

Flow-Induced Structures
in
Semidilute Polymer Solutions

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Chapter 1

General Introduction

1-1. Background

1-1-1. Motivation and Objectives of This Study

For the last several decades, miscibility, phase transitions and structure formation have been intensively studied for many polymer systems, e.g. polymer solutions, polymer blends, block copolymers, polymer gels and polymer liquid crystals. Recently, effects of flow on these phenomena have been attracting a great deal of attention from both experimental and theoretical viewpoints. Several important studies of the phase transition under a flow field, especially shear-induced phase separation, have been carried out,¹⁻³ although they were far from complete, and the underlying mechanisms are still left to be unveiled. Hence, I tried to elucidate the mechanism with *in situ* observations of phase separation phenomena in polymer systems under the flow. For that purpose I developed and improved *in situ* optical microscopy and small-angle light scattering method under shear flow which enable us to pursue the real-space and reciprocal-space analyses. The optical microscopy under shear flow (shear-microscopy) has the advantage of directly capturing detailed features of the structures, and the small-angle light scattering under

shear flow (shear-SALS) has the advantage of analyzing statistical features of the structures in the systems. By using both methods complementarily, I attempted to clarify the mechanism of shear-induced phase separation, structure formation in the systems and its time evolution in detail.

1-1-2. Universality of Butterfly Patterns

Before starting on the main subject of this thesis, I would like to review the “**Butterfly Pattern**”. The “butterfly pattern” is one of the most important key words in this thesis. In this section I am going to show the butterfly patterns observed for several systems and to show their universality.

The butterfly patterns are typical scattering patterns which we observed for semidilute polymer solutions under shear flow by using small-angle light scattering (SALS). Butterfly patterns cannot be observed in quiescent state. They appear only under external fields.

In the case of polymer solutions, they appear under shear flow as a consequence of shear-enhanced concentration fluctuations along the flow direction. Its theoretical explanation will be discussed in the next section (Sec. 1-1-3). First the butterfly patterns for high molecular weight polystyrene (PS) solutions with dioctyl phthalate (DOP) as a solvent (PS/DOP) were observed.⁴⁻⁶ Subsequently, it was confirmed that the butterfly patterns could be observed for other PS solutions as well, e.g. high molecular weight polystyrene/dibutyl phthalate (PS/DBP), high molecular weight polystyrene/Tricresyl phosphate (PS/TCP), high molecular weight polystyrene/cyclohexane (PS/cyclohexane), and high molecular weight polystyrene/diethyl

malonate (PS/DEM) solutions.⁷ Furthermore, the butterfly patterns could be observed in crystallizable polymer solutions, semidilute solutions comprised of ultrahigh molecular weight polyethylene as a solute and paraffin as a solvent (UHMWPE/paraffin).^{8,9} Here, UHMWPE and paraffin have the same chemical structure, $(-\text{CH}_2-)_n$, and differ only in the degree of polymerization. Thus this result suggests that elastic deformation of entangled polymer chains plays an important role in the generation of butterfly patterns and hence shear-induced concentration fluctuations or phase separation. Figure 1-1 shows the butterfly patterns from the sheared polymer solutions mentioned above. Therefore butterfly patterns are universal phenomena for sheared semidilute polymer solutions when they have concentration fluctuations or phase separation induced by shear flow.

In fact, we can observe the butterfly patterns in other systems besides semidilute polymer solutions. The butterfly patterns can be universally observed when anisotropic concentration or density fluctuations occur in systems under flow or uniaxial elongation. Figure 1-2 introduces some examples. Figure 1-2a is the butterfly pattern observed for elongated swollen gels using small-angle neutron scattering (SANS).^{10,11} It is considered that this butterfly pattern arises from the density fluctuations of the crosslinking points of the gels (and hence concentration fluctuations in the gels) under elongation. Moreover, Figures 1-2b and 1-2c are the butterfly patterns from colloidal dispersions under shear flow.^{8,12} The butterfly pattern in Figure 1-2b was observed during shear flow in polydimethylsiloxane liquids ($M_n = 36,000$) filled with colloidal silica (radius = 50 nm), whose concentration was 7.5 vol%. The butterfly pattern in Figure 1-2c arose from a silica particle

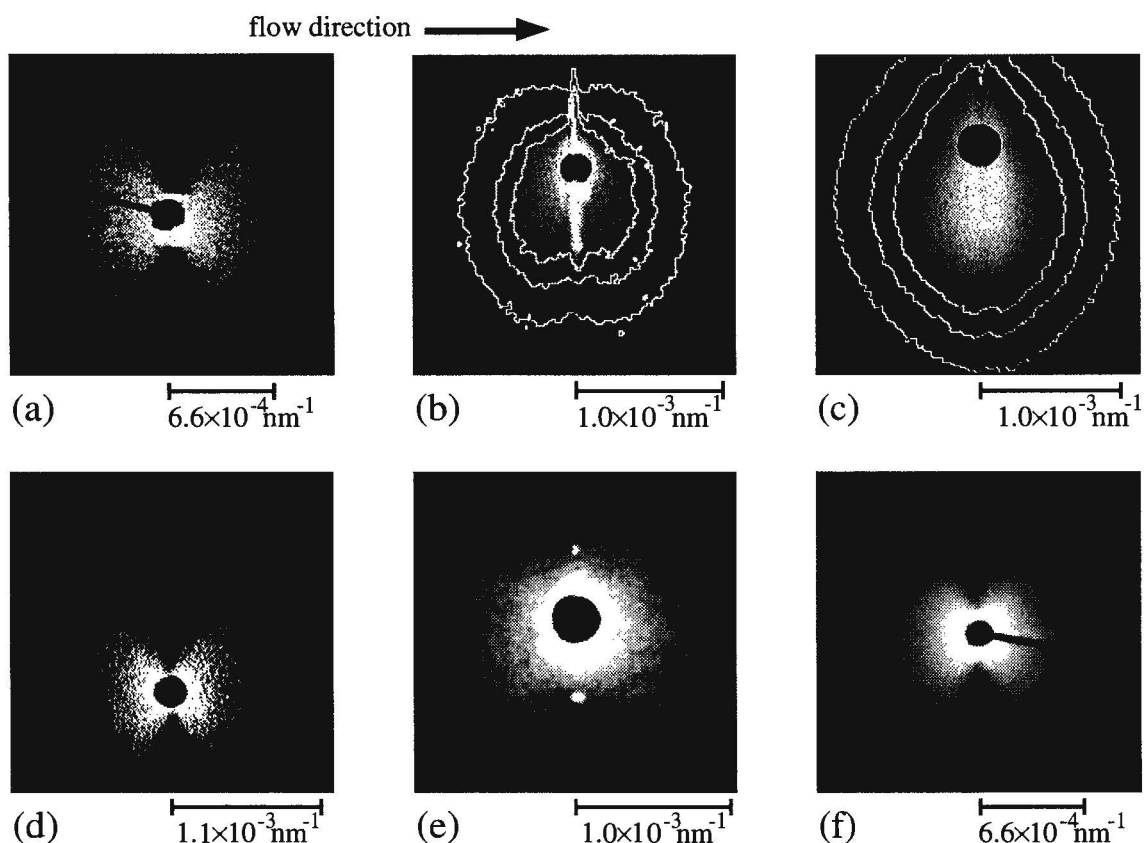


Figure 1-1 Butterfly patterns from several semidilute polymer solutions: (a) PS548/DOP 6.0 wt% at 27 °C, $\dot{\gamma} = 0.23 \text{ s}^{-1}$, (b) PS548/DBP 6.0 wt% at 27 °C, $\dot{\gamma} = 316 \text{ s}^{-1}$, (c) PS548/TCP 6.0 wt% at 27 °C, $\dot{\gamma} = 316 \text{ s}^{-1}$, (d) PS548/Cyclohexane 6 wt% at 27 °C, $\dot{\gamma} = 1.0 \text{ s}^{-1}$, (e) PS548/DEM 6.0 wt% at 27 °C, $\dot{\gamma} = 100 \text{ s}^{-1}$, (f) UHMWPE/paraffin 5 wt% at 150 °C, $\dot{\gamma} = 46 \text{ s}^{-1}$. PS548 and UHMWPE are high molecular weight polystyrene and polyethylene, whose weight-average molecular weight, M_w , are 5.48×10^6 and 2.0×10^6 , respectively. In patterns (b) and (c) contour plots of the scattered intensity distribution were superposed on scattering patterns because their butterfly patterns were obscure. All butterfly patterns are not symmetrical perpendicular to the flow direction, because they are due to the shape of a window of the temperature enclosure for a scattered beam (see Sec. 6-2-2 for details).

(radius = 50 nm)/decalin (cis-trans mixture) solution, whose concentration was 12 vol%. These butterfly patterns are considered to arise from enhanced concentration fluctuations of particles along the flow direction.

As mentioned above, the butterfly patterns are quite universal phenomena in systems which have anisotropic fluctuations under shear flow or uniaxial deformation. In this thesis I investigated the structure formation in systems, mainly the semidilute polymer solutions, under shear flow, based on *in situ* observations of butterfly patterns in Fourier space and corresponding optical images in real space.

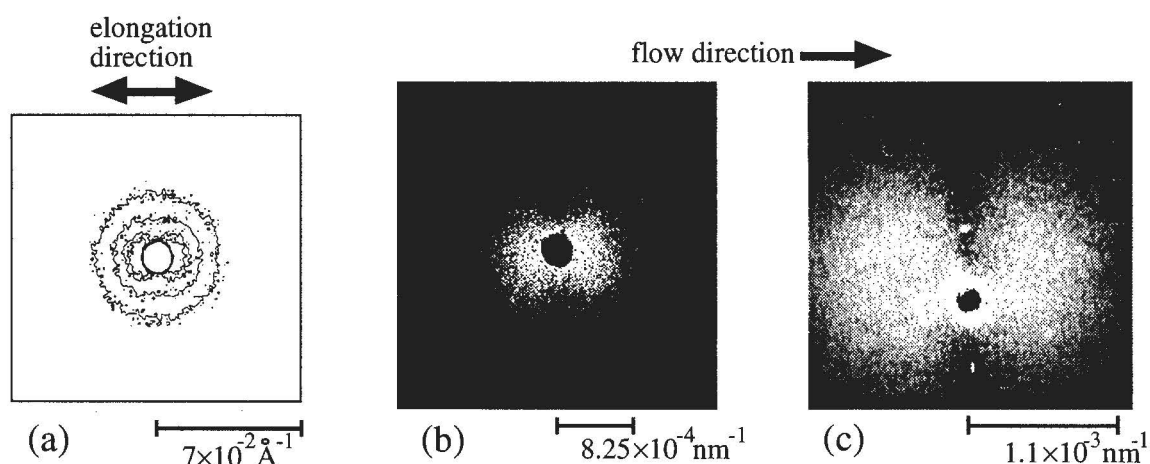


Figure 1-2 Butterfly patterns from several systems: (a) Elongated swollen gel,¹¹ (b) Silica particle/Polydimethylsiloxane (PDMS), at RT, $\dot{\gamma} = 23 \text{ s}^{-1}$ (c) Silica particle/Decalin at 25 °C, $\dot{\gamma} = 50 \text{ s}^{-1}$.

1-1-3. Theoretical Background

In this section, I will review some recent theoretical studies of shear-induced concentration fluctuations or phase separation.

Early theoretical and experimental approaches to shear-induced **phase separation** were reviewed by Rangel-Nafaile et al.³ They developed a quasithermodynamic theory to describe the effect of flow on the phase-separation behaviors of polymer solution, i.e., the stored elastic free energy of a flowing polymer solutions increased its Gibbs free energy and thereby changed the phase equilibrium from that of a quiescent solution. They obtained the Gibbs free energy of macromolecules in quiescent solutions from the Flory-Huggins theory, and computed changes with deformation state from Marrucci's analysis for a dilute solution of elastic dumbbells.¹³

Afterwards, Helfand and Fredrickson presented a phenomenological theory for the dynamics of concentration fluctuations of polymer solutions under shear flow.¹⁴ Subsequently, Onuki also presented a dynamical model which describes the phase transition of deformed polymers in solvent under shear flow.¹⁵ They pointed out that the former theory developed by Rangel-Nafaile et al. had no basis in statistical mechanics and neglected much of the physics that they believed to be essential to the observed phenomena. They indicated the non-equilibrium statistical mechanics: a coupling between concentration fluctuations and stress exists in the system as a result of the concentration dependence of viscosity and normal stress coefficients. They set up the following dynamic equations for local polymer concentration ϕ and velocity field v ,

$$\frac{\partial}{\partial t}\phi = -\nabla \cdot (\phi v) + \lambda_0 \nabla^2 (\mu_0 + \mu_{el}) + \theta \quad (1-1)$$

$$\rho \frac{\partial}{\partial t} v = -\nabla p - \phi \nabla \frac{\partial}{\partial \phi} F_0 + \nabla \cdot \sigma + \eta_s \nabla^2 v + \zeta \quad (1-2)$$

where $\mu_0 + \mu_{el}$ is chemical-potential difference between the polymer and solvent consisting of the usual part $\mu_0 = \delta F_0 / \delta \phi$ and the elastic part $\mu_{el} = \delta F_{el} / \delta \phi$. ρ , p , and σ are mass density, pressure, and stress tensor, respectively. λ_0 and η_s are, respectively, the kinetic coefficients related to the power spectra of the random source term θ and ζ via the fluctuation-dissipation relations. From scaling theory $\lambda_0 \sim a^2 / 6\pi\eta_s$ for $\phi \gtrsim \phi^*$. Furthermore Helfand and Fredrickson mentioned that experimental observations of turbidity in polymer solutions above the equilibrium phase transition point under shear flow would not mean a true shift in the phase transition, but just large shear-induced **concentration fluctuations**.

Based on the latter theory, we consider the mechanism of the concentration fluctuations in semidilute polymer solutions under shear flow as follows. As shown Figure 1-3a, in the quiescent state (no shear flow) only thermal concentration fluctuations exist in the system. The thermal concentration fluctuations are averaged out to zero on time- and space- average, and their spatial distribution is isotropic. When shear flow is imposed on the system, polymer molecules in the solution behave differently depending on the shear rate. If the shear rate $\dot{\gamma}$ is smaller than τ_{rep}^{-1} , where τ_{rep} is the reptation time of polymer molecules under a given condition, the polymer chains can diffuse in reptation tubes before chains are elongated. Therefore, in this case the concentration fluctuations are not enhanced by shear flow and the system

is still isotropic (Figure 1-3b). If the shear rate $\dot{\gamma}$ is larger than τ_{rep}^{-1} , the system changes from the previous state. The polymer molecule chains cannot diffuse within the deformation time, thus they are elongated and elastic free energy are stored. This situation is quite unstable, and as a consequence the stored elastic free energy are relaxed through a process that solvent molecules are squeezed from polymer chains (Figure 1-3c) and thereby polymer chains can take relaxed conformation. In this way the system would release the elastic free energy even if it pays a penalty of combinatorial entropy. Consequently, the concentration fluctuations are enhanced along the flow direction, but in the perpendicular direction of the shear flow the concentration

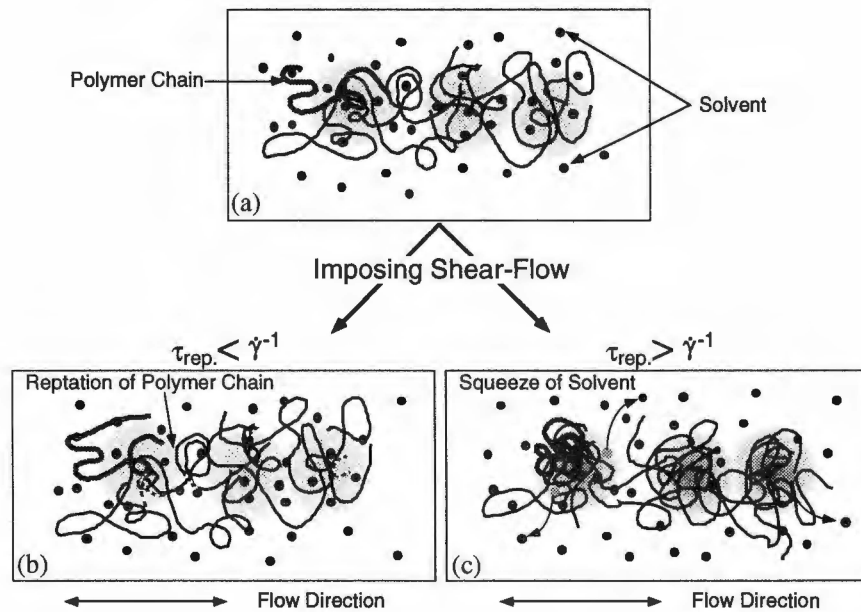


Figure 1-3 Sketches of concentration fluctuations developed in polymer solutions: (a) in the quiescent state (no shear flow); (b) under shear flow at $\dot{\gamma} < \dot{\gamma}_c$. Polymer chains can diffuse by disentangling via reptation, so the concentration fluctuations are not enhanced. (c) under shear flow at $\dot{\gamma} > \dot{\gamma}_c$, where reptation of polymer chains cannot occur within the deformation time, thus the concentration fluctuations are enhanced along the flow.

fluctuations are unaffected by the shear flow. Therefore such shear-enhanced concentration fluctuations along the flow are believed to give rise to the butterfly patterns in the shear-small-angle light scattering experiments.

1-2. Apparatus for Small-Angle Light Scattering under Shear Flow

Two apparatuses for small-angle light scattering under shear flow (shear-SALS), which have been developed in our laboratory, were used in most of the experiments in this thesis. The new shear-SALS apparatus can measure shear-SALS and simultaneously measure the development of the supramolecular structure under an optical microscope (shear-microscopy), the details of which will be explained in Chapter 2.¹⁶ The details of the older shear-SALS apparatus were described elsewhere.¹⁷

The old shear-SALS apparatus was constructed by modifying an existing rheometer (IR-200, Iwamoto Seisakusho, Co. Ltd., Kyoto, Japan).¹⁷ Figure 1-4 shows a schematic diagram of this apparatus. The rheometer can measure rheological properties, i.e., shear stress and shear viscosity of polymers under steady state and oscillatory shear flow, under “saw-tooth” shear flow consisting of two periods with linearly increasing and decreasing shear rates, and during recovery after cessation of the flow. However, this apparatus cannot measure normal force, therefore rheological measurements of this thesis were mainly performed by other rheometers (e.g. Rheometrics®, RMS-800, RDA-II and RFS-II rheometer) in order to obtain quantitative rheological properties.

The shear-SALS measurements were made possible by using a set of optically transparent cone (a) and plate (b) or of parallel plates made of quartz

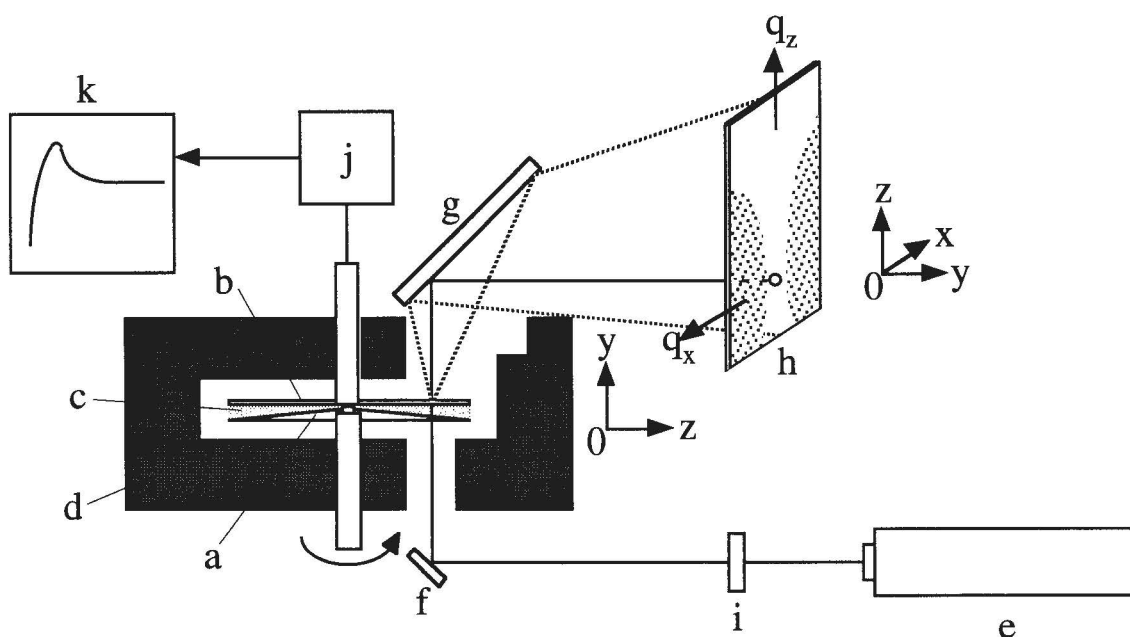


Figure 1-4 Schematic diagram of the shear-small-angle laser light scattering apparatus: (a) sample cell (cone), (b) sample cell (plate) (c) sample, (d) temperature enclosure, (e) laser unit, (f) and (g) mirror, (h) photographic film, (i) neutral density filter, (j) transducer for torque measurement, and (k) chart recorder.

or BK glass. The cones and plates have the same radius of 40 mm, but we used cones with different angles ranging from 1.0° to 2.6° in order to adjust for the varying transparency of the samples. These cones and plates are of same size for the new apparatus, so we can use them for both apparatuses. The sample (c), cone and plate were covered by a temperature enclosure (d) with windows for the incident and scattered beam paths. The temperature enclosure was a double-chamber construction made by modifying the single-chamber type temperature enclosure previously used.^{4,17} This new temperature enclosure was almost same as the new shear-SALS apparatus¹⁸ (see Chapter 2). It can control the temperature of the samples in the range of 0°C to 200°C with an accuracy of $\pm 0.3^\circ\text{C}$. For low temperature experiments below

room temperature, dried cold air was fed to a temperature enclosure using an air-cooler and an air compressor.

A He-Ne CW gas laser (e) was used as an incident light source ($\lambda_0 = 632.8$ nm). The incident beam was reflected by a mirror (f), passed through the cone (a) and irradiated the sample (c) between the cone and the plate. The scattered light from the sample was passed through the plate (b) and again reflected by a mirror (g), and detected by a photographic film (h) or by a TV-camera with a VCR-monitor system described elsewhere¹⁹ or with a dynamic image digitizing system previously developed in our laboratory.²⁰ The scattering-angular range in air (θ in the Figure 1-5) covered by the present apparatus is typically from 0 to 25 °, which is wider than that previously used^{4,17} as a result of redesigning the windows of the new temperature

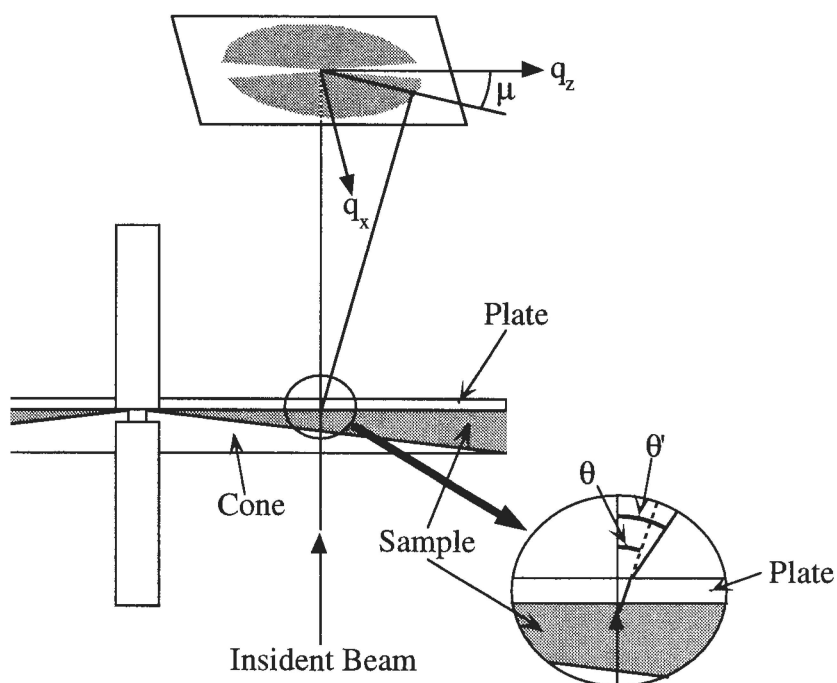


Figure 1-5 Schematic diagram of cone-and-plate type sample cell, scattering angle, and coordinate system.

enclosure. The incident light intensity level was controlled by a neutral density filter (i) in order to adjust the scattering intensity level to the appropriate range of the detector.

