}^{-1}$), show a slight change in the intensity profile as a result of shear (solid versus dashed lines in Figure 4.29). The microemulsion peak has shifted to smaller angles, reflecting a small increase in the B μ E domain size. In addition, the intensity has increased at $q \rightarrow 0$, suggesting that some of the larger length scale structures remain in the sample long after cessation of flow. Allowing the sample to anneal for 2.5 hours at the shear temperature ($T = 130^\circ\text{C}$) resulted in partial recovery of the initial intensity profile (dotted line). Due to time constraints at the x-ray facility, we did not anneal for longer times in attempt to achieve greater recovery. Since the change in the quiescent intensity profile is not drastic, we assume that the long-lasting changes in the microstructure are not significant enough to affect the qualitative behavior of the microemulsion in additional shear experiments. However, as a precaution, the sample was annealed at 130°C for 2.5 hours in between all shear experiments at rates greater than 0.04 s^{-1} . Recall that in our rheological experiments, we had annealed the sample at a higher temperature (150°C) to recover the initial sample morphology (see Figure 4.24). These SAXS experiments were performed prior to the rheological experiments in which we employed the higher temperature annealing.

The scattering anisotropy factor and orientation angle of the PS-PI B μ E during shear inception at various rates is shown in Figure 4.30. As expected, the anisotropy

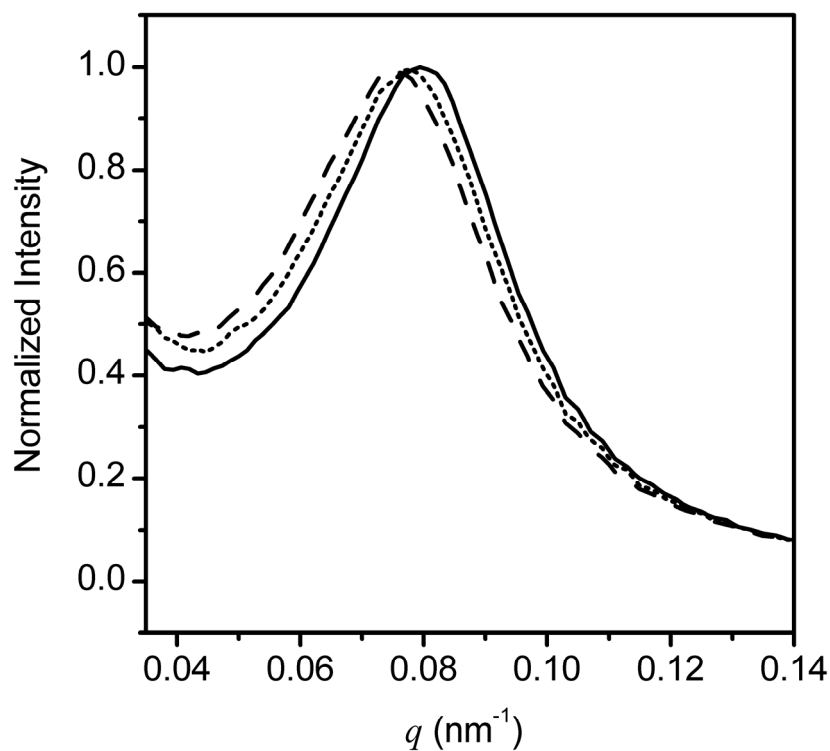


Figure 4.29. Intensity versus scattering vector for the PS-PI BμE at 130°C and quiescent conditions. Data were collected
 (—) prior to shear at rates above 0.04 s⁻¹,
 (---) 10 minutes of relaxation following cessation of steady shear at 0.1 s⁻¹,
 (....) 2.5 hours of relaxation following cessation of steady shear at 0.1 s⁻¹.
 Intensity values have been normalized by the microemulsion peak intensity at $q = q_{\text{max}}$; the parasitic scattering at low- q has *not* been subtracted from these data.

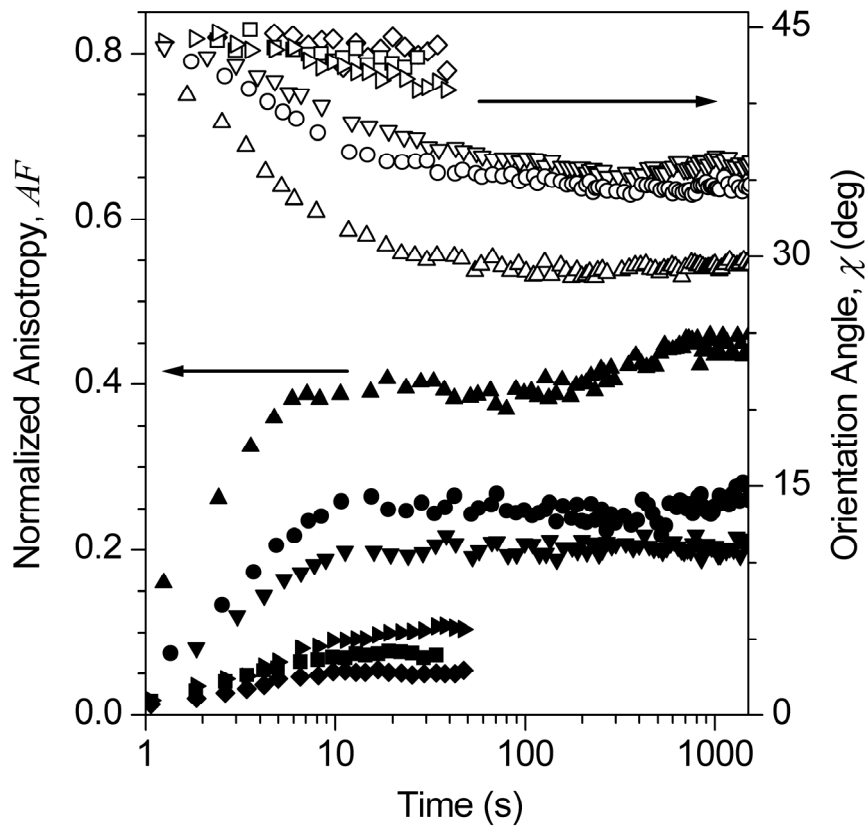


Figure 4.30. Scattering anisotropy factor (solid symbols) and orientation angle (open symbols) versus time for the PS-PI B μ E ($T = 130^\circ\text{C}$) during shear inception at rates of ($\blacklozenge$) 0.02, ($\blacksquare$) 0.03, ($\blacktriangleright$) 0.04, ($\blacktriangledown$) 0.07, ($\bullet$) 0.10, and ($\blacktriangle$) 0.20 s^{-1} .

increases and the orientation angle decreases with increasing shear rate. Only data corresponding to $\leq 0.20 \text{ s}^{-1}$ are shown. At shear rates greater than these values, the sample begins to eject itself from the x-ray shear cell and, consequently, measurements at steady-state could not be obtained.

For shear rates of $0.02, 0.03, \text{ and } 0.04 \text{ s}^{-1}$, AF grows monotonically with time and then plateaus at the steady-state value. The SAXS patterns at these shear rates show no sign of low- q scattering at any point during shear. The evolution in AF at rates of $0.07, 0.10, \text{ and } 0.20 \text{ s}^{-1}$, over short to intermediate times, look similar to the behavior at lower shear rates. At these higher shear rates, low- q scattering became apparent in the 2-D SAXS patterns at times ≤ 10 seconds. More specifically, the appearance of low- q scattering occurred at a strain of $\gamma \sim 0.7$ (where $\gamma = \dot{\gamma}t$) in all cases. There are no distinct features in the anisotropy factor (or χ) with time that we can associate with this event; note that the second moment tensor $\langle \mathbf{qq} \rangle$ naturally weights large- q scattering more heavily, so that the data in Figure 4.30 are likely dominated by the microemulsion structural dynamics, with only weak influence from the low- q scattering. For rates of $0.10 \text{ and } 0.20 \text{ s}^{-1}$ at long times, AF begins to increase again. In the case of 0.20 s^{-1} , this growth eventually levels off to the steady-state value. This long-term feature is similar to that observed at long times in the mechanical shear stress. It appears that data at 0.10 s^{-1} were not collected for long enough times to reach steady-state.

Figure 4.31 shows the scattering analog of the shear stress with time during shear inception at various rates. The top graph shows data for all applied shear rates at short times, whereas the bottom graph presents only data at higher shear rates over much

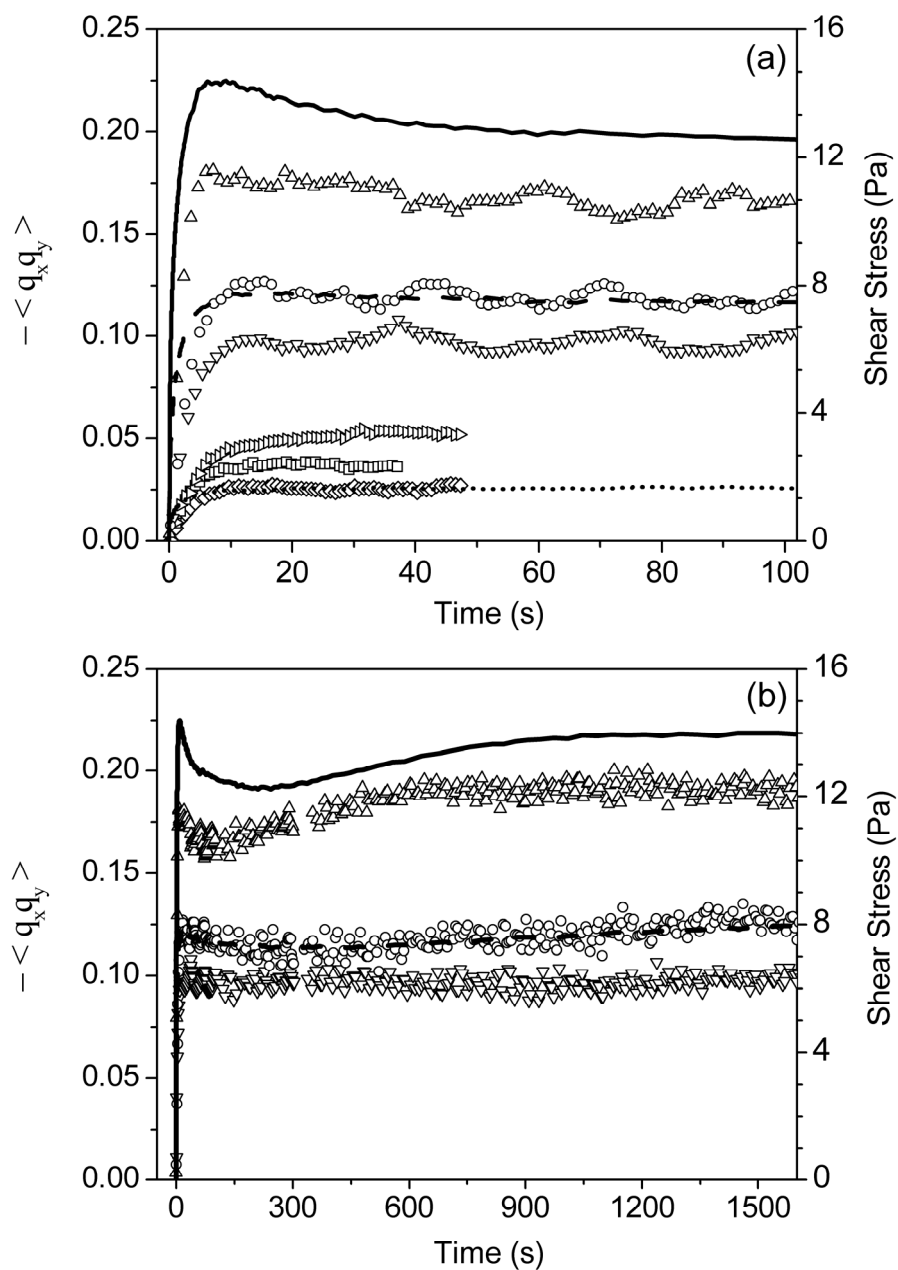


Figure 4.31. Scattering analog of the shear stress versus time for the PS-PI B μ E ($T = 130^\circ\text{C}$) during shear inception at rates of ($\diamond$) 0.02, ($\square$) 0.03, ($\triangleright$) 0.04, (∇) 0.07, ($\circ$) 0.10, and ($\triangle$) 0.20 s^{-1} . Mechanical shear stress at ($\cdots$) 0.02, ($-$) 0.1, and ($-$) 0.2 s^{-1} are also plotted. (a) Data at short times. (b) Data at long times.

longer times. The mechanical shear stress for the cases of 0.02, 0.10, and 0.20 s⁻¹ are also plotted for comparison. Interestingly, the evolution of the mechanical shear stress, with time and shear rate, is qualitatively similar to the behavior of the scattering analog. Both quantities exhibit a linear response at low shear rates (0.02 s⁻¹). At higher shear rates, an overshoot followed by an undershoot are apparent, becoming more pronounced with increasing shear rate. The similarities in the mechanical shear stress and the scattering analog suggest that both techniques are probing the same structural processes in the sample. Since we were unable to collect scattering data at long times for shear rates greater than 0.20 s⁻¹, we are uncertain whether these features diminish with further increase in shear rate as was observed in the mechanical response (see Figure 4.23).

The 2-D scattering patterns at selected time points during shear inception at 0.20 s⁻¹ are shown in Figure 4.32. The BμE scattering peak quickly orients upon start-up of flow (0 – 3 sec). At 7 seconds of shear, which corresponds to the peak of the stress overshoot, scattering at smaller angles has already become apparent and is oriented along the same direction as the BμE peak. This event strongly suggests the onset of shear-induced phase separation. As time proceeds, the orientation of the BμE peak remains constant as the low-*q* scattering feature becomes more intense and rotates until it is nearly parallel with the velocity gradient direction. This growth and alignment of the low-*q* scattering corresponds to the decrease in stress following the overshoot (7 – 50 sec) and implies that as phase-separation is occurring, the larger structures orient along the flow direction and reduce the stress in the system. Note that the anisotropy factor and orientation angle (Figure 4.30) remain nearly constant during these changes in the

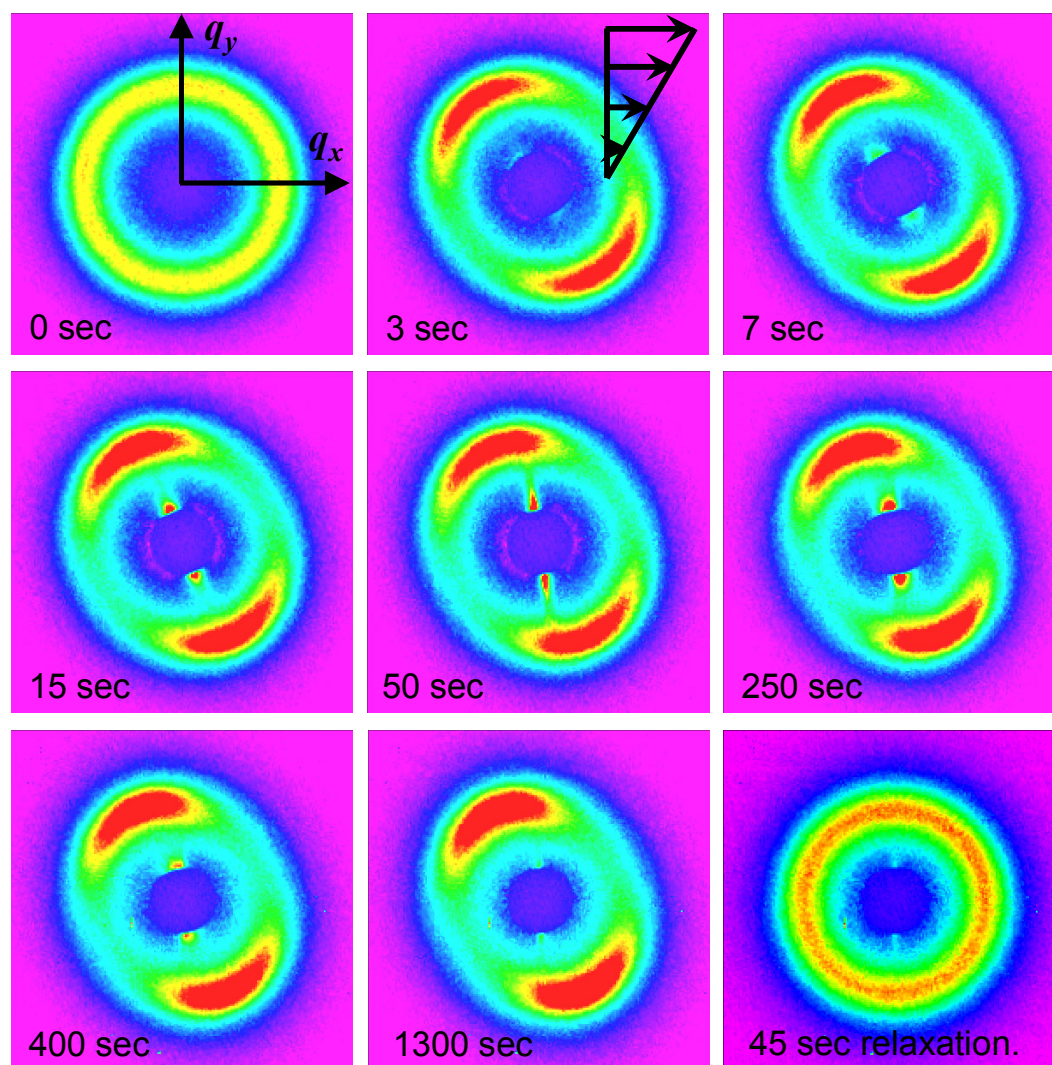


Figure 4.32. SAXS patterns of the PS-PI BμE collected at various time points during shear inception at 130°C and 0.20 s⁻¹. The bottom, right-hand pattern corresponds to 45 seconds after cessation of shear flow. The intensity scale is the same in all images. The q -range in these images is $|q_x, q_y| \leq 0.136$ nm⁻¹.

low- q scattering. Therefore, AF and χ appear to be dominated by the B μ E scattering peak over this time interval.

Interestingly, once the minimum in the stress undershoot is reached (250 sec), the low- q scattering feature has become less anisotropic. Over longer times, as the stress (and AF) increases and plateaus at its steady-state value, the low- q scattering weakens and seems to disappear. Upon cessation of flow, the B μ E peak returns to an isotropic ring and a small amount of anisotropy is still apparent in the remaining weak low- q scattering oriented along the velocity gradient direction. The behavior at long times is intriguing, and it is not readily apparent from the 2-D patterns as to what structural changes are occurring. The scattering pattern corresponding to steady-state (1300 sec) shows that a bicontinuous microemulsion phase still exists during shear, but it is uncertain as to what happened to the phase-separated structures. The sequence of changes in the scattering patterns with time is qualitatively similar to the observed behavior at rates of 0.07 and 0.10 s⁻¹. However, the anisotropy in the B μ E peak and the intensity of the low- q scattering is weaker at these lower shear rates (see Figure 4.28(b) for 0.07 s⁻¹).

Comparison of the quiescent patterns in Figure 4.32, obtained before and after shear at 0.20 s⁻¹, show that the intensity of the B μ E peak has increased slightly. This change is more clearly illustrated in the 1-D scattering data extracted from these patterns, which are plotted in Figure 4.33. Also as a result of shear, the microemulsion peak has broadened significantly and shifted slightly to smaller scattering vector. The shift in the peak position corresponds to an increase in the average domain size, and the peak

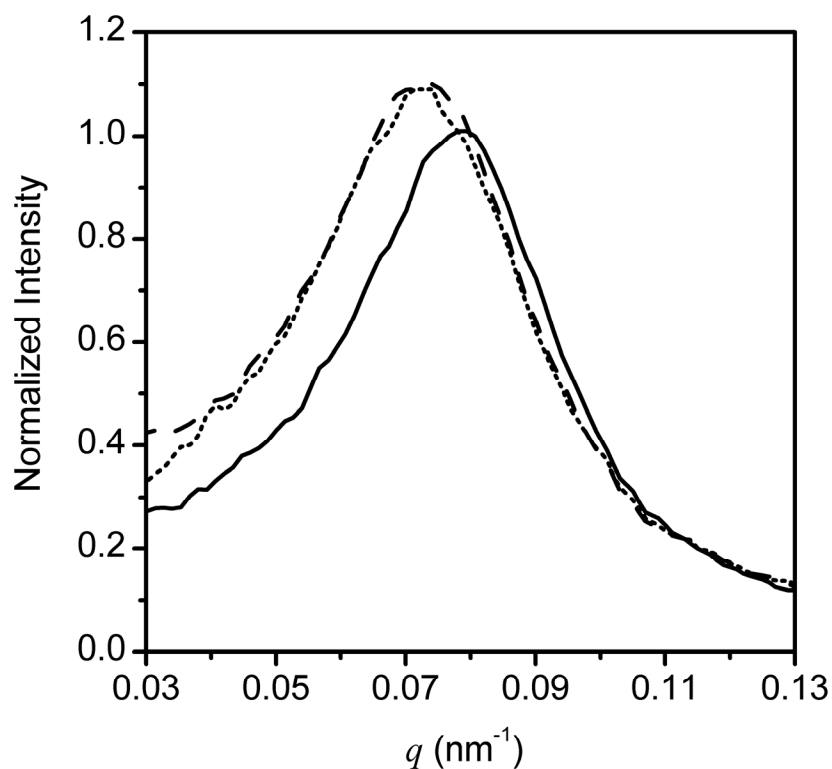


Figure 4.33. Intensity versus scattering vector extracted from corrected 2-D patterns of the PS-PI B μ E at 130°C. Data were obtained at quiescent conditions: (—) prior to shear at 0.20 s⁻¹, (····) 45 seconds after cessation of steady shear at 0.20 s⁻¹ and along the q_x -direction, (— —) 45 seconds after cessation of steady shear at 0.20 s⁻¹ and along the q_y -direction.

broadening suggests a widening of the domain size distribution. The reason for the increase in the peak intensity is less clear. Possibly, the sample thickness illuminated by the x-ray beam has increased during shear, leading to a proportional increase in the scattered intensity. The sample is exposed on the outer edge of the shear cell (see Figure 2.7), and shearing may cause the sample to accumulate slowly at the back end of the shear cell (which is tilted at a 2.5° angle) where it is intersected by the incident beam. If this process was in fact occurring, we expect that the sample would continuously accumulate with time. However, the scattering data plateau at long times (Figures 4.30 and 4.31(b)), suggesting that shear-induced changes in the sample microstructure are related to the increased intensity.

To further investigate the structural changes occurring during shear, we have computed the average intensity as a function of azimuthal angle φ in the low- q region (defined by the dashed circles in the scattering pattern of Figure 4.34) at various time points. At quiescent conditions ($t = 0$), the intensity is flat over all values of φ . Upon start-up of shear, the intensity begins to grow near $\varphi = 135^\circ, 315^\circ$. These peaks grow further in intensity with time and shift towards $\varphi = 90^\circ, 270^\circ$ (*i.e.*, the q_y axis). At the time corresponding to the minimum of the stress curve ($t = 250$ sec), the peaks remain at $\varphi = 90^\circ, 270^\circ$, but begin to weaken with time as expected from Figure 4.33. As this is occurring, the average intensity at all angles φ begins to increase. Although the anisotropy in the low- q scattering has nearly vanished by the time steady-state is reached, the amount of overall intensity is larger with respect to the initial condition ($t = 0$). This is consistent with the increased intensity in the B μ E peak in Figure 4.33.