For the quantitative measurement of the scattered intensity distribution, a photodiode array system was employed, as shown in Figure 1-6. We measured the intensity profiles parallel and perpendicular to the shear flow over an angular range of 1 to 16 ° in medium (θ in the Figure 1-5), which corresponds to the magnitude of the scattering vector q from 2×10^{-4} to $4 \times 10^{-3} \text{ nm}^{-1}$ where

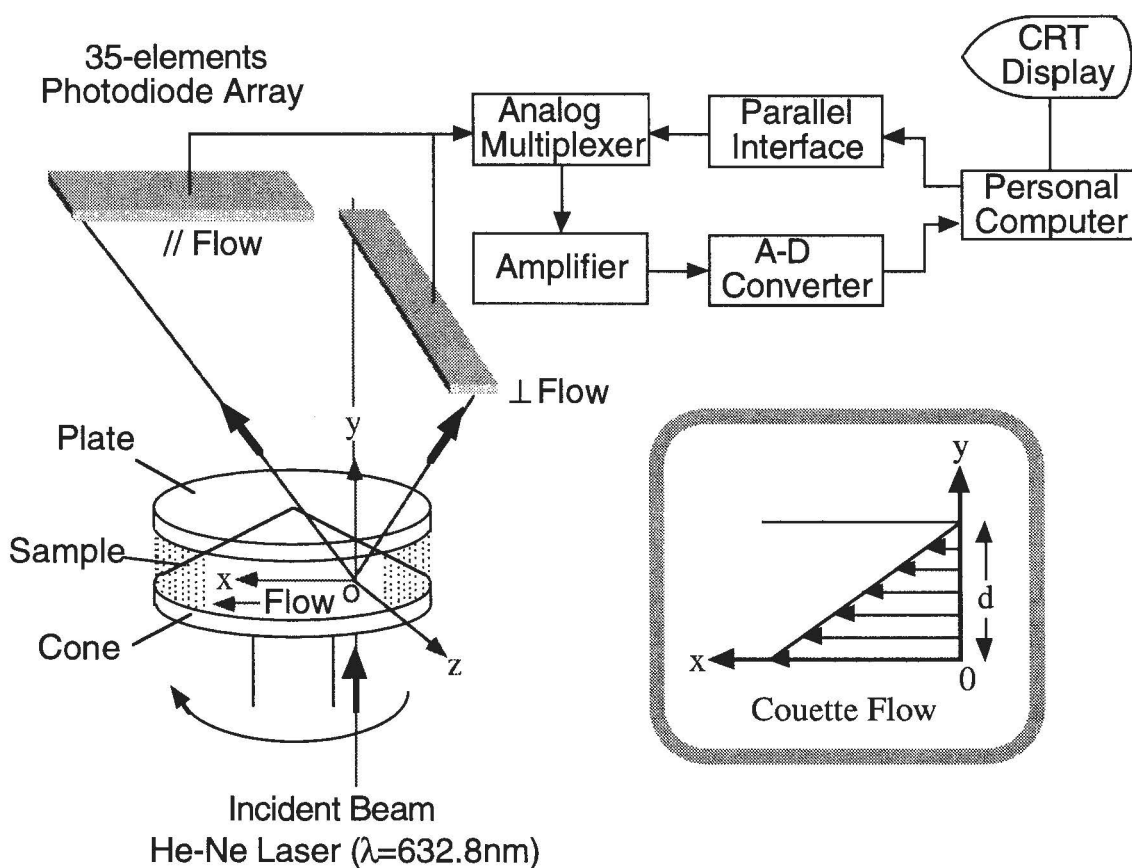


Figure 1-6 Schematic diagram of cone-and-plate rheometer to generate Couette type shear flow, photodiode arrays and photocurrent detecting system to measure small-angle light scattering, and coordinate system.

$$q = (4\pi / \lambda) \sin(\theta/2). \quad (1-3)$$

Here λ and θ are the wavelength and scattering angle in the medium, respectively. The photocurrent from the diode was passed through an analog multiplexer, amplified, digitized with a 12-bit analog-to-digital converter, and stored in a personal computer memory.

Shear flow was imposed on the sample by applying steady state rotations or oscillatory rotations to the cone (a), and the torque exerted on the plate (b) was measured by a conventional method. The cone was placed on the incident beam side in order to avoid complex reflection of the scattered beam at the oblique surface which could occur if the cone was placed on the scattered beam side. This cone and plate setting is opposite to that of normal rheometer for easy sample handling.

Figure 1-7 represents the definition of the coordinate system in the shear-SALS experiments. Note that the coordinate system shown here is different from that of previous reports.^{4-6,16,17} In the previous reports we used the coordinate system based on traditional scattering studies. However the coordinate system used in recent reports^{9,18,21,22} and here is based on the rheological tradition. I used the latter in this thesis in order to avoid confusion. The velocity gradient of the flow exists in the plane parallel to Oxy , the incident beam is irradiated through the velocity gradient direction, parallel to Oy , and the small angle scattering profiles are detected in the plane Oxz perpendicular to Oy axis and to the shear plane Oxy . The Ox axis is set parallel to the flow direction.

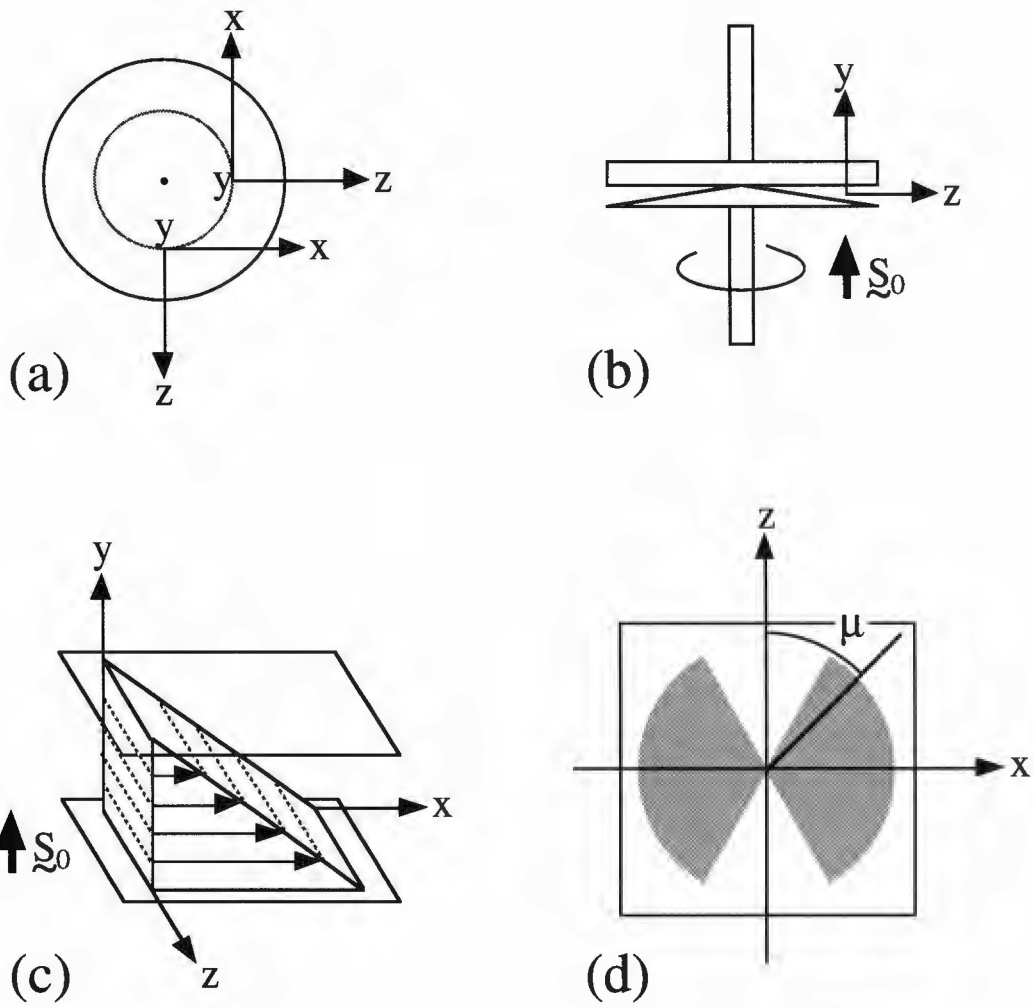


Figure 1-7 Definition of the coordinate system in the flow light scattering experiment. Oy is parallel to the propagation direction of incident beam (unit vector S_0), and Ox is parallel to the flow direction. The velocity gradient of the shear flow exists in the plane parallel to Oxy and the scattering profiles are detected in the plane Oxz either by a photographic film or by a TV camera coupled with a VCR or the dynamic image analyzer.

1-3. Outline of This Thesis

In this Chapter 1, I am going to review the earlier studies and theoretical background of shear-induced concentration fluctuations or phase separation, the apparatus for the shear-small-angle light scattering (“shear-SALS”) previously developed in our laboratory, and my motivations and objectives for this thesis. Moreover the butterfly patterns, the most important key word of this thesis, are shown to be quite universal phenomena, and to be not always in semidilute polymer solutions even though polymer solutions are mainly used as experimental systems in this thesis.

In Chapter 2, a new apparatus developed in our laboratory will be explained, which makes it possible to measure small-angle light scattering and to observe the development of the supramolecular structure by an optical microscope (“shear-microscopy”) under shear flow. It simultaneously provides information on reciprocal space from SALS and on real space from optical microscopy. Therefore, the development of the supramolecular structure in systems such as polymer solutions and polymer mixtures as well as liquid crystals and colloidal systems under shear can be investigated in depth. Shear-induced phase separation and shear-induced homogenization of some polymer solution systems were investigated using this apparatus.

In Chapter 3, the effects of simple shear flow on concentration fluctuations in semidilute solutions of high molecular weight polystyrene are investigated by shear-SALS. The shear-rate ($\dot{\gamma}$) dependence of scattering in steady state flow was found to fall into four regimes: Regime I at $\dot{\gamma} < \dot{\gamma}_c$ where the scattering is that of homogeneous semidilute solutions, and Regimes II to IV at $\dot{\gamma} > \dot{\gamma}_c$,

where $\dot{\gamma}_c$ being the critical shear rate for the shear-enhanced concentration fluctuations. In Regime II, a unique butterfly-type scattering pattern with a dark streak perpendicular to the flow direction appears. The intensity parallel to the flow increases by about 100 times with increasing $\dot{\gamma}$. In Regime III at higher shear rates, the intensity increase with $\dot{\gamma}$ tends to saturate, and finally in Regime IV at even higher shear rates, the intensity further increases and the butterfly pattern changes into a two-point pattern elongated perpendicular to the flow, with a broad intensity maximum along the flow. This anomalous pattern change is closely related to anomalies in rheological behavior.

Chapter 4 focuses on the concentration fluctuations in a semidilute polymer solution induced by steady shear flow, which were directly visualized for the first time. The spatial structure corresponding to the “butterfly pattern” observed by light scattering is elucidated, being the result of hydrodynamic rippling waves which have a distribution of tilt angles. The minimal tilt angle depends on shear rate in a power law fashion, causing the butterfly to almost close upon itself at high shear rates. The concentration waves have a time scale related to a shear rate $\dot{\gamma} \sim 1 \text{ s}^{-1}$ and periodicity $\lambda \sim 10 \text{ }\mu\text{m}$, indicating a link to reptation processes.

In Chapter 5, the shear-induced concentration fluctuations in semidilute solutions of polystyrenes with high molecular weights ($\sim 10^6$) are studied under steady state shear flow as a function of shear rate $\dot{\gamma}$ by means of light scattering and transmission optical microscopy. Special attention will be focused on the formation of string-like structure at high shear rate (string phase). The solutions, which are homogeneous in the quiescent state, show enhanced concentration fluctuations parallel to the flow axis at $\dot{\gamma} > \dot{\gamma}_c$, giving rise to

unique butterfly-type scattering patterns, as reported in Chapter 3 and 4. Upon further increasing $\dot{\gamma}$, it was found for the first time that the solutions form long strings parallel to flow using shear microscopy. The string formation occurs in parallel to the onset of rheological anomalies and to the appearance of strong streak-like small-angle scattering at $\dot{\gamma} > \dot{\gamma}_a$, the critical shear rate above which the string and the rheological anomalies are clearly discerned.

In Chapter 6, transient scattering and rheological behaviors, i.e., the time evolution of structures induced after imposing shear flow on semidilute solutions of high molecular weight polystyrene (PS) investigated by means of both shear-light scattering and rheology are studied. After imposing shear flow with a shear rate $\dot{\gamma} > \dot{\gamma}_c$, the unique butterfly-type scattering pattern appeared with an elapse of time. The pattern had a scattering maximum along the flow direction. The wave number q_m decreased and the intensity I_m at the scattering maximum increased with time and eventually reached steady state values. The rheological experiments that were carried out on the same solution under the same shear flow revealed two stress overshoots. The second overshoot was found to be related to the development of the butterfly pattern and its time change, i.e., to the formation and growth of shear-induced structures.

In Chapter 7, shear-induced structure formation and molecular orientation in the structure in semidilute solutions of high molecular weight polystyrene (PS) will be discussed in further detail, which was investigated by using shear-dichroism and shear-birefringence in addition to shear-SALS, shear-microscopy and rheology. At the shear rate $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$, negative dichroism, almost zero (weakly negative) birefringence, and the butterfly-type LS patterns

were observed. All these results are consistent with the optical images captured by shear-microscopy and show the shear-induced concentration fluctuations with the following characteristics: the amplitude of the fluctuations is enhanced along the flow direction and the domain structure (regions rich in polymer concentration) formed is extended normal to flow. However, at the shear rate $\dot{\gamma} > \dot{\gamma}_a$, the dichroism became positive and the absolute values of both the dichroism and the birefringence increased drastically. The changes in the dichroism and the birefringence are believed to be related to formation of the string-like structures and molecular orientation, both parallel to flow.

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Chapter 2

A New Apparatus for Simultaneous Observation of Optical Microscopy and Small-Angle Light Scattering Measurements of Polymers under Shear Flow

2-1. Introduction

The mixing or demixing phenomena of polymers have been studied theoretically and experimentally since the 1970s. Recently, the effect of shear flow has attracted much attention.¹⁻²² The essence of this subject is the topic of open non-equilibrium systems. Several methods, such as transmitted light intensity,^{2,12} flow form dichroism,^{10,12,13} small-angle light scattering,³⁻¹³ and small-angle neutron scattering,¹⁴ have been used to understand these phenomena. These methods are indirect methods, having the advantage of providing information that is a statistical average over the systems as a whole, but it is difficult to get detailed features of the structures. In contrast, optical microscopy is a direct method but it can investigate only a rather small part of the system. It does not always cover all of the system, i.e., it is not statistical. Thus the two approaches are complementary to each other. Therefore the small-angle light scattering method was combined with optical microscopy to understand the supramolecular structures of polymeric solutions and polymer mixtures developed under shear flow. A new shear-small-angle light

scattering apparatus with an optical microscope was constructed for this purpose. The structures of polymeric systems as a liquid and in solution can be simultaneously investigated by the shear-small-angle light scattering (designated hereafter as “shear-SALS”) and by optical microscopy (designated hereafter as “shear-microscopy”). The shear-SALS technique gives fundamental information on the nature of supramolecular structures developing under shear flow. It is, however, hard to obtain an image of the structures in the system by the shear-SALS when the structures are too complicated because phase information is lost in the scattering image. Thus the scattering pattern does not have a one-to-one correspondence to the structure. In this case, the optical microscope measurement provides helpful information about the structure. Therefore it is believed that this is an important and effective technique to study the shear flow effects.

2-2. New Rheo-Optical Apparatus of Combined Shear-Microscopy and Shear-SALS

The new apparatus was constructed by modifying an existing rheometer (IR-200, Iwamoto Seisakusho, Co., LTD., Kyoto, Japan). Figure 2-1 shows a schematic diagram of the whole apparatus. Unlike the apparatus previously developed (see Sec. 1-2),³ this new apparatus does not have a transducer which measures the rheological properties of samples. Therefore there is free space above the temperature enclosure. The apparatus previously developed has a large mirror to reflect the scattering light above the temperature enclosure, because the transducer disturbs the detection of the scattered light. The new

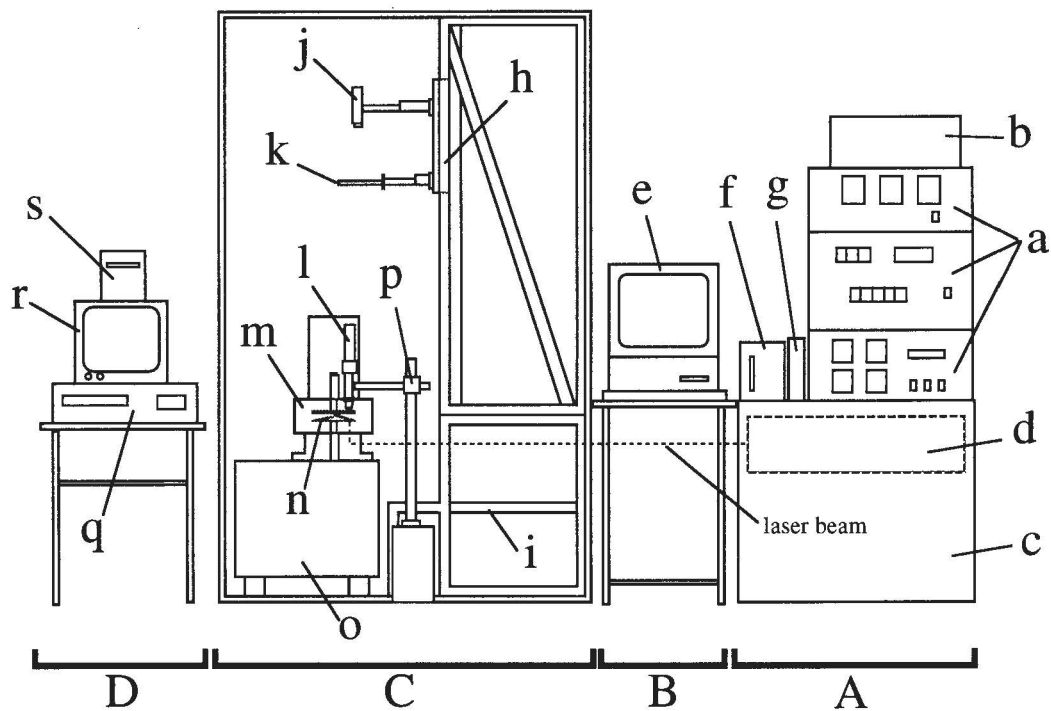


Figure 2-1 Schematic representation of the new shear-small-angle laser light scattering apparatus and the shear-microscopy apparatus. Part A: (a) control units for the shear cell, (b) power supply for the laser unit, (c) power supply for the shear cell, (d) laser unit. Part B: (e) personal computer (Macintosh), (f) MO disk drive, (g) hard disk drive. Part C: (h) and (i) optical benches, (j) CCD camera, (k) screen, (l) optical microscope, (m) temperature enclosure, (n) shear cell, (o) motor unit, (p) microscope bench. Part D: (q) VCR, (r) TV monitor, and (s) video printer.

apparatus does not have such a mirror. The scattered light can be directly detected without an upper mirror, and artifacts due to the mirror can thus be avoided.

This apparatus consists of four main parts, A to D, as shown in Figure 2-1. Part A is made of several control units (a) for the shear cell, power supplies (b and c) for the laser unit and for the motor that drives the shear cell, and the laser unit (d). A He-Ne CW gas laser is used as an incident light

source ($\lambda_0 = 632.8$ nm, 15 mW) for the scattering measurements. A halogen white lamp, on an optical bench (i), is used as a light source for microscope observation. Part B is composed of a personal computer (Macintosh) (e) with an MO disk drive (f) and a hard disk drive (g) in order to capture images from the CCD camera and immediately analyze digital images. A frame grabber board is set up in the Macintosh computer for capturing images. In digital image analyses the image program, NIH Image, developed by Wayne Rasband at NIH²³ was used extensively. Part C is the core of this apparatus: an optical bench (h) carries the CCD camera (j) and screen (k) up and down, which detect two-dimensional scattering profiles. When necessary, an analyzer is placed in front of a screen (k) for depolarized light scattering experiments. The halogen white lamp unit, which was mentioned above, and a polarizer to polarize incident light beam from the lamp are put on an optical bench (i) for shear-microscopy. For shear-SALS, neutral density filters, pinholes and a half wavelength plate to rotate polarization direction of incident laser beam are put on the optical bench (i). The optical microscope (l) is supported by the microscope bench (p), and by rotating its arm the microscope can be easily removed when scattering profiles are taken. Thick rubber is set under the microscope bench (p) to avoid the vibration from the motor unit. The temperature enclosure (m), shear cell (n) and motor unit (o) will be discussed in detail later. Part D is composed of the VCR (q), TV monitor (r) and video printer (s) to display or record scattering patterns or microscopic images.

Figure 2-2 shows a schematic diagram of the shear cell and represents a flow chart of the video signal in optical microscopy. Optically transparent cone and plate or parallel plates made of quartz or BK glass are used as a

shear cell. The cone is placed on the incident beam side so as to avoid complex reflection of the scattering light at the oblique surface which could occur if the cone is placed in the scattered beam side. The cones and plates have the same radius of 40 mm, but cones with different angles ranging from 1.0° to 2.6° are used in order to adjust for the varying transparency of the samples. Objective lenses used are Nikon 10 $\times$, 20 $\times$, 40 $\times$ and 60 $\times$ long focus type. The shear flow is imposed on the sample by applying steady state rotations, oscillatory rotations, or “saw-tooth” rotations to the lower cone or plate as was done before with the apparatus previously constructed.³ In this new

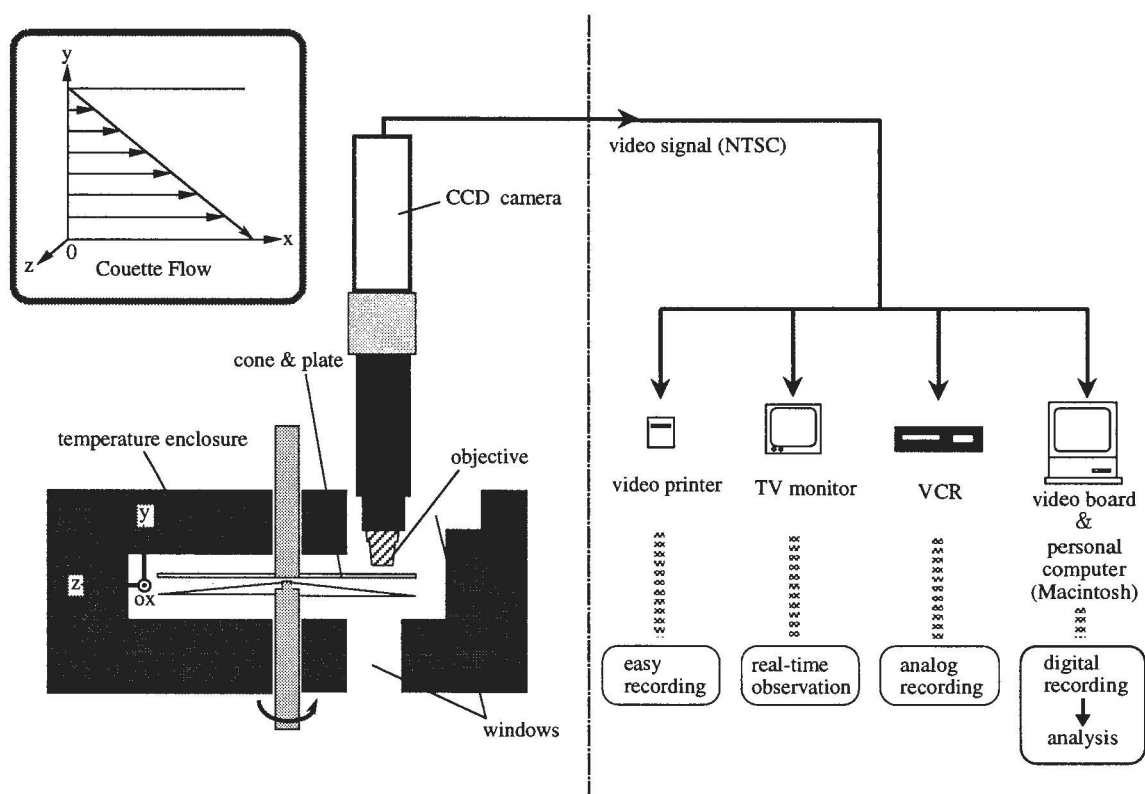


Figure 2-2 Schematic diagram of the shear-microscopy and a flow chart of the video signal. The temperature enclosure corresponds to (m) in Figure 2-1. The inset at the top left-hand corner shows a schematic diagram of Couette flow in the sample. The Ox , Oy and Oz axes are parallel to the flow direction, the velocity gradient direction and the neutral axis, respectively.

apparatus the rotation can be reversed. Transient step-wise shear flow can be also imposed on the sample. The definition of the coordinate system is the same as those shown in Figure 1-3, 1-4, 1-5 and 1-6 of Sec. 1-2. The inset at the top left-hand corner of Figure 2-2 shows a schematic diagram of Couette flow in the sample. Oy is parallel to the propagation direction of the incident beam, and to the velocity gradient direction, whilst Ox is parallel to the flow direction and Oz is the neutral axis.

To the optical microscope a fast shutter ($\sim 1/10,000$ s) CCD video camera (Sony SSC-M370) is connected, which is connected in parallel to a video printer, a TV monitor, a SVHS VCR (Victor HR-S6600), and a Macintosh computer with a frame grabber board (RasterOps 24STV or Data Translation QuickCapture). For the observation of samples under shear flow by optical microscope, a fast shutter CCD camera is needed because the samples quickly flow out of sight of the microscope. The video printer allows easy and quick recording. Focus and real-time observation are made using the TV monitor. The VCR carries out analog and continuous recording. The Macintosh computer is used for digital image capturing and processing, e.g., contrast enhancement, background subtraction and correction of artifacts. For digital image capturing, the largest size of the captured images is 640×480 pixels, and their resolution is 8 bits. It takes a few seconds to capture the largest size image and save it onto the hard disk. For digital image processing, several filtering operations are carried out on captured images (see Sec. 2-3-1 below for details). Furthermore image analyses, e.g., fast Fourier transform (FFT), can be easily carried out using digital images.

The temperature enclosure is a double-chamber enclosure which can

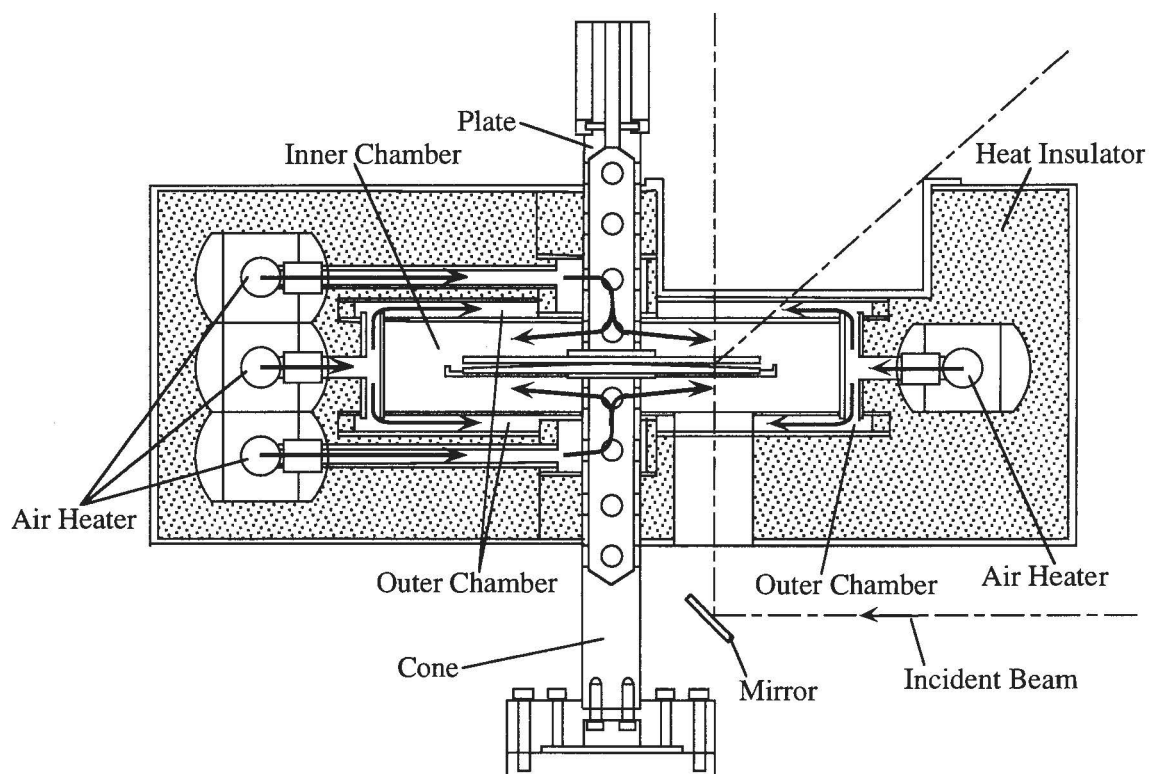


Figure 2-3 Cross sectional view of the double-chamber temperature enclosure. Solid arrows indicate flow of temperature-controlled air. The shafts holding the cone-and-plate are made out of a pipe with holes, through which the temperature-controlled air circulates in the inner chamber and the pipe. Other temperature-controlled air is also circulated in the outer chamber.

control the temperature of the samples in the range of 0 °C to 200 °C with accuracy of ± 0.3 °C (Figure 2-3). Such accuracy is necessary because critical phenomena, which are very sensitive to temperature, are treated. Before experiments the temperature accuracy was checked by using a specially made quartz plate in which three platinum resistance thermometers were embedded along the radial direction. The temperatures at the three points along the radial direction of the cone-and-plate shear cell filled with the DOP were measured by using the special plate. In order to make the temperature variation along the radial direction of the shear cell as small as possible, a metal pipe

with holes for the metal shafts holding the cone and the plate is used , as shown in Figure 2-3. Through the holes the temperature-controlled air is circulated in the inner chamber and the pipe. Other temperature-controlled air is also circulated in the outer chamber. Below room temperature a cooling system is used, which cools the air before entering the temperature enclosure. Small windows are opened on the upper and lower sides of the temperature enclosure to insert the optical microscope or to let incident and scattered beams pass. These windows define the angular range of scattering measurements from ca. 0 to 30° (in the medium).

For quantitative measurements of light scattering the CCD camera and screen are used. The flow chart of the video signal after the CCD camera is the same as for shear-microscopy. Thus scattering profiles can be handled as digital data, i.e., contrast enhancement, background subtraction and correction for artifacts are possible as in shear-microscopy. Moreover, photographic films can be used instead of the screen (k in Figure 2-1) to detect the scattering profiles for qualitative observation.

For both shear-microscopy and shear-SALS measurements, experiments under various polarization conditions are possible. For shear-microscopy, the polarizer is used, which is set on the top of the halogen white lamp and analyzer in the microscope. For light scattering, the laser beam is polarized, thus polarizer is not necessary. The half wavelength plate, which is put on the optical bench (i in Figure 2-1), can rotate the orientation of the electric vectors of the incident laser beam. The analyzer is put between the screen and temperature enclosure. Therefore H_V , V_H , H_H , and V_V components of the scattering profiles and microscopic images can be detected, with large H , V

defining analyzer orientation and subscript H, V denoting polarizer orientation.

Since shear-SALS and shear-microscopy are combined, the information obtained by them can be very effectively used. Calculating the 2D-FFT of microscopic images²⁴ and comparing them with scattering profiles confirm whether microscopic images are a true representation or not. Furthermore, when the dominant wave numbers, $q = (4\pi/\lambda)\sin(\theta/2)$ (λ and θ being the wavelength and scattering angle in the medium, respectively), of the system are known, other structures arising from unimportant wave numbers by performing filtering operations on the microscopic images can be eliminated and images of the dominant structures can be obtained. Some examples are shown in the next section.

2-3. Application of Shear-SALS and Shear-Microscopy to Polymeric Systems

2-3-1. Shear-Induced Phase Separation in Semidilute Polymer Solutions

Effects of shear flow on the phase transition and self-assembly of multicomponent mixtures have been attracting a great deal of attention from both theoretical and experimental viewpoints as an intriguing subject in statistical physics.¹⁻²² Shear-induced phase separation in semidilute polymer solutions is one of the striking results of combining hydrodynamics with the special elastic and viscous properties of polymers, and has been the focus of a concentrated effort in recent years.^{2,6-10,12-14} More recently, it has attracted much theoretical interest in the non-equilibrium statistical physics of

polymers.¹⁸⁻²² Using the shear-SALS apparatus previously constructed,³ a strong anisotropy of the scattering pattern with respect to the flow direction and anomalies have been found at high shear rates. Here the merits of applying this apparatus to studying the shear-induced structure formation are demonstrated. The details were described elsewhere.²⁵

In this section, polystyrene (PS) with weight average molecular weight M_w of 5.48×10^6 and heterogeneity index $M_w/M_n = 1.15$ (M_n is the number average molecular weight) was dissolved at a concentration of 6.0 wt% in dioctyl phthalate (DOP), a θ -solvent at 22 °C. This concentration is about 40 times higher than the overlap concentration²⁶ c^* , and its cloud point is 13.8 °C. The experiment was done in the one phase region at 27 °C.

Figure 2-4 shows two light scattering patterns recorded on photographic films in the quiescent state and the steady shear state. The shear rates of (a) and (b) were 0 s⁻¹ and 0.23 s⁻¹, respectively. The pattern (a) has almost no scattering intensity, the only signal resulting from the direct beam, so that the solution is in the one-phase region at zero shear. The pattern (b), which was taken in the plane of Oxz with the incident beam parallel to the velocity gradient direction (see Figure 2-2), has a strong intensity along the flow, but no intensity perpendicular to the flow. This unique pattern has been designated as the “butterfly pattern”.^{6,8} The butterfly pattern has also been observed in other polymer systems, e.g., stretched elastomeric block copolymer films, polymer gels, entangled polymer melts and silica colloids in polymer matrix, and is attracting much attention (see Sec. 1-1 in detail).²⁷⁻³⁵ It suggests that spatial heterogeneities of concentration fluctuations of polymer molecules, block copolymer microdomains or colloidal particles are enhanced in the direction

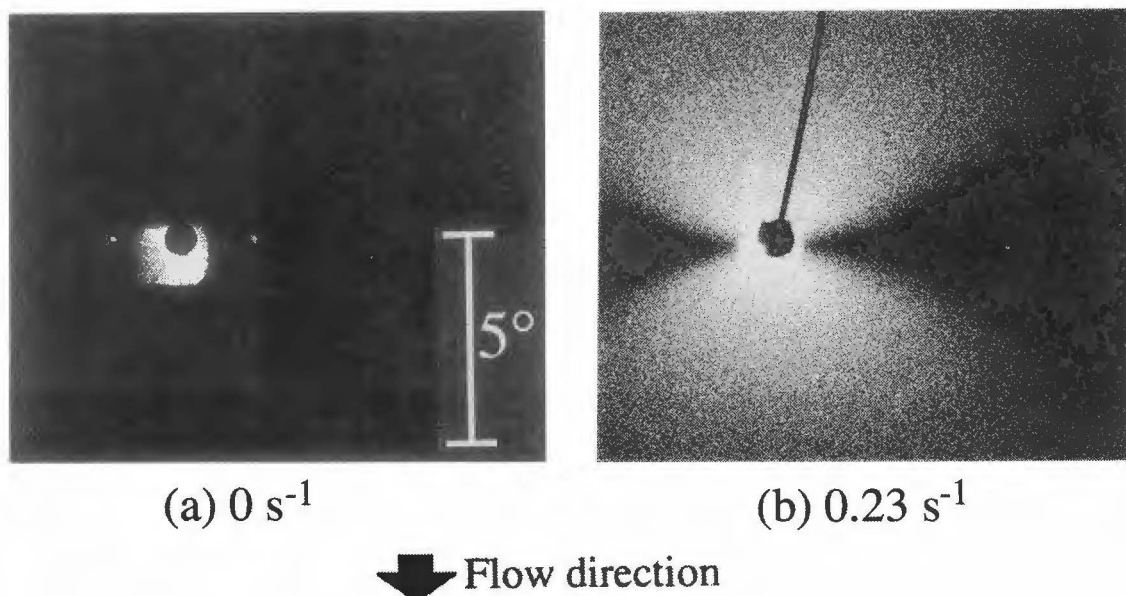


Figure 2-4 SALS patterns of a PS/DOP solution (6.0 wt%) show the features of the butterfly pattern at 27 °C: shear rate = 0 s^{-1} (a) and 0.23 s^{-1} (b). The halo around the beam stop at 0 s^{-1} is parasitic scattering.

of shear flow, while the heterogeneities remain essentially unaltered from the homogeneous solution in quiescent state in the direction perpendicular to shear flow, leading to a proposal⁸ of the model shown in Figure 2-5. Figure 2-5a schematically shows that the dark regions are clusters in semidilute polymer solution in the quiescent state which have higher polymer concentration and hence more entanglement points and which are less deformed than less entangled regions having lower polymer concentration (the bright region). In the quiescent state these clusters, which are generated by thermal concentration fluctuations, are undetectable by scattering because the intracluster correlations compensate (screen) exactly the intercluster correlations, as proposed by Bastide et al.³⁰ In shear flow the clusters are less deformed than the interstitial medium, resulting in separation of the clusters

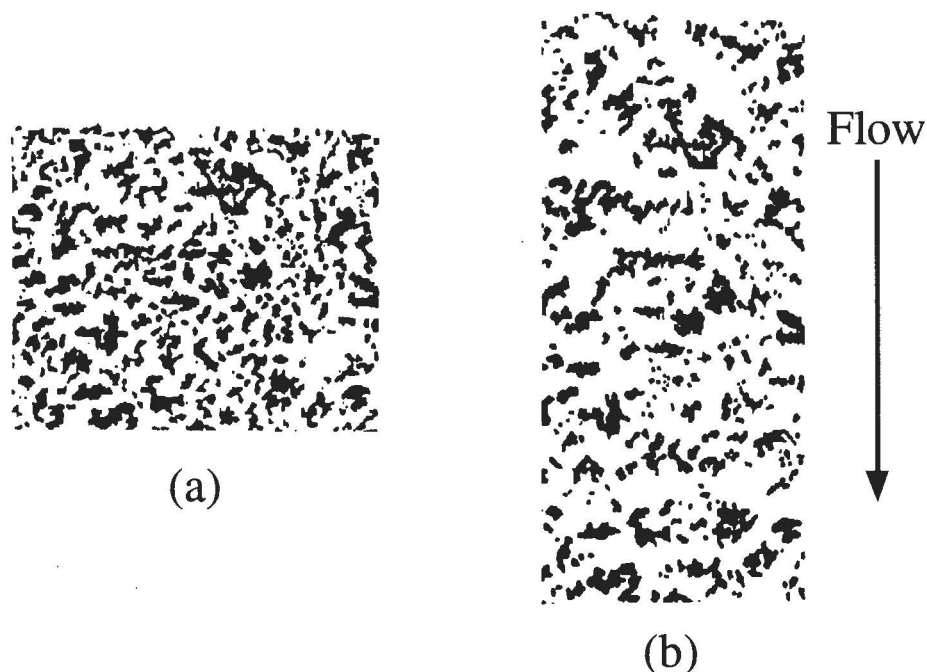


Figure 2-5 Sketches of concentration fluctuations in polymer solutions. The clusters (the dark regions containing more entanglements and less subjected to deformation) are shown in the quiescent state or at $\dot{\gamma} < \dot{\gamma}_c$ (a) and at $\dot{\gamma} > \dot{\gamma}_c$ (b), where $\dot{\gamma}_c$ is a critical shear rate above which shear-enhanced concentration fluctuations and scattering are observed.

parallel to the flow and higher interpenetration of the clusters perpendicular to it, as schematically shown in Figure 2-5b. Thus the clusters are detectable along the flow but remain undetectable normal to it. In other words, the concentration fluctuations are enhanced along the flow but remain unaffected or even suppressed normal to it, which explains the butterfly patterns observed in scattering experiments.

The microscope visualization of the structures in the flow is presented in Figure 2-6. The images of (a) and (b) are raw microscopic images at shear rates of 0 s^{-1} and 0.23 s^{-1} , respectively. Moreover, the images of (c) and (d) are contrast-enhanced images from those of (a) and (b), respectively. The

image of zero shear (c) has no distinctive features, but the image (d) under shear flow has some enhanced contrast variation and hence concentration fluctuations along the shear flow. The image (e) is filtered from the image (d) using a bandpass “Mexican hat” filter which causes both smoothing and edge detection. The size of the bandpass filter is selected, which correspond to the dominant structures using scattering information. Thus the image of (e) is that of the dominant structures at 0.23 s^{-1} . Furthermore, the thresholded image of (e) is the binary image (f). The binary image enables the distribution of waves at different angles to be calculated.²⁵

Nevertheless, it is important to confirm whether or not the structure observed in Figure 2-6d reflects the true structure occurring in the sheared solution. For this purpose the two-dimensional fast Fourier transform (2-D FFT) patterns were calculated from the structure in Figures 2-6c and 2-6d and the FFT patterns were compared with real scattering patterns. Figures 2-7a and 2-7b show 2-D FFT images corresponding to Figures 2-6c and 2-6d, respectively. To reconstruct the light scattering representation of q -space (wave number or Fourier space) of Figure 2-6, a logarithmic gray scale representation with constant contrast enhancement is used in Figure 2-7. It is evident that the calculated 2-D FFT patterns are basically similar to the patterns obtained by light scattering, showing that the microscopic image in Figure 2-6d is a true representation in real space of the butterfly-type scattering pattern. Thus the image in Figure 2-6d is believed to be the direct visualization of the concentration fluctuations induced by shear flow, which is obtained for the first time for this system. This image directly confirms the conjecture shown in Figure 2-5b from the light scattering pattern.

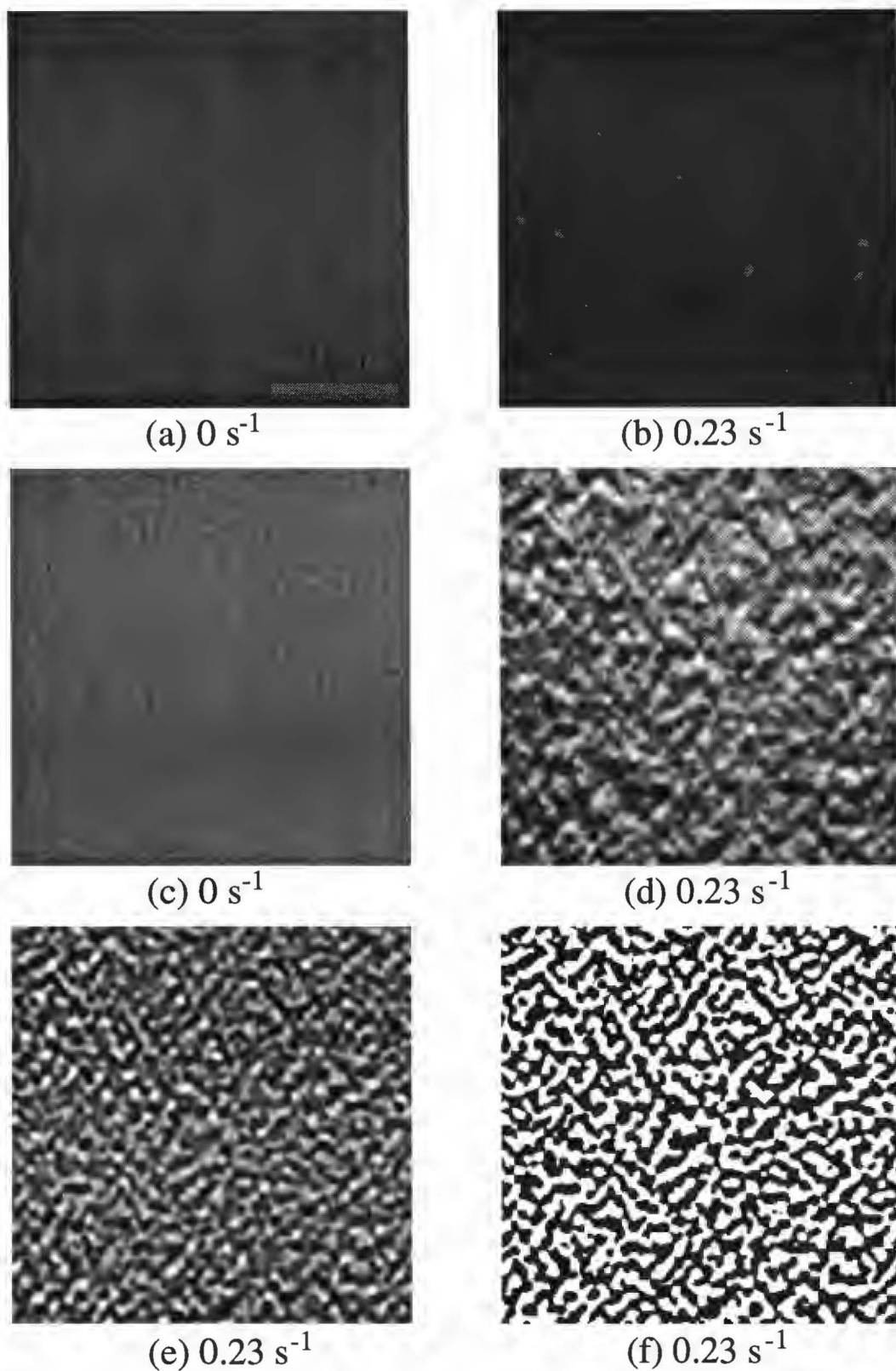


Figure 2-6 Microscopic images of the concentration fluctuations. (a, c) Quiescent state. (b, d, e, f) Shear rate 0.23 s^{-1} ($> \dot{\gamma}_c$). (a, b) Raw images. (c, d) Contrast-enhanced from (a) and (b), respectively. (e) Image of dominant fluctuations extracted from (d). (f) Binary image thresholding of (e).