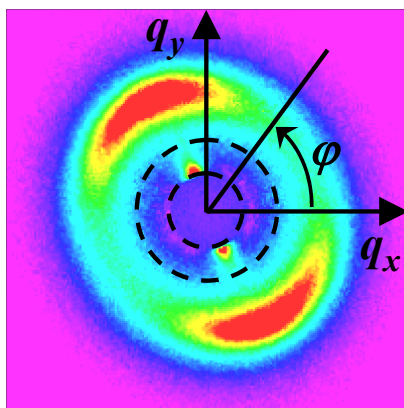
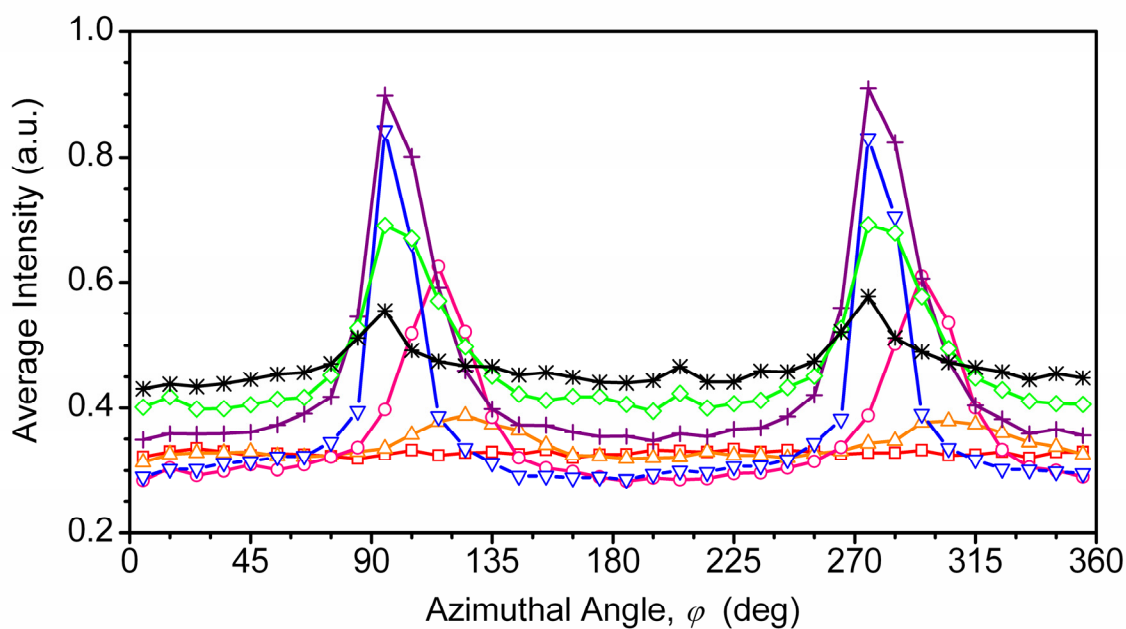


Figure 4.34. Top: Average intensity versus azimuthal angle of the low- q scattering from the PS-PI B μ E ($T = 130^\circ\text{C}$) during shear inception at 0.2 s^{-1} . Data correspond to the following time points during shear: $t = 0$ ($\square$), 3.5 (Δ), 10 ($\circ$), 50 ($+$), 250 (∇), 400 ($\diamond$), and 1300 seconds ($*$). Bottom: Representative scattering pattern illustrating the region from which the low- q intensity data were obtained (between the dashed circles). The azimuthal angle is given with respect to the q_x axis.

The occurrence of partial phase separation at short times appears to serve as an immediate route for limiting the stress in the system. The combined results in Figures 4.31 - 4.34, in a way, suggest that these larger length scale structures eventually break down under shear with time and then slowly reorganize back into the B μ E phase. For example, as the anisotropy in the low- q scattering declines at long times, the overall anisotropy factor and the scattering analog of the shear stress increases (Figures 4.30 and 4.31). It therefore seems as though the scattering anisotropy lost by the phase-separated structures has transitioned back into the microemulsion peak. The mechanical shear stress also increases at long times. If the phase-separated structures, in fact, reorganize back into the B μ E phase, the recovery of the interconnected structure along the velocity gradient direction may be sufficient to cause this growth in stress. The much broader, shifted intensity profile obtained after shear (Figure 4.33) implies that the “recovered” B μ E morphology consists of a larger average domain size with a much broader distribution. With larger domains, the microemulsion structure may be capable of withstanding shear at 0.20 s^{-1} . Perhaps at larger shear rates, for which the sample does not exhibit recovery in the shear stress over long times, shear is sufficiently strong that recovery of the B μ E phase does not occur.

We emphasize at this point that much of the above discussion regarding the shear-induced structural changes in the sample is speculative. Although the low- q scattering at steady-state is nearly unobservable, this does not imply that the larger phase-separated structures are no longer present. For example, if these structures continued to grow in size with time during shear, the scattering would shift to smaller scattering vectors that

are inaccessible via SAXS. Therefore, additional characterization techniques are required to obtain more conclusive answers regarding the microstructure in the sample.

The final set of SAXS data that we present shows relaxation of the scattering shear stress analog following cessation from steady shear (Figure 4.35). For low shear rates (0.02 and 0.04 s⁻¹), the data roughly follow single-exponential relaxation with an average relaxation time ($\lambda = 4.5$ sec) that is slightly shorter than indicated by step strain and oscillatory shear experiments ($\lambda = 8.4$ sec). This is in contrast to rheological data (Figures 4.27), which show a distribution of relaxation times. For higher shear rates, the scattering shear stress analog begins to deviate from single-exponential relaxation, potentially relating to the complex structural changes that have occurred at these rates.

In Situ Optical Microscopy

To obtain further insight into the shear-induced structural dynamics of the PS-PI microemulsion, we have conducted *in situ* optical microscopy experiments, which allow for direct visualization of the micron-sized structures in the sample. Whereas the x-ray cone and plate flow cell provides access to the plane of the flow velocity (x) and velocity gradient (y) directions, the flow cell used in our microscopy experiments allows for observation in the plane of the flow velocity (x) and vorticity (z) directions. Due to the low-limit resolution of the shear cell motor, the lowest reliable shear rate achievable in these experiments is 0.05 s⁻¹.

Microscopy images collected during shear inception at the lowest applied rate of 0.05 s⁻¹ are shown in Figure 4.36. In the quiescent image obtained prior to start-up of

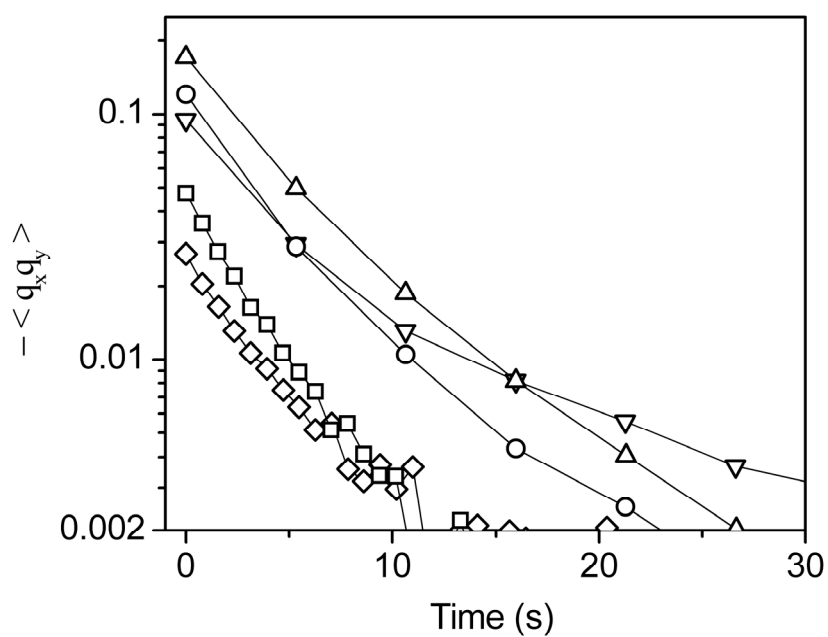


Figure 4.35. Relaxation of the scattering shear stress analog in the PS-PI B μ E following cessation of steady shear flow at 130°C and rates of ($\diamond$) 0.02, ($\square$) 0.04, (∇) 0.07, ($\circ$) 0.10, and (Δ) 0.20 s⁻¹. The thin lines are aids to the eye.

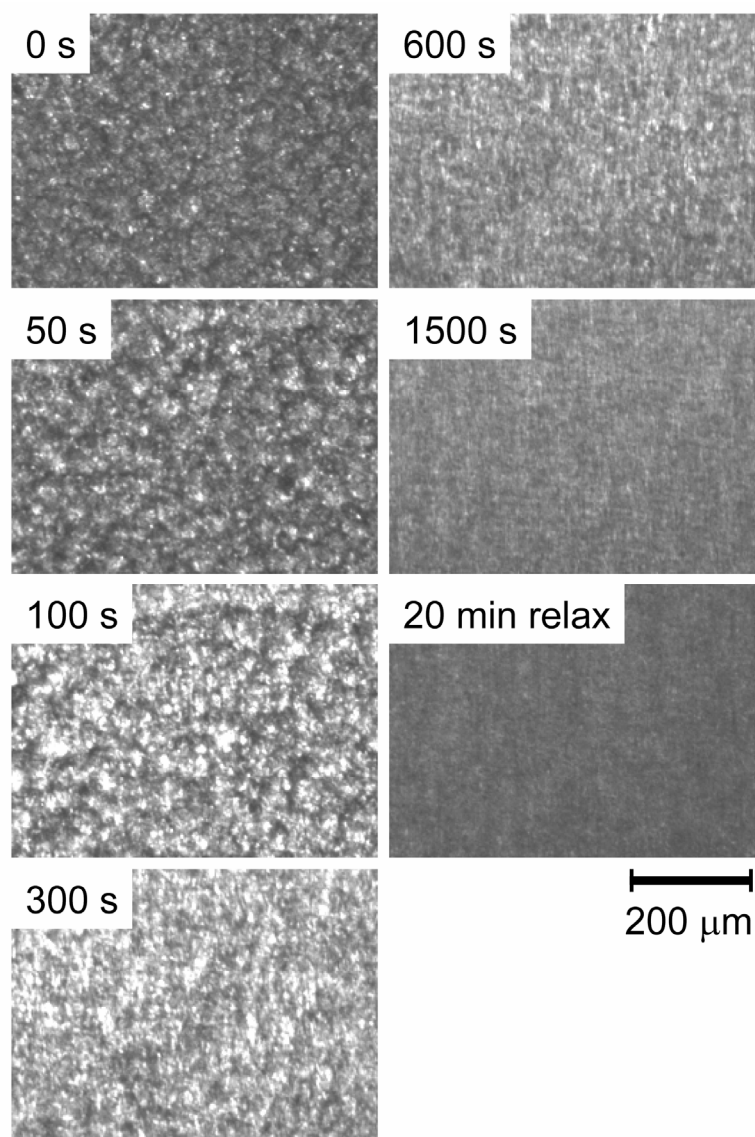


Figure 4.36. Microscopy images of the PS-PI BμE during shear inception at 130°C and 0.05 s⁻¹. The numbers in each image represent the time after start of flow, and the last image corresponds to 20 minutes following cessation of flow. The intensity scale is equal for all images, and the flow direction is vertical.

shear ($t = 0$), the presence of large phase-separated structures are clearly evident. This image was collected at 130°C prior to any shear experiments and after annealing at 150°C for 1 hour. Therefore, these structures, some of which are 50 μm in size, seem to exist in equilibrium with the B μ E phase. Referring back to Figure 4.1, the coexistence of phase-separated structures with the B μ E phase places our sample within the region of the isopleth diagram denoted by 3P. The presence of the phase-separated structures were probably not reflected in the SAXS patterns at equilibrium or moderate shear conditions because the structures are so large that they scatter at experimentally inaccessible small angles. The discovery of the large structures in the equilibrium morphology is surprising considering the strong behavioral similarities between the PS-PI and PEE-PDMS[§] systems in response to linear and moderately non-linear flow conditions. These similarities suggest that the rheology and scattering behavior of the PS-PI sample under the less severe conditions is dominated by the B μ E phase. The following microscopy results, however, indicate that the phase-separated structures have a much greater impact in the rheology and scattering behavior under more non-linear conditions, such as steady shear flow.

During the early to intermediate stages of shear inception at 0.05 s^{-1} (0 – 300 sec), the larger structures become stretched along the flow direction. Over longer times (> 300 sec), the larger structures break down into much smaller structures. The reason for the increased brightness of the images at early times is unclear. The phase-separated structures seem to remain at micron-sized length scales during shear, so we therefore do

[§] Microscopy images of the PEE-PDMS microemulsion showed no phase-separated structures at equilibrium [Krishnan *et al.* (2002a, 2002b)].

not expect a decrease in the sample turbidity. Because the image intensity at steady-state (1500 sec) is comparable to that prior to start-up of shear, we cannot determine whether the B μ E phase has undergone any level of additional phase-separation. Significant amounts of phase-separation of the B μ E microstructure would result in higher sample turbidity, and thus a darker micrograph. Quiescent SAXS intensity profiles collected after steady shear at rates of $< 0.04 \text{ s}^{-1}$ do not show noticeable changes from the quiescent profile before shear, suggesting that the B μ E phase does not undergo phase-separation for this lower range of shear rates. Long after cessation of shear, however, the microscopy image has in fact darkened. Perhaps the phase-separated structures coarsen to some extent after flow is stopped.

Before conducting additional shear experiments, the sample was annealed for 1.5 hours at 150°C and then cooled back down to 130°C. The image corresponding to $t = 0$ in Figure 4.37 shows the state of the phase-separated morphology after the annealing process. Apparently, annealing has led to further coarsening of the phase-separated structures, and the morphology seems to have returned to its state prior to shear at 0.05 s^{-1} . Recall the low shear rate viscosity measurements (*i.e.*, within the linear regime at 0.02 s^{-1}) in Figure 4.24, which were collected before and after shear at a higher shear rate. The low shear rate viscosity had *increased* as a result of shear, perhaps due to the fact that the total surface area in the sample had increased due to the break-up of the phase-separated structures. The initial viscosity value was “recovered” by annealing at higher temperatures, which is consistent with the return of the larger, coarsened structures observed in microscopy.

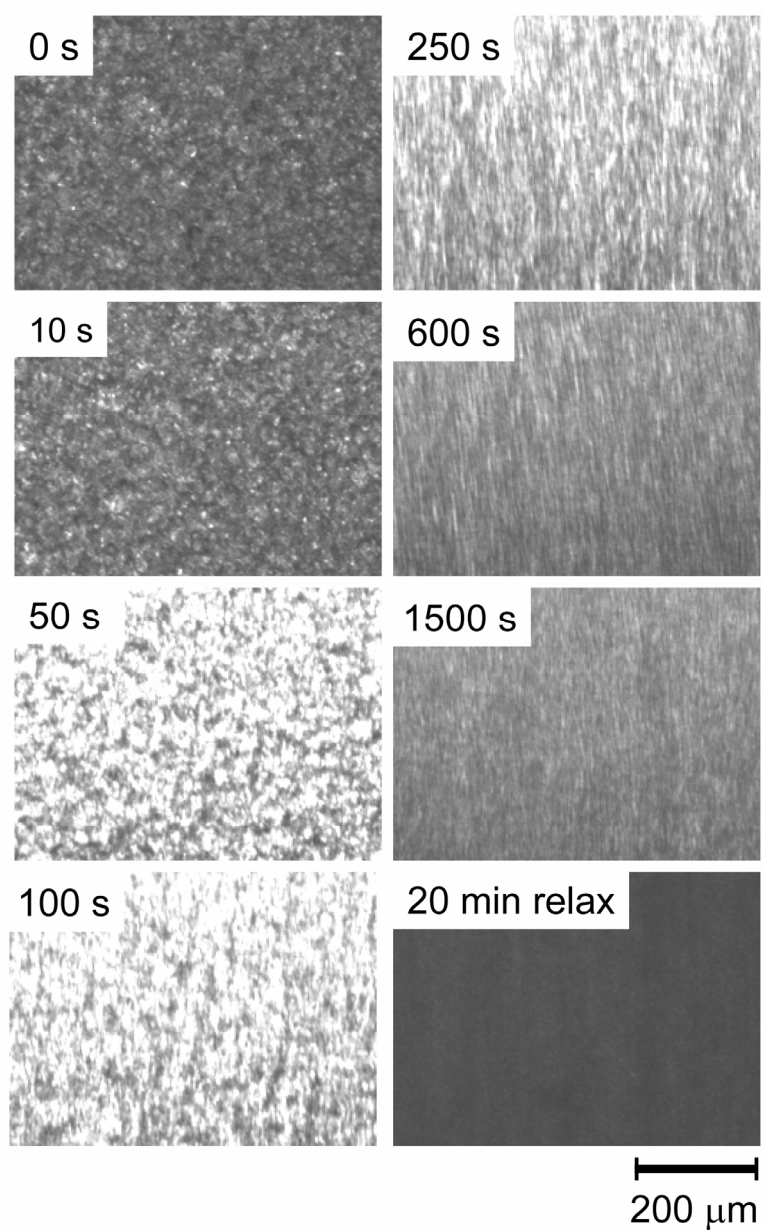


Figure 4.37. Microscopy images of the PS-PI BμE during shear inception at 130°C and 0.20 s^{-1} . The numbers in each image represent the time after start of flow, and the last image corresponds to 20 minutes following cessation of flow. The intensity scale is equal for all images, and the flow direction is vertical.

The microscopy images in Figure 4.37 for $t > 0$ were collected during start-up of shear at 0.20 s^{-1} . The changes occurring in the phase-separated structures are similar to the changes during shear at 0.05 s^{-1} , except the process occurs more quickly at the higher shear rate and the structures are more stretched. Comparison of the images in Figures 4.36 and 4.37 corresponding to the time long after cessation of flow shows that higher sample turbidity resulting from shear at 0.20 s^{-1} . This observation suggests the B μ E phase has undergone a small degree of phase-separation.

The sample was annealed again for 1.5 hours at 150°C and cooled back to 130°C . The morphology of the phase-separated structures after annealing is shown in Figure 4.38 for $t = 0$. This image shows higher turbidity and larger structures in comparison to the image obtained prior to shear at 0.20 s^{-1} . This observation further indicates that shearing at 0.20 s^{-1} leads to additional phase-separation of the B μ E phase, which is not fully recovered by annealing at the higher temperature.

The remaining images in Figure 4.38 correspond to various time points during shear inception at an even higher rate of 1.0 s^{-1} . The evolution in the morphology is similar to the observed changes at lower shear rates. As expected, the structures are more stretched and break up more rapidly at this higher shear rate. Figure 4.39 shows microscopy images collected over time following cessation from steady-shear at 1.0 s^{-1} . Within 2 minutes of relaxation, the phase-separated structures appear to have contracted slightly. Also, the increased image darkness indicates that the structures have begun to coarsen, which continues with time. Unfortunately, due to the occurrence of melt fracture in the x-ray flow cell at this shear rate, we were unable to obtain complementary SAXS

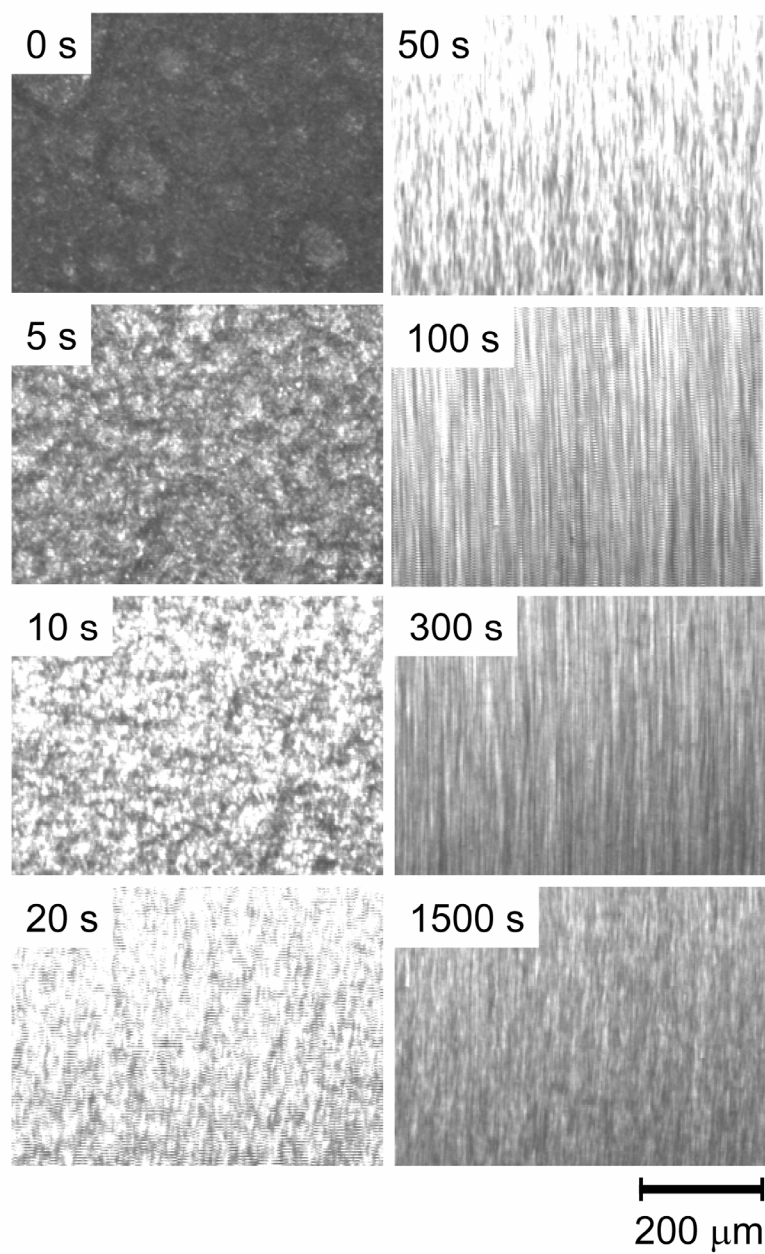


Figure 4.38. Microscopy images of the PS-PI BμE during shear inception at 130°C and 1.0 s^{-1} . The numbers in each image represent the time after start of flow. The intensity scale is equal for all images, and the flow direction is vertical.

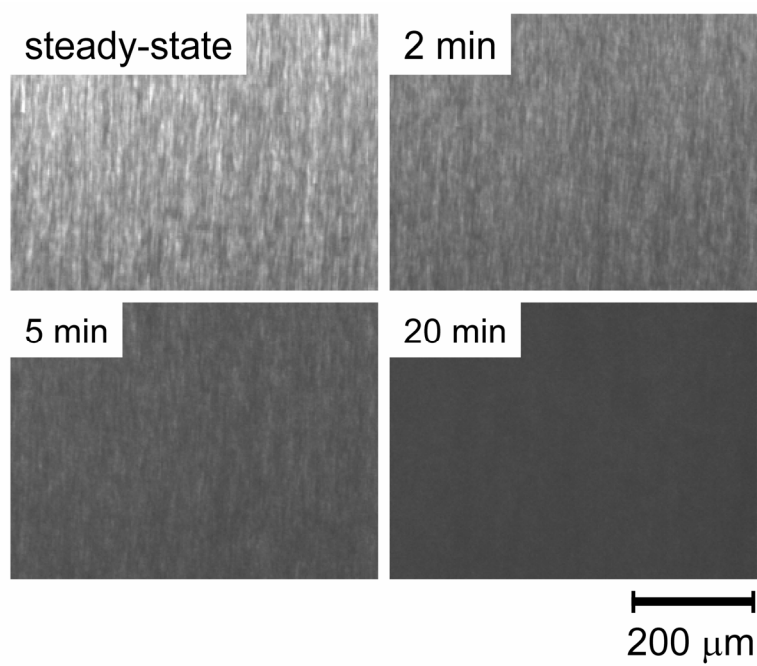


Figure 4.39. Microscopy images of the PS-PI BμE following cessation from steady shear at 130°C and 1.0 s^{-1} . The numbers in each image represent the time after cessation of flow.

data to investigate the extent of phase-separation of the B μ E phase at this higher shear rate.

Discussion

The microscopy results presented in Figures 4.36 – 4.39 provide a clearer picture of the shear-induced structural changes leading to the observed rheological and x-ray scattering behavior of the PS-PI microemulsion. We now know that micron-sized structures exist in the sample *prior* to application of shear and are not solely produced during shear. Thus, the appearance of the streak at low- q in the SAXS patterns (Figure 4.32) immediately upon start-up of shear likely corresponds to the stretching and alignment of the already present phase-separated structures. The gradual weakening of the low- q streak over longer times appears to be related to the break-up of these structures. Since smaller structures deform less under shear than larger structures, break-up will yield lower anisotropy in the associated scattering. Close inspection of the SAXS images in Figure 4.32 for $t = 50 - 1300$ seconds shows that the intensity associated with the low- q streak, in fact, appears to be spreading out along the azimuthal direction with time. This is also illustrated in Figure 4.33. A decrease in the size of the phase-separated structures will also shift the associated scattering to larger q . Figure 4.33 indeed shows an overall increase in intensity on the low- q side of the B μ E peak as a result of shear. Therefore, the increased intensity in this q -range is potentially associated with the smaller phase-separated structures rather than the B μ E structure itself.

The increase in overall anisotropy factor (Figure 4.30) and the scattering analog of the shear stress (Figure 4.31) at long times also may be related to the break-up of the phase-separated structures. In the definition of the second moment tensor (eqn. 2.14), from which AF and $\langle q_x q_y \rangle$ are computed, the intensity values at larger scattering vector are weighted more than the intensities at smaller q -values. Thus, the movement of intensity toward larger q as the phase-separated structures break-up would lead to an increase in these values. The microscopy images at steady-state indicate that the large structures maintain some degree of orientation even after break-up.

In regards to the rheological response to shear inception, recall that the transient shear stress exhibits a distinct overshoot, followed by a minimum before slowly growing towards the steady-state value (Figure 4.23). Interestingly, this behavior has been reported in immiscible binary blends, and is associated with the stretching and break-up of droplets during shear [Takahashi and Noda (1995); Vinckier *et al.* (1997)]. Microscopy images suggest that the shear stress response of the PS-PI microemulsion is also related to the break-up of larger structures into smaller ones. SAXS and microscopy images indicate that the overshoot is associated with stretching and orientation of both the B μ E and phase-separated structures. However, the breakup of the larger structures leads to an increased amount of interface in the system, resulting in the observed stress growth over longer times.

At the highest applied shear rates in rheological measurements, the undershoot and subsequent growth in stress become less pronounced. Potentially, these rates lead to significant shear-induced phase-separation of the B μ E phase. The loss in interface from

the B μ E structure may be comparable to the gain in interface from break-up of the much larger structures, resulting in a minimal change in shear stress following the overshoot. Due to experimental limitations, SAXS data could not be collected at high shear rates to confirm this possibility.

One of the original objectives of these transient experiments was to complete our investigation of the universality of the shear-induced behavior of polymer bicontinuous microemulsions. However, the micron-sized structures, which are present in the equilibrium morphology of the PS-PI microemulsion sample, dominate the rheology and x-ray scattering response under steady-shear in the non-linear regime. As a consequence, we cannot make conclusive generalizations regarding the behavior, particularly with respect to phase transitions, in B μ E systems under these stronger shear conditions. Nonetheless, these experiments have yielded interesting results that provide insight into the flow properties of fluids exhibiting multiple phases. The sample used in these studies contains 10% block copolymer. Perhaps a single-phase bicontinuous microemulsion can be achieved using slightly higher concentration of the diblock. It would be interesting to replicate the flow studies with a pure B μ E phase in the PS-PI blend system and compare to the 3-phase PS-PI system presented here and the PEE-PDMS B μ E by Krishnan *et al.* (2002b).

An additional objective of the SAXS flow experiments was to obtain time-resolved, simultaneous measurements of scattering from the B μ E phase and phase-separated structures during shear. Measurement of scattering from phase-separated structures was not possible in the previous SAXS experiments of the PEE-PDMS B μ E

due to strong parasitic scattering in the low- q region from the x-ray shear cell (Figure 2.9). However, the parasitic scattering was less significant in our case due to the stronger scattering power of the PS-PI blend, and we were in fact able to accomplish our objective. The installation of the mica window in the shear cell, as discussed in Section 2.4.3 eliminates the parasitic scattering from future experiments, providing the opportunity to investigate the shear-induced phase-separation process in polymer bicontinuous microemulsions with weaker scattering power (including the PEE-PDMS system).

4.5.3. Summary

The shear-induced structural behavior of a PS-PI bicontinuous microemulsion has been characterized using rheology and *in situ* SAXS. In effort to identify characteristics that may be general to all polymer B μ E systems, in depth comparisons were made to the flow behavior of the previously reported PEE-PDMS B μ E [Caputo *et al.* (2002b); Krishnan *et al.* (2002a, 2002b)]. The scattering response to step strain and oscillatory shear at moderate strain and frequency shows strong similarities to the PEE-PDMS B μ E subjected to similar flow conditions. During start-up of continuous shear, both B μ E systems exhibit a linear response in the shear stress at very low shear rates and a more complex response at higher shear rates that occurs over long times. However, the *shapes* of the observed shear stress with time at the higher shear rates are dramatically different, which indicates a difference in the evolution of microstructure at more severe shear conditions.

Using *in situ* neutron scattering, SALS, and optical microscopy techniques, Krishnan *et al.* (2002a, 2002b) discovered that the stress response in the PEE-PDMS system corresponds to a shear-induced transition of the B μ E phase to a micron-sized phase-separated morphology. On the other hand, optical microscopy images of the PS-PI system revealed the existence of micron-sized phase-separated structures with the B μ E phase at *equilibrium*, prior to application of shear flow. *In situ* optical microscopy and SAXS measurements suggest that the stress response in the PS-PI system is strongly associated with the stretching and break-up of these large structures rather than with phase-separation of the B μ E morphology. Changes in the shear stress response with increasing shear rate suggest that higher shear rates eventually lead to phase-separation of the B μ E structure in addition to the break-up of the very large, already existing phase-separated structures; however, this could not be confirmed in SAXS measurements.

The results of our study shows complex, interesting flow behavior of a PS-PI blend exhibiting a multi-phase morphology, which exists near the homopolymer-rich side of the bicontinuous microemulsion channel within the isopleth phase diagram. The B μ E phase within the blend appears to dominate the rheology and x-ray scattering at low to moderate shear deformation. This is indicated by the striking similarities to the previously documented PEE-PDMS system, which exhibits a single-phase B μ E morphology. At stronger shear conditions, deformation of the coexisting larger structures in the PS-PI system becomes significant and results in a rheological response that strongly differs from the response of the PEE-PDMS microemulsion. Consequently, the presence of phase-separated structures in the equilibrium morphology of our PS-PI blend

prevents us from investigating possible shear-induced phase transitions of the bicontinuous microemulsion phase. Presumably, a “pure” B μ E phase can be obtained in the PS-PI blend system by using slightly higher concentration of copolymer.

CHAPTER 5.

RHEOLOGY AND SHEAR-INDUCED STRUCTURE IN A POLYMER SPONGE PHASE

5.1. Introduction

Polymer sponge phases are characterized by two cocontinuous domains of a single homopolymer separated by a randomly oriented, multiconnected bilayer membrane formed by block copolymer [Falus *et al.* (2004a); Laurer *et al.* (1997)]. As in the similarly structured bicontinuous microemulsion, the characteristic domain spacing is on the order of 10s of nanometers. Therefore, polymer sponge phases also show promise for the development of new materials that benefit from their nanoscale, cocontinuous morphology. To date, the rheology and shear-induced structural behavior of polymer-based sponge phases has not been documented.

Considering the bicontinuous morphology of the sponge phase, one might expect the rheology and shear-induced structural response to be similar to the polymer bicontinuous microemulsion under low to moderate shear deformation. As in the polymer B μ Es, one may also anticipate a break down of the interconnected structure of the sponge phase under strong shear flow conditions. Studies of water/surfactant sponge

phases have shown a transition to a lamellar phase at very high shear rates ($>10^2 \text{ s}^{-1}$)

[Mahjoub *et al.* (1998); Porcar *et al.* (2003); Yamamoto and Tanaka (1996)].

Unfortunately, the fast dynamics in these small molecule systems prevent more detailed characterization of the rheology and time-evolution of the structural changes during flow.

The final objective of this dissertation is to investigate the flow behavior of *polymer* sponge phases, which exhibit slow dynamics due to the larger constituent polymer molecules.

This Chapter begins by briefly reviewing previous studies of water/surfactant sponge phases. The phase behavior of two-component systems consisting of a surfactant and solvent is presented, followed by a discussion of the flow behavior of aqueous-based sponge systems. We then discuss the phase behavior of a polymer sponge phase developed by Falus *et al.* (2004a, 2006). Our studies, which comprise the remainder of this chapter, probe the flow behavior of this polymer-based system by Falus *et al.* using rheology and *in situ* small-angle x-ray scattering.

5.2. Background

5.2.1. Water/Surfactant Sponge Phases

As discussed in Chapter 4, ternary mixtures of a surfactant and two incompatible fluids yield complex phase behavior (see Figure 4.1). Binary systems consisting of a surfactant and a single solvent also exhibit a large array of interesting morphologies. Figure 5.1 shows, for example, the phase diagram for a system composed of water and C_{12}E_5 (n-

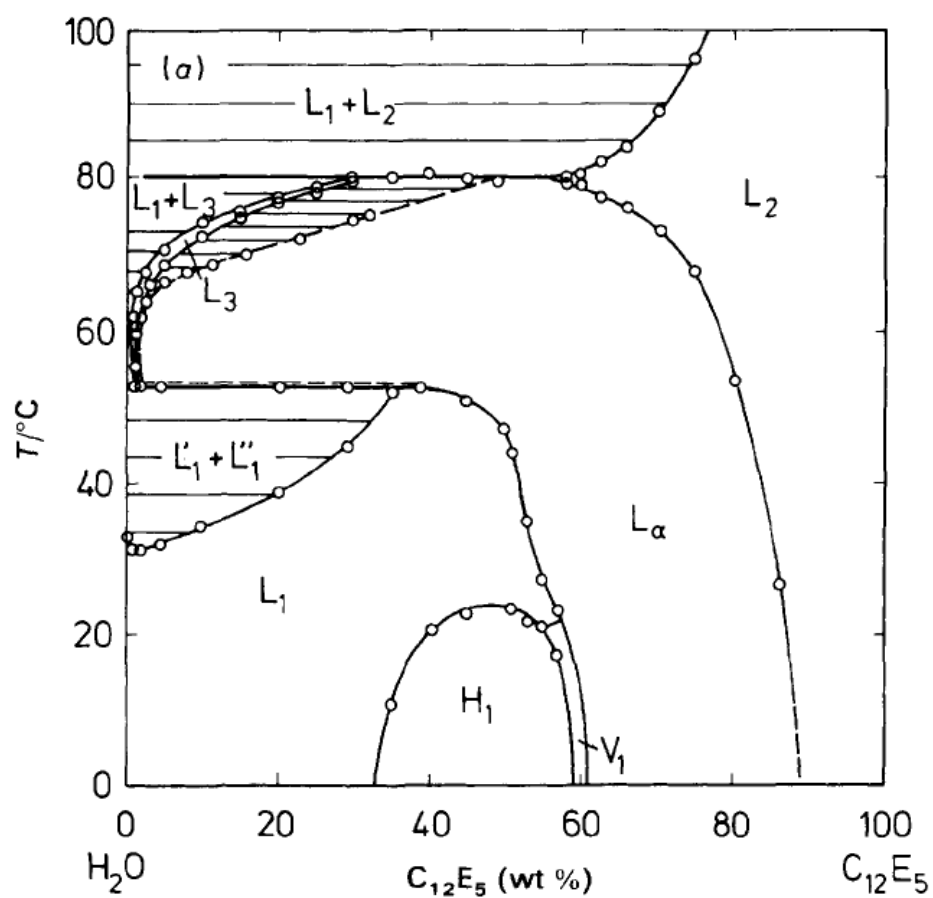


Figure 5.1. Phase diagram of the water-C₁₂E₅ system. L₁ and L₂ represent disordered micellar and inverse micellar phases, respectively. H₁ is a hexagonal phase, and V₁ is a cubic phase. L_α is a lamellar phase, and L₃ is a sponge phase [from Strey *et al.* (1990)].

dodecyl pentaoxyethylene glycol ether) [from Strey *et al.* (1990)], which forms disordered micellar (L_1), inverse micellar (L_2), ordered hexagonal (H_1), cubic (V_1), and lamellar phases (L_α). In the lamellar phase, the surfactants self-assemble into extensive, flexible sheets of bilayer membranes. At sufficient dilution of the L_α phase, within the intermediate temperature range (55 - 80°C), thermal undulations of the sheets lead to the formation of a sponge phase (L_3), in which the membranes form a continuous, three-dimensional network. Further dilution (*i.e.*, increase in water concentration) results in a biphasic L_1 - L_3 morphology. Illustrations of the L_3 and L_α morphologies are shown in Figure 5.2.

The flow behavior of the L_3 sponge phase in aqueous-based systems has been experimentally investigated by several groups [Diat and Roux (1995); Gomati *et al.* (2002); Leon *et al.* (2001); Mahjoub *et al.* (1996, 1998) ; Porcar *et al.* (2002, 2004); Snabre and Porte (1990); Tanaka *et al.* (2006); Yamamoto and Tanaka (1996)]. These systems generally exhibit a Newtonian response with low viscosities over a wide range of shear rates, implying that the connections in the extensive, continuous membrane rapidly break and reform to relieve stress during shear. For dilute or “swollen” sponge phases, the viscosity depends linearly on the volume fraction of membrane ($\eta \sim \phi_m$) [Snabre and Porte (1990)]. Above a critical concentration of membrane, the sponge viscosity deviates from this linear relationship and increases exponentially with ϕ_m [Gomati *et al.* (2002)].

At very high shear rates ($> 100 \text{ s}^{-1}$), aqueous sponge phases exhibit strong shear thinning, which is associated with a shear-induced transition to a lamellar structure [Porcar *et al.* (2002); Tanaka *et al.* (2006)]. Cates and Milner (1989) predicted that shear

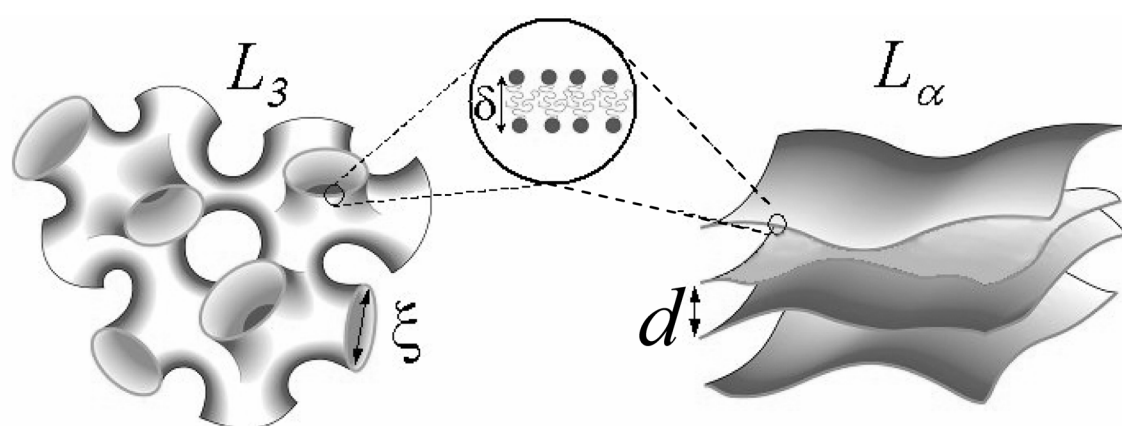


Figure 5.2. L_3 and L_α membrane structures and their respective characteristic dimensions [from Porcar *et al.* (2002)].

flow suppresses fluctuations in isotropic phases, such as a sponge morphology, leading to the creation of a lamellar phase at a critical shear rate $\dot{\gamma}_c$. This transition is expected to follow the relationship

$$\dot{\gamma}_c \sim \frac{k_B T}{\eta_s \xi^3} \sim \frac{k_B T}{\eta_s} \left(\frac{\phi_m}{\delta} \right)^3 \quad (5.1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, η_s is the solvent viscosity, ξ is the domain size, and δ is the membrane thickness. The scaling relationship $\dot{\gamma}_c \sim \phi_m^3$ in eqn. 5.1 has been found to hold in different sponge systems by Diat and Roux (1995), Porcar *et al.* (2002), and Tanaka *et al.* (2006). However, the experimentally observed *orientation* of the lamellar structure is in disagreement with the theory. Whereas the Cates and Milner theory predicts orientation of the lamellar normals perpendicular to the flow velocity and velocity gradient directions (known as “perpendicular” orientation), the shear-induced lamellae in sponge systems are generally reported to orient with the layer normals parallel to the velocity gradient direction (“parallel” orientation) [Porcar *et al.* (2002); Yamamoto and Tanaka (1996)]. Mahjoub *et al.* (2006) observed in a sponge system “perpendicular” orientation of the shear-induced lamellar phase at a low critical shear rate, which transitions to “parallel” orientation at a higher critical shear rate.

The mechanisms driving the sponge-lamellar transition remain unclear, and the fast dynamics of aqueous sponge phases render these issues difficult to resolve experimentally. In the documented studies, only steady-state data were reported.

Polymer-based sponge phases provide opportunities to study the time-evolution of shear-induced structure in these types of systems.

5.2.2. Polymer Sponge Phases

To our knowledge, sponge phases have been created in only two polymer systems [Falus *et al.* (2004a); Laurer *et al.* (1997, 1998)]. The sponge phase developed by Falus *et al.* (2004a) consists of polystyrene homopolymer (PS) and a poly(styrene-ethylene/butylene-styrene) symmetric triblock copolymer (PSEBS). In this system, the ethylene/butylene mid-block of the copolymer is immiscible with polystyrene and segregates to form membranes. The phase behavior or arrangement of membranes in the PS/PSEBS blend has the following dependence on copolymer concentration. High concentrations of PSEBS yield a lamellar (L_α) phase. At lower copolymer concentration, thermal undulations bring the membrane sheets into contact, resulting in a sponge phase (L_3). With further decrease in PSEBS concentration, the interconnected structure of the sponge cannot be maintained, leading to the formation of vesicle phase (L_4). The transition in these morphologies is gradual with copolymer concentration, and the PS/PSEBS system exhibits biphasic regions (*i.e.*, L_α - L_3 and L_3 - L_4) in between the compositions of the pure phases. This transition is evident in static SAXS measurements later on.

Figure 5.3 shows representative cryotransmission electron (CTEM) micrographs [from Falus *et al.* (2004a)] of vesicle and sponge morphologies in blends with weight fraction of copolymer $\phi_{\text{PSEBS}} = 0.07$ and $\phi_{\text{PSEBS}} = 0.19$. The existence of membranes is evident in these images. For $\phi_{\text{PSEBS}} = 0.07$ (top image), the membranes form loops,

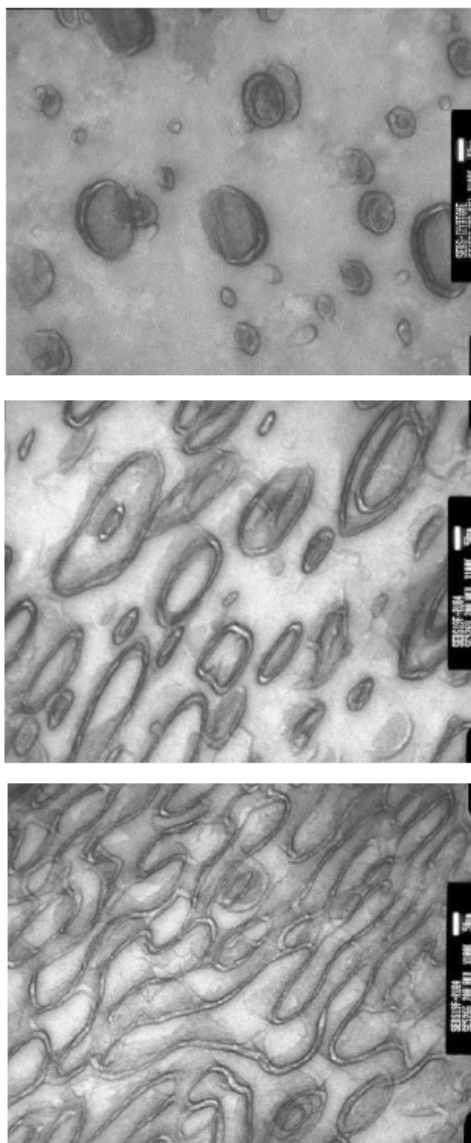


Figure 5.3. CTM micrographs of PS/PSEBS blends with $\phi_{\text{PSEBS}} = 0.07$ (top) and $\phi_{\text{PSEBS}} = 0.19$ (middle and bottom). The top and middle micrographs show the L_4 (vesicle) morphology, and the bottom shows the L_3 (sponge) morphology. The white scale bar in each image represents 50 nm [from Falus *et al.* (2004b)].

characteristic of vesicle structures, ranging from 50 to 300 nm in diameter. The $\phi_{\text{PSEBS}} = 0.19$ blend exhibits a biphasic morphology, which consists of 95% vesicle regions (middle image) and 5% sponge regions (bottom image) with an average domain size of ~ 80 nm. For $\phi_{\text{PSEBS}} = 0.22 - 0.25$, Falus *et al.* reported a symmetric, single-phase sponge morphology. We have performed rheology and *in situ* SAXS experiments to characterize the flow behavior of the PS/PSEBS sponge phase.

5.3. Experiment

5.3.1. Materials

Polystyrene homopolymer with a molecular weight of $M_w = 4100$ and a polydispersity of $M_w/M_n = 1.09$ was obtained from Polymer Source, Inc. (Dorval, QC, Canada). We note that Falus *et al.* used a PS homopolymer with a slightly higher molecular weight $M_w = 4820$ and similar polydispersity. Poly(styrene-ethylene/butylene-styrene) symmetric triblock copolymer (Kraton G1652) with $M_w = 80,700$ and $M_w/M_n = 1.07$ is produced by Kraton Polymers (Houston, TX). The PSEBS copolymer consists of a weight fraction ethylene/butylene midblock of $w_{\text{EB}} = 0.70$.

Using similar procedures documented by Falus *et al.* (2004a), blends were prepared with copolymer weight fractions of $\phi_{\text{PSEBS}} = 0.20, 0.25, 0.28, 0.30$, and 0.35 . To facilitate mixing, the polymers were co-dissolved in toluene (90:10 solvent to polymer ratio) using a magnetic stir bar. The solution was precipitated in cold isopropanol ($> 5:1$ isopropanol : toluene). The precipitate was collected on filter paper (Whatman

International, 8 μm porosity) and dried under vacuum at 60°C for 1 hour. Prior to rheology or SAXS experiments, the blends were annealed under vacuum for 2 hours at 200°C and then 12 hours at 160°C.

5.3.2. Rheology

Linear viscoelastic measurements of the PS homopolymer and PS/PSEBS blends ($\phi_{\text{PSEBS}} = 0.20, 0.25, 0.28, \text{ and } 0.35$) were conducted using a Rheometric Scientific ARES strain-controlled rheometer with cone and plate fixtures (50 mm diameter, 0.04 radian cone angle) and a nitrogen atmosphere. A limited number of shear inception/cessation experiments were performed for the blend $\phi_{\text{PSEBS}} = 0.25$. Blends with higher concentration of copolymer were susceptible to melt fracture, even at low shear rates.

5.3.3. X-Ray Scattering

SAXS experiments were performed at beamline 5ID-D of the Advanced Photon Source using 15 keV undulator radiation. Prior to conducting flow experiments, static SAXS measurements were collected to characterize the morphology of all prepared PS/PSEBS blends. *In situ* SAXS measurements during flow were collected for three of the prepared blends exhibiting a sponge phase ($\phi_{\text{PSEBS}} = 0.20, 0.25, \text{ and } 0.28$).