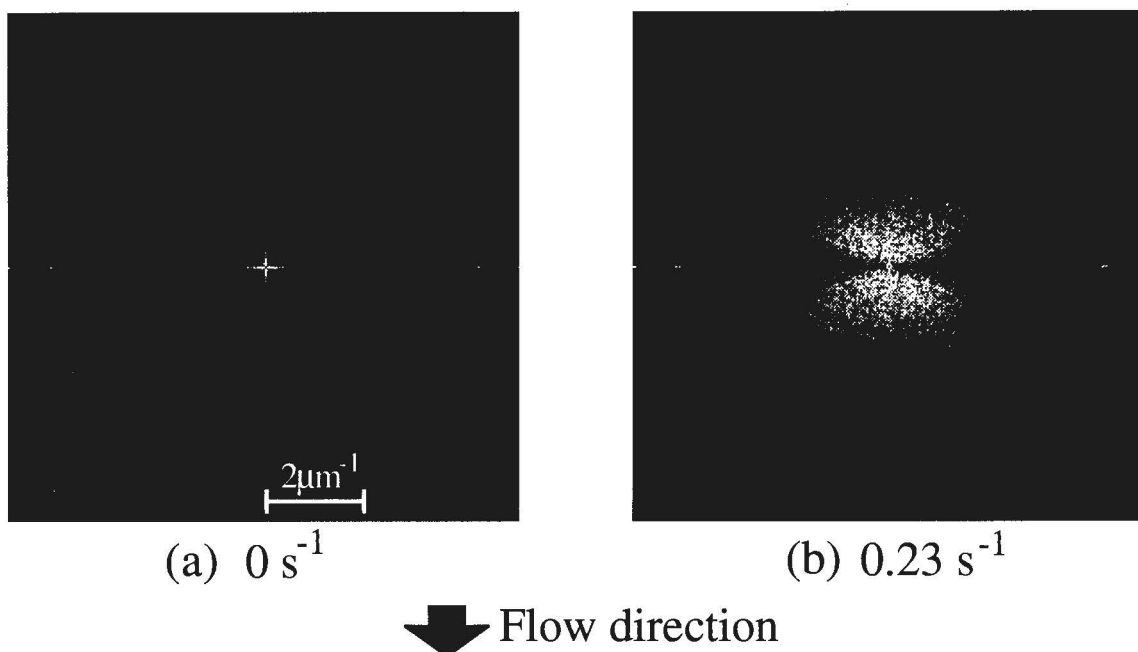


Figure 2-7 2D-FFT patterns. (a, b) Calculated from the microscopic images in Figures 2-6c and 2-6d, respectively. These images are basically similar to the patterns obtained by light scattering, shown in Figure 2-4.

Thus it has been demonstrated that images of concentration fluctuations of semidilute, high molecular weight polymer solutions can be directly taken under shear flow with shear-microscopy, and shown that the origin of the butterfly pattern is the existence of hydrodynamic modes (or ripples) or concentration fluctuations along the flow direction.

2-3-2. Shear-Induced Homogenization in Semidilute Solutions of a Polymer Mixture

Effects of the shear on ternary system consisting of polystyrene (PS), polybutadiene (PB), and dioctyl phthalate (DOP) were studied using the shear-

SALS apparatus previously constructed.^{4,5,11} Some models have been proposed for the structures occurring in the sheared solutions. These, however, have never been directly confirmed by real space analysis. Here the merits of using the apparatus for the solution with a near critical composition are demonstrated.⁴

PS with $M_w = 2.14 \times 10^5$ and heterogeneity index $M_w/M_n = 1.05$, and PB with $M_w = 3.13 \times 10^5$ and $M_w/M_n = 1.90$ were used. These samples were mixed at a ratio of 50/50 by weight (46/54 by volume), and a solution containing 3.3 wt% of the mixture in DOP was prepared. At this concentration, the ternary system satisfies $c/c^* \cong 2$, where c^* is the overlap concentration,²⁶ and its cloud point is at 74 °C in quiescent state. The experiment was done in the two-phase region at 66 °C ($\Delta T = 8$ K). More detailed results are described elsewhere.³⁶

Figure 2-8 shows a set of light scattering patterns obtained under different steady shear flows at shear rates between 0.0033 and 40 s⁻¹ recorded by the CCD camera. These patterns are the same as the patterns in the previous work (Figure 1 in ref. 5), indicating that those results are reproducible. According to the model of self-assembled domain structure in the previous work (Figure 14 in ref. 5 reproduced here as Figure 2-9.), the shear rate can be classified into five regimes from I to V by the scattering pattern variation. The shear rates between 0.0033 and 40 s⁻¹, which are treated here, correspond to regimes II, III and IV. These regimes are the two-phase regions below the critical shear rate $\dot{\gamma}_c (= 127 \text{ s}^{-1})$.¹¹ Though not shown here, in the regime I (i.e., quiescent state or very low $\dot{\gamma}$), the solution separated into two macroscopic phases, a PB-rich DOP solution (on top) and a PS-rich DOP solution (below

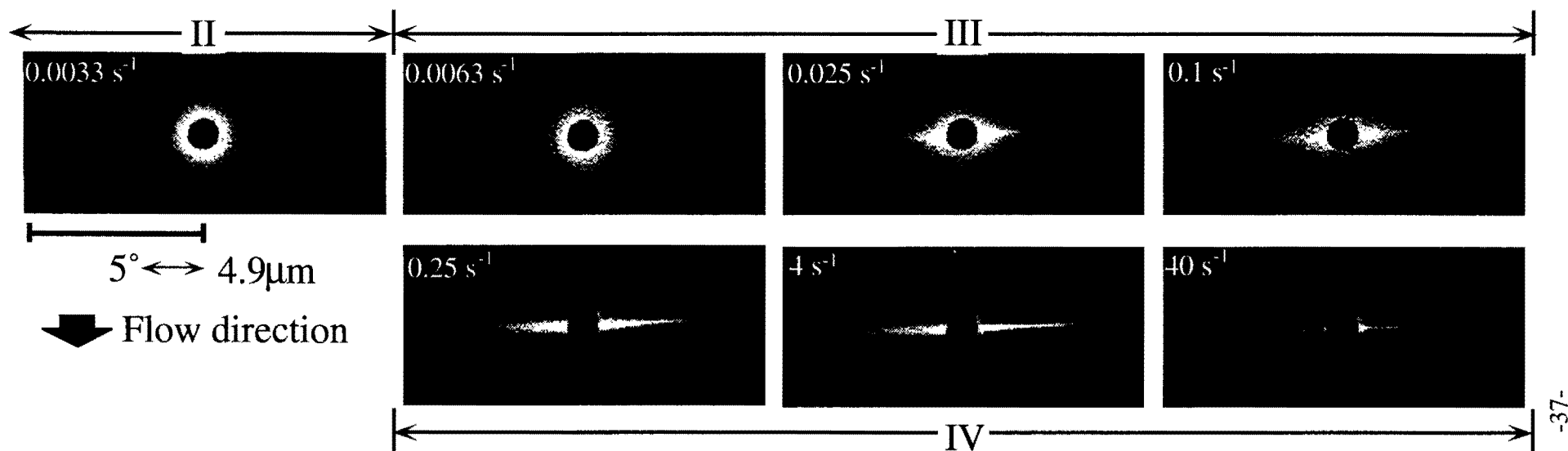


Figure 2-8 SALS patterns of a PS/PB/DOP system at different shear rates (s^{-1}) under steady shear flow. The ratio of PS to PB is 50:50. The concentration of polymers is 3.3 % by weight. The temperature is 66°C , which is 8 K lower than the cloud point. Regime II, III and IV are the two-phase regions below the critical shear rate $\dot{\gamma}_c (= 127 \text{ s}^{-1})$. Regime II is the low shear region, $0 < \dot{\gamma} < 0.0063 \text{ s}^{-1}$. Regime III is $0.0063 < \dot{\gamma} < 0.25 \text{ s}^{-1}$. Regime IV is the high shear region, $0.25 \text{ s}^{-1} < \dot{\gamma} < \dot{\gamma}_c$.

it). In regime II (the low shear region, $0 < \dot{\gamma} < 0.0063 \text{ s}^{-1}$), the scattering patterns are circular, so it is expected that the domains are isotropic. In regime III ($0.0063 < \dot{\gamma} < 0.25 \text{ s}^{-1}$), the scattering patterns are elongated in the direction normal to shear flow, hence domains are elongated in the direction of shear flow. In regime IV (the high shear region, but lower than $\dot{\gamma}_c$), the elongated scattering patterns change into sharp streaks perpendicular to the flow direction. This suggests that the elongated domains change into long percolated structures oriented along the flow direction. Furthermore, the lateral size of the elongated domains and the contrast between domains and matrix decrease with increasing $\dot{\gamma}$, and eventually shear-induced single phase formation occurs in regime V ($\dot{\gamma} > \dot{\gamma}_c$). However, it was previously impossible to obtain direct images of these structures.

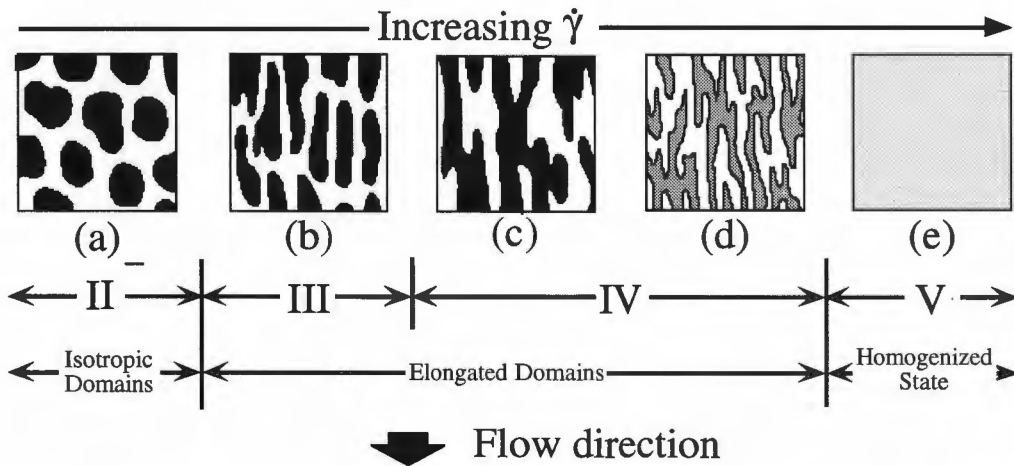


Figure 2-9 Schematic summary of the self-assembled domain structures deduced from the SALS results in previous experiments. This figure is the same as Figure 14 in ref. 5. The flow direction is vertical in the panels (a) to (e). The definition of regime II, III and IV are the same as for Figure 2-8. Regime V is the one phase region (homogenized state) above the critical shear rate $\dot{\gamma}_c$ ($= 127 \text{ s}^{-1}$).

Figure 2-10 shows the variation of the structures of the same solution as what used for the shear-SALS (Figure 2-8) under steady shear observed by the shear-microscopy. The same solution was simultaneously observed by the shear-SALS and the shear-microscopy. These images indicate that domains changed from spherical droplets into long elongated domains oriented along the flow direction. At the lowest shear rate, $\dot{\gamma} = 0.0033 \text{ s}^{-1}$ (regime II), structures in the sample are spherical domains. At the shear rate between $\dot{\gamma} = 0.0063$ and 0.1 s^{-1} (regime III), domains are elongated along the shear direction. At the shear rate above 0.25 s^{-1} (regime IV), domains are elongated much more, and change into string-like domains which extend along the flow direction. Since the sample composition is PS/PB 50/50 wt%, the sample structure is expected to be bicontinuous or percolated at $\dot{\gamma} = 0.0033 \text{ s}^{-1}$ (regime II). However, note that the ratio of two phases in Figure 2-10 is not 46/54 vol%, the ratio of polymer components dissolved into DOP solution. In this case the two coexisting phases are PS-rich phase (solution) and PB-rich phase (solution). It was found that the ratio of PS-rich phase to PB-rich phase is ca. 40/60 vol% after the solution completes phase separation and gravity divides it into top (PB-rich) and bottom (PS-rich) solution phases, i.e., after it has been kept for a few weeks at the measuring temperature. This is because the PS/PB/DOP phase diagram is not symmetrical, in a way that makes the dispersed domains and matrix the PS-rich phase and PB-rich phase, respectively, at lower shear rates. This expectation was proven by transmission optical microscopy with the solution stained by OsO_4 .³⁶ In the high shear regime (regime IV), however, their ratio probably changes, because of a downward shift of the coexistence curve with shear.¹¹

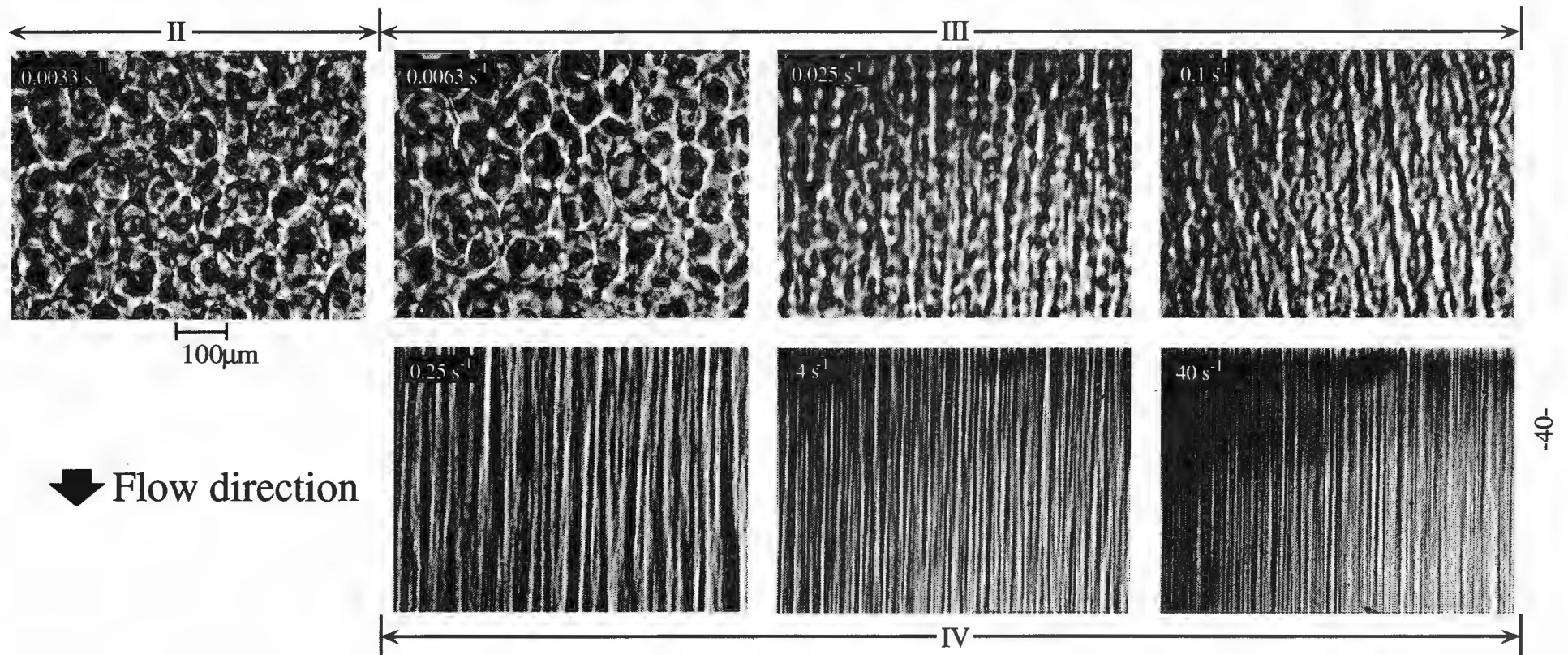


Figure 2-10 Microscopic images at different shear rates under steady shear flow. The sample and experimental conditions are the same as those in Figure 2-8.

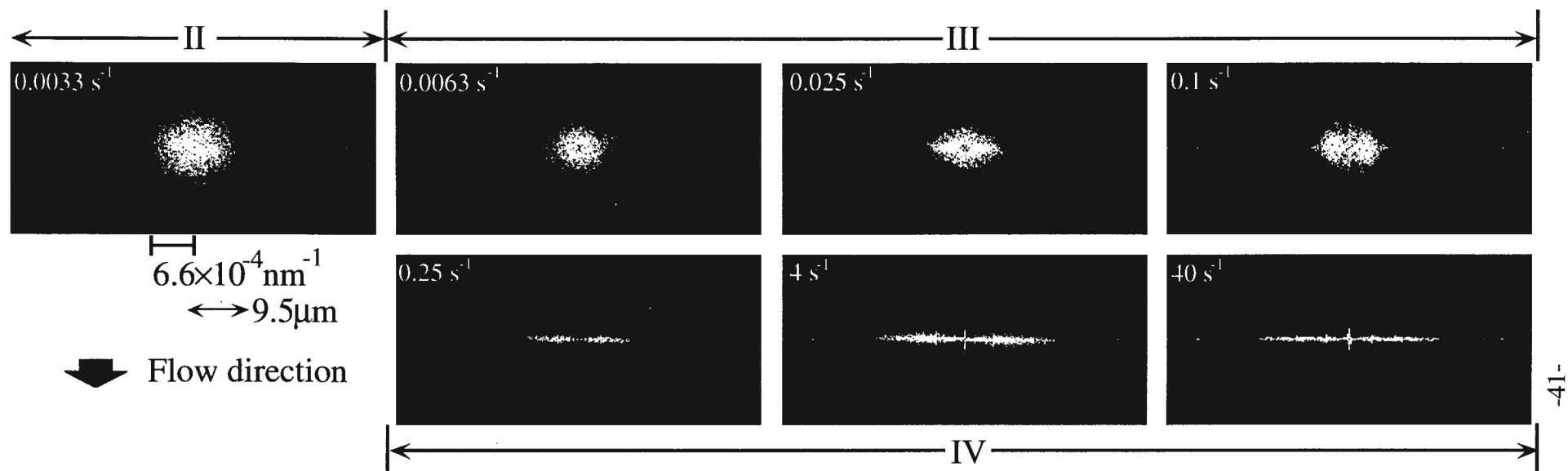


Figure 2-11 2D-FFT patterns calculated from the visualization images in Figure 2-10. These images are basically similar to the patterns obtained by light scattering in Figure 2-8.

Figure 2-11 shows 2-D FFT patterns calculated from images of Figure 2-10 which are consistent with the corresponding SALS pictures in Figure 2-8. Therefore it was able to confirm again that the images captured really reflect the domain structures in the sample under shear flow. Thus the combined shear-microscopy and shear-SALS technique gives a new model, as shown in Figure 2-12. The schematic pictures (a), (b), (c), and (f) are same as those (a), (b), (c), and (e) in Figure 2-9, respectively. However, the picture (d) in Figure 2-9 should be replaced by the pictures (d) and (e) in Figure 2-12. These latter pictures constitute new models in Regime IV which the shear-microscopy study indicates. In this regime, the string-like domains oriented along the shear flow can be macroscopically long while their diameters are less than 10 μm . The contrast between the two phases becomes weak and the diameter of the strings become small with further increasing shear rates, as shown in (d)

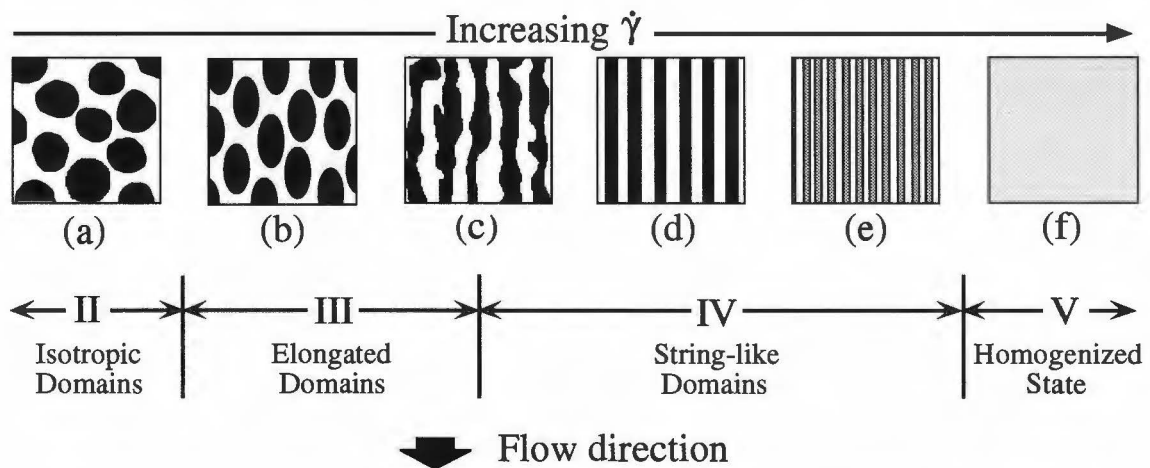


Figure 2-12 Summary of the self-assembled domain structures observed by shear-microscopy under steady state shear flow. The flow direction is vertical in the panels (a) to (f). The new model adds the new features as shown in the panels (d) and (e) in Figure 2-12 to the previous model obtained by the shear-SALS (Figure 2-9).

and (e) in Figure 2-12. Surprisingly the surface undulation of the strings is very much suppressed at higher shear rates in Regime IV. In summary, it was able to confirm and add detail to the previous model describing a solution of polymer mixtures under the shear flow with the use of shear microscopy.

In these experiments, it was also found a limit for using shear-microscopy. When the shear rate is higher than 100 s^{-1} , even using a shutter speed of $1/10000 \text{ s}$, the pattern travels about $10 \text{ }\mu\text{m}$ during the exposure time, and it is difficult to image the supramolecular structure of the sample by means of CCD, not only because the contrast between two phases becomes too weak to capture the images, but also because the spatial structures quickly move away from the sight of microscope at high shear rate. However it is still possible to explore the development of the supramolecular structure in the polymer solutions at high shear rate using shear-SALS.

2-4. Summary

The new apparatus which simultaneously provides information by using shear-SALS and shear-microscopy was introduced. It was shown that the shear-microscopy technique enabled us to observe the concentration fluctuations and its structure formation induced by shear flow more directly and exactly than using shear-SALS alone. Thus both shear-SALS and shear-microscopy techniques complementarily helped us to investigate the development of the supramolecular structures in polymeric systems under shear flow.

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Chapter 3

“Butterfly” Light Scattering Pattern and Shear-Enhanced Concentration Fluctuations in Polymer Solutions and Anomalies at High Shear Rates

3-1. Introduction

An intriguing phenomenon has been reported recently on shear-induced turbidity and a related change of rheological behavior in semidilute polymer solutions.¹⁻⁷ This shear effect has been theoretically interpreted as thermodynamic instability of the solutions induced by shear stretching of polymer coils.^{1,3,5,8-12} To gain insight into the physics underlying this non-equilibrium phenomenon, some attempts have been made to investigate, by scattering methods,¹³⁻¹⁵ the structure factor of the solutions subjected to shear flow. As a first trial, some results on shear-small-angle light scattering experiments for semidilute solutions of high molecular weight polystyrene (PS) in dioctyl phthalate (DOP) were reported.¹³ Recently it was found that the scattering pattern appearing upon increasing the shear rate $\dot{\gamma}$ has a unique feature, designated as the “**butterfly pattern**”, in that the pattern has a strong intensity along the flow and a “**dark streak**” normal to it. In this chapter this butterfly pattern is analyzed and similarities and dissimilarities with the butterfly pattern reported for small-angle neutron scattering (SANS) from

swollen and stretched polymer gels¹⁶⁻¹⁸ are presented.

3-2. Experimental Section

The polystyrene used in this study, coded PS548, has a weight-average molecular weight M_w of 5.48×10^6 and a heterogeneity index $M_w/M_n = 1.15$ where M_n is the number-average molecular weight. Solution containing 6.0 wt% of PS548 was prepared using dioctyl phthalate (DOP) as a solvent. The value of c/c^* was about 40, where c^* is the overlap concentration. The cloud point of the solutions were determined by the same method as described previously¹³ and was 13.8 °C.

The apparatus,^{19,20} the optical setup and coordinate system used in this chapter were the same as those previously used (see Figure 1-3, 1-4, 1-5 and 1-6 in Chapter 1). Simple shear flow was generated with a cone-and-plate rheometer where the flow direction is taken along the Ox axis, the velocity gradient exists in the plane of Oxy , and the Oy axis is along the velocity gradient. The incident beam was sent along the Oy axis and the scattering intensity distribution was observed in the Oxz plane as a function of the scattering vector $\mathbf{q} = (q_x, q_z)$, where $\mathbf{q}$ is defined by $|\mathbf{q}| = (4\pi/\lambda)\sin(\theta/2)$, λ and θ are the wavelength of light and the scattering angle in the medium, respectively, and q_x and q_z are the x - and z - components of $\mathbf{q}$.