The annular cone and plate shear device, with the mica window installed in the bottom plate, was mounted on a translation table using the general setup shown in Figure 2.8. The sample area was enclosed using acrylic plates and purged with Helium gas to provide an inert atmosphere. The PS/PSEBS blends were subjected to step strain and

oscillatory shear in addition to start-up, reversal, and cessation of unidirectional shear flow. Time-resolved two-dimensional scattering patterns were collected at a rate of ~ 1.25 frames/sec using a Roper CCD detector positioned 8.04 meters downstream from the sample. Using a Mar CCD detector, additional scattering measurements were collected for a small number of shear experiments. The Mar is a much larger detector than the Roper and provides access to a larger q -range. However, the Roper offers greater time resolution than the Mar and was therefore employed for most shear experiments. Changes in the incident beam flux were monitored using an ion chamber positioned upstream from the sample. Here, we only present *in situ* SAXS results for $\phi_{\text{PSEBS}} = 0.20$ and 0.25 subjected to start-up, reversal, and cessation of unidirectional shear flow.

5.4. Results

5.4.1. Static X-Ray Scattering

Within a sponge phase, the membranes divide the solvent into two distinct continuous domains. In the case of bicontinuous microemulsions, the domains consist of two dissimilar solvents whose differing electron densities give rise to the observed scattering peak. This contrast does not exist in the sponge phase; rather, scattering results from electron density contrast between the solvent and membrane. Theoretical descriptions of sponge phases predict two scattering peaks: one at zero scattering vector, and the other at

non-zero scattering vector ($q = q^*$) that varies linearly with membrane concentration ϕ_m [Gompper and Schick (1994)].

The scattering profiles for the PS/PSEBS blends are shown in Figure 5.4. The shapes of the profiles and their dependence on copolymer concentration are nearly identical with the PS/PSEBS system by Falus *et al.* (2004a). At large q , oscillations are evident for all blend compositions. Falus *et al.* noted that the locations of the oscillation minima, occurring every 0.32 nm^{-1} , correspond to the existence of membranes of thickness $\delta \sim 19 \text{ nm}$.

The scattering profiles at smaller q are much more dependent on copolymer concentration and reflect the larger scale arrangement of the membranes within the blend. For $\phi_{\text{PSEBS}} = 0.20$, the scattering shows a peak at $q \rightarrow 0$ and then decreases monotonically before oscillating at large q . In addition to the peak at $q \rightarrow 0$, $\phi_{\text{PSEBS}} = 0.25$ and 0.28 exhibit a broad, second peak at non-zero scattering vector ($q = q^* \approx 0.055 \text{ nm}^{-1}$), consistent with expectations of a sponge phase. Thus, the development of a second peak for $\phi_{\text{PSEBS}} > 0.20$ suggests a transition from a vesicle phase to a sponge phase. Note that $\phi_{\text{PSEBS}} = 0.20$ shows a slight shoulder at q^* , which suggests a small amount of sponge morphology coexisting with the vesicle phase at this concentration. The peak at q^* persists for $\phi_{\text{PSEBS}} = 0.30$ indicating the existence of a sponge phase at this composition as well. The peak at $q \rightarrow 0$ is not shown because data were not measured at lower scattering vectors for this sample (or $\phi_{\text{PSEBS}} = 0.35$). For $\phi_{\text{PSEBS}} = 0.35$, the peak at q^* is very weak, and an additional, more pronounced peak has developed at higher q ($\sim 0.15 \text{ nm}^{-1}$). This third peak is attributed to the formation of a lamellar phase [Falus *et al.* (2004a)].

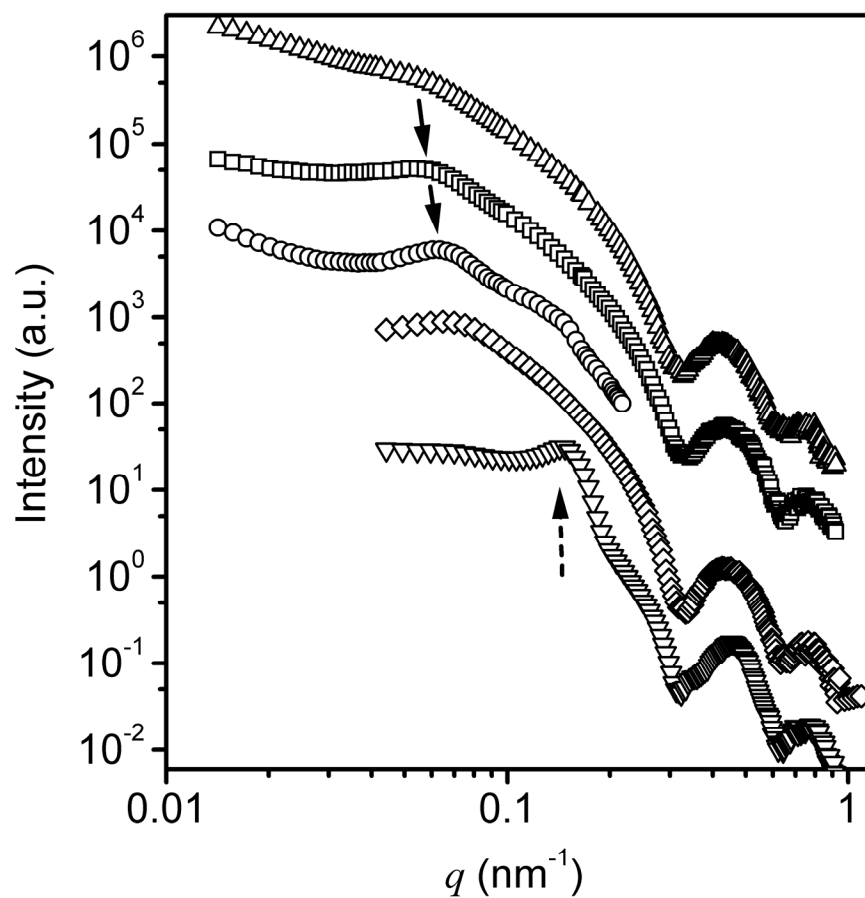


Figure 5.4. One-dimensional intensity profiles of PS/PSEBS blends: $\phi_{\text{PSEBS}} = 0.20$ (Δ), 0.25 ($\square$), 0.28 ($\circ$), 0.30 ($\diamond$), 0.35 (∇). Data have been shifted vertically from each other to provide clarity. The arrows highlight peaks associated with sponge (solid lines) and lamellar (dashed line) structures.

Figure 5.5 shows two-dimensional quiescent scattering patterns for $\phi_{\text{PSEBS}} = 0.20$, 0.25, and 0.28. The pattern corresponding to $\phi_{\text{PSEBS}} = 0.20$ (top) is isotropic and exhibits strong intensity at $q \rightarrow 0$ with no signs of an additional peak at $q > 0$. The peaks observable in the patterns for $\phi_{\text{PSEBS}} = 0.25$ (middle) and $\phi_{\text{PSEBS}} = 0.28$ (bottom) correspond to $q = q^*$ and are associated with the sponge structure. By definition, sponge phases at equilibrium (in a relaxed state) are isotropic. Interestingly, $\phi_{\text{PSEBS}} = 0.25$ and 0.28 both show some anisotropy in the sponge peak, indicating an average orientation of the sponge structure along the horizontal (q_x) direction.

Anisotropy of the sponge peak under quiescent conditions was *not* reported by Falus *et al.* However, their scattering measurements included only a quadrant of the full 2-D scattering plane [Falus *et al.* (2004c)], and the anisotropy may be low enough such that it was not apparent in these measurements. Mochrie (2007) noted that CTEM micrographs of their samples show slight anisotropy in the sponge morphology (see bottom image of Figure 5.3), but this was not verified using additional methods. The quiescent scattering patterns in Figure 5.5 were collected after loading the samples into the shear cell. It is possible that the anisotropy has resulted from deformation imposed on the sample during loading, and this anisotropy is extremely slow to relax (longer than experimental time scales).

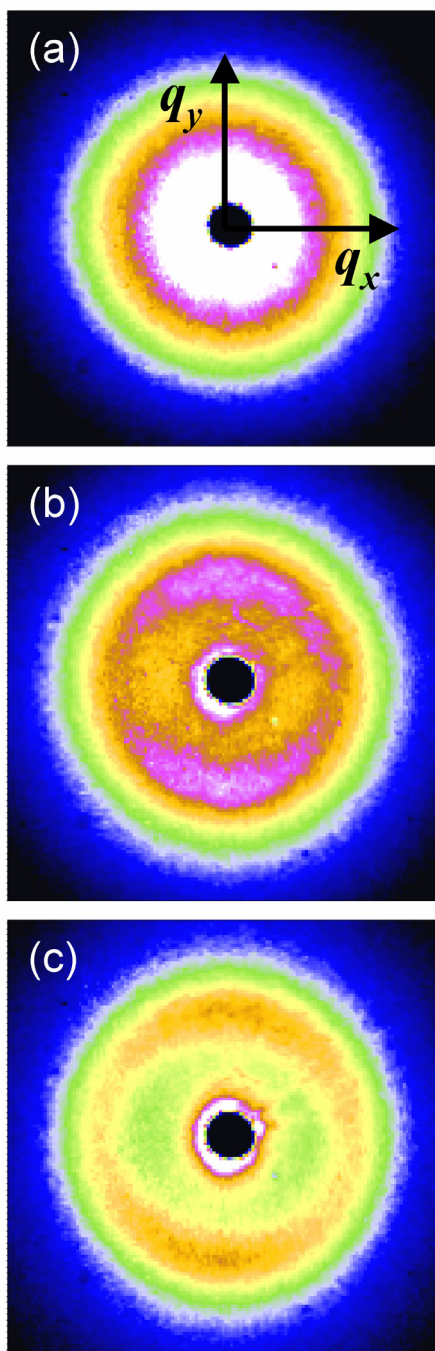


Figure 5.5. Quiescent scattering patterns of PS/PSEBS blends at 150°C: (a) $\phi_{\text{PSEBS}} = 0.20$, (b) 0.25, and (c) 0.28. The q -range in these images is $|q_x, q_y| \leq 0.11 \text{ nm}^{-1}$. The intensity scale is the same in all images. The 1-D profiles in Figure 5.4 were obtained by averaging the intensity data in these 2-D patterns along the azimuthal direction.

5.4.2. Rheology

Linear viscoelastic measurements of the PS/PSEBS blends began with strain sweep measurements (at 10 rad/s) to determine the linear viscoelastic regime of each blend. Figure 5.6 shows the storage modulus G' as a function of strain for $\phi_{\text{PSEBS}} = 0.20, 0.25$, and 0.35 at 150°C. In all blends, G' does not approach a constant value at low strains, and therefore does not exhibit a clear linear regime within the range of applied strains. However, the changes in G' are not huge, and we proceeded with frequency sweep experiments at (150°C) using a strain of 3% for $\phi_{\text{PSEBS}} = 0.20$, 0.5% for $\phi = 0.25$ and 0.28, and 0.1% for $\phi = 0.35$. Slightly higher strains were used at higher temperatures. The low strain-dependence in the measured response is further illustrated in Figure 5.7. Frequency sweeps of the $\phi = 0.20$ blend conducted at different strains of 0.5% and 3% show a negligible difference in G' .

The complex viscosity, $|\eta^*|$, and phase angle, δ , as a function of angular frequency for different blend compositions and PS homopolymer at 150°C are shown in Figure 5.8. The blends appear to exhibit three regimes. The viscosity shows shear-thinning at low frequencies, a shoulder at intermediate frequencies, and shear-thinning at high frequencies. The extent of shear-thinning increases and the shoulder becomes less distinct with increasing copolymer (membrane) concentration in the blends. The low molecular weight homopolymer is Newtonian over the entire range of applied frequencies and therefore does not likely contribute to the observed elastic response of the blends.

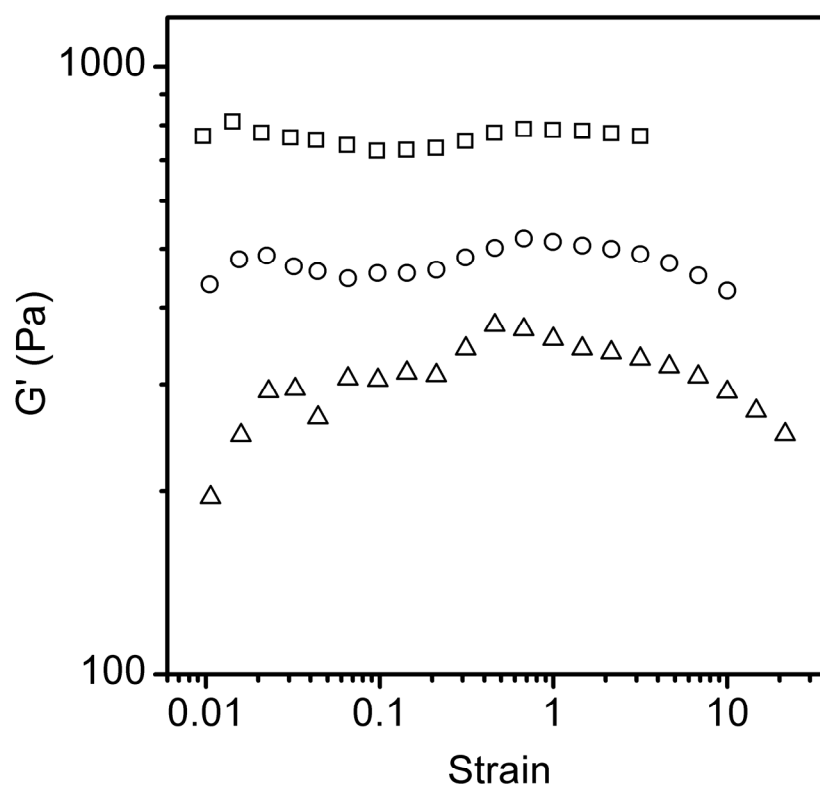


Figure 5.6. Storage modulus as a function of strain in SP/PSEBS blends at 150°C: $\phi_{\text{PSEBS}} = 0.20$ (Δ), 0.25 ($\circ$), 0.35 ($\square$). Measurements were conducted at an applied frequency of 10 rad/s. Data corresponding to $\phi_{\text{PSEBS}} = 0.25$ and 0.28 have been divided by factors of 4 and 16, respectively.

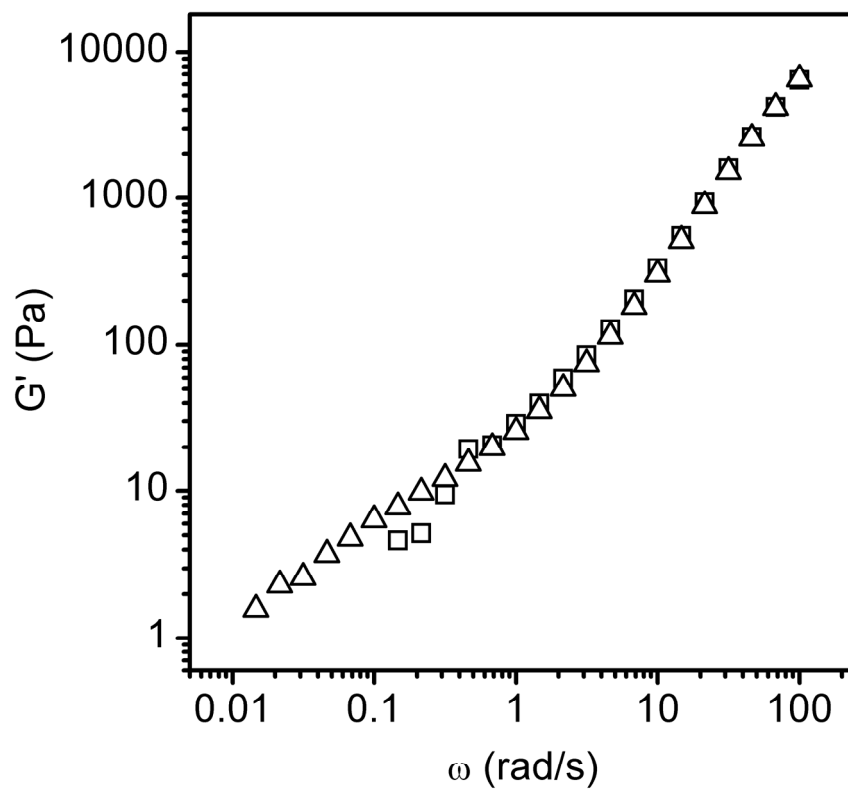


Figure 5.7. Storage modulus as a function of angular frequency in a PS/PSEBS blend ($\phi_{\text{PSEBS}} = 0.20$) at 150°C. Data were collected using ($\square$) 0.5% and (Δ) 3% strain.

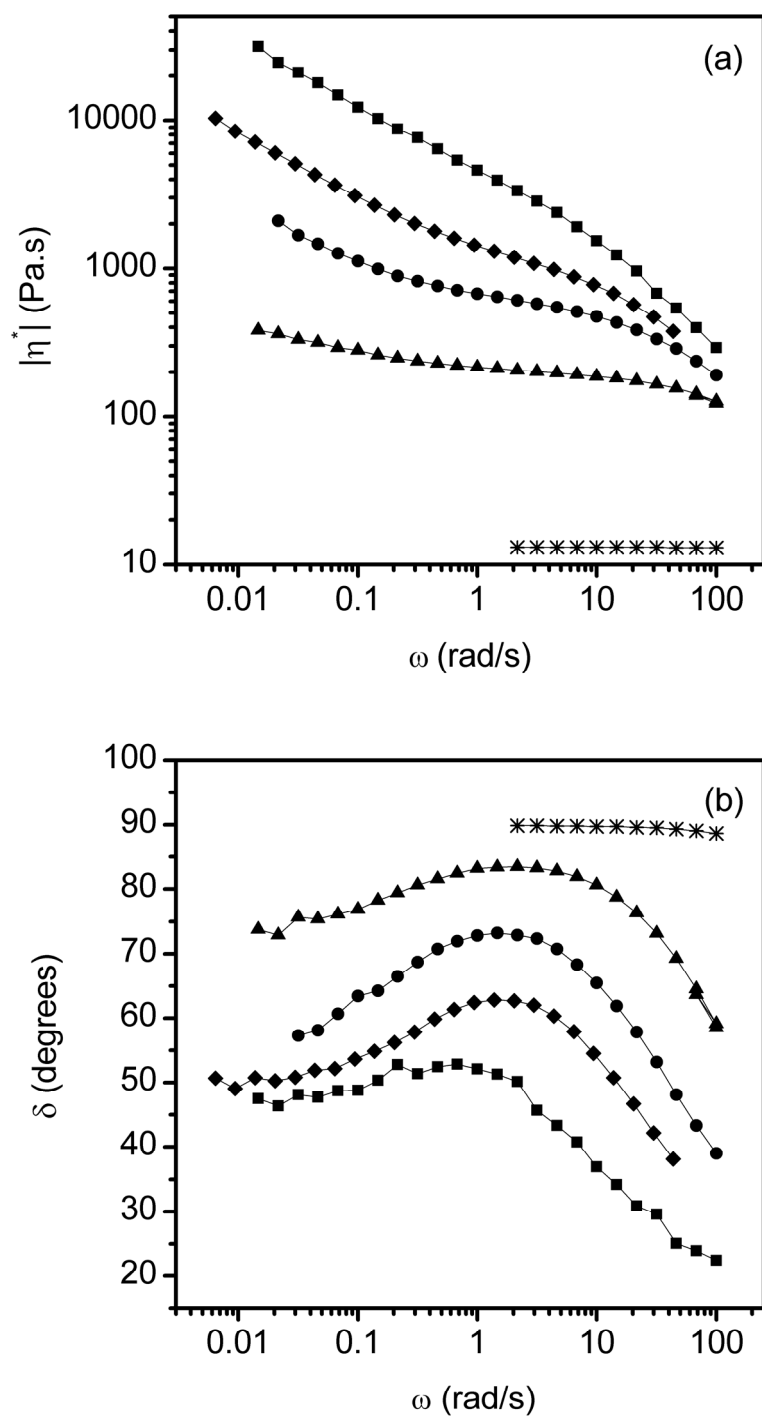


Figure 5.8. (a) Complex viscosity and (b) phase angle as a function of angular frequency in PS/PSEBS blends at 150°C: $\phi_{\text{PSEBS}} = 0.20$ (▲), 0.25 (●), 0.28 (◆), 0.35 (■). (*) represents PS homopolymer.

The three regimes are also reflected in the phase angle. At low frequencies, δ appears to become constant. The range of measured δ values within this regime corresponds to a fluid exhibiting both viscous and elastic character. At intermediate frequencies, the phase angle increases (exhibiting more liquid-like behavior) and reaches a maximum. Higher frequencies lead to a decline in δ , corresponding to an increase in elasticity. The downward vertical shift in the phase angle profile with increasing copolymer concentration reflects an overall increase in the elastic character of the system.

The general behavior of our blends at intermediate and high frequencies (*i.e.*, a viscosity plateau followed by shear-thinning) is commonly observed in viscoelastic fluids, including flexible, entangled polymers. However, the shear-thinning response at low frequencies is more unusual and is likely associated with the macroscale structural organization in the blend. The lack of a terminal, Newtonian regime in the PS/PSEBS blends is further shown in plots of the storage and loss moduli (G' and G'' , respectively) in Figure 5.9. Whereas terminal behavior is characterized by $G' \sim \omega^2$, $G'' \sim \omega$ at low frequencies, the PS/PSEBS blends show $G' \sim G'' \sim \omega^{1/2}$.

The response of the membrane phases in the PS/PSEBS blends over the entire range of applied frequencies is remarkably similar to the behavior of unoriented lamellae in diblock copolymer melts [Koppi *et al.* (1992); Rosedale and Bates (1990)]. In the case of unoriented lamellae, the elastic behavior at low frequencies is related to the disturbance of “defects” in the orientations of the lamellar grains. More specifically, the solid-like response is largely associated with grains whose lamellar planes are aligned perpendicular to the flow direction. The layers aligned in this direction are quite rigid in

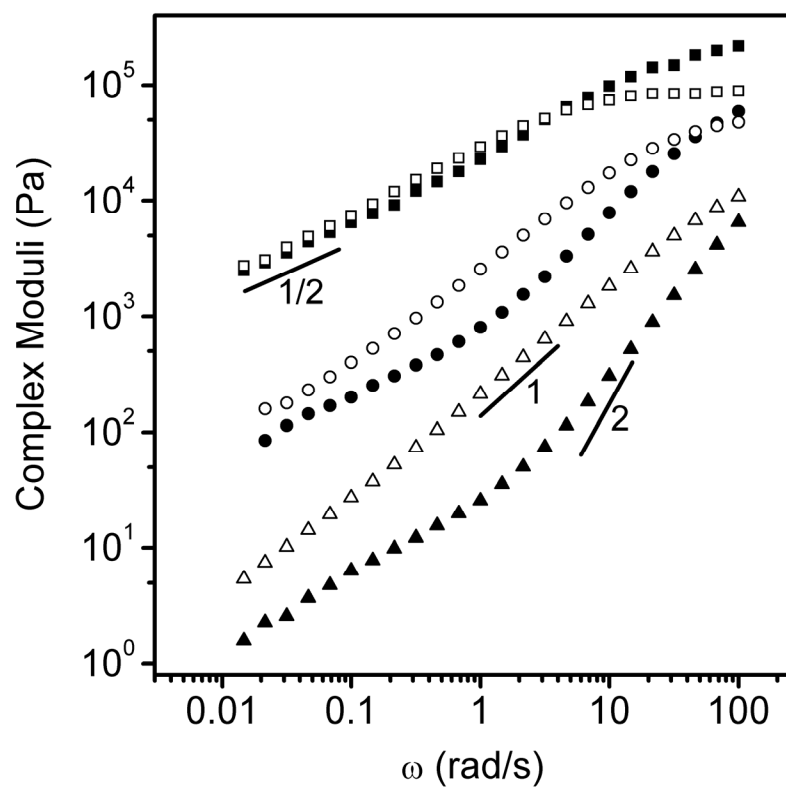


Figure 5.9. Storage modulus (solid symbols) and loss modulus (open symbols) as a function of angular frequency in PS/PSEBS blends at 150°C: $\phi_{\text{PSEBS}} = 0.20$ ($\blacktriangle, \triangle$), 0.25 ($\bullet, \circ$), 0.35 ($\blacksquare, \square$). Data corresponding to $\phi_{\text{PSEBS}} = 0.25$ and 0.35 have been multiplied by factors of 4 and 8, respectively.

response to flow, in part, because the domains are narrow and tightly packed in these systems. In *oriented* lamellar diblock systems, where the planes are oriented normal to the velocity gradient (or vorticity direction), the lamellar layers (and chain blocks within each layer) are able to flow past each other, and a liquid-like, terminal response is achieved at low frequencies.