The scattered intensity distribution $I(\mathbf{q}) = I(q_x, q_z)$ was qualitatively detected by a photographic film or by a CCD camera and a dynamic image digitizing system constructed in our laboratory. A linear photodiode array detector with 35 pixels (1 mm/pixel) was used for quantitative measurements

of $I(\mathbf{q})$. The detector was rotated in the Oxz plane to measure the intensity distributions, $I_{//}(\mathbf{q}) \equiv I(q_x = q, q_z = 0)$ and $I_{\perp}(\mathbf{q}) \equiv I(q_x = 0, q_z = q)$, parallel and normal to the flow direction, respectively. To avoid smearing of $I(\mathbf{q})$ along the window height (10 mm) of the photodiode array, a height-limiting slit with a 2 mm width was placed in front of the photodiode array. The temperature enclosure for the shear cell was improved to attain better temperature control. The temperature was held constant to within ± 0.1 °C. The rheological experiments were performed using a Rheometrics® Mechanical Spectrometer 605. A cone-and-plate geometry was used, and both the shear stress and the first normal stress difference were measured. Most experiments were performed with a cone angle of 0.04 rad.

3-3. Results and Discussion

Figure 3-1 shows the steady state properties of PS548/DOP 6.0 wt% at 27 °C as a function of $\dot{\gamma}$. $\mathcal{I}_{//}(\dot{\gamma})/\mathcal{I}_{//}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma})/\mathcal{I}_{\perp}(\dot{\gamma}=0)$ are, respectively, the integrated scattered intensity of the solution at a given $\dot{\gamma}$ parallel and perpendicular to the flow direction, normalized with respect to the respective integrated intensity of the quiescent solution. The integrated intensity was defined previously.¹³ (see equation 5-1 and 5-2 in Sec. 5-3.) η and ψ_1 are the shear viscosity and the coefficient of the first normal stress difference. The steady state properties were measured at more than $20/\dot{\gamma}$ s after the specified shear rate was attained in the cycle of increasing the shear rate from the quiescent state.

The scattering and rheological behaviors as a function of $\dot{\gamma}$ can be

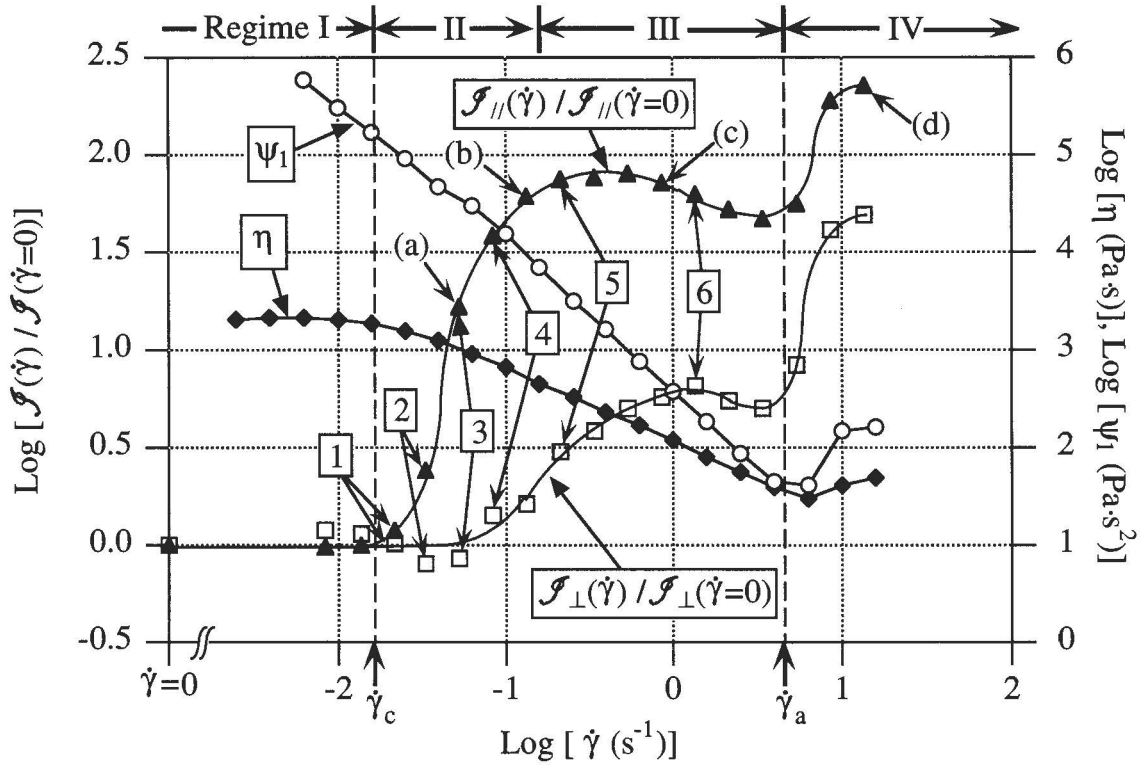


Figure 3-1 Shear viscosity η , coefficient of the first normal stress difference ψ_1 , normalized integrated scattered intensity parallel and perpendicular to the flow, $\mathcal{J}_{||}(\dot{\gamma}) / \mathcal{J}_{||}(\dot{\gamma}=0)$ and $\mathcal{J}_{\perp}(\dot{\gamma}) / \mathcal{J}_{\perp}(\dot{\gamma}=0)$, as a function of shear rate $\dot{\gamma}$ in steady state simple shear flow. $\dot{\gamma}_c$ and $\dot{\gamma}_a$ are the critical shear rates for the onset of the shear-enhanced concentration fluctuations and of the anomalies in the rheological and scattering behaviors.

classified into four regimes, as shown in Figure 3-1. In Regime I the concentration fluctuations, and hence the scattering, are essentially identical to those in the quiescent state, and η is nearly independent of $\dot{\gamma}$. Regimes II to IV exist at $\dot{\gamma} > \dot{\gamma}_c$, a critical shear rate above which shear-enhanced concentration fluctuations and scattering are observed concurrently with the decrease of η and ψ_1 . The scattering strongly depends on the direction of observation, $\mathcal{J}_{||}$ being much stronger than $\mathcal{J}_{\perp}$. In Regime II, a dramatic shear-enhanced scattering occurs along the flow direction, as seen by an approximately 100-

fold increase of $\mathcal{J}_{||}$. The intensity $\mathcal{J}_{\perp}$ normal to the flow tends to be slightly **suppressed** in the beginning and then enhances with further increase of $\dot{\gamma}$. In Regime III, $\mathcal{J}_{||}$ does not vary much with $\dot{\gamma}$, while $\mathcal{J}_{\perp}$ still gradually increases with increasing $\dot{\gamma}$, and the values of η and ψ_1 keep decreasing. In Regime IV (at $\dot{\gamma} > \dot{\gamma}_a$), an anomaly is observed in both the scattering and rheological behaviors. The **scattering anomaly** is the strong increase of the intensity of both $\mathcal{J}_{||}$ and $\mathcal{J}_{\perp}$ above $\dot{\gamma}_a$, the shear rate above which the anomaly starts to develop. This **second-stage enhancement** of the intensity at $\dot{\gamma} > \dot{\gamma}_a$, in contrast to the **first-stage enhancement** of the intensity at $\dot{\gamma} > \dot{\gamma}_c$, is accompanied by **rheological anomalies**. Upon increasing $\dot{\gamma}$ into Regime IV from a lower shear rate, both η and ψ_1 momentarily increase dramatically. In the original paper of this chapter,¹³ it was stated that there is no anomaly in η even in Regime IV for the PS548/DOP 6.0 wt% solution (though there is a definite anomaly in ψ_1), because the first overshoot of shear stress decays to the level expected from the $\dot{\gamma}$ -dependence of η in the lower $\dot{\gamma}$ regime, if the solution is kept under shear. However it was found that this solution exhibits the second overshoot on its approach toward steady state, if the solution is kept under shear even longer and that the steady state values are larger than those reported previously. Therefore this solution was found to exhibit the anomaly in both η and ψ_1 , as shown in Figure 3-1 and Yanase et al.¹⁵ The anomaly is also observed as an upturn of the steady state value of ψ_1 with increasing $\dot{\gamma}$. A large transient stress overshoot was also observed in the first normal stress difference. The steady state value of ψ_1 (more than $10^2 \text{ Pa}\cdot\text{s}^2$) at the highest shear rate is the lower limit of the true value, i.e., ψ_1 is larger than this value but measurement was stopped beyond the range of this apparatus.

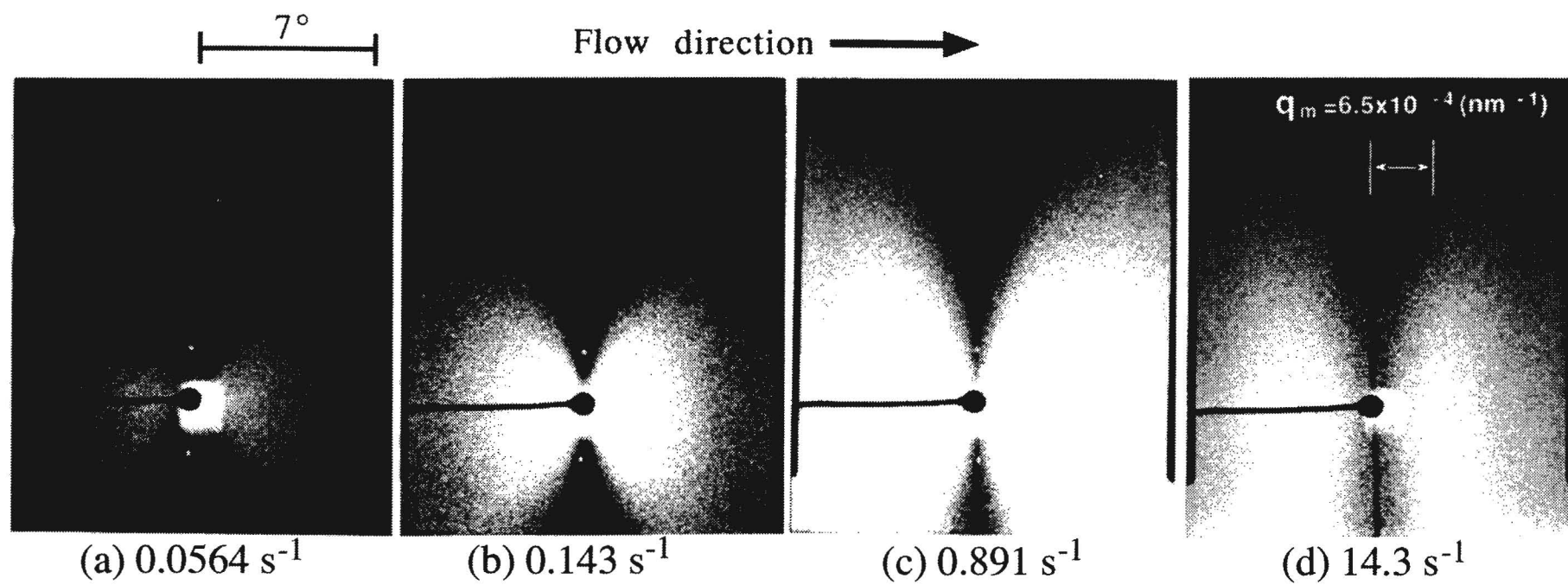


Figure 3-2 Steady state scattering patterns at various shear rates.

A characteristic change of the steady state scattering pattern with shear is shown in Figure 3-2 where patterns (a) - (d) were obtained at $\dot{\gamma}$ marked (a) - (d) in Figure 3-1, and the flow direction was horizontal in the figure. Each pattern was taken with an exposure time of 1/30 s, except for pattern (d) for which the exposure time was 1/500 s. The scattering pattern in Regime I shows no appreciable scattering on the photograph and hence is not included in Figure 3-2. At $\dot{\gamma} > \dot{\gamma}_c$, strong anisotropic scattering appears. Patterns (a) - (c) have the same “butterfly” characteristics as reported previously,¹³ a strong intensity parallel to the flow direction and the dark streak normal to it. The butterfly pattern changes its shape in Regime II, its wings becoming wider with increasing $\dot{\gamma}$ (patterns (a) and (b)). In Regime III its shape is essentially unchanged (pattern (c)), except for a sharpening of the dark streak with increasing $\dot{\gamma}$. In Regime IV, where the anomalies were observed, the butterfly pattern is changed into an “**elongated two-point pattern**” (pattern (d)) which has a broad scattering maximum along the flow direction at $q_x = q_{mx} \cong 6.5 \times 10^{-4} \text{ nm}^{-1}$. The two-point pattern is elongated normal to the flow so that the scattered intensity $I(q_x=q_{mx}, q_z)$ only weakly depends on q_z . The scattering maximum implies that a pseudoperiodic structure with a spacing of $2\pi/q_{mx} = 9.7 \text{ } \mu\text{m}$ is formed along the flow direction. It is impressive that there still remains a very sharp dark streak normal to the flow.

The scattering intensity distributions, $I_{//}(q)$ and $I_{\perp}(q)$, measured quantitatively with the photodiode array detector, displayed on a double-logarithmic scale in Figure 3-3 where $I_{\perp}(q)$ is shown by the data points with open circles or asterisk and $I_{//}(q)$ is shown by the data points with filled diamonds. Curves 1 to 6 were obtained at the shear rates marked 1 to 6 in

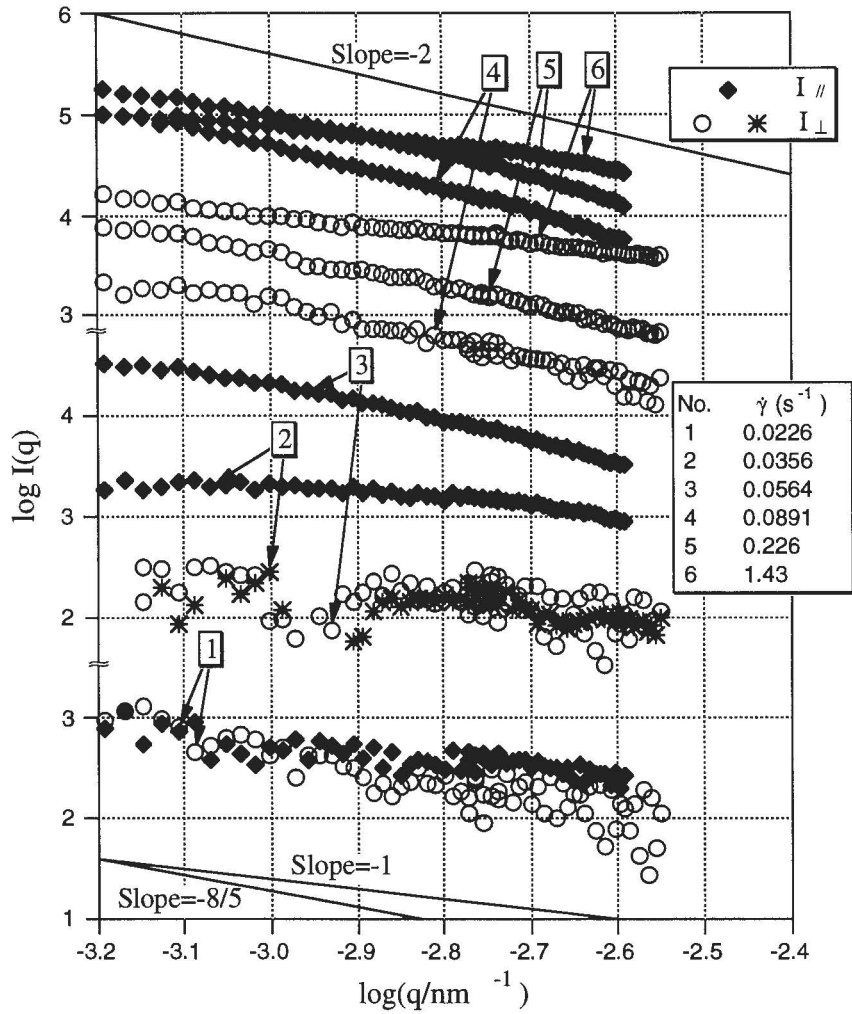


Figure 3-3 Double-logarithmic plots of the intensity distributions with q , parallel ($I_{||}$) and perpendicular to the flow ($I_{\perp}$).

Figure 3-1. Thus curves 2 to 4 correspond to the shear rates in Regime II, while curves 5 and 6, to the shear rates in Regime III. At $\dot{\gamma} < \dot{\gamma}_c$, the scattering is weak and directionally independent, characteristic of scattering from homogeneous semidilute solutions (curve 1 in Regime I). However, at the shear rates in Regime II, anisotropy of the scattering increases, as seen in curves 2 to 4, $I_{||}/I_{\perp}$ increasing from about 10 for curve 2 to 100 for curves 3 and 4. The anisotropy tends to decrease with further increase of $\dot{\gamma}$, as seen in curves 5 to 6.

A dramatic increase of $I_{//}(q)$ with increasing $\dot{\gamma}$ is obvious, and a similar trend is also observed for $I_{\perp}(q)$, except for $I_{\perp}(q)$ at the lower shear rates of 0.0356 and 0.0564 s⁻¹ (curves 2 and 3, respectively). The intensity $I_{\perp}$ at these shear rates tends to become lower than $I_{//}$ or $I_{\perp}$ at $\dot{\gamma} = 0.0226$ s⁻¹, consistent with the decrease of $\mathcal{F}_{\perp}(\dot{\gamma}) / \mathcal{F}_{\perp}(\dot{\gamma}=0)$ in Figure 3-1, despite the fact that $I_{//}$ dramatically increases with $\dot{\gamma}$. $I_{\perp}$ at these shear rates tends to have a weaker q -dependence than at the smaller rate of 0.0226 s⁻¹. The decrease of $I_{\perp}$ and of its q -dependence suggest that the thermal correlation length $\xi_{\perp}$ for the concentration fluctuations normal to the flow decreases with $\dot{\gamma}$. The decrease of $\xi_{\perp}$, in turn, may imply that the solution tends to become more homogeneous in the direction normal to the flow with increasing $\dot{\gamma}$. The curves for both $I_{//}(q)$ and $I_{\perp}(q)$ at different $\dot{\gamma}$ in Regime II were found to be superposable by horizontal and vertical shifts on the double-logarithmic scale. The shear-rate dependence of the shift factors for $I_{//}(q)$ suggests that the correlation length $\xi_{//}$ for the concentration fluctuations along the flow increases with increasing $\dot{\gamma}$, while that for $I_{\perp}(q)$ suggests that the correlation length $\xi_{\perp}$ decreases with increasing $\dot{\gamma}$. In all cases the scattering shows only very weak q -dependence both parallel and perpendicular to flow over the q -range covered, which may be a consequence of the fact that a part of the simple Lorentzian or squared Lorentzian scattering functions²¹ or of the scattering function predicted for the gels¹⁶ is being just observed.

The unique features of our butterfly patterns, especially those found in Regime II, may be qualitatively interpreted on the basis of the model proposed for uniaxially stretched swollen gels.¹⁶⁻¹⁸ Our butterfly was observed for entangled semidilute solutions subjected to steady state shear at $\dot{\gamma}$ satisfying

$\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$, whilst the butterfly for the gels was seen for randomly cross-linked semidilute solutions subjected to uniaxial stretching. Our butterfly was observed by light scattering (LS) with the q -range from approximately 6×10^{-4} to $3 \times 10^{-3} \text{ nm}^{-1}$, whilst the other butterfly was observed by SANS with the q -range from about 3×10^{-2} to $3 \times 10^{-1} \text{ nm}^{-1}$. Both butterflies have common features, as summarized in parts (a) and (b) of Figure 3-4: a strong enhancement of the scattered intensity parallel to the flow (or stretching) direction, but the scattered intensity normal to it is unaffected or even suppressed by the applied fields.

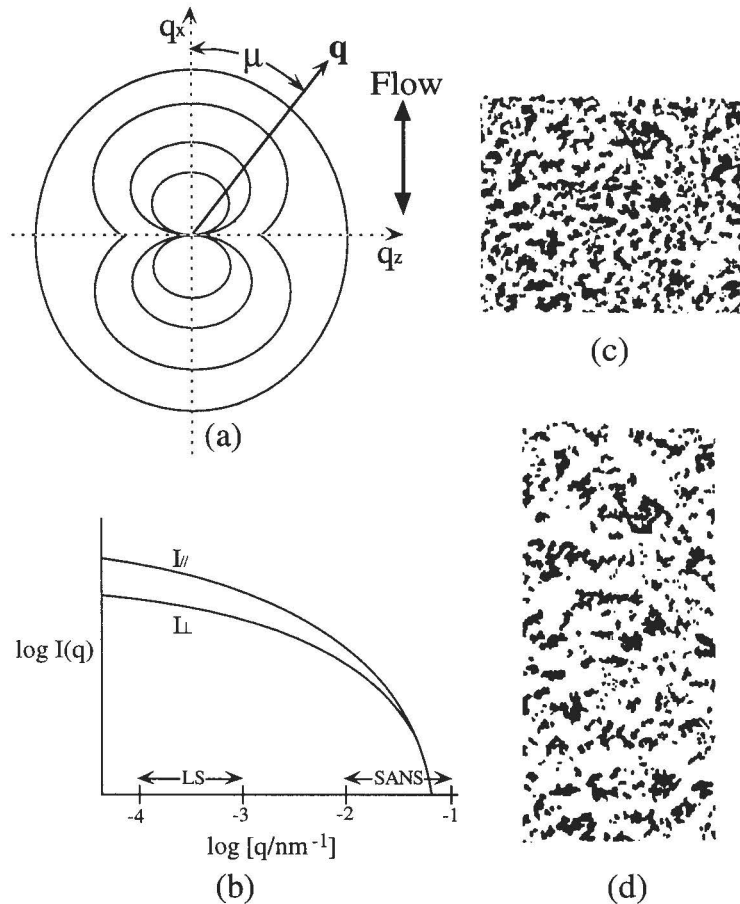


Figure 3-4 (a) Sketches of butterfly pattern, (b) the intensity distributions $I_{\parallel}(q)$ and $I_{\perp}(q)$, clusters (the dark regions containing more entanglements and less subjected to deformation) (c) in the quiescent state or at $\dot{\gamma} < \dot{\gamma}_c$ and (d) at $\dot{\gamma} > \dot{\gamma}_c$.

Corresponding to the clusters in the gels¹⁶ which contain more cross-linking points and which are less deformed than less cross-linked interstitial regions, there are clusters in our semidilute solution which have higher polymer concentrations and hence more entanglement points and which are less deformed than less entangled regions, as schematically shown by the dark regions in Figure 3-4(c). In the quiescent state these clusters which are generated by thermal concentration fluctuations are undetectable by scattering because the intracluster correlations compensate (screen) exactly the intercluster correlations, as proposed by Bastide et al.¹⁶ In our systems there exists coupling⁹⁻¹² between concentration fluctuations and stress as a result of the concentration dependence of viscosity and normal stress coefficients. In this situation the clusters are less deformed than the interstitial medium, resulting in separation of the clusters parallel to the flow and higher interpenetration of the clusters perpendicular to it, as schematically shown in Figure 3-4(d). Thus the clusters are detectable along the flow but remain undetectable normal to it. In other words, the concentration fluctuations are enhanced along the flow but remain unaffected or even suppressed normal to it, which explains the butterfly patterns. The weak q -dependence of $I_{//}$ and $I_{\perp}$ and the increase of $\xi_{//}$ and the decrease of $\xi_{\perp}$ with increasing $\dot{\gamma}$ are consistent with this prediction of the percolation cluster model proposed for stretched swollen gels.¹⁶

There are fundamental differences in the two systems. In our system concentration fluctuations are built up by coupling between the fluctuations and stress,⁹⁻¹² viz., chains are not permanently cross-linked, thus a part of the more stretched chains in the interstitial medium having lower local

concentrations has the freedom to make “**uphill diffusion**” into the clusters which have higher concentrations, more entanglements and less stretched chains. The uphill diffusion relaxes the cost of free energy due to chain stretching by flow and enhances a further build up of concentration fluctuations and a growth of the cluster domains, resulting in intensity increases of a factor of 100 in Regime III or 250 in Regime IV. For the gels, however, uphill diffusion is essentially hindered because of the permanent cross-links, and hence the enhancement of the scattered intensity is limited to several times that for the unstretched gels.¹⁶⁻¹⁸ The concentration fluctuations are convected under the shear flow in such a way that the wave vector of each Fourier component changes length and rotates.⁹⁻¹² This convection may be a possible origin of the dark streak along the Oz direction. This dark streak was not reported for uniaxially stretched gels.