Considering the behavior of unoriented lamellae in diblock melts, the observed low-frequency response in the PS/PSEBS blends seems reasonable for the case of $\phi_{\text{PSEBS}} = 0.35$, which exhibits an unoriented lamellar morphology of stacked sheets of membrane spaced by PS homopolymer. For $\phi_{\text{PSEBS}} = 0.20 - 0.30$, on the other hand, which exhibit sponge and vesicle phases, one might expect greater mobility and flexibility of the membrane sheets leading to a terminal response at low frequency. The lack of a terminal regime within the experimental range of frequencies suggests, however, that the membranes are not so flexible and the topological relaxation (*i.e.*, breaking and reformation of connections between membrane sheets) is extremely slow within the PS/PSEBS sponge phase. The slow dynamics in the topology appear to be related to the persistent anisotropic state at quiescent conditions (Figure 5.5).

Although the anisotropy in the scattering patterns (Figure 5.5) is quite evident, the intensity of the sponge peak is fairly diffuse along the azimuthal direction. This indicates a fairly broad distribution in the orientation of the sponge domains. In the rheological response at low frequencies and as a result of the slow topological relaxation, the partially aligned sponge phase behaves similarly to a lamellar system exhibiting a distribution in grain orientation. That is, the “defects” in the orientation of membranes in

the sponge phase yield the observed elasticity. With lower concentration of membrane (ϕ_{PSEBS}), the flexibility of the membranes increases, leading to a lower elasticity in this low frequency regime.

Whereas the low frequency response of the PS/PSEBS blends is governed by dynamics associated with macroscale organization of the membranes, the behavior at higher frequencies corresponds to structural dynamics on a more local scale. The more liquid-like response at intermediate frequencies, characterized by the shoulder in the viscosity and the maximum in the phase angle, is potentially related to the flow of the Newtonian PS homopolymer within the domains confined by sheets of membrane. The shear-thinning at higher frequencies is likely associated with chain dynamics of the long ethylene/butylene midblock of the copolymer within the membranes. With increasing concentration of copolymer, the dynamics associated with the macroscale organization of membranes becomes more dominant at faster time scales, leading to the viscous shoulder associated with the solvent domains becoming less distinct.

Figure 5.10 shows the temperature-dependence of the complex viscosity and phase angle for $\phi_{\text{PSEBS}} = 0.25$. The viscosity shoulder and the maximum in δ shift to higher frequencies with increasing temperature, reflecting a speeding up of the membrane dynamics. At the same time, the viscosity shoulder becomes less distinct and the magnitude of the maximum in δ is more suppressed at higher temperatures. Perhaps the time scales of the membrane dynamics are becoming comparable to those of the chain dynamics in the mid-block of the copolymer at higher temperatures, resulting in an overall higher elasticity in this range of time scales. Interestingly, the phase angle at

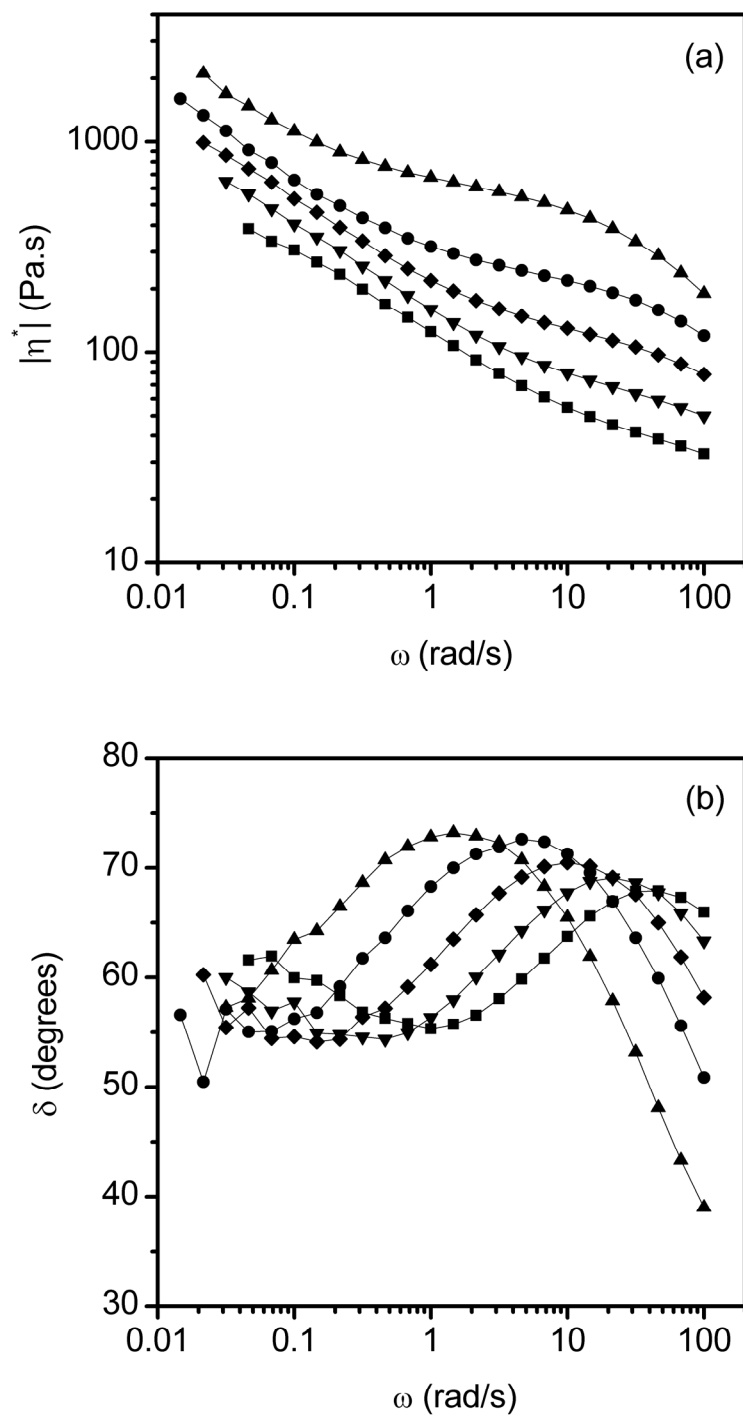


Figure 5.10. (a) Complex viscosity and (b) phase angle as a function of angular frequency in a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$) at 150 ($\blacktriangle$), 160 ($\bullet$), 170 ($\blacklozenge$), 180 ($\blacktriangledown$), and 190°C ($\blacksquare$).

higher temperatures begins to exhibit an upturn to a more liquid-like state at low frequencies. The upturn in δ at low frequency is also apparent at higher temperatures for $\phi_{\text{PSEBS}} = 0.28$, which exhibits a sponge morphology as well (Figure 5.11). The lamellar morphology corresponding to $\phi_{\text{PSEBS}} = 0.35$, on the other hand, shows no indication of this upturn and plateaus at $\delta \sim 45^\circ$ for all temperatures; this remains consistent with expectations for unoriented lamellar systems (below the T_{ODT}).

The upturn in phase angle observed for $\phi_{\text{PSEBS}} = 0.25$ and 0.28 suggests the possible existence of a terminal regime ($\delta \rightarrow 90^\circ$) at even lower frequencies in the PS/PSEBS sponge system. The incredibly long time scales necessary to reach this regime, as mentioned earlier, may correspond to extremely slow relaxation of the membrane topology. The existence of a terminal regime would also indicate that the anisotropy observed in the scattering data was imposed during sample preparation or loading into the shear cell, but that this anisotropy would eventually relax over *very* long times yielding an isotropic sponge structure. As a consequence of the very slow relaxation, this sponge system appears to behave, on experimental time scales, similarly to systems exhibiting a partially ordered morphology.

The crossplot of G'' versus G' for $\phi_{\text{PSEBS}} = 0.25$ in Figure 5.12 shows that this sponge system nearly obeys time-temperature superposition over the range of measured temperatures and applied frequencies. This observation suggests that the membrane morphology is fairly insensitive to changes in temperature. Based on static SAXS measurements over a broad temperature range ($T = 120 - 200^\circ\text{C}$), Falus *et al.* (2004a)

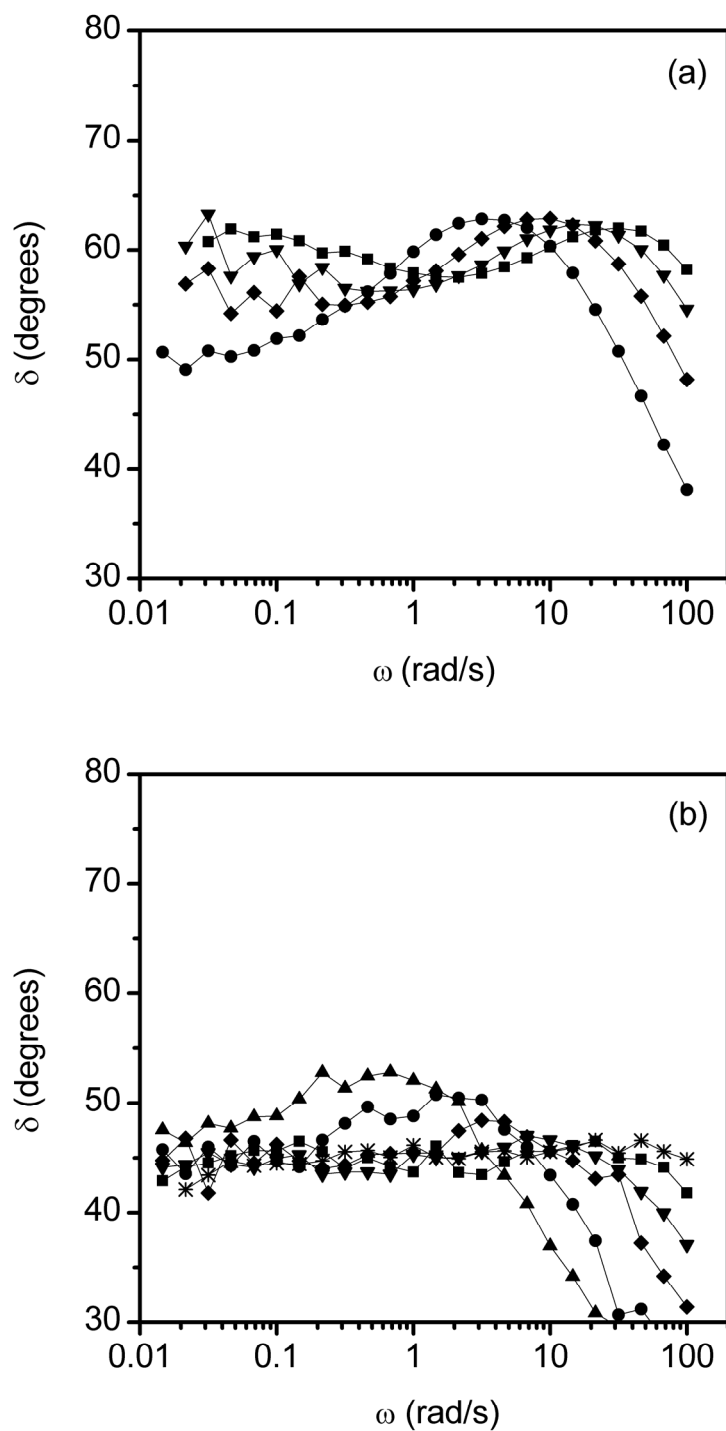


Figure 5.11. Temperature dependence of the phase angle in PS/PSEBS blends: (a) $\phi_{\text{PSEBS}} = 0.28$, (b) $\phi_{\text{PSEBS}} = 0.35$. (▲) 150, (●) 160, (◆) 170, (▼) 180, (■) 190, and (*) 200°C.

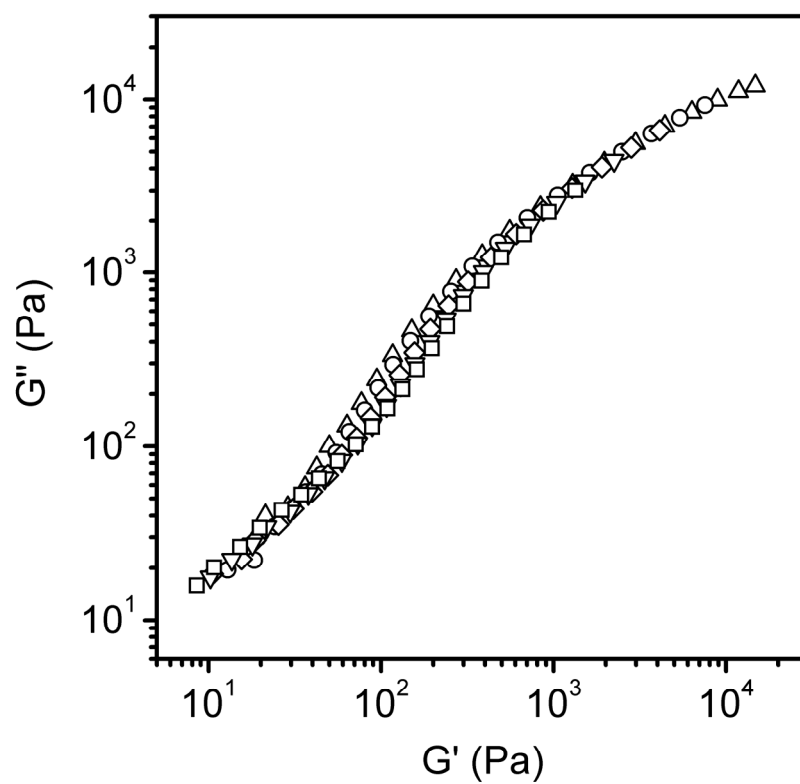


Figure 5.12. Crossplot of G'' and G' for a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$) at 150 (Δ), 160 ($\circ$), 170 ($\diamond$), 180 (∇), and 190°C ($\square$).

reported minimal temperature-dependence in the phase behavior of the PS/PSEBS blends.

The transient viscosity and shear stress of the PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$) during start-up of steady shear are shown in Figure 5.13. Even for the lowest applied shear rate of 0.05 s^{-1} , a broad overshoot is apparent upon flow inception. This overshoot, which becomes more pronounced with increasing shear rate, is potentially associated with the deformation and alignment of the sponge structure under flow. Measurements were only conducted for shear rates of $\leq 0.5 \text{ s}^{-1}$ since higher shear rates led to the occurrence of melt fracture.

Relaxation of shear stress after cessation of flow is shown in Figure 5.14. For all applied shear rates, two relaxation modes are apparent: a faster relaxation process at short times followed by a slower process over longer times. Following shear at the highest applied shear rates (0.20 and 0.50 s^{-1}), the slower mode at longer times relaxes more quickly than following shear at lower rates. The relaxation behavior of this polymer sponge phase is very similar to the observed behavior in polymer bicontinuous microemulsions that have undergone partial phase-separation at higher shear rates [Figure 4.27; Krishnan *et al.* (2002b)]. In the case of polymer B μ Es, the short-term relaxation mode is attributed to retraction of the stretched, micron-sized phase-separated droplets [Krishnan *et al.* (2002b)]. Perhaps the short-term mode in the polymer sponge system is associated with relaxation of large vesicles that may coexist with the sponge morphology in this sample. We have performed *in situ* SAXS experiments to obtain insights into the shear-induced structural processes occurring in the PS/PSEBS sponge system.

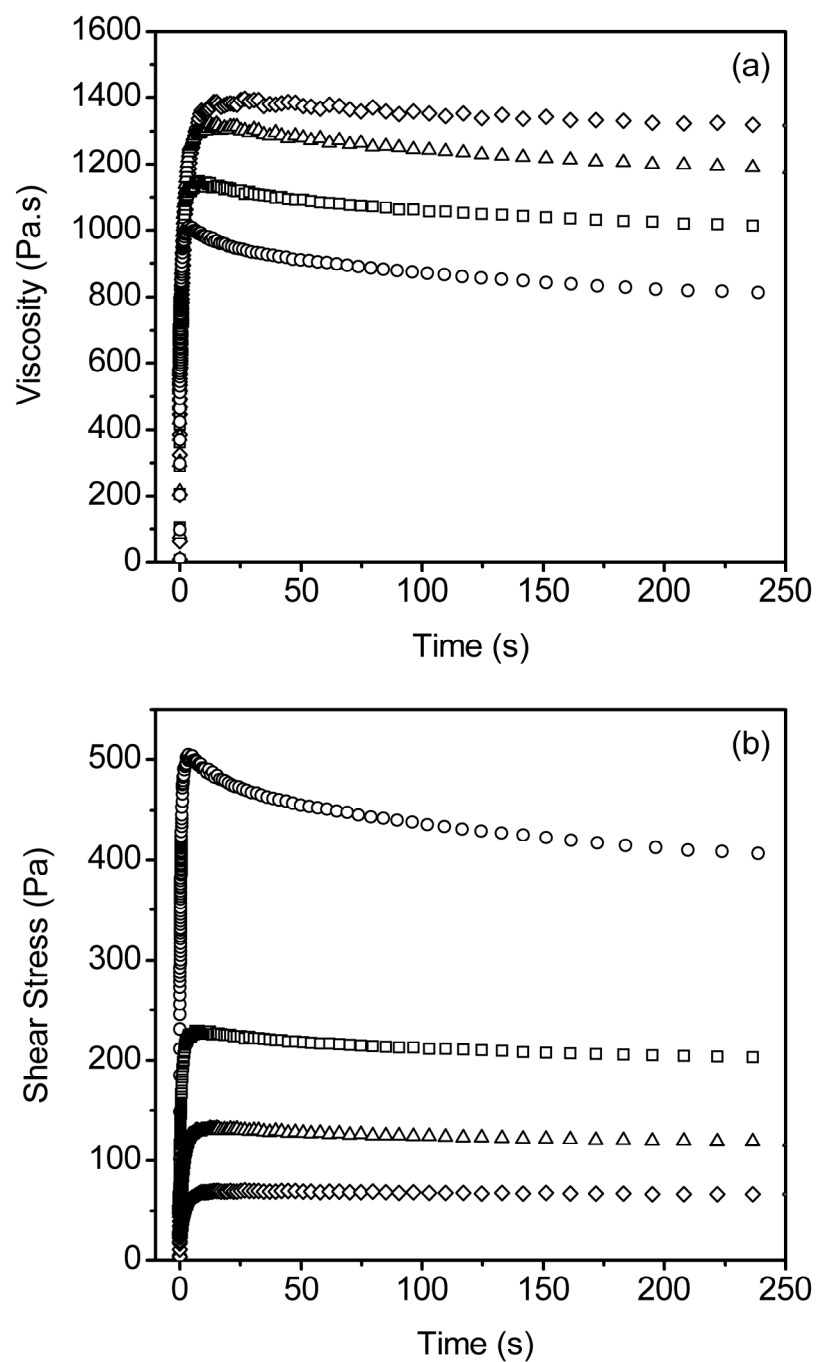


Figure 5.13. (a) Transient viscosity and (b) transient shear stress of the PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) during start-up of shear flow at rates of ($\diamond$) 0.05, (Δ) 0.10, ($\square$) 0.20, ($\circ$) 0.50 s⁻¹.

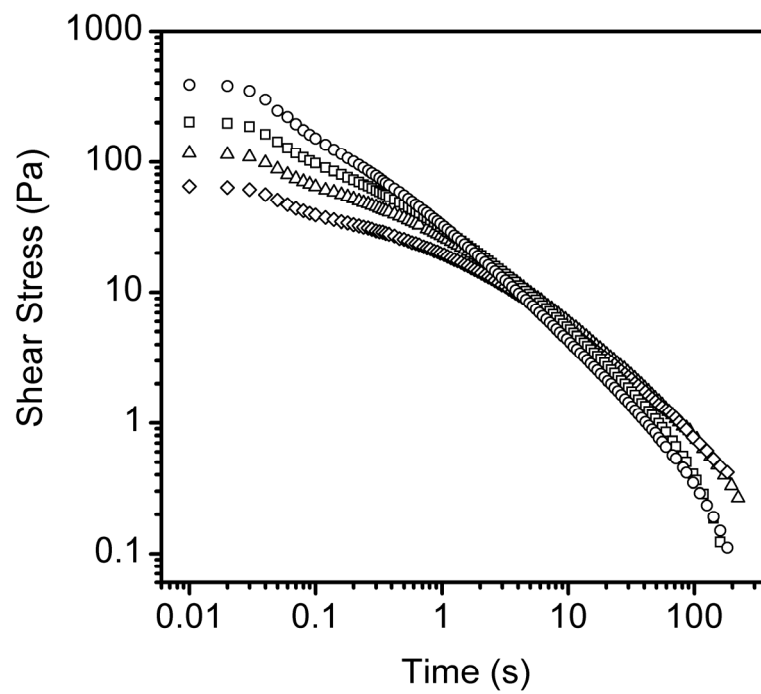


Figure 5.14. Shear stress relaxation of the PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) following cessation of shear flow at rates of (◇) 0.05 , (Δ) 0.10 , (□) 0.20 , (○) 0.50 s^{-1} .

5.4.3. *In Situ* X-Ray Scattering

Two-dimensional x-ray scattering patterns of the blends, collected during shear flow, were characterized using a second moment tensor analysis. Using the definition in eqn. 2.14, $\langle \mathbf{q}\mathbf{q} \rangle$ was computed for each scattering pattern over the range $|q_x, q_y| \leq 0.165 \text{ nm}^{-1}$. For a series of quiescent patterns collected prior to each shear experiment, the average of the diagonal components was calculated:

$$\frac{1}{2}\langle qq \rangle_0 = \frac{1}{2}[\langle q_x q_x \rangle_0 + \langle q_y q_y \rangle_0] \quad (5.2)$$

where the subscript 0 denotes the values obtained under initial, quiescent conditions.

Then, $\langle \mathbf{q}\mathbf{q} \rangle$ at all time points within a shear experiment was normalized by its corresponding value of $\frac{1}{2}\langle qq \rangle_0$. Finally, the principal anisotropy factor, AF , and the orientation angle, χ , were computed from the quiescent-normalized $\langle \mathbf{q}\mathbf{q} \rangle$ using eqns. 2.16 and 2.17, respectively.

We first present the shear-induced scattering behavior of a PS/PSEBS blend ($\phi_{\text{PSEBS}} = 0.20$) exhibiting a vesicle phase coexisting with small amounts of sponge morphology. Figure 5.15 shows the normalized anisotropy factor and orientation angle during inception, reversal, and cessation of shear at a rate of 0.05 s^{-1} . The anisotropy factor indicates fairly low deformation of the microstructure at this low shear rate, which is consistent with the nearly isotropic scattering patterns collected at various time points during shear. Upon inception of flow ($t = 0$), AF increases and grows toward the steady-state value as the structure orients at an average angle of $\chi \sim 25^\circ$ with respect to the flow direction. Upon flow reversal ($t \sim 135 \text{ s}$), AF decreases and then grows again as the

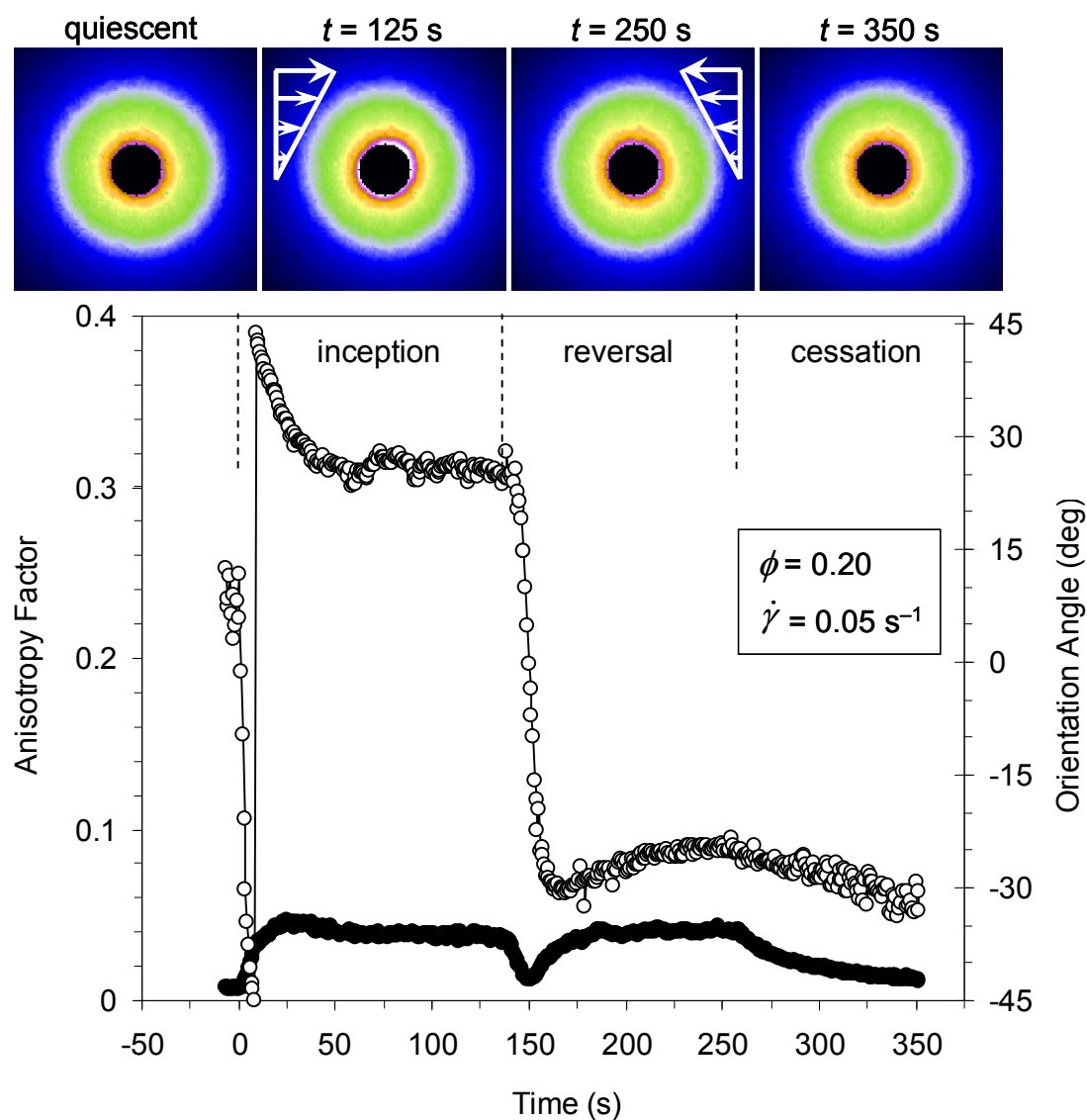


Figure 5.15. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS vesicle phase ($\phi_{\text{PSEBS}} = 0.20$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 0.05 s^{-1} . Shear inception begins at time = 0 seconds. The images above the plot show representative scattering patterns collected during shear. The q -range in these patterns is $|q_x, q_y| \leq 0.10 \text{ nm}^{-1}$. The q -range and intensity scale in these images are the same for all patterns corresponding to the $\phi_{\text{PSEBS}} = 0.20$ blend in Figures 5.15 – 5.18.

microstructure rotates and re-orientes itself along the opposite direction. Following cessation of shear, the anisotropy factor relaxes back to its initial state.

By definition, isotropic scattering yields $AF = 0$. In these experiments, however, AF under quiescent conditions (before and after shear, when an isotropic microstructure is expected) has a small, non-zero value. We are uncertain at this time whether this residual anisotropy is associated with some experimental artifact or with the sample microstructure. The “baseline” AF value does not vary significantly over the course of all shear experiments conducted with this sample, suggesting that the residual anisotropy may indeed be an experimental artifact.

Figures 5.16 – 5.18 show results for higher shear rates of 0.5, 2.0, and 10 s^{-1} . As expected, higher shear rates yield larger anisotropy and closer alignment of the microstructure to the flow direction. The steady-state values of AF and χ as a function of shear rate are summarized in Figure 5.19. As evident in the scattering patterns in Figure 5.18, the degree of shear-induced anisotropy remains fairly low, even at the highest applied shear rate of 10 s^{-1} .

In general, the behavior of this system at lower shear rates ($< 2 \text{ s}^{-1}$) is what we may expect for a system consisting of discrete objects, such as vesicles, dispersed in a matrix phase. That is, the initially (almost) isotropic vesicle structures establish a steady-state orientation (AF and χ) over fairly rapid time scales during shear inception, re-establish an equal degree of orientation over similar time scales in the opposite direction upon shear reversal, and then relax (returning to a nearly isotropic state) upon cessation of shear. The scattering behavior is slightly different at the highest applied shear rates

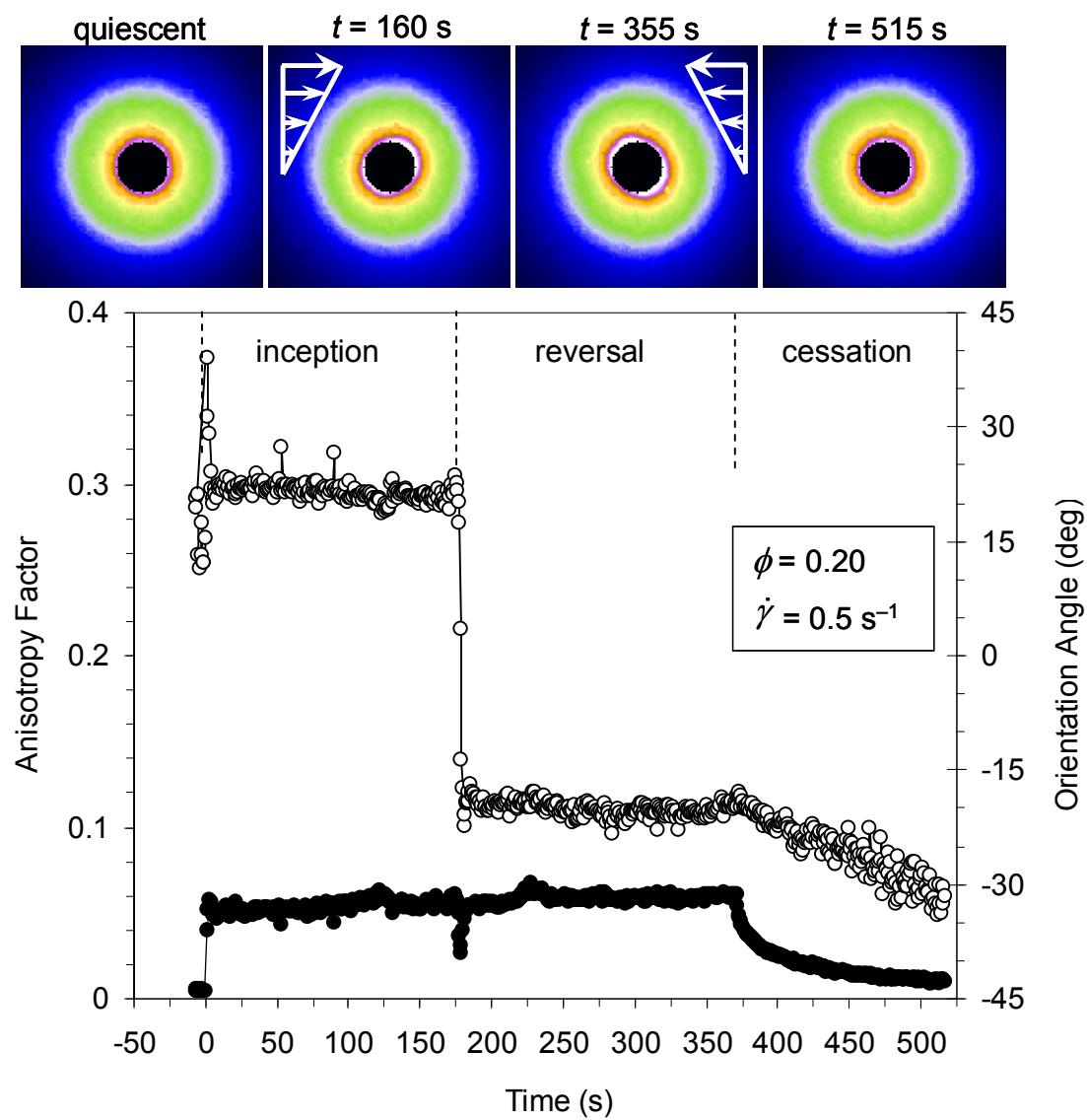


Figure 5.16. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS vesicle phase ($\phi_{\text{PSEBS}} = 0.20$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 0.50 s^{-1} .

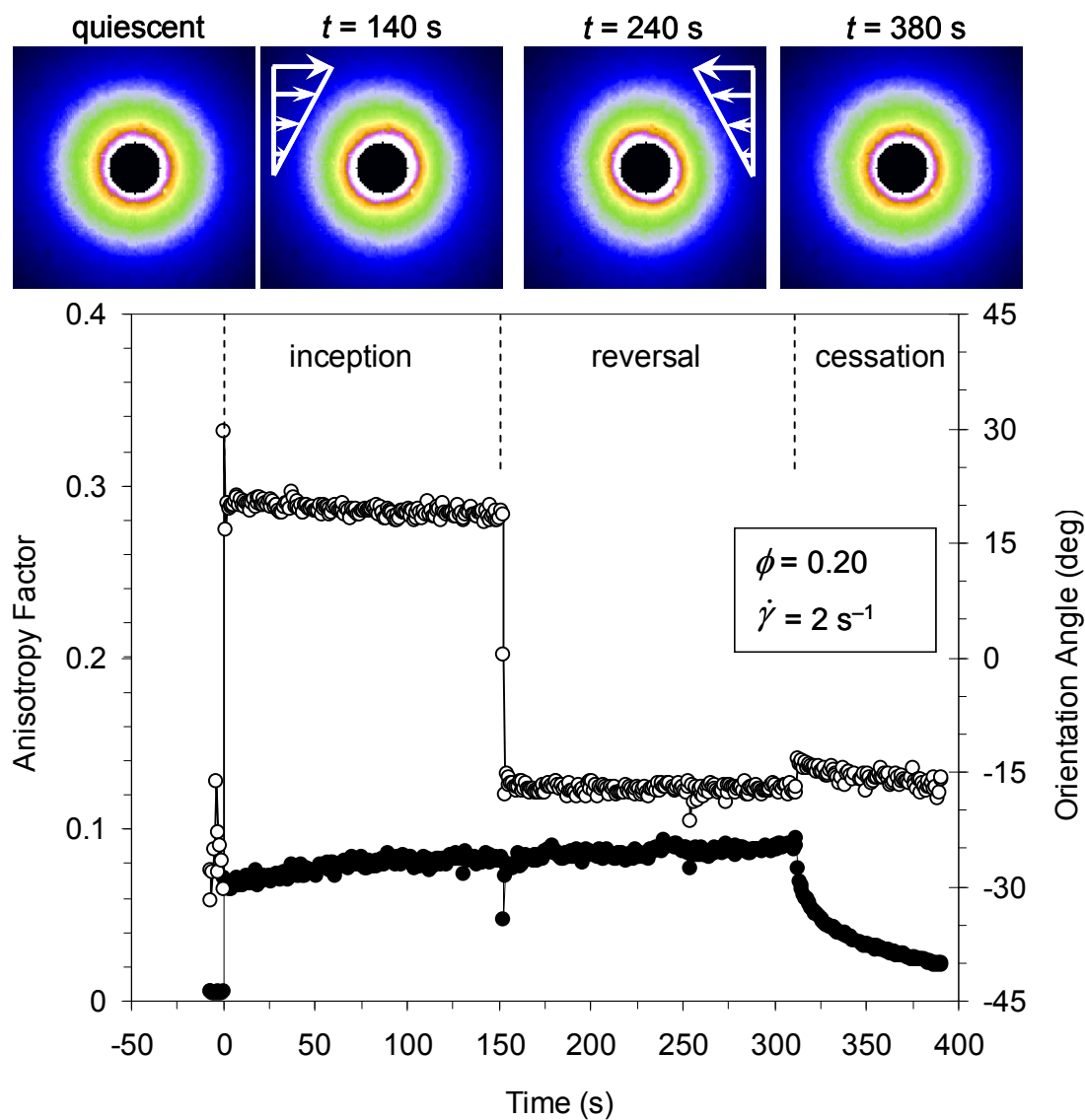


Figure 5.17. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS vesicle phase ($\phi_{\text{PSEBS}} = 0.20$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 2.0 s^{-1} .

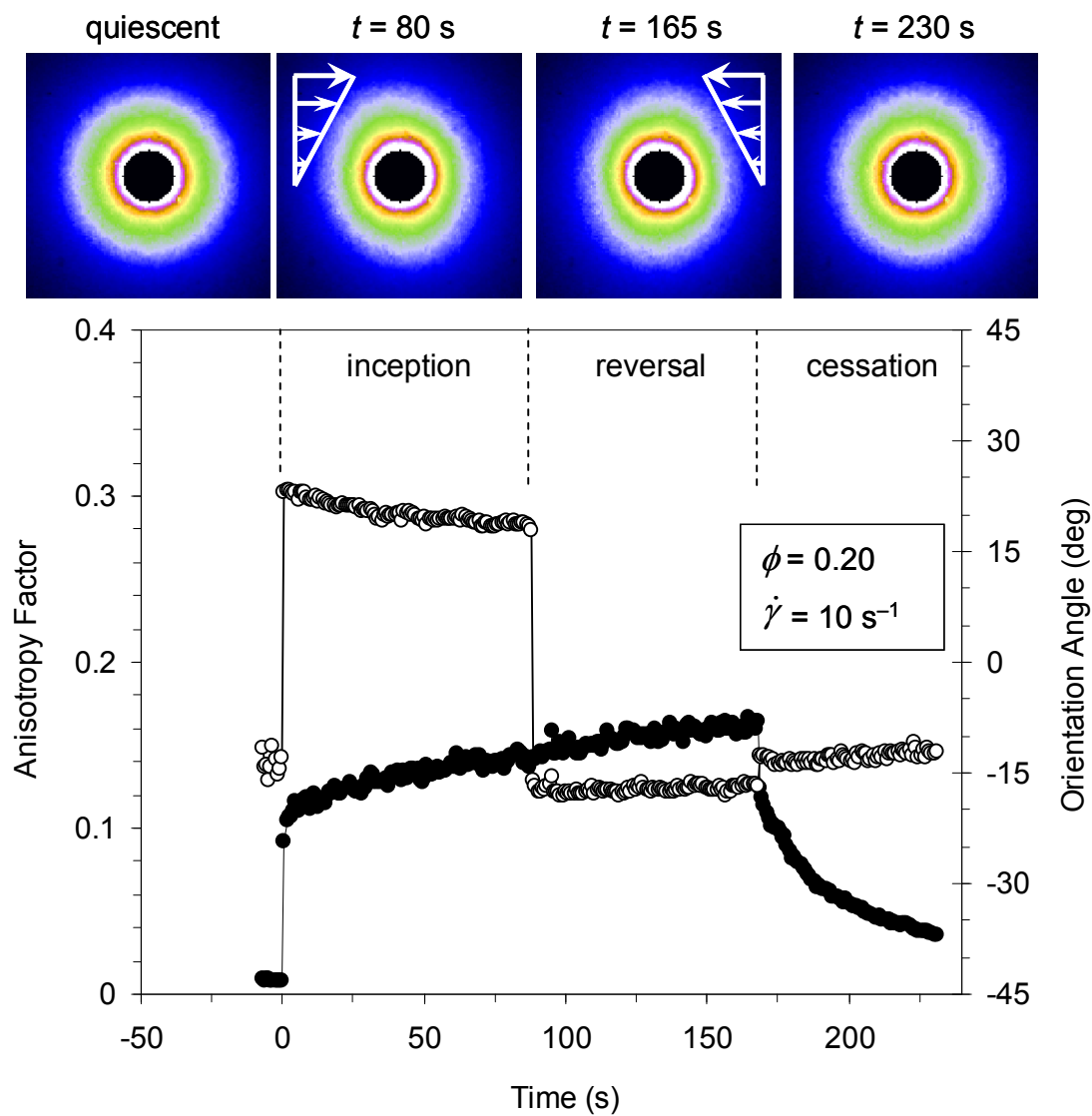


Figure 5.18. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS vesicle phase ($\phi_{\text{PSEBS}} = 0.20$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 10 s^{-1} .

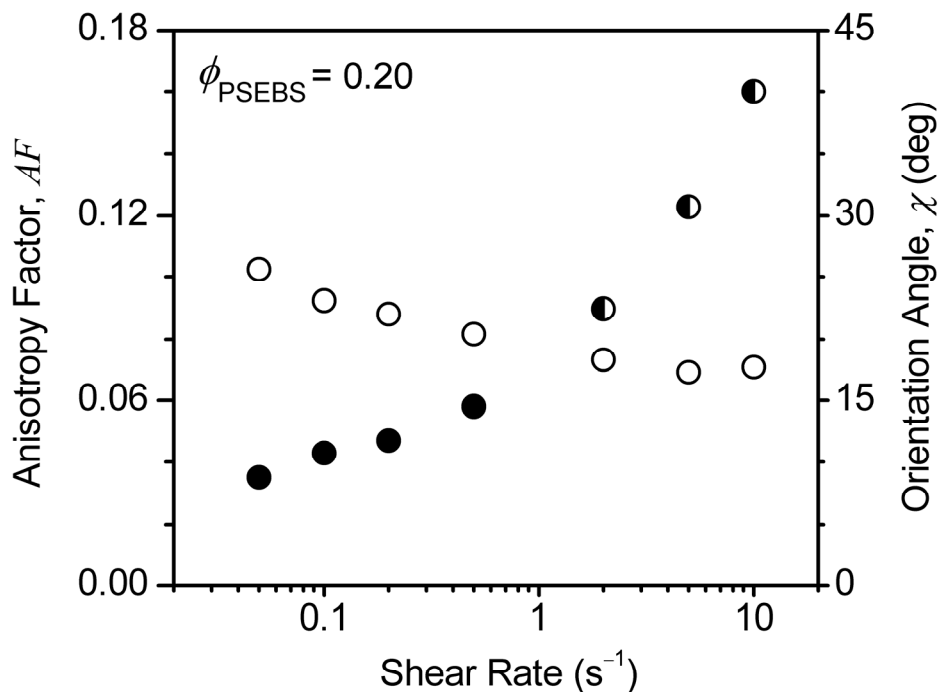


Figure 5.19. Steady-state values of the normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS vesicle phase ($\phi_{\text{PSEBS}} = 0.20$, $T = 150^\circ\text{C}$) during continuous shear. For $\dot{\gamma} > 1 \text{ s}^{-1}$, steady-state values of AF were not achieved within the time scales of the experiments. The half-filled symbols at these higher shear rates correspond to AF values achieved immediately prior to cessation of flow.

(2 and 10 s⁻¹). Whereas the steady-state orientation angle is quickly established upon shear inception and reversal, the anisotropy factor continues to increase with time during shear (Figures 5.17 and 5.18). One-dimensional intensity scans extracted from 2-D patterns before and after shear at the higher shear rates suggest that the gradual long-term growth in AF may be related to changes in the morphology during shear (Figure 5.20).

Prior to shear experiments, the intensity profile of the $\phi = 0.20$ sample shows a strong peak at $q \rightarrow 0$ largely associated with the vesicle structures, and a shoulder at $q^* \sim 0.05 \text{ nm}^{-1}$ associated with a small concentration (< 10%) of sponge phase in the system (Figure 5.4). Shear experiments began with inception/reversal of steady shear at 0.01 s⁻¹. This experiment was repeated using progressively higher shear rates, up to 0.5 s⁻¹. Very little change was observed in the quiescent intensity profile as a result of shear at these low rates (Figure 5.20), indicating that the equilibrium sample morphology has not been significantly affected by shear.

Following shear at 0.5 s⁻¹, some oscillatory shear experiments were conducted using 100% strain and various frequencies (data not presented here). As a result of oscillatory shear, the quiescent scattered intensity *increased* at $q \rightarrow 0$ and *decreased* at the shoulder at $q = q^*$. Shear inception/reversal experiments were then conducted at higher shear rates of 2, 5, and 10 s⁻¹. The shoulder intensity at q^* was found to decrease further with increasing shear rate. The decreased intensity at the shoulder, accompanied by the increased intensity at $q \rightarrow 0$ suggests that the connectivity in the membranes of the sponge structure is breaking down under shear at these higher shear rates, possibly resulting in the formation of large vesicles. The scattering profiles show *no* indication of

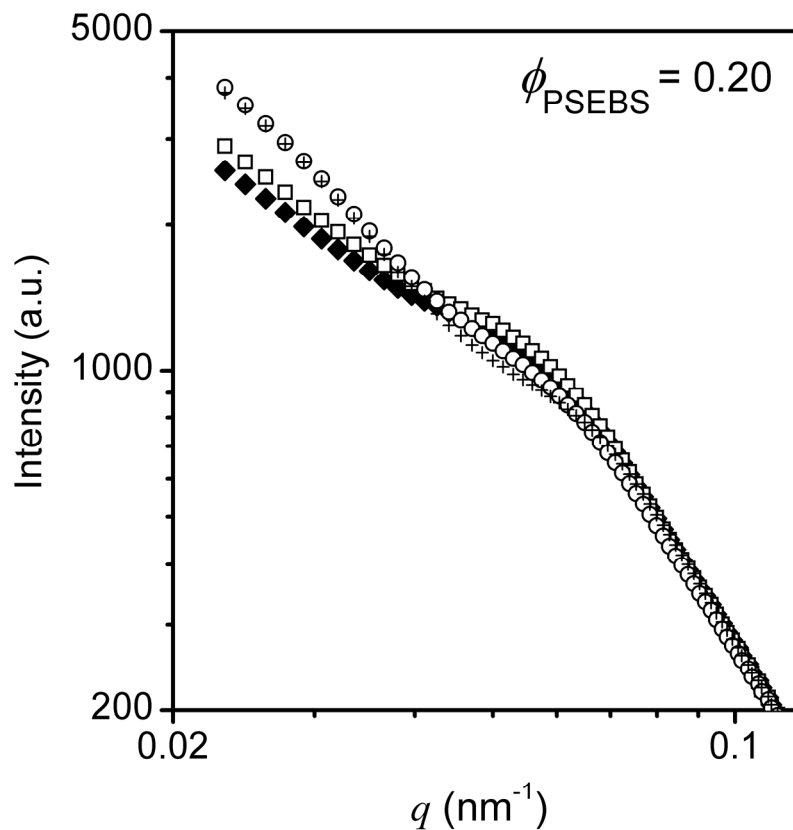


Figure 5.20. One-dimensional intensity profiles of a PS/PSEBS blend ($\phi_{\text{PSEBS}} = 0.20$, $T = 150^\circ\text{C}$) obtained from 2-D patterns averaged along the azimuthal direction. Data correspond to the following experiments, which were conducted in chronological order:

- ($\blacklozenge$) at quiescent conditions before shear,
- ($\square$) after shearing at rates between 0.01 and 0.5 s^{-1} ,
- ($\circ$) after several oscillatory shear experiments at 100% strain and various frequencies,
- ($+$) after shearing at rates of 2 , 5 , and 10 s^{-1} .

the development of new peaks within the range $q \leq 0.20 \text{ nm}^{-1}$ as would be expected for the creation of a lamellar structure. The lower degree of connectivity between membranes, in the form of large vesicles, provides greater mobility under shear allowing a greater degree of alignment to be achieved. Therefore, the gradual growth in the anisotropy factor during shear at these rates (Figures 5.17 and 5.18) may directly correspond to the gradual breakdown of the sponge structure. Based on these observations, we expect to observe similar, but more pronounced behavior for the $\phi = 0.25$ sample.