In addition to the fundamental difference discussed above, there is another difference in the two butterfly patterns: the azimuth-angle (μ) dependence of scattering intensity at a given q tends to decrease with increasing q so that the iso-intensity contour at a higher q becomes more or less circular for the SANS patterns from the gels, whilst the μ -dependence is strong over all q 's for the LS patterns from our solutions. The difference may be partially attributed to the difference in q -region covered in the two experiments, as seen in Figure 3-4(b).

The increase in the intensity $I_{\perp}$ with $\dot{\gamma}$ in Regimes III and IV may be a consequence of an increasing degree of unscreening of the intracluster correlations (from the intercluster correlations) even in the direction normal to flow. A possible mechanism of the lateral unscreening is schematically

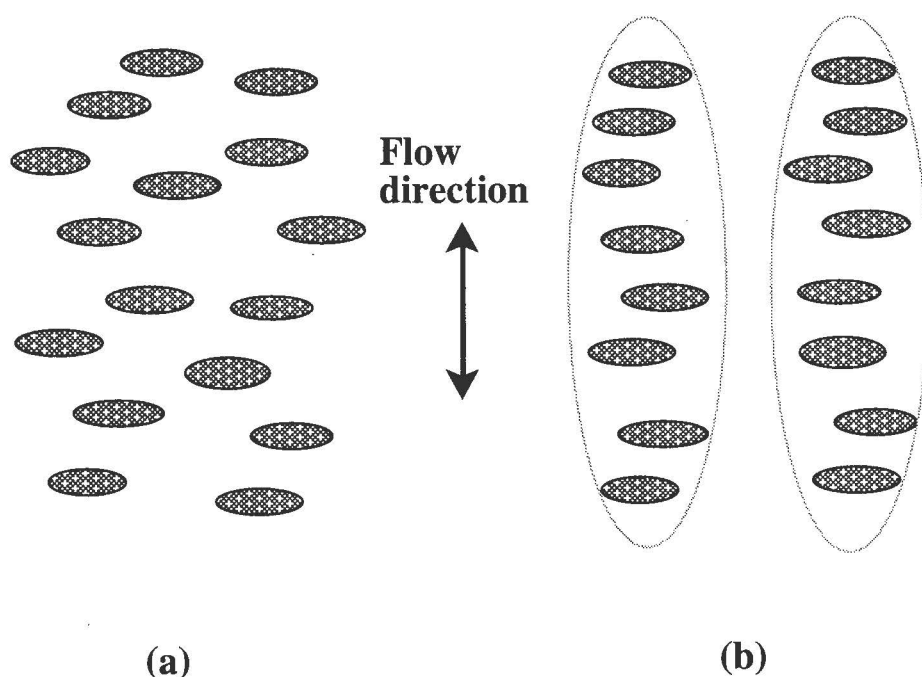


Figure 3-5 Sketches showing a possible mechanism of unscreening of the intracluster correlations in the direction normal to flow, (a) screened and (b) unscreened. The dark regions schematically correspond to the clusters shown in Figure 3-4(d).

presented in Figure 3-5 where part (a) has screening in the lateral direction but unscreening along the flow, whilst part (b) shows unscreening in both directions. The lateral unscreening may develop rows of clusters oriented parallel to the flow, as shown in Figure 3-5(b), the tendency of which is experimentally confirmed in the pattern shown in Figure 3-6 for the sheared solution with a lower concentration, PS548/DOP 3.0 wt%. The pattern at $\dot{\gamma} = 89.1 \text{ s}^{-1}$ ($> \dot{\gamma}_c$) exhibits the sharp bright streak at $q_x = 0$ and normal to the flow, superposed on the butterfly pattern. This streak scattering may arise from the assembly of a row of clusters developed along the flow and may be associated with the positive form dichroism at high shear rates or with the change of sign with increasing shear rates in the rheo-optical studies reported by Yanase

et al.¹⁵ (I will discuss experiments of PS548/DOP 3.0 wt% in Chapter 5 and shear-dichroism and birefringence of PS/DOP system in Chapter 7. See these chapters for details.) The lateral unscreening should occur more readily with decreasing concentration and for the uncross-linked semidilute solutions composed to the cross-linked gels.

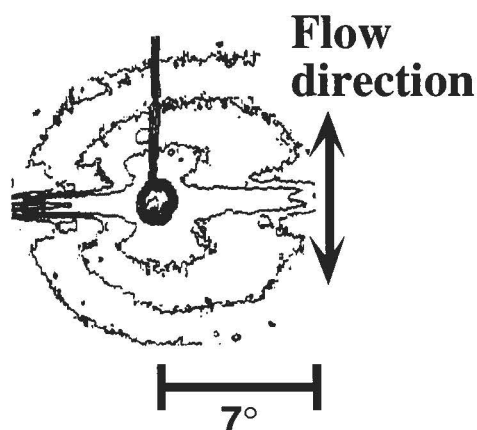


Figure 3-6 Isointensity contour pattern for the butterfly pattern with a sharp bright streak normal to flow, observed for PS548/DOP 3.0 wt% at $\dot{\gamma} = 89.1 \text{ s}^{-1}$ and at 25 °C.

3-4. Summary

The butterfly-type light scattering patterns and anomaly in scattering and rheological behavior at high shear rates in a semidilute polystyrene solution under shear flow were presented. The scattering and rheological behaviors were classified into four regimes depending on shear rate. The butterfly pattern also changed into the elongated two-point pattern at high shear rate (in Regime IV at $\dot{\gamma} > \dot{\gamma}_a$), and its intensity increased substantially. These scattering anomalies are believed to relate to those in rheological behavior.

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Chapter 4

Shear-Microscopy of the “Butterfly Pattern” in Polymer Mixtures

4-1. Introduction

Shear-induced phase separation is one of the striking results of combining hydrodynamics with the special elastic and viscous properties of polymers, and has been the center of a concentrated effort in recent years.¹⁻¹¹ It originates in the profound effects of entanglement and coil stretching upon the flow of semidilute, high molecular weight polymer solutions. While our notion of mixing by shear flow is intuitively consistent with shear-induced homogenization in lower molecular weight systems,¹²⁻¹⁴ the appearance of systems where shear induces phase separation was quite remarkable. When shear-induced phase separation was first observed experimentally,^{1,2} it was attributed to an elastic term in the free energy.² Such a contribution could move the critical curve sufficiently to allow phase separation at elevated temperatures. More recently, Helfand and Frederickson (HF) suggested³ that this separation is not a thermodynamic phase transition, but rather a non-equilibrium result of the coupling between the stress field and the polymer concentration field.

A first clue to the hydrodynamic origin of the separation can be found in

light scattering experiments, which showed a strong anisotropy of the scattering pattern with respect to the flow direction.^{6,9} In these experiments the salient feature is the “butterfly pattern” obtained from small-angle light scattering (SALS) experiments. It is characterized by a dark streak in the direction perpendicular to the flow, where there is no enhancement of the scattering. In the direction of the flow a strong enhancement of the scattering occurs that is limited in width to an opening angle 2α which increases with shear rate (Figure 4-1). Such anisotropy would not occur if the transition were a thermodynamic phase transition. A qualitative confirmation of the HF theory was given in a Couette flow light scattering experiment,⁸ where the experimental axes of the scattering rays were made to correspond to those in the calculation of HF. In this chapter the first direct observation and visualization of the actual participating hydrodynamic modes are presented.

The butterfly pattern has also been observed in other polymer systems, and is attracting much attention.¹⁵⁻²⁰ It has appeared in stretched rubber, polymer gels and polymer melts. There it is found by neutron scattering at much smaller wavelengths. It is worth noting that the butterfly pattern was also reported for stretched block copolymer films containing spherical microdomains of polystyrene in a rubbery matrix of polyisoprene.²¹ A feature universal to the butterfly pattern is that spatial heterogeneities (concentration fluctuations of polymer molecules or centers of spherical domains) are built up in the direction of the applied fields, while the heterogeneities remain essentially unaltered in the direction perpendicular to the fields.

To elucidate the structure which yields the butterfly pattern, a new measurement for semidilute polymer solutions, a flow visualization that could

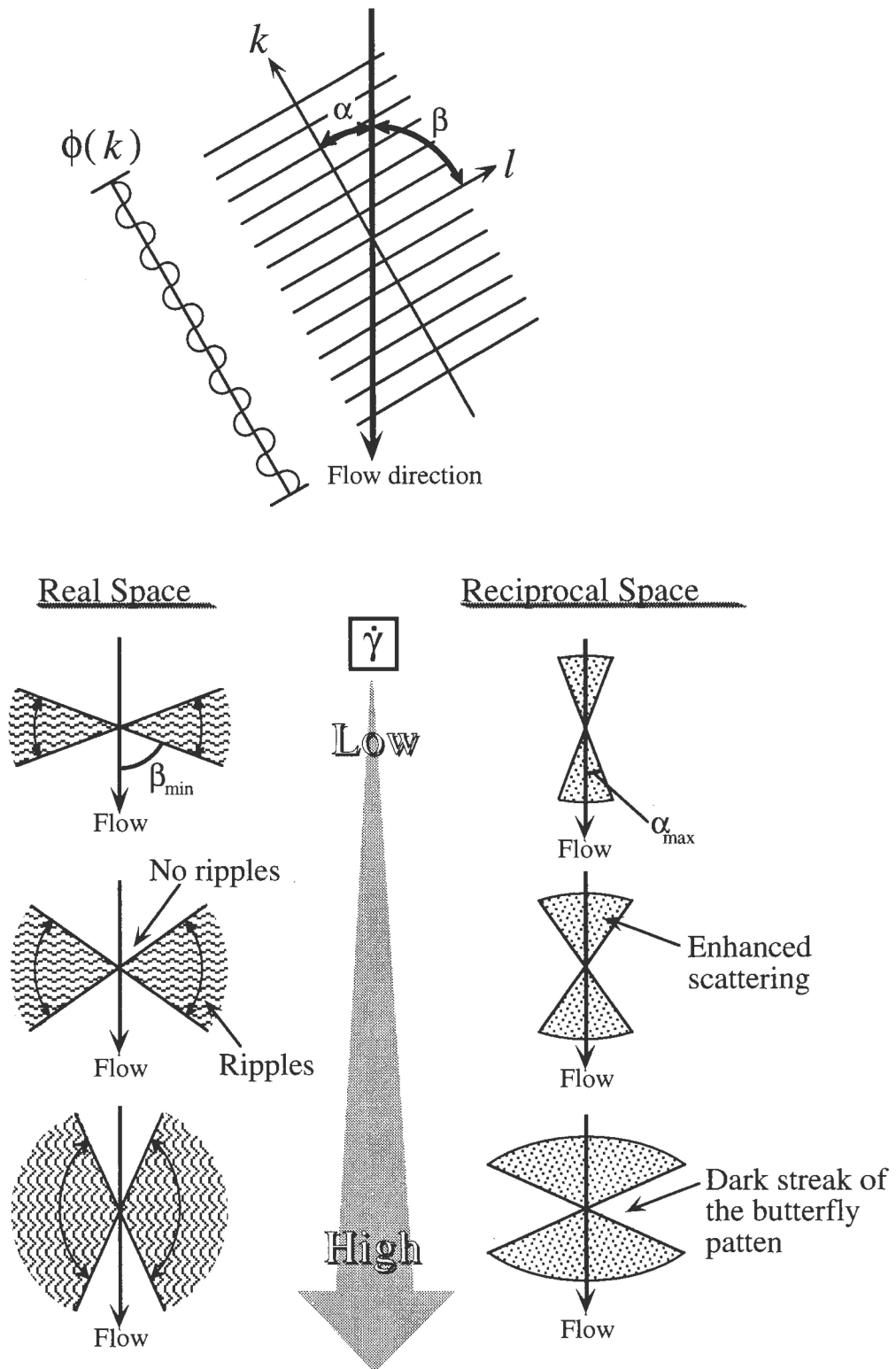


Figure 4-1 Schematic representation of plane wave fluctuations (upper), and development of their angular distribution in real space and small-angle light scattering patterns in reciprocal space with increasing shear rate (lower). k is an unit vector of a certain plane wave fluctuation and l is perpendicular to it.

be operated in conjunction with the SALS, was introduced. This enabled a direct measurement of the concentration fluctuations through their effect on the index of refraction. Then computer enhanced video techniques^{22,23} were used to identify the participating hydrodynamic modes. It was found that the butterfly pattern is the effect of ripples, i.e., plane wave fluctuations, that are tilted at varying angles β with respect to the flow direction, but are limited by a minimal angle $\beta_{\min}$ which decreases with the shear rate.

4-2. Experimental Section

Experimental setup is a modified version of the one described in ref. 6 (see Chapter 2). A cone and plate rheometer with glass components made out of quartz (the cone angle used was 2.6°) was used. The cone and plate are encased in a temperature regulated volume, with long term stability of ± 0.1 K. Apertures in the temperature enclosure (~ 1 cm diameter) allow illumination from below and the insertion of a modified Nikon microscope from above (white light and Nikon 10 $\times$, 20 $\times$ and 60 $\times$, $a = 6$ mm objectives were used). For scattering measurements the microscope was removed, He-Ne laser light used, and a photographic film placed ~ 30 cm above the plate. The polymer solution is sheared between the fixed top plate and the rotating cone below, in a gap which goes continuously from ~ 100 μm to ~ 3 mm. The conical wedge ensures a constant shear rate so long as the flow is simple shear. For visualization a fast shutter (1/10,000 s) charge-coupled-device (CCD) video camera (Sony SSC-M370) connected in parallel to a Macintosh IIfx with a frame grabber (RasterOps 24STV) and to a SVHS VCR (Victor HR-S6600)

was used. For technical reasons the shutter limits the use to single fields, decreasing the effective spatial resolution by half.

In shear flow, a flow direction (x axis) along which the velocity is constant, a direction in which the dominant, shearing flow velocity gradient exists (y axis) and a neutral direction (z axis) are distinguished. In the cone and plate experiment the dominant velocity gradient lies in the vertical gap between the (fixed) top plate and the (rotating) cone. The incident light beams which are used for visualization or for scattering enter through the transparent cone at the bottom of the apparatus, traverse the sample along the y axis and exit the cell through the transparent top. The data are recorded above the cell, onto a screen (for light scattering) or into the microscope (for visualization). Thus they are observed in the x - z plane which contains the flow (tangential) and neutral (radial) directions. Note that HF treat the x - y plane, which is also the one visualized in ref. 8.

Polystyrene used has a weight average molecular weight M_w of 5.48×10^6 and heterogeneity index $M_w/M_n = 1.15$, where M_n is the number average molecular weight, and was dissolved at 6.0 wt% in dioctyl phthalate (DOP), a θ solvent at 22 °C. This concentration is about 40 times the overlap concentration c^* . The cloud point was at 13.8 °C, and experiments were carried out in the one phase region at 27 °C, which is the same condition as those in Chapter 3.

4-3. Results and Discussion

Figure 4-2 shows the butterfly pattern as observed by SALS for three

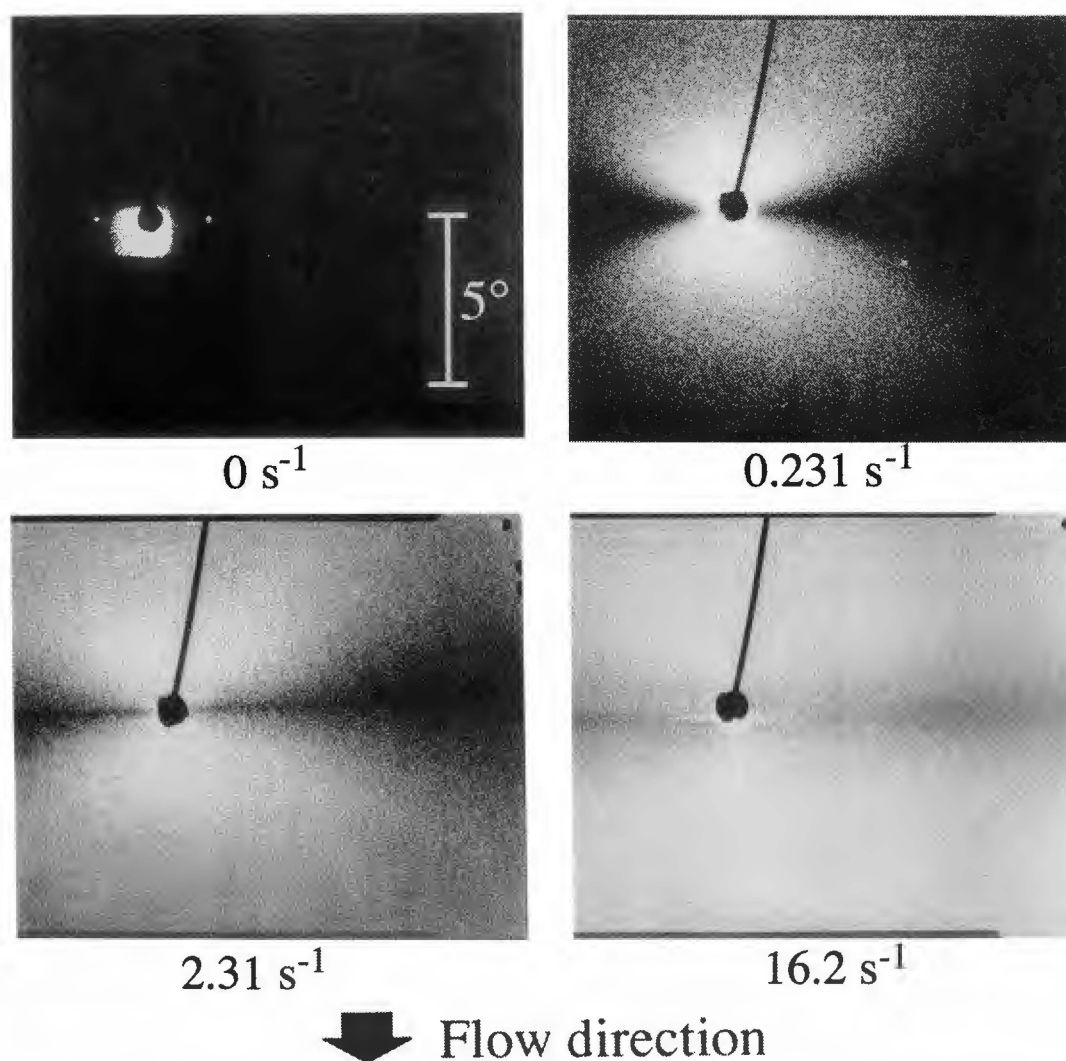
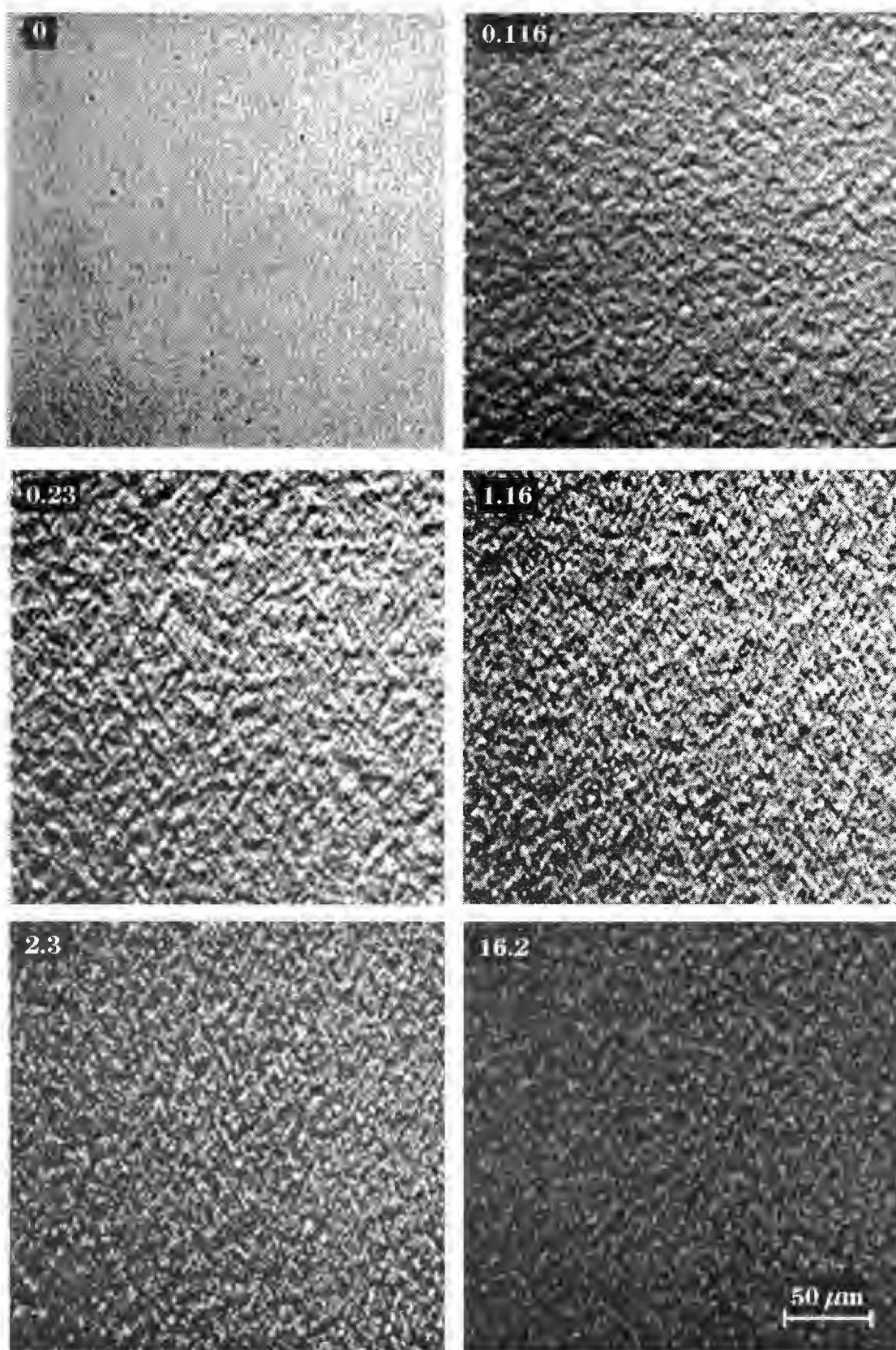


Figure 4-2 SALS patterns show the appearance and development of the butterfly pattern. Photographs taken at $1/250 \text{ s}$ shutter speed, except for 0 s^{-1} , taken at $1/30 \text{ s}$. The halo around the beam stop at 0 s^{-1} gives an indication of the parasitic scattering.

shear rates. For reference, the signal at no shear are also presented, where the only signal comes from the direct beam, and no scattering is apparent. This indicates that prior to shearing the solution is indeed in the homogenous, one phase region. Once the shear rate is high enough, a characteristic anisotropic pattern appears, whose dominant feature is the dark streak perpendicular to the flow direction. In the direction of the flow there is enhanced scattering,



 Flow direction

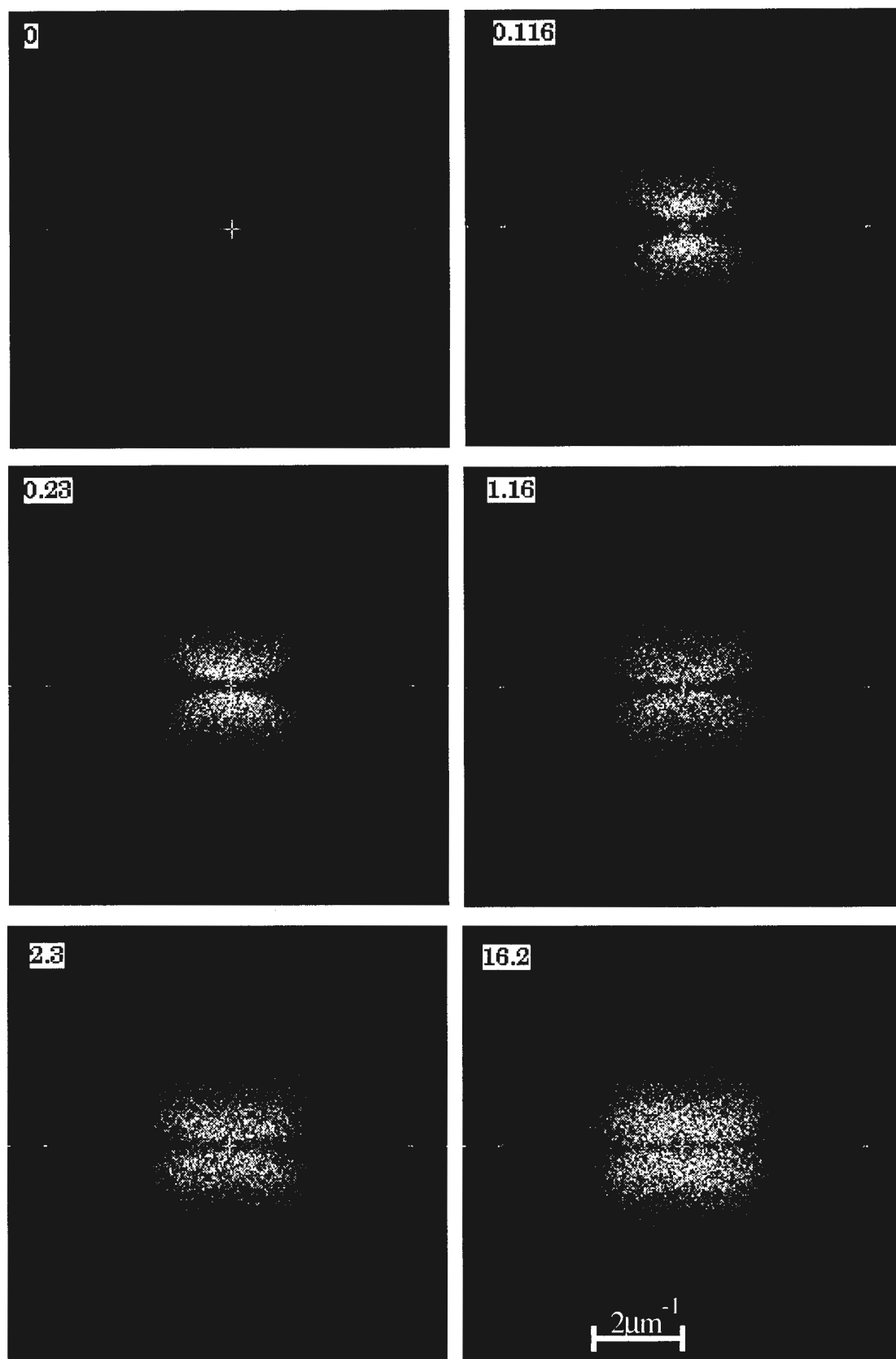
Figure 4-3 Microscope visualization images of the concentration fluctuations.
Numbers indicate shear rate in s^{-1} .

indicative of a structure with periodicity in the flow direction and extent in the direction perpendicular to the flow. This enhancement extends out to the “butterfly wings”, indicating that the periodicity exists at the distribution of angles with respect to the flow direction. As the shear rate increases, the “wings” spread and invade into the dark streak, which almost disappears for the high shear rate.