The scattering behavior for $\phi_{\text{PSEBS}} = 0.25$ during inception, reversal, and cessation of shear at 0.05 s^{-1} is shown in Figure 5.21. The greater degree of membrane connectivity (sponge phase) in this system yields *much* slower time-evolution of the anisotropy factor and orientation angle than observed for the $\phi = 0.20$ blend at the same shear rate. Unfortunately, we did not perform measurements for long enough times to reach steady-state (even in the orientation angle). The slow structural response during shear is consistent with the slow evolution of viscosity and shear stress measured during shear inception in rheological experiments (Figure 5.13). The viscosity/shear stress shows a very gradual decline with time and also does not reach steady-state within the time scales of these experiments.

As evident in the 2-D scattering patterns in Figure 5.21, the sponge structure in the $\phi = 0.25$ blend exhibits some anisotropy under quiescent conditions, prior to application of shear. This anisotropy yields a significant, non-zero “starting” value for AF . With inception of shear, the sponge structure deforms and realigns close to the flow

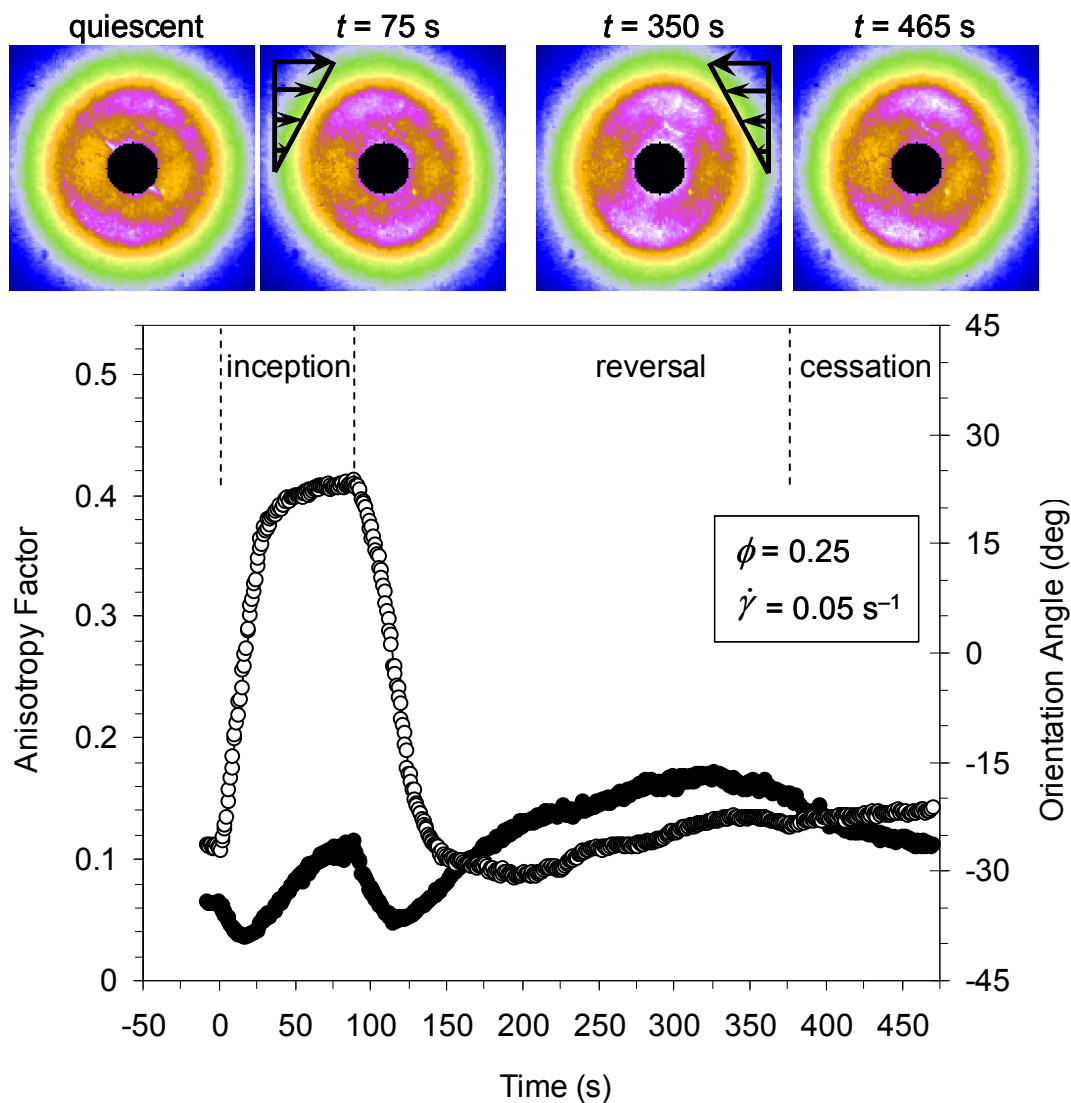


Figure 5.21. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 0.05 s^{-1} . The q -range in the scattering patterns is $|q_x, q_y| \leq 0.10 \text{ nm}^{-1}$. The q -range and intensity scale in these images are the same for all patterns corresponding to the $\phi_{\text{PSEBS}} = 0.25$ blend in Figures 5.21 – 5.26.

direction, and then rotates toward the opposite direction upon flow reversal. Following cessation of flow, the anisotropy relaxes. Since we did collect data for longer times, we do not know whether the sponge structure returns to its initial anisotropic state (*i.e.*, “starting” values of AF and χ) prior to shear.

The scattering response of the sponge phase at a slightly higher rate of 0.1 s^{-1} (Figure 5.22) shows no significant changes from the behavior at 0.05 s^{-1} over the measured time period. We again note that the sample was not sheared for long enough times to reach steady-state, and that data was not collected long enough after flow cessation to observe the full relaxation process. Therefore, we cannot fully assess the impact of continuous shear at these rates on the morphology. The “starting” values of AF and χ measured before shear at 0.1 s^{-1} are close to the final measured values after cessation of shear at the previous rate of 0.05 s^{-1} . Only 2 – 3 minutes had elapsed between these measurements, and we do not know if the anisotropy accumulated during shear at 0.05 s^{-1} would continue to relax back to the initial state (at a noticeable rate) beyond this time frame. Regardless of whether or not the anisotropy would relax further over longer times, the “starting” anisotropy at 0.1 s^{-1} has been impacted by the previous shear experiment. All additional shear experiments discussed below were also performed with short 2 – 3 minute “breaks” between data collection for each experiment, which corresponds to about 5 – 6 minutes between the stopping of flow in one experiment and the start of flow in the next. As will be evident in the following results, the “initial” anisotropy of the sample (and perhaps the response during shear) in each experiment shows a dependence on the final measured state in the previous experiment. For the $\phi =$

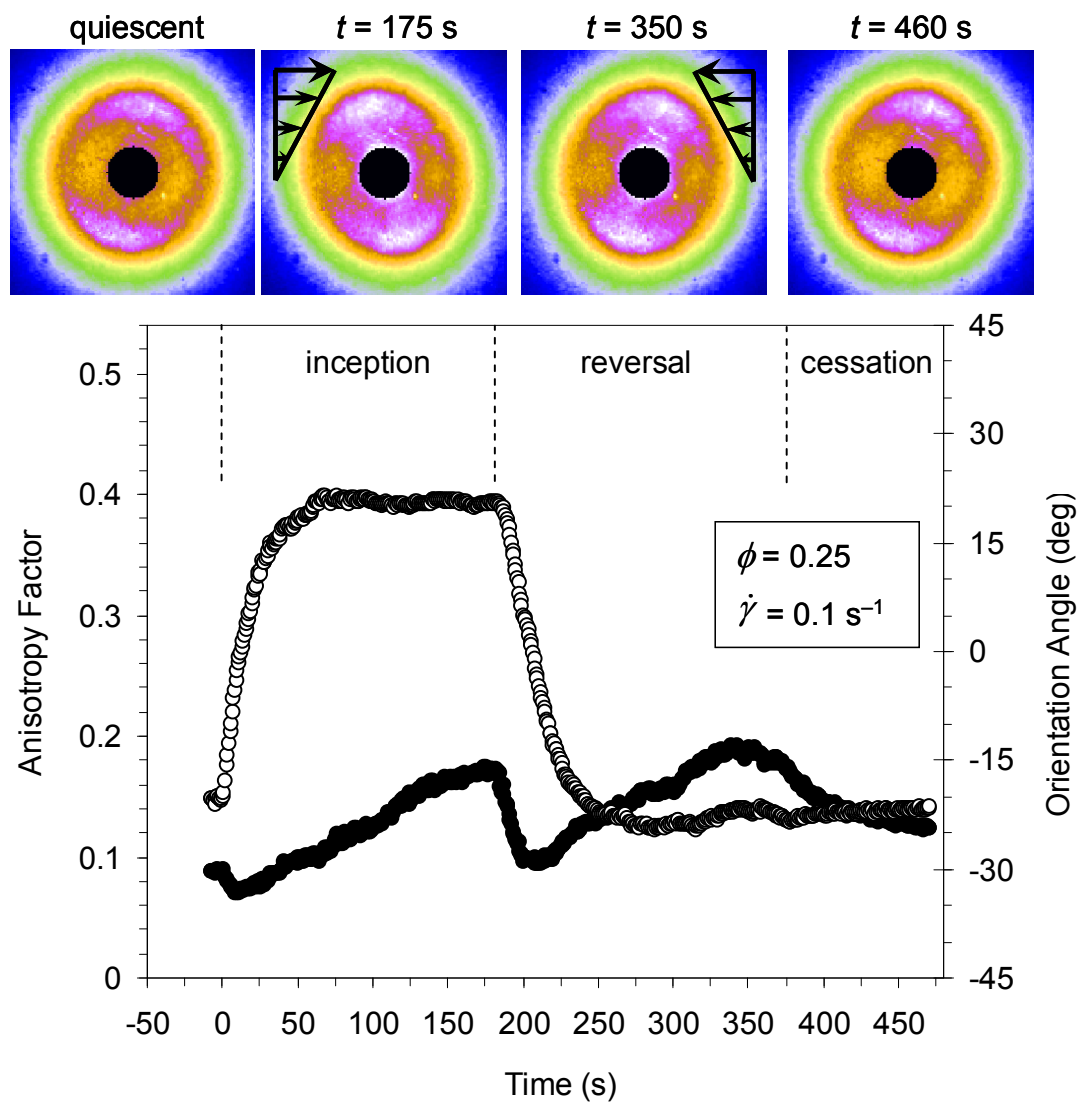


Figure 5.22. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 0.1 s^{-1} .

0.20 blend, the starting condition was nearly the same in all shear experiments; therefore, shear history was less significant in this system, whose morphology consists mainly of vesicles.

Shearing the $\phi = 0.25$ sample at 0.2 s^{-1} shows some differences in the scattering behavior in comparison to results obtained at lower shear rates. Inception/reversal experiments were conducted twice at 0.2 s^{-1} . Unfortunately, scattering data collected during the first shear experiment at this rate were lost due to problems with the data acquisition system. Figure 5.23 presents results from the *second* experiment conducted at 0.2 s^{-1} . Comparison of the starting quiescent scattering pattern in Figure 5.23 to the final quiescent pattern in Figure 5.22 shows a slightly weakened sponge peak resulting from the *first* shear experiment at 0.2 s^{-1} . (This change in the sponge peak is more distinct in 1-D intensity profiles in Figure 5.27 presented later on.) The general behavior in Figure 5.23 is also beginning to resemble the behavior of the $\phi = 0.20$ blend at higher shear rates. Particularly, the degree of anisotropy continues to increase even after the orientation angle has essentially reached steady-state. The weakened sponge peak, along with the similar trends in AF and χ in comparison to the $\phi = 0.20$ blend at higher shear rates, suggest that the sponge structure is starting to break down due to shear.

Possible changes in the microstructure of the $\phi = 0.25$ blend during shear at 0.2 s^{-1} are also indicated by the shear stress relaxation behavior measured in rheological experiments following cessation of shear (Figure 5.14). Stress relaxation is faster following shear at 0.2 s^{-1} relative to shear at lower rates. The faster relaxation may

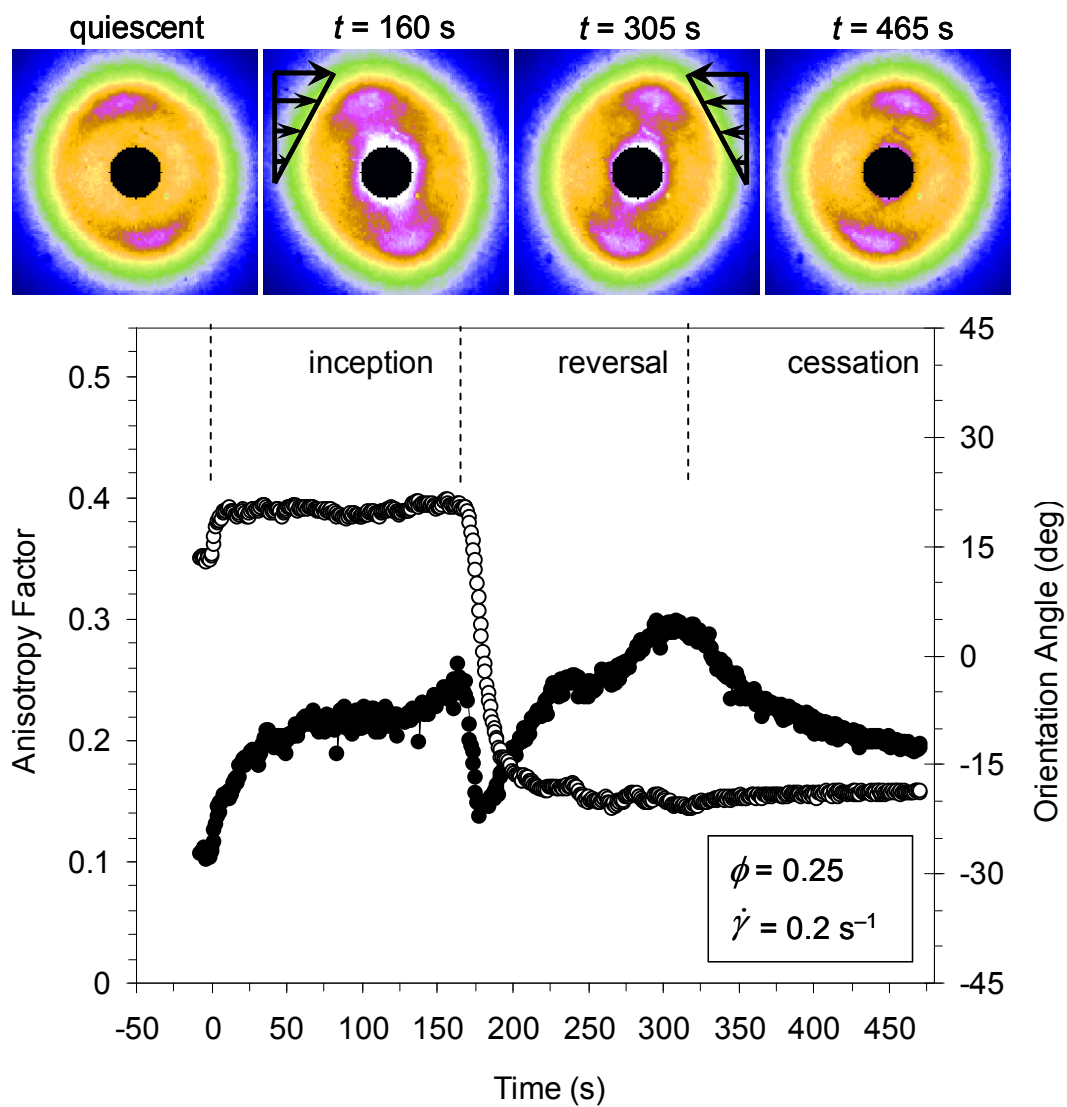


Figure 5.23. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 0.2 s^{-1} .

reflect a greater concentration of vesicles in the system that has resulted from the breakdown of the sponge structure during shear.

After the second scattering shear experiment at 0.2 s^{-1} , additional experiments were conducted in sequence of increasing shear rate, using 0.5 , 1 , 2 , 5 , and 10 s^{-1} . We were again faced with technical problems that resulted in the loss of all data corresponding to these experiments. The starting quiescent scattering pattern in Figure 5.24, obtained after these lost series of experiments, reveals substantial changes in the $\phi = 0.25$ blend morphology resulting from shear at these high rates. The intensity has increased significantly at $q \rightarrow 0$ and the sponge peak has nearly diminished, indicating a significant loss in the amount membrane connectivity in the system. Since we have no scattering data for any time point within or between the lost data sets, we cannot determine the shear rate at which these changes became significant.

Figures 5.24 – 5.26 show time-resolved measurements corresponding to *repeat* experiments at 0.5 , 1 , and 2 s^{-1} , which were conducted in sequence. (At higher shear rates, sample loss from the shear cell became significant, yielding unreliable scattering results.) The data collected during shear look very similar to the $\phi = 0.20$ blend at higher shear rates (Figure 5.18), where AF continues to grow long after χ reaches steady-state. However, at equivalent shear rates, the $\phi = 0.25$ blend achieves a much greater degree of anisotropy and relaxes more slowly upon flow cessation than the $\phi = 0.20$ blend. Also, as indicated earlier, the starting AF values in the $\phi = 0.25$ blend are influenced by the anisotropy achieved in the previous experiment and tend to increase gradually with each shear experiment.

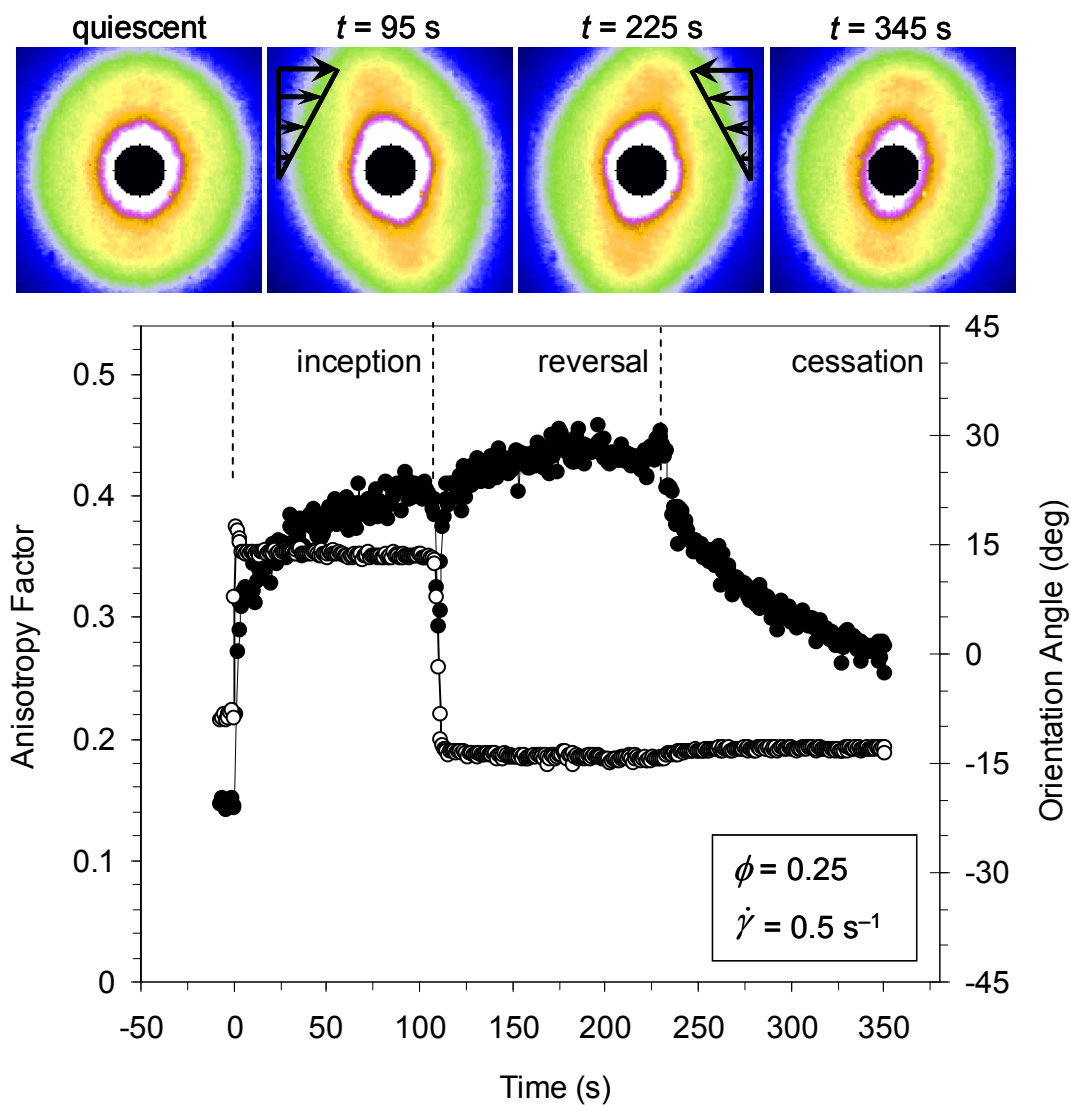


Figure 5.24. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 0.5 s^{-1} .

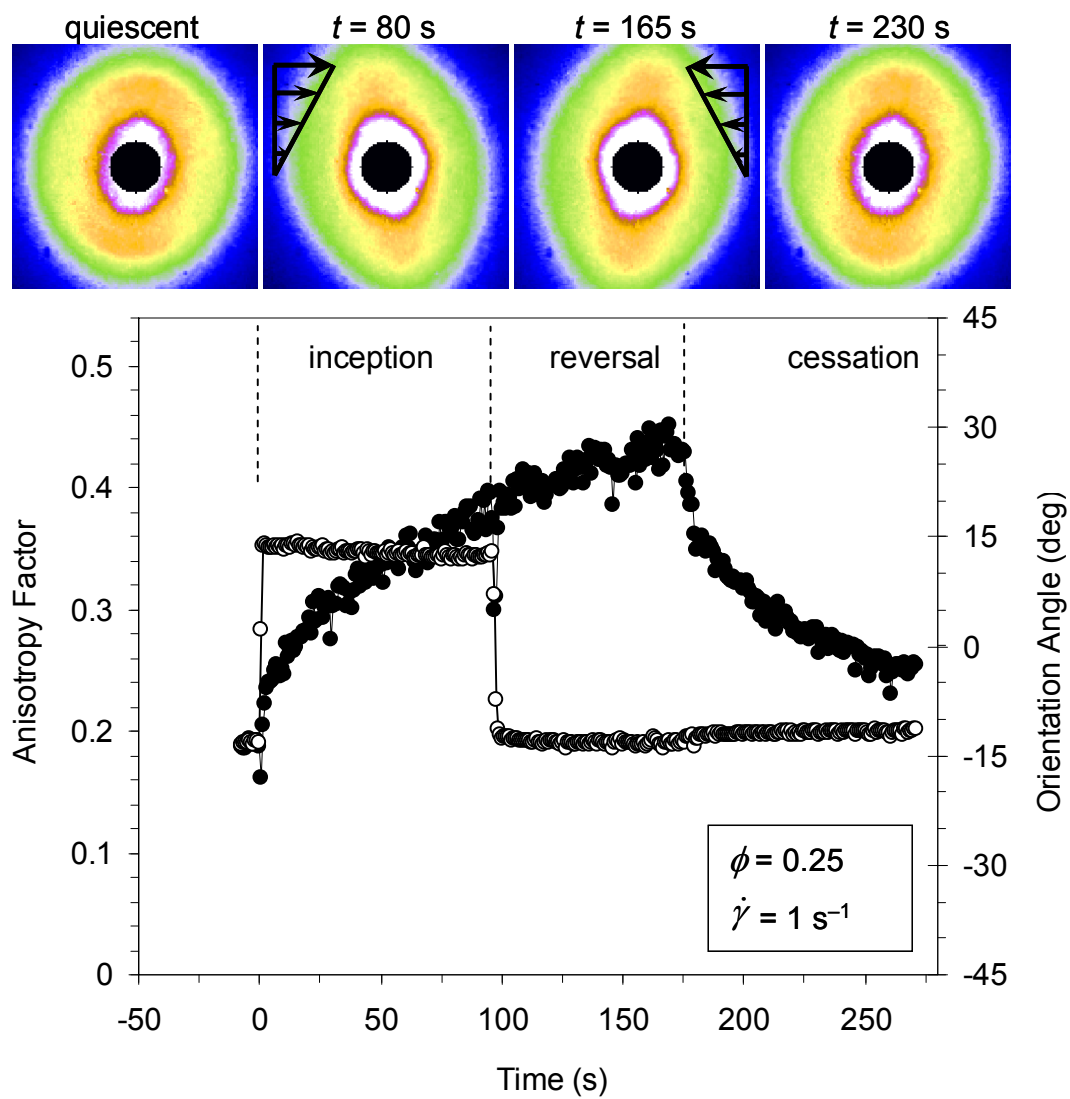


Figure 5.25. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 1.0 s^{-1} .

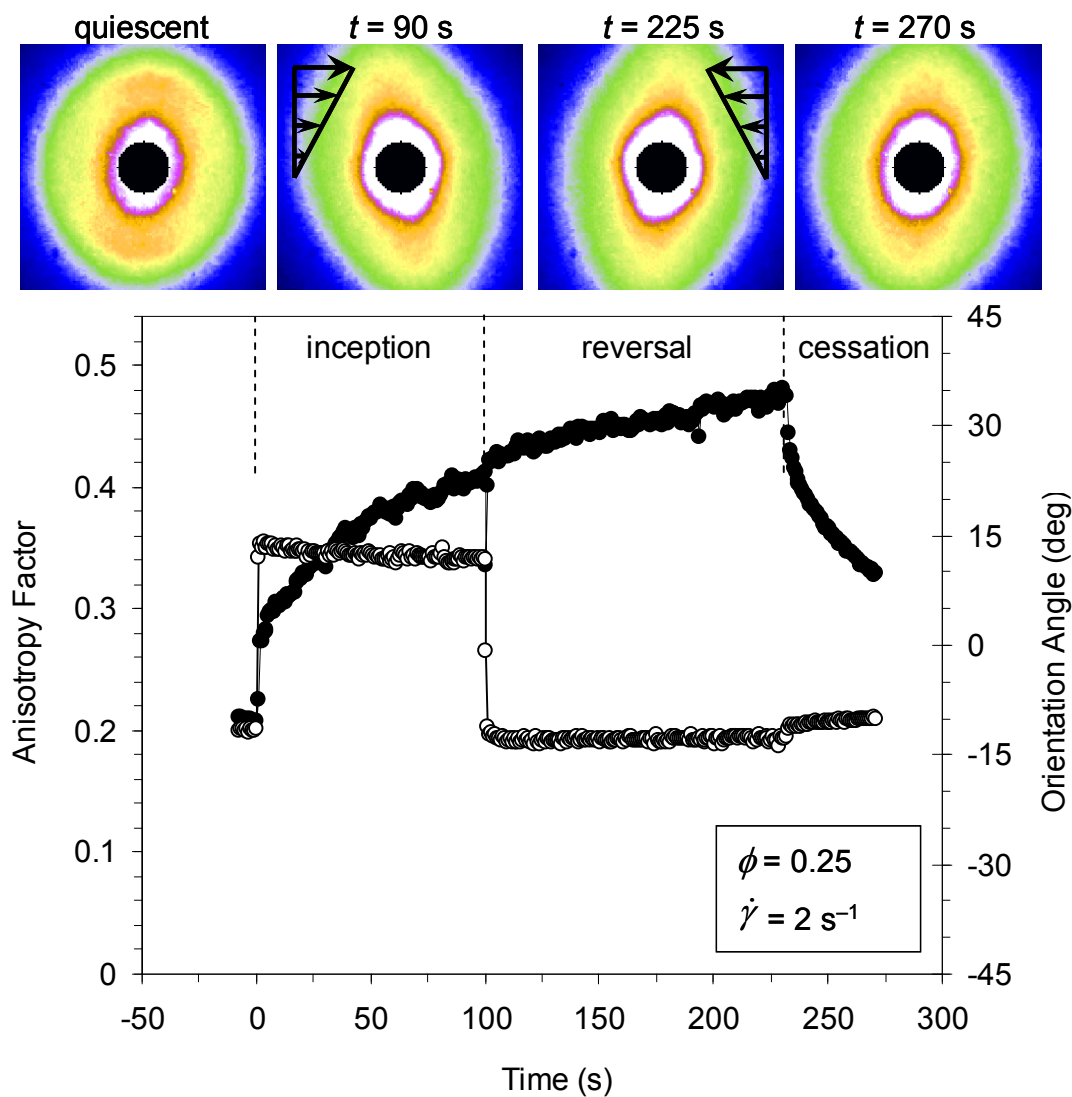


Figure 5.26. Normalized anisotropy factor (solid symbols) and orientation angle (open symbols) of a PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) during inception, reversal, and cessation of shear flow at 2.0 s^{-1} .

One-dimensional intensity data extracted from 2-D patterns of the $\phi = 0.25$ blend before and after various shear experiments are presented in Figure 5.27. These data more clearly illustrate the loss in sponge structure due to shear. Shear experiments conducted using shear rates up to 0.1 s^{-1} do not result in any significant changes in the intensity profile. We recognize, however, that shearing for longer times to reach steady-state could lead to changes in the sponge morphology. A small decrease in the sponge peak intensity results from shear at 0.2 s^{-1} and suggests that the membrane connectivity in the sponge structures is beginning to break under shear. Shear experiments at higher rates yields more dramatic changes in the intensity profile. The intensity at $q \rightarrow 0$ has significantly increased while the sponge peak at $q \sim 0.06 \text{ nm}^{-1}$ has reduced to a shoulder. As in the case of $\phi = 0.20$, these changes indicate a possible transition of the sponge morphology to a vesicle phase. The scattering profiles for $q \leq 0.20 \text{ nm}^{-1}$ show no signs of new peaks that may suggest a transition to a lamellar phase.

5.4.4. Discussion

The linear viscoelastic measurements of the PS/PSEBS blends show strong elastic character persisting to very low frequencies. These results indicate very slow relaxation of the membrane topology, which is further supported by the slow shear-induced structural response of the sponge morphology measured by *in situ* SAXS experiments. One-dimensional intensity data suggest that continuous shear over long enough times and/or at sufficiently high rates leads to a gradual breaking of connections between sheets

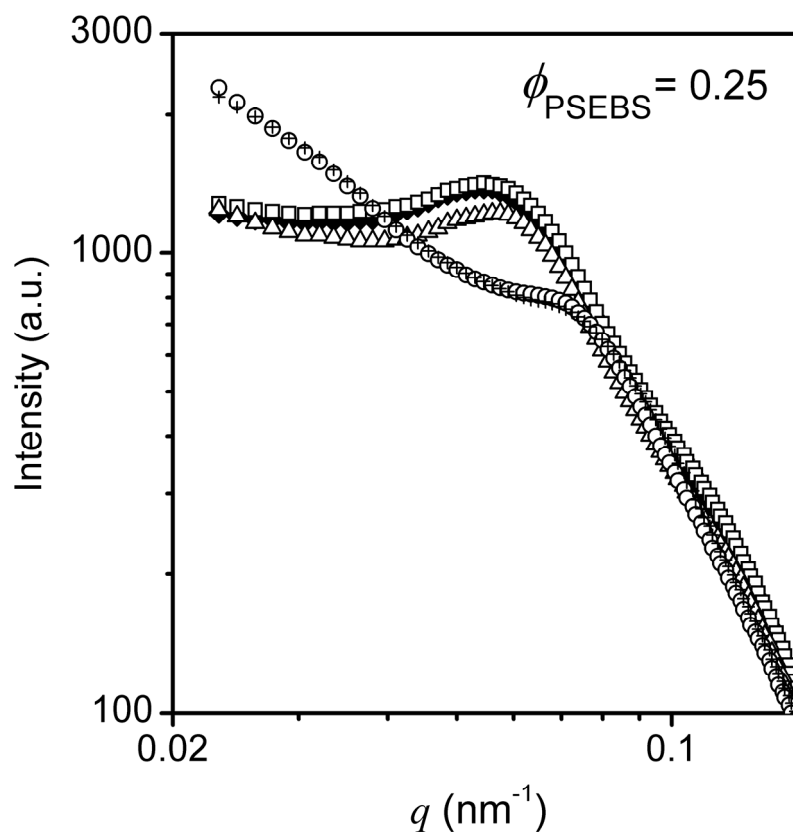


Figure 5.27. One-dimensional intensity profiles of a PS/PSEBS blend ($\phi_{\text{PSEBS}} = 0.25$, $T = 150^\circ\text{C}$) obtained from 2-D patterns averaged along the azimuthal direction. Data correspond to the following experiments, which were conducted in chronological order:

- ($\blacklozenge$) before shear at quiescent conditions and after shearing at rates up to 0.1 s^{-1} ,
- ($\square$) after shearing at 0.2 s^{-1} ,
- ($\circ$) after shearing at rates of 0.5 , 1 , 2 , 5 , and 10 s^{-1} ,
- ($+$) after shearing again at rates of 0.5 , 1 , and 2 s^{-1} .

of membrane in the sponge phase. Since the topological dynamics are very slow, *new* membrane connections are *not* created within observable time scales, even after flow has been stopped.

The slow topological dynamics are likely related to the fairly high molecular weight of the copolymer mid-block, which forms the internal membrane structure. For example, the breaking of connections during shear may be significantly slowed by entanglements between chains in the membrane. If the characteristic diffusion time of the long polymer chains in the copolymer mid-block is much longer than the average contact time between the undulating sheets of membrane in the sponge phase, the probability is very low that new connections will be created within experimental time scales. Although chain dynamics provide a reasonable explanation for the slow breaking and formation of membrane connections in the sponge phase, the inability of the structural anisotropy to relax over reasonable time scales remains less clear. We cannot offer any insight at this time as to what causes the persistent anisotropy.

The *in situ* SAXS results presented here show a gradual shear-induced transition of the sponge morphology to a vesicle phase. However, we cannot be certain of the final steady-state morphology; the eventual formation of a lamellar phase is not an impossibility. Additional experiments should be performed, where the samples are sheared for long enough times to reach steady-state.

5.5. Summary

The rheology and shear-induced structural dynamics in a polymer sponge phase have been investigated. Scattering measurements collected under quiescent conditions, prior to shear experiments, show some persistent anisotropy in the sponge structure that does not appear to relax. The linear viscoelastic behavior of the partially aligned sponge phase is very similar to the behavior of unoriented lamellae in diblock copolymer melts [Koppi *et al.* (1992); Rosedale and Bates (1990)] and exhibits strong elasticity at the lowest applied frequencies. In contrast to lamellar systems, however, the polymer sponge phase shows signs of a terminal regime at very low frequencies that are difficult to access experimentally. The potential existence of a terminal regime in the sponge phase suggests that the membrane structure will eventually relax over very long times and achieve an isotropic state. The slow membrane dynamics may be largely attributed to slow diffusion of the high molecular weight copolymer chains that comprise the membrane structure. Perhaps as a consequence of the slow membrane dynamics, this sponge system appears to behave as a partially aligned system, such as unoriented lamellae, within experimental time scales.

In situ SAXS measurements of the sponge phase ($\phi = 0.25$) and of a vesicle phase ($\phi = 0.20$), which also contains a small amount of sponge morphology, were performed during inception, reversal, and cessation of shear flow. For $\phi = 0.20$, at lower shear rates, steady-state is established fairly quickly upon inception and reversal of shear flow, and the structure relaxes following shear cessation and returns to its initial isotropic state. During shear at higher rates, the degree of anisotropy continues to increase over fairly

long times and does not reach steady-state within the time scales of the experiment.

Intensity profiles of the $\phi = 0.20$ sample show that shearing at these higher rates begins to induce changes in the small amounts of sponge structure existing in this system.

Specifically, the intensity data suggest the connections between sheets of membrane in the sponge phase are breaking under shear, resulting in the formation of more vesicles.

The sponge structures appear to remain intact at lower shear rates.

For $\phi = 0.25$, the scattering data show a much slower shear-induced structural response than the $\phi = 0.20$ blend, and steady-state was not reached within the time scales of the experiment, even at low shear rates. The more sluggish response of the $\phi = 0.25$ blend is attributed to a higher degree of membrane connectivity in this system. As in the $\phi = 0.20$ blend, intensity profiles obtained after shearing at higher rates suggest a reduction in the level of connectivity in the sponge phase, yielding a higher concentration of vesicle structures. Since the sample was not sheared for long enough times, the final, steady-state morphology is unknown at this time. In addition, the relaxation behavior following cessation of shear is not fully understood since data were not collected for sufficiently long times to capture this behavior. Of course, these issues may possibly be addressed by performing repeat experiments of the same blend systems using much longer shear times and allowing much longer relaxation times.

CHAPTER 6.

CONCLUDING REMARKS AND FUTURE DIRECTIONS

Rheology and small-angle x-ray scattering techniques were used to probe structural dynamics in three types of polymer blend systems: immiscible homopolymer blends, bicontinuous microemulsions, and sponge phases. In the case of immiscible blends, we have established the feasibility of using SAXS for characterization of morphological changes in this class of blends. Two experimental studies were performed with blends of polystyrene and poly(methyl methacrylate), and information regarding the quantity or orientation of interface in the blend was extracted from scattering measurements in the Porod regime. In the first experiment, Porod scattering measurements were used to monitor droplet growth as a function of time in isotropic blends subjected to high-temperature annealing. The results of this particular study demonstrated that, for immiscible blends consisting of relaxed spherical droplets, SAXS may serve as a simpler, more objective alternative to laborious, time-consuming electron microscopy techniques for determination of an absolute droplet size.

The second experiment of immiscible blends involved characterization of shear-induced droplet deformation via *in situ* SAXS measurements in the Porod regime. The

scattering model of a single ellipsoid by Wu (1980) was investigated as a potential model for quantifying droplet shape. However, results suggest a need for more complex theoretical descriptions for these concentrated blend systems to account for polydispersity in droplet shape. Despite the lack of an available model for determination of shape, we have successfully characterized changes in the orientation and degree of alignment of *interface* using a second moment tensor analysis. This study shows the promising potential of *in situ* SAXS techniques as a new route for studying structural dynamics in immiscible blends.

During the *in situ* flow studies of immiscible blends, fluctuations in the incident beam intensity could not be accounted for in the scattering measurements. Accounting for these fluctuations in future studies will allow for observation of changes in the total scattered intensity associated with rotation of interface (into or out of the measured 2-D plane) or changes in the total interfacial area in the blend. For example, the ability to monitor changes in total scattered intensity provides the opportunity to conduct *in situ* studies of flow-induced coalescence or breakup in concentrated systems. Additionally, it would be interesting to investigate conditions of strong deformation, in which the droplets transition from ellipsoidal to fibrillar or cylindrical-shaped particles. Scattering theory suggests that this transition should be marked by a change from $I \sim q^{-4}$ (Porod's law) to $I \sim q^{-2}$ along the directions perpendicular to the planar faces of the droplets [Guinier and Fournet (1955)].

Since Porod scattering from immiscible blends occurs at very small angles, the presence of voids or air bubbles in the blend results in strong scattering that overwhelms

the scattering from the two-phase structure. Therefore, samples need to be carefully prepared to minimize air, moisture, or low molecular weight volatiles in the system. The difficulty associated with eliminating voids in systems exhibiting significant viscoelastic behavior may be the largest limiting factor in successfully conducting *in situ* SAXS measurements. If the presence of voids is sufficiently low, *in situ* SAXS techniques may provide significant opportunities to study the behavior of immiscible blends in more complex flow fields that more closely resemble those used in commercial processes.

In regards to bicontinuous microemulsions, we have conducted an extensive study of structural dynamics in a B μ E system composed of polystyrene, polyisoprene, and the corresponding diblock copolymer. The equilibrium dynamics at length scales comparable to the B μ E domain size were characterized using x-ray photon correlation spectroscopy. These measurements showed stretched-exponential relaxation of the dynamic structure factor and an Onsager coefficient that depends strongly on scattering vector. Values of the Onsager coefficient corresponding to zero scattering vector ($q = 0$) and the peak of the static structure factor ($q = q_{\text{max}}$) were independently used to test rheological predictions for bicontinuous microemulsions by Pätzold and Dawson. The theory, which is based on Landau-Ginzburg model, describes the shape of the relaxation spectrum and predicts the temperature dependence of the rheological properties quite well. However, for either case of the Onsager coefficient (at $q = 0$ and $q = q_{\text{max}}$), the theory fails to predict the *absolute* values of the zero-shear viscosity and average relaxation time of the microemulsion. The general failure of the model to predict the absolute values of the rheological parameters is consistent with observations by

Burghardt *et al.* (2002) for a PEE-PDMS B μ E. In the Pätzold-Dawson theory, the presence of amphiphile and the coupling between the hydrodynamic flow field to the order parameters were neglected. The results of our study underscore the need to account for these factors in theoretical descriptions of bicontinuous microemulsion rheology. Of course, the development of such theory is a significant challenge. A complete theoretical description would also include the effects of chain dynamics in polymer B μ E systems.

The shear-induced structural dynamics of the PS-PI B μ E were investigated using rheology, *in situ* SAXS, and *in situ* optical microscopy. In general, the rheology and scattering behavior of the PS-PI B μ E nearly parallels the behavior of the previously documented PEE-PDMS B μ E [Caputo *et al.* (2002b); Krishnan *et al.* (2002a)] under linear and moderately non-linear shear conditions. Under more severe conditions, such as inception of steady shear flow at “high” shear rates, significant differences in the response of the two B μ E systems are evident. Initially, it was anticipated that the PS-PI microemulsion undergoes phase-separation at high shear rates (as occurs in the PEE-PDMS B μ E), and that the differences in the observed responses were associated with differences in the phase-separation process. Optical microscopy, however, revealed the presence of micron-sized phase-separated structures coexisting with the B μ E phase in the PS-PI system at *equilibrium*, prior to application of shear flow. This is in contrast to the PEE-PDMS system, which appears to exhibit a single-phase B μ E morphology. The different response observed in the PS-PI system, relative to the PEE-PDMS system, is attributed to the break-up of the already existing large phase-separated structures with time during shear. Although the phase-separated structures dominate the rheology and

scattering behavior of the PS-PI system under strong shear conditions, the B μ E phase within the blend appears to dominate the response under moderate shear, as indicated by the strong similarities to the PEE-PDMS microemulsion under moderate flow conditions.

One original objective of our B μ E shear studies was to investigate shear-induced phase transitions in this class of blends. The presence of phase-separated structures in the equilibrium morphology of the PS-PI B μ E system has inhibited our efforts to achieve this particular goal. Consequently, the PEE-PDMS B μ E remains the only polymer bicontinuous microemulsion system for which a shear-induced transition has been observed experimentally and documented in detail. Additional studies of other polymer B μ Es are still required to determine if the shear-induced phase separation process is universal to these systems and to better understand the mechanisms driving this transition. The PS-PI blend used in our studies contains 10% copolymer; for the same system of polymers, a blend containing slightly higher copolymer concentration may yield a single-phase B μ E and thus serve as a model system for studying shear-induced dynamics. Both the PEE-PDMS and PS-PI systems show large viscosity contrasts between their constituent homopolymers, which may facilitate phase-separation at higher shear rates or alter the mechanisms through which this process occurs. Therefore, studies of a B μ E system with more closely matched homopolymer viscosities would help to identify the shear-induced processes that are solely associated with the bicontinuous microemulsion structure. However, one must also keep in mind the possible effects of chain dynamics, even in the absence of viscosity contrast and when using very low molecular weight polymers [Narayanan *et al.* (2006)].

Our final set of experiments involved the investigation of the rheology and shear-induced structural dynamics in a polymer-based sponge phase previously developed by Falus *et al.* (2004a). This sponge system consists of a polystyrene homopolymer and a poly(styrene-ethylene/butylene-styrene) triblock copolymer with a fairly high molecular weight mid-block, which forms the membrane structure. Static SAXS measurements revealed anisotropy in the sponge structure under quiescent conditions that does not relax within observable time scales. Considering the low viscosity of the Newtonian PS homopolymer, the inability of the membrane structure to relax and achieve an isotropic state seems a bit surprising. Unfortunately, we are unable at this time to offer a potential explanation for this intriguing behavior.

The linear viscoelastic behavior of the PS/PSEBS sponge phase ($\phi_{\text{PSEBS}} = 0.25$) closely resembles the behavior of unoriented lamellae in diblock copolymer melts [Koppi *et al.* (1992); Rosedale and Bates (1990)]. Whereas unoriented lamellar systems do not show any indication of a terminal regime at low frequencies, the sponge system shows a trend towards Newtonian behavior existing at extremely slow time scales that are difficult to access experimentally. If a terminal regime exists, we expect the sponge structure to eventually achieve an isotropic state if annealed for a *very* long time, potentially days or weeks. Even for a blend with lower concentration of membrane ($\phi_{\text{PSEBS}} = 0.20$), which mostly consists of vesicle structures with small amounts of sponge phase, a terminal regime was not observed at the lowest applied frequencies. These results indicate very slow topological dynamics (*i.e.*, the connections between sheets of membrane break and reform at a very low rate).

In situ SAXS measurements of the sponge phase show a slow structural response to shear flow. Intensity profiles obtained before and after shear experiments indicate that continuous shear leads to a gradual breaking of membrane connections in the sponge structure, leading to the formation of vesicles. Unfortunately, this sample was not sheared for long enough times to reach steady-state, and we cannot be certain the vesicle structures define the shear-induced steady-state morphology. Perhaps a lamellar phase is eventually achieved. Furthermore, as a result of the slow topological dynamics, the membrane connectivity lost during shear does not appear to recover within experimental time scales after cessation of flow. The slow topological dynamics may possibly be attributed to slow diffusion of the long-chain mid-block of the copolymer. If the diffusion is slow, long contact times between membrane sheets are necessary for the copolymer chains to move and form a stable connection between the sheets.

As far as we are aware, our studies of the PS/PSEBS blend represent the first investigation of the flow behavior of polymer sponge phases. Repeat experiments of the PS/PSEBS blends using longer shear times (as well as longer relaxation times following flow cessation) are clearly required to obtain more definitive answers regarding the shear-induced dynamics of this system. The development and characterization of other polymer sponge systems should provide further insight in the dynamics of these systems. For example, studies of other polymer sponge phases will help to address the question regarding the persistent anisotropy in the PS/PSEBS system in the absence of flow. Will a partially aligned sponge phase be observed in other blend systems? A sponge phase has also been reported in a blend consisting of a homopolymer and a gradient diblock

copolymer [Laurer *et al.* (1997, 1998)]. How does the flow behavior of this type of system compare to our homopolymer/triblock copolymer system?

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