The microscopic images of the structures in the flow are presented in Figure 4-3. Again the zero shear picture emphasizes the appearance of a structure as the shear is applied. A signal can be discerned already at a shear rate $\dot{\gamma}$ of 0.116 s^{-1} , and at 0.231 s^{-1} the appearance of a periodic structure with a length scale of approximately $10 \text{ }\mu\text{m}$ is clearly detected. These ripples were observed at low shear rates to form and disappear on a time scale of $\sim 1 \text{ s}$, and their lateral extent is much longer than the periodicity. At the lower shear rates the waves are mostly oriented perpendicular to the flow. As the shear rate increases, the waves tilt with respect to the direction of the flow. The smallest accessible angle $\beta_{\min}(\dot{\gamma})$ decreases, until the shear rate of 16.2 s^{-1} at which the waves can be almost parallel with the flow ($\beta_{\min} \cong 20^\circ$).

To ascertain that the microscopic images are a true representation in real space of the butterfly pattern, the fast Fourier transform (FFT) of the patterns are calculated. The spectra corresponding to the pictures of Figure 4-3 are presented in Figure 4-4. To reconstruct the light scattering representation in k space of Figure 4-2, a logarithmic gray scale representation with constant contrast enhancement is used in Figure 4-4. The similarity of the Fourier spectra with the signal obtained by light scattering is apparent.

These pictures constitute the real space explanation for the appearance



 Flow direction

Figure 4-4 FFT spectra of the images as in Figure 4-3. Numbers indicate shear rate in s^{-1} .

of the butterfly pattern: The dark streak perpendicular to the flow (in the z direction) in the SALS pattern arises because there is no periodicity (no concentration fluctuations) in that direction (the solution remains homogeneous in that direction). Waves that are perpendicular to the flow direction contribute a scattering intensity parallel to the flow (x direction), while those waves that are oriented in the range of allowed angles fill up the “wings” of the pattern, up to a maximal angle determined by $\alpha_{\max}(\dot{\gamma})$, with the connection to the (minimal) spatial angle given by $\alpha_{\max} = 90^\circ - \beta_{\min}$. Beyond $\alpha_{\max}$ no periodicity exists and the dark streak begins.

The periodicity of $\sim 10 \mu\text{m}$ observed in the pictures is consistent with the peak in the SALS pattern at a similar wavelength ($\sim 9.3 \mu\text{m}$)⁹ that shows up at high shear rates. A bandpass filter centered around $\lambda = 9 \mu\text{m}$ by digital convolution was applied, followed by binary thresholding of the filtered signal to enhance the contrast. The results of this process are presented in Figure 4-5, spanning over two decades in shear rate.

Close inspection of the filtered data shows the distribution of waves at different angles. The waves of largest lateral extension have similar orientation, at $\pm\beta_{\min}(\dot{\gamma})$ with respect to the flow direction. The lateral extent of the waves can go from as short as $20\text{-}30 \mu\text{m}$ up to a few hundred μm , which is the whole field of view. Waves with high angles exist, up to 90° with respect to the flow, but their extent is short.

To evaluate the angular distribution of the waves, the figures were skeletonized, keeping the edges of the resulting graph as relevant segments. This caused a loss of long range correlations, but the angular dependence is still strong. In order to reduce high frequency noise, segments shorter than a

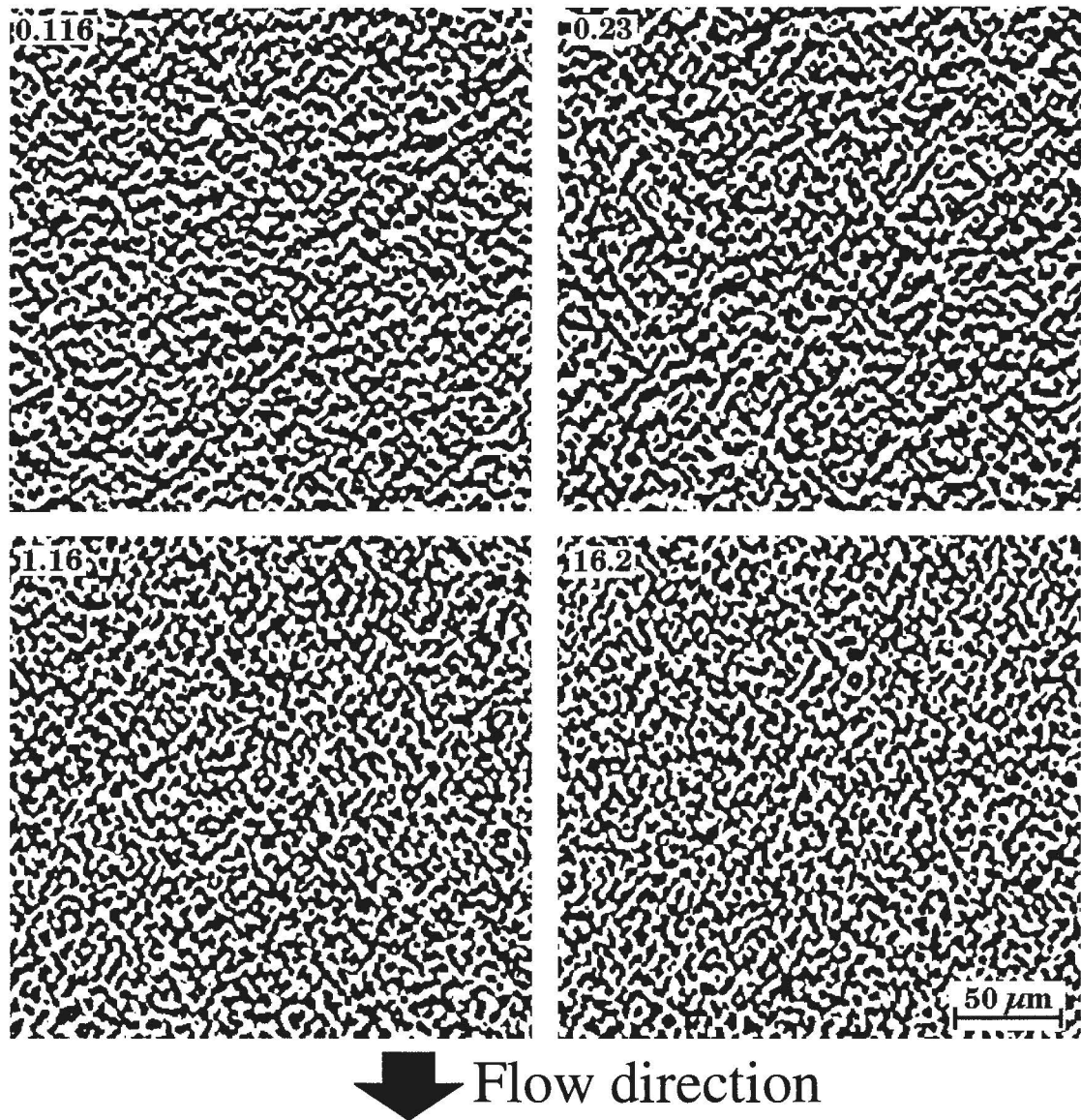


Figure 4-5 Microscopic images after bandpass convolution and thresholding. Numbers indicate shear rate in s^{-1} .

wavelength of $\sim 9 \mu m$ were discarded and angles were computed from the remaining segments. To eliminate scatter originating in the pixel matrix, short distances were discarded, then renormalized by an isotropic distribution and data smoothing was applied. The resulting distributions are presented in Figure 4-6. Since there was no apparent asymmetry in the plus or minus β distribution, the modulus of the angle was plotted.

The angle is identified, at which the peak in the angular distributions

begins (or shoulder for $\dot{\gamma} = 0.116 \text{ s}^{-1}$) with $\beta_{\min}(\dot{\gamma})$. The inset to Figure 4-6 shows the trend of a power law over the two decades spanned, with $\beta_{\min} \rightarrow 0$ as $\dot{\gamma} \rightarrow \infty$. Approaching the limit, however, is impractical, due to the appearance at $\dot{\gamma} \geq \dot{\gamma}_a \cong 5 \text{ s}^{-1}$ of a rheological anomaly.⁹ As a guide to the eye a best fit to a power law $\beta_{\min} = 0.5 \dot{\gamma}^{-1/7}$ is given, with $\beta_{\min}$ in radians and $\dot{\gamma}$ in s^{-1} .

The origin of the wavelength (and the length scale observed by SALS at $\dot{\gamma} \geq \dot{\gamma}_a$) is an interesting question. One explanation is that a reptation process is dominating the hydrodynamic structures which are observed.²⁴ The time scale for reptation τ_{rep} of polymer used in this chapter is on the order of 1-10 s. The argument (based on the work of Brochard and de Gennes²⁵) is that in

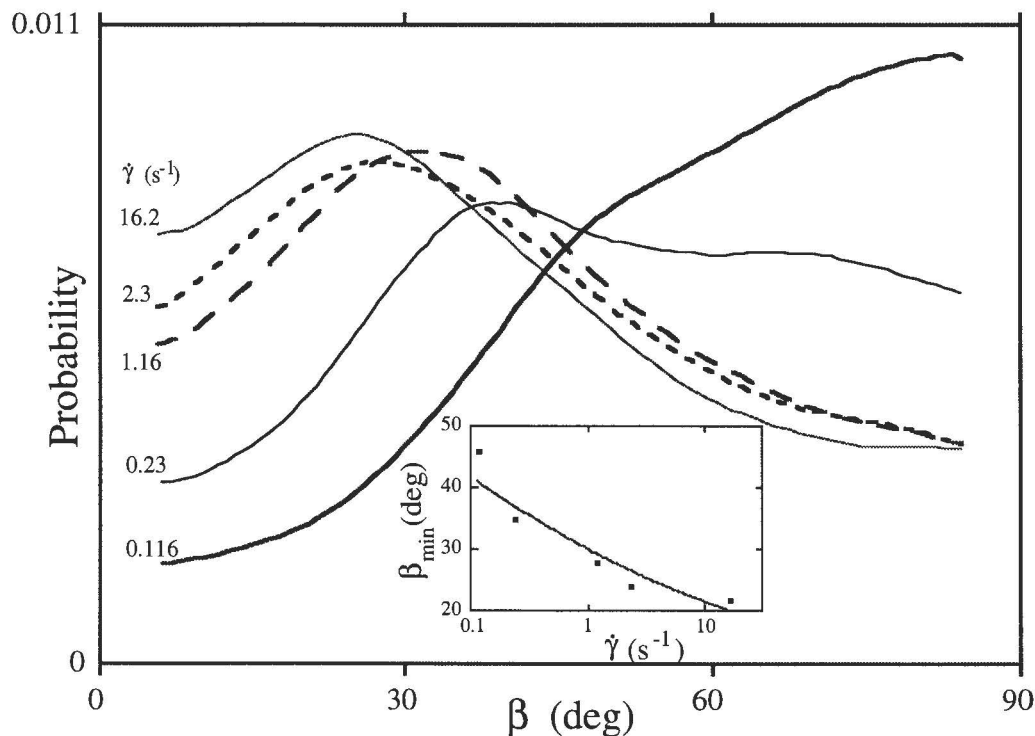


Figure 4-6 Normalized probability histograms of the angular distribution of segments from skeletonized microscopic images for various shear rates. Flow direction is at 0° . Inset: Shear rate dependence of the minimal angle $\beta_{\min}$. Solid line is the fit to a power law.

the absence of shear fluctuations decay by cooperative diffusion (with coefficient⁸ $D_{\text{fluid}} \sim 10^{-6} \text{ cm}^2/\text{s}$). In the presence of shear the flow of solvent into polymer-rich regions produces a transient elastic deformation which reduces the thermodynamic force driving the solution to equilibrium and effectively arrests the relaxation of a density fluctuation. The transient stress decays after a typical relaxation time determined by reptation, τ_{rep} . This defines a viscoelastic length scale $\lambda = (D_{\text{fluid}}\tau_{\text{rep}})^{1/2}$ on which the slowing down of the decay of fluctuations is most pronounced, i.e., on which fluctuations are enhanced.²⁶ Thus $\lambda \cong 10\text{-}30 \text{ }\mu\text{m}$ is obtained, close to the length scale measured (a similar argument in ref. 8 yielded $\sim 1 \text{ }\mu\text{m}$ for that system).

Note that the rotation of the scattering pattern with increasing shear rate described by HF and observed in ref. 8 occurs in the x - y plane, while rotation of the spatial pattern with increasing shear rate in the x - z plane was reported. Three dimensional effects are clearly important, and should be taken into consideration in any theoretical treatment which would endeavor to explain the waves and their tendency to tilt.

4-3. Summary

It was demonstrated that the spatial origin of the butterfly pattern in shear flow of semidilute, high molecular weight polymer solutions is the existence of hydrodynamic modes, or ripples, which have a distribution of tilt angles. The FFT of the patterns obtained by shear-microscopy reproduces well the light scattering pattern. There exists a minimal angle β_{min} with respect to the flow, beyond which no wave can tilt. This causes a dark streak with

angle $2\beta_{\min} = 180^\circ - 2\alpha_{\max}(\dot{\gamma})$, in the direction perpendicular to the flow, which is the salient characteristic of the butterfly pattern. $\beta_{\min}$ tends to 0° at high shear rates, causing the butterfly to almost close upon itself. The wavelength of the waves is $\sim 10 \mu\text{m}$, and a time scale which arises from viewing the lifetime of the ripples, from a peak in the scattering intensity, from rheological measurements,⁸ from the rotation of the scattering pattern⁸ and from an argument about reptation is $\tau_{\text{rep}} = 1 \text{ s}$, or $\dot{\gamma} = 1 \text{ s}^{-1}$.

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Chapter 5

String Phase in Semidilute Polystyrene Solutions under Steady Shear Flow

5-1. Introduction

Shear-induced concentration fluctuations or phase separation¹⁻²⁰ have been studied quite extensively for semidilute solutions of high molecular weight polystyrenes, typically higher than 10^6 , as an intriguing phenomenon concerning the non-equilibrium statistical mechanics of polymers. A polymer solution which is homogeneous and in the single phase state without shear flow exhibits strong concentration fluctuations at shear rates, $\dot{\gamma}$, larger than a critical shear rate, $\dot{\gamma}_c$. These shear-enhanced fluctuations were confirmed by measurements of changes in the turbidity or transmitted intensity,^{2-4,11,16,18} rheological properties^{2,11,16,17} and form dichroism^{11,14,16,18} with $\dot{\gamma}$.

The fluctuations induced were found to be highly anisotropic, with strong fluctuations along flow but fluctuations normal to the flow or the neutral axis of the flow being nearly identical to those at $\dot{\gamma} = 0$, giving rise to the unique butterfly-type scattering patterns.^{8,12,14,19,20} The anisotropic concentration fluctuations were further confirmed by a direct visualization with **shear-microscopy**,¹⁹ i.e., by *in situ* observation with optical microscopy. The images obtained by shear-microscopy were confirmed as representing true structural

entities by comparing the real light scattering patterns, simultaneously recorded by **shear-light scattering**, and the Fast Fourier Transform (FFT) patterns corresponding to the microscopic images.

In this chapter it is an aim to report a novel experimental result on the formation of long strings parallel to flow at shear rates much higher than $\dot{\gamma}_c$. The string phase was directly visualized by shear-microscopy and confirmed by shear-light scattering which gives a streak-like scattering pattern normal to the flow direction. The string formation will be shown to be intimately related to the anomalies found in the rheological properties of these solutions.

5-2. Experimental Section

As in previous experiments, semidilute polymer solutions of high molecular weight polystyrene (PS) with dioctyl phthalate (DOP) were used.^{8,12,19} The PS/DOP system has a UCST-type phase diagram, and its θ temperature (T_θ) is 22 °C. Two PS samples were used in this chapter. PS548

Table 5-1. Polymers and polymer solutions used in this chapter

polymer code	c: concentration (wt%)	$c/c^{*1)}$	cloud point ²⁾ (°C)
PS548	3.0	20	16.3
PS548	6.0	40	13.8
PS1000	2.0	20	15.9

1) c^* : overlap concentration

2) The cloud points of the solutions were determined by the same method as described previously.⁸

is a standard sample supplied by TOSOH Co. Ltd., which has weight average molecular weight (M_w) of 5.48×10^6 and a heterogeneity index (M_w/M_n) of 1.15. PS1000 is a sample supplied by Japan Synthetic Rubber Co. Ltd., which has a molecular weight in the range $9-14 \times 10^6$. These polystyrenes were dissolved into solutions using prescribed amounts of DOP and an excess of methylene chloride, and then the PS/DOP solutions were prepared by completely evaporating the methylene chloride. The solutions used in this study are listed in Table 5-1.

The small-angle light scattering and optical microscopy measurements under shear flow were performed by the two types of rheo-optical apparatuses which were constructed in our laboratory.^{21,22} (See also Sec. 1-2 and Chapter

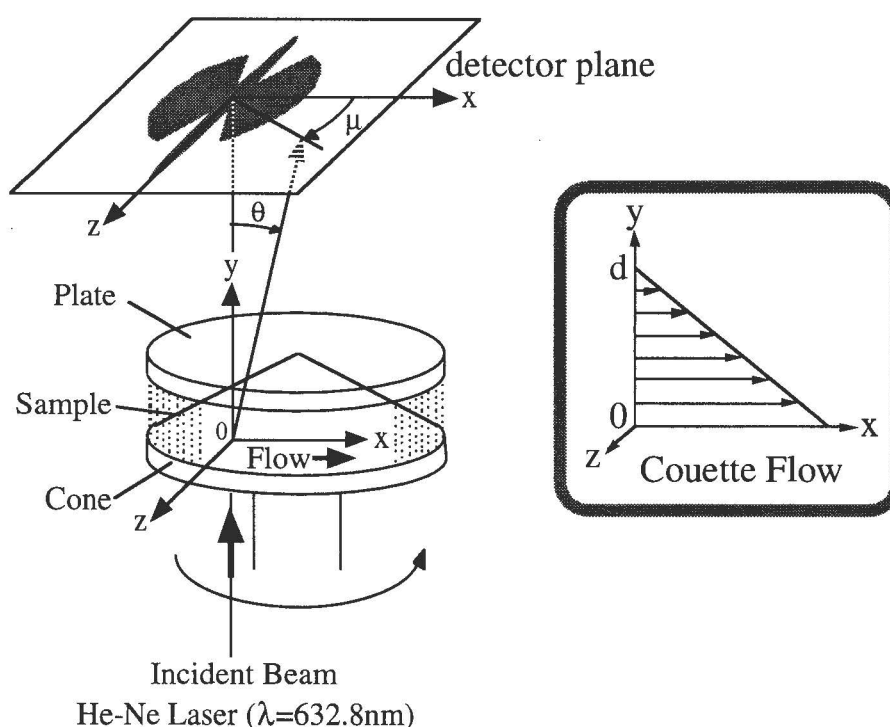


Figure 5-1 Cone-and-plate type sample cell to generate Couette flow, the coordinate system, and definition of the scattering angle, θ , and azimuthal angle, μ .

2.) Transparent cone-and-plate type sample cells which were made of quartz were used. The optical setup and coordinate system in this chapter, shown in Figure 5-1, are the same as those previously used. The velocity gradient exists in the plane Oxy , where Ox is the flow direction. The incident beam is sent along the Oy axis, and the scattering profiles were detected in the plane Oxz . The temperature of the sample cell was controlled with an accuracy of ± 0.1 °C.

The rheological measurements were performed with a mechanical spectrometer, RMS-800, and a fluid spectrometer, RFS II (both from Rheometrics®, Inc.). The sample cells used also have a cone-and-plate geometry. The steady state properties at various shear rates, $\dot{\gamma}$, were measured more than $20/\dot{\gamma}$ seconds after the specified shear rate was attained, in the cycle of increasing shear rate from a quiescent state. It was confirmed that the scattering intensity at a given $\dot{\gamma}$ didn't change after shearing for the specified period of time.

5-3. Results

Figure 5-2 shows various properties under steady state shear flow as a function of shear rate for the 3.0 wt% DOP solution of PS548 plotted on a double logarithmic scale: η and ψ_1 are shear viscosity and coefficient of the first normal stress difference, respectively; $\mathcal{I}_{//}(\dot{\gamma})$ and $\mathcal{I}_{\perp}(\dot{\gamma})$ are the integrated scattered intensity parallel to x and z axis, respectively, and $\mathcal{I}_{//}(\dot{\gamma} = 0)$ and $\mathcal{I}_{\perp}(\dot{\gamma} = 0)$ are the corresponding quantities in the quiescent state. Here the quantities $\mathcal{I}_{//}$ and $\mathcal{I}_{\perp}$ were defined by

$$\mathcal{I}_{\parallel} = \int_{q_{\parallel S}}^{q_{\parallel L}} I_{\parallel}(q) dq \quad (5-1)$$

$$\mathcal{I}_{\perp} = \int_{q_{\parallel S}}^{q_{\parallel L}} I_{\perp}(q) dq \quad (5-2)$$

where $I_{\parallel}(q)$ and $I_{\perp}(q)$ are the scattered intensities parallel to the x and z axes, respectively, and q is the magnitude of scattering vector defined by $q = (4\pi/\lambda)\sin(\theta/2)$, with θ and λ being scattering angle and wavelength of

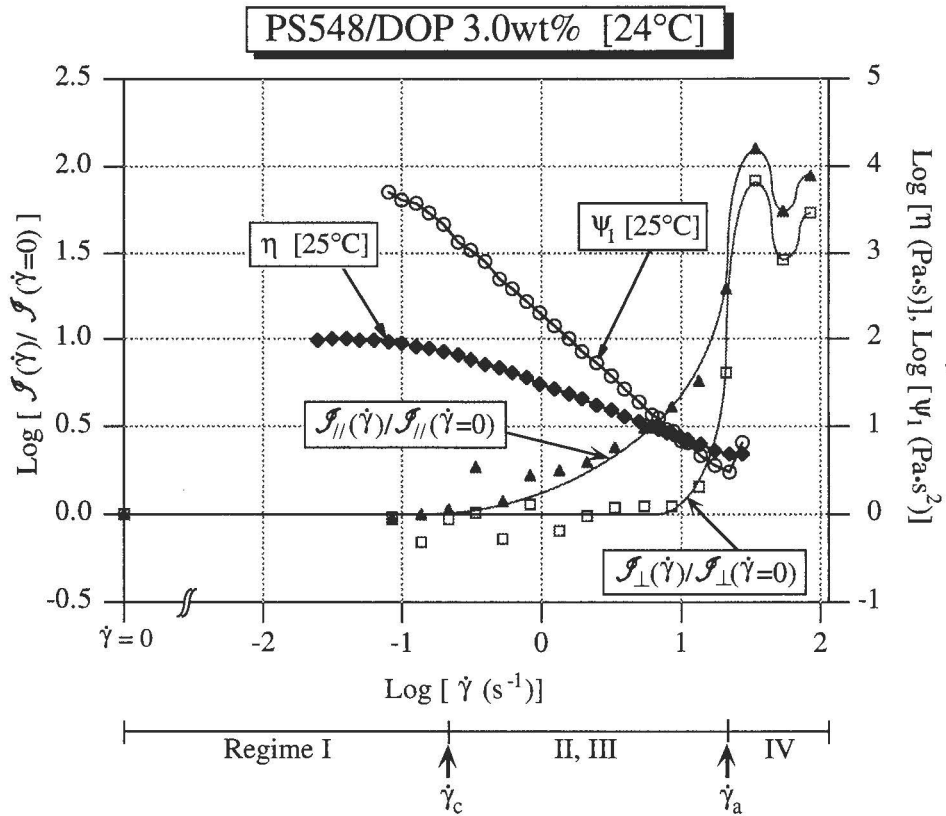


Figure 5-2 Shear viscosity, η , coefficient of the first normal stress difference, ψ_1 , normalized integrated scattered intensity parallel and perpendicular to flow, $\mathcal{I}_{\parallel}(\dot{\gamma})/\mathcal{I}_{\parallel}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma})/\mathcal{I}_{\perp}(\dot{\gamma}=0)$ for the PS548/DOP 3.0 wt% solution, as a function of shear rate $\dot{\gamma}$ in steady state shear flow. $\dot{\gamma}_c$ and $\dot{\gamma}_a$ are the critical shear rates for the onset of the shear-enhanced concentration fluctuations, and of the anomalies in the rheological and scattering behaviors, respectively.

light in the medium, respectively. The solution was sheared at 24 °C for light scattering experiments and 25 °C for the rheological experiments, 7.7 and 8.7 °C above the cloud point, respectively.

The solution, which is in a single-phase state at $\dot{\gamma} = 0$, exhibits remarkable shear-enhanced concentration fluctuations as observed in the change of light scattered intensity. At a shear rate smaller than the critical shear rate, $\dot{\gamma}_c$, the scattered intensities $\mathcal{I}_{//}(\dot{\gamma})$ and $\mathcal{I}_{\perp}(\dot{\gamma})$ are the same as those at $\dot{\gamma} = 0$, and hence the concentration fluctuations are not affected by shear (Regime I). However at $\dot{\gamma} > \dot{\gamma}_c$, a tremendous increase in the scattered intensities is observed, indicating the shear-enhanced concentration fluctuations reported earlier.^{8,12} The critical shear rate, $\dot{\gamma}_c$, for the shear-enhanced concentration fluctuations is 0.2 s⁻¹ for this solution. In parallel to the change in the scattered intensities $\mathcal{I}_{//}$ and $\mathcal{I}_{\perp}$ the rheological properties undergo remarkable change with $\dot{\gamma}$. At $\dot{\gamma} > \dot{\gamma}_c$, both η and ψ_1 drop with $\dot{\gamma}$, which may be approximated by the following power laws,

$$\eta \sim \dot{\gamma}^{-0.61 \pm 0.02} \quad \text{and} \quad \psi_1 \sim \dot{\gamma}^{-1.47 \pm 0.02} \quad (5-3)$$

The power law behavior given by equation 5-3 starts to break at $\dot{\gamma} > \dot{\gamma}_a$ (Regime IV), a critical shear rate (20 s⁻¹ for this solution) for the rheological anomaly as reported earlier¹²: the decrease of η with $\dot{\gamma}$ starts to level off²³ and deviates from equation 5-3; ψ_1 starts to increase with $\dot{\gamma}$. This anomaly appears to occur in parallel to that in the scattered intensities $\mathcal{I}_{//}$ and $\mathcal{I}_{\perp}$: (i) a sharp increase in $\mathcal{I}_{//}$ and $\mathcal{I}_{\perp}$ with $\dot{\gamma}$ ($\dot{\gamma}_a$ appears to be an inflection point for $\mathcal{I}_{//}(\dot{\gamma})$ and $\mathcal{I}_{\perp}(\dot{\gamma})$) and (ii) a sharp decrease in the scattering anisotropy ($\mathcal{I}_{//}(\dot{\gamma}) - \mathcal{I}_{\perp}(\dot{\gamma})$)

with $\dot{\gamma}$.

In the previous report¹² (Chapter 3) on 6.0 wt% solution of PS548 in DOP, it was indicated that the shear-rate dependence of the properties at $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$ can be further classified into Regime II and III: in Regime II both $\mathcal{I}_{//}$ and $\mathcal{I}_{\perp}$ start to increase sigmoidally and reach certain saturated intensity levels, and in Regime III these intensity levels stay nearly constant. In this 3.0 wt% solution, it was unable to distinguish Regimes II and III clearly in the same way as in the 6.0 wt% solution.

Figure 5-3 shows the change of the scattering patterns with $\dot{\gamma}$ observed in the Oxz plane. The solution examined is the 3.0 wt% PS548 in DOP solution at 25 °C. The solution exhibits no strong small angle scattering at $\dot{\gamma} < \dot{\gamma}_c$, as shown in Figure 5-3a, but a typical strong anisotropic scattering designated as the butterfly pattern^{8,12} is exhibited at $\dot{\gamma} > \dot{\gamma}_c$, as shown in Figures 5-3b and 5-3c. The butterfly pattern has characteristics of a strong intensity parallel to the flow but a weak intensity along the neutral axis (Oz axis). The intensity along the Oz axis is as weak as that at $\dot{\gamma} = 0$, giving rise to the unique feature called the “dark streak”.¹² Upon further increasing $\dot{\gamma}$ beyond $\dot{\gamma}_a$, a strong streak-like pattern appears at small-angle regions in the direction parallel to Oz axis, as seen in Figures 5-3d to 5-3g. The appearance of the streak-like scattering pattern upon increasing $\dot{\gamma}$ occurs in parallel to the onset of the rheological anomaly.

Figure 5-4 represents contour plots of the scattered intensity distributions at various $\dot{\gamma}$, measured by the CCD camera system previously reported.²¹ The features demonstrated in Figure 5-3 are more quantitatively shown in this figure. It is clearly shown that the intensity of the streak pattern along the

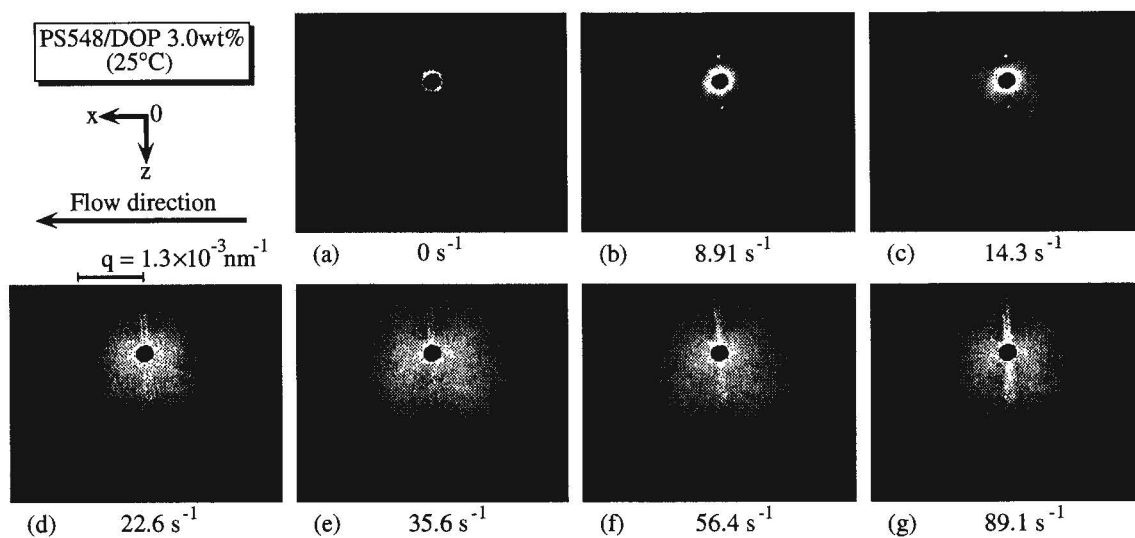


Figure 5-3 Steady state scattering patterns at various shear rates for the solution shown in Figure 5-2.

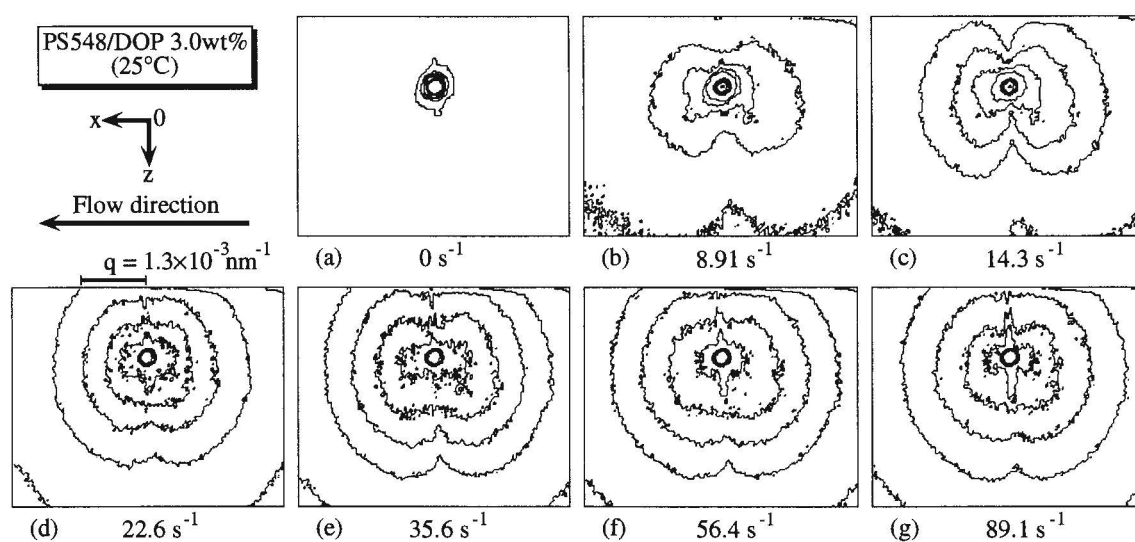


Figure 5-4 Contour plots of the scattered intensity distribution for the solution shown in Figure 5-2.

neutral axis increases with $\dot{\gamma}$ beyond $\dot{\gamma}_a$, as seen in Figures 5-4d to 5-4g. It is also observed that, superimposed on the streak pattern, the butterfly pattern appears at q regions larger than those where the streak pattern appears.

Figure 5-5 represents a direct visualization of the structure at $\dot{\gamma} = 89.1 \text{ s}^{-1}$ ($> \dot{\gamma}_a$) by means of shear-microscopy (a) and its FFT image (b). The image in part a (a snap shot taken with a shutter speed of 10^{-3} s) shows long strings of length about $50 \mu\text{m}$ or longer oriented along flow (Ox axis). The corresponding FFT image shows a strong streak parallel to the z axis, consistent with the real scattering pattern shown in Figure 5-4g. The spread of the streak shown in the FFT image is approximately equal to that observed in the real light scattering pattern. Therefore the image shown in Figure 5-5a seems to reflect

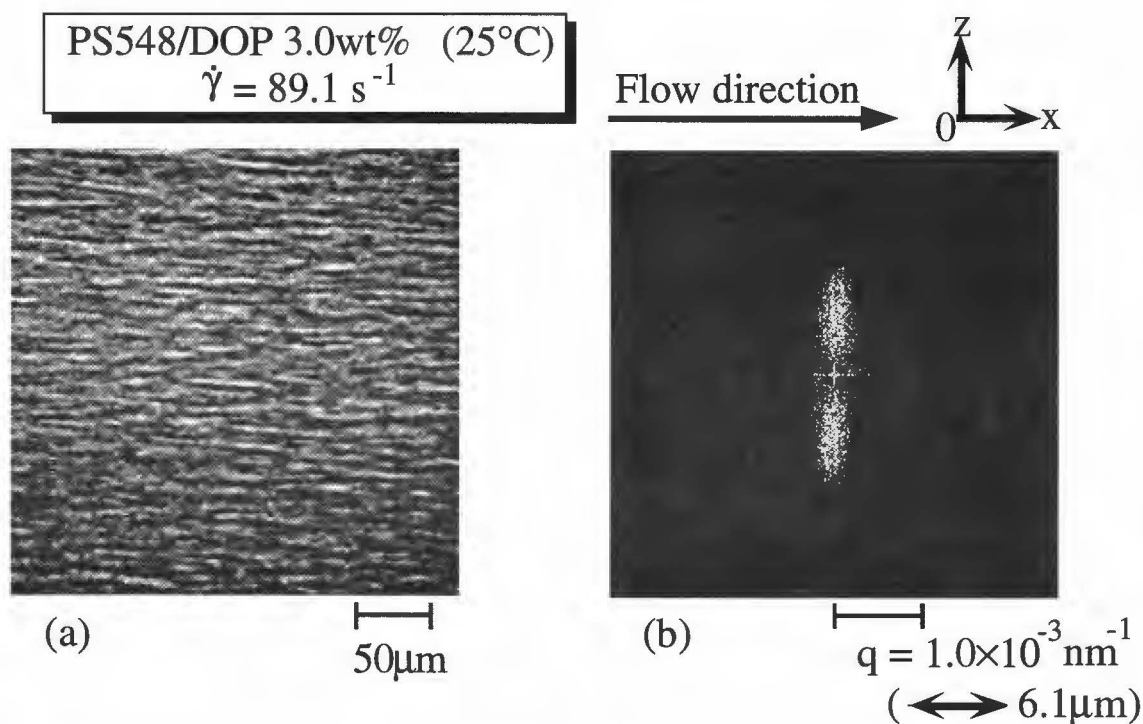


Figure 5-5 Microscopic image of concentration fluctuations (a) and its 2D-FFT pattern (b) at $\dot{\gamma} = 89.1 \text{ s}^{-1}$ which correspond to Figure 5-3g and Figure 5-4g. The microscopic image is a snap shot taken at a shutter speed of 10^{-3} s .

the true structural entity corresponding to the streak-like scattering. Unfortunately it was unable to recover the butterfly-type scattering pattern in the FFT image shown in Figure 5-5b from the optical image shown in Figure 5-5a. This may be due to the fact that the intensity of the butterfly-type scattering pattern is much weaker than that of the streak-type scattering pattern, i.e., the concentration difference between the strings and their matrix associated with the streak scattering are much greater than the concentration fluctuations within the strings associated with butterfly pattern (see discussion related to Figure 5-8 later).¹⁹

Figures 5-6 and 5-7 show formation of the string phase or the streak-like scattering pattern in other systems such as the 2.0 wt% solution of PS1000 in DOP at 25 °C and the 6.0 wt% solution of PS548, at 27 °C, respectively. The former and the latter may represent effects of molecular weight and concentration on the string phase formation, when compared with the results obtained for the 3.0 wt% solution of PS548. The streak-like scattering patterns in Figures 5-6b and 5-6c and in Figure 5-7 imply that the string phase is

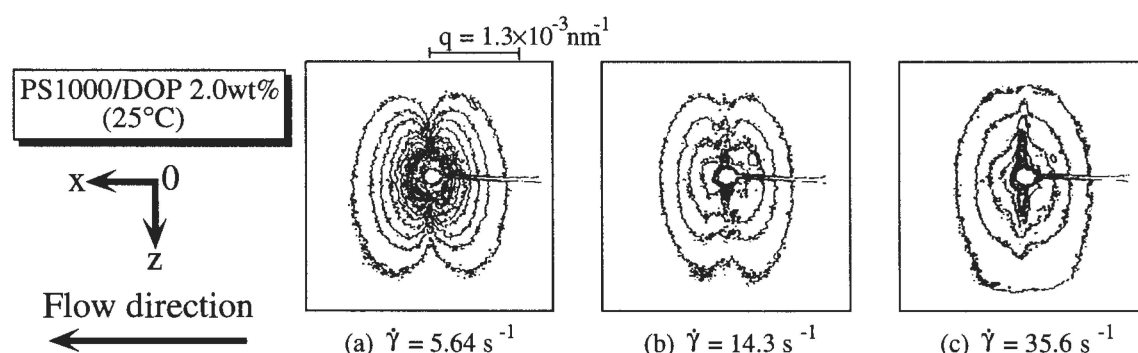


Figure 5-6 Contour plots of the scattered intensity distribution for the PS1000/DOP 2.0 wt% solution at $\dot{\gamma} = 5.64$ (a), 14.3 (b) and 35.6 s⁻¹ (c) in the steady state.

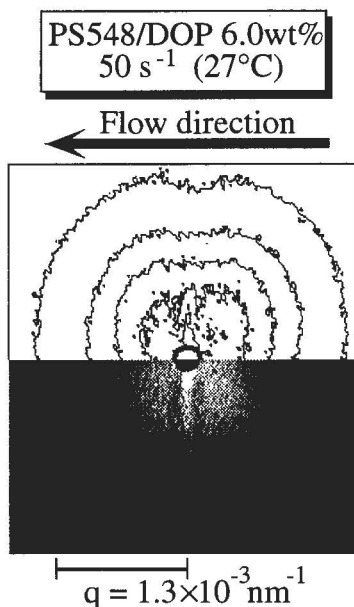


Figure 5-7 Steady state scattering pattern (lower half) and contour plot of the intensity distribution (upper half) for the PS548/DOP 6.0 wt% solution at $\dot{\gamma} = 50 \text{ s}^{-1}$.

formed in these solutions as well, implying that the string phase formation may be a general phenomenon.

5-4. Discussion

The rheological anomaly as observed in the upturn of ψ_1 and η at $\dot{\gamma} > \dot{\gamma}_a$ (Figure 5-2) was found to be intimately related to the appearance of the streak-like scattering pattern normal to flow and along the neutral axis (Oz axis) as shown in Figures 5-3 and 5-4 (patterns d - g). A simultaneous observation under shear-light scattering and shear-microscopy for the same solution further clarified that this anomaly is related to the formation of the strings aligned parallel to flow (see Figures 5-4 and 5-5).

The preliminary results indicate that the critical shear stress at the shear rate $\dot{\gamma}_a$ for the onset of the anomaly appears to increase with the concentration, e.g., 120 and 300 Pa for the 3.0 and 6.0 wt% DOP solution of

PS548, respectively. Thus the higher the concentration, the harder the formation of the string phase. The string formation implies a build-up of the concentration fluctuations along the Oz axis, normal to flow. The higher the concentration, the larger the osmotic pressure and hence larger the mechanical energy required to generate the concentration fluctuations normal to flow. The critical stress for the onset of butterfly formation at $\dot{\gamma}_c$ was found²⁴ to be almost independent of concentration (nearly equal to 20 Pa for PS548 in the concentration range of 1.5 to 6.0 wt%).

The fact that the streak-like scattering appears at small scattering angles and the butterfly appears at large scattering angles in Figure 5-4g suggests that the strings are larger than the concentration fluctuations responsible for the butterfly pattern. Moreover the micrograph in Figure 5-5a shows the structure uniformly composed of the strings but not a two-phase structure composed of the strings and the structure responsible for butterfly pattern.

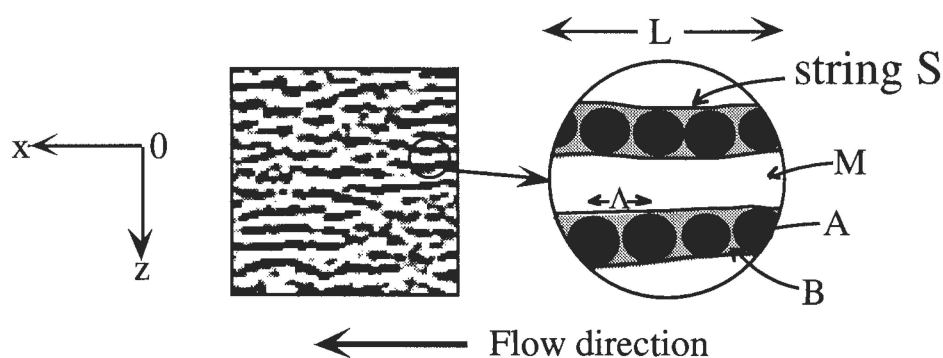


Figure 5-8 Sketch of concentration fluctuations in polymer solutions at $\dot{\gamma} > \dot{\gamma}_a$. Λ and L are a length scale of the internal fluctuations and an average length of the strings, respectively. Strings, S , have polymer concentrations higher than that of matrix, M . Regions, A , in the strings, S , have higher polymer concentrations than region B .

Thus the results in Figure 5-4g and 5-5a may suggest the model shown in Figure 5-8 for a self-assembly at $\dot{\gamma} > \dot{\gamma}_a$.

This model consists of the long strings oriented parallel to flow. The strings, S, have polymer concentration higher than that of the matrix, M. These concentration fluctuations give rise to the strong streak-like scattering along the Oz axis. The strings also may have internal concentration fluctuations along their axes as schematically illustrated by regions A and B having a higher and a lower concentration, respectively. These internal concentration fluctuations are expected to be responsible for the butterfly pattern. Moreover the length scale for the internal fluctuations, Λ , is shorter than the average length, L , of the strings, which account for the fact that butterfly patterns appear at larger scattering angles than the streak-like scattering patterns.

In order to better demonstrate the unique scattering pattern composed of a superposition of the butterfly-type and streak-like scattering patterns, scattering patterns and optical micrographs obtained simultaneously from a very different system are presented in Figure 5-9. The system to be considered here is a DOP solution of an 80/20 wt%/wt% (77/23 vol%/vol%) mixture of polystyrene (PS)/polybutadiene (PB). The polymer concentration, c , is 3.3 wt% which is about twice as large as the overlap concentration, c^* . The PB has a weight-average molecular weight of $M_B = 3.13 \times 10^5$ and PS has $M_S = 2.14 \times 10^5$. Figure 5-9 shows the steady state structure (a) and the scattering pattern from the solution sheared at $\dot{\gamma} = 4 \text{ s}^{-1}$ (b) and at 14 °C below the cloud temperature $T_{cl} = 58 \text{ °C}$ of the quiescent solution. It also shows the transient change of the structure (c and e) and scattering pattern (d and f) after cessation of the steady shear.

PS/PB(80:20)/DOP 3.3wt%
After Cessation of Shear from 4 s^{-1}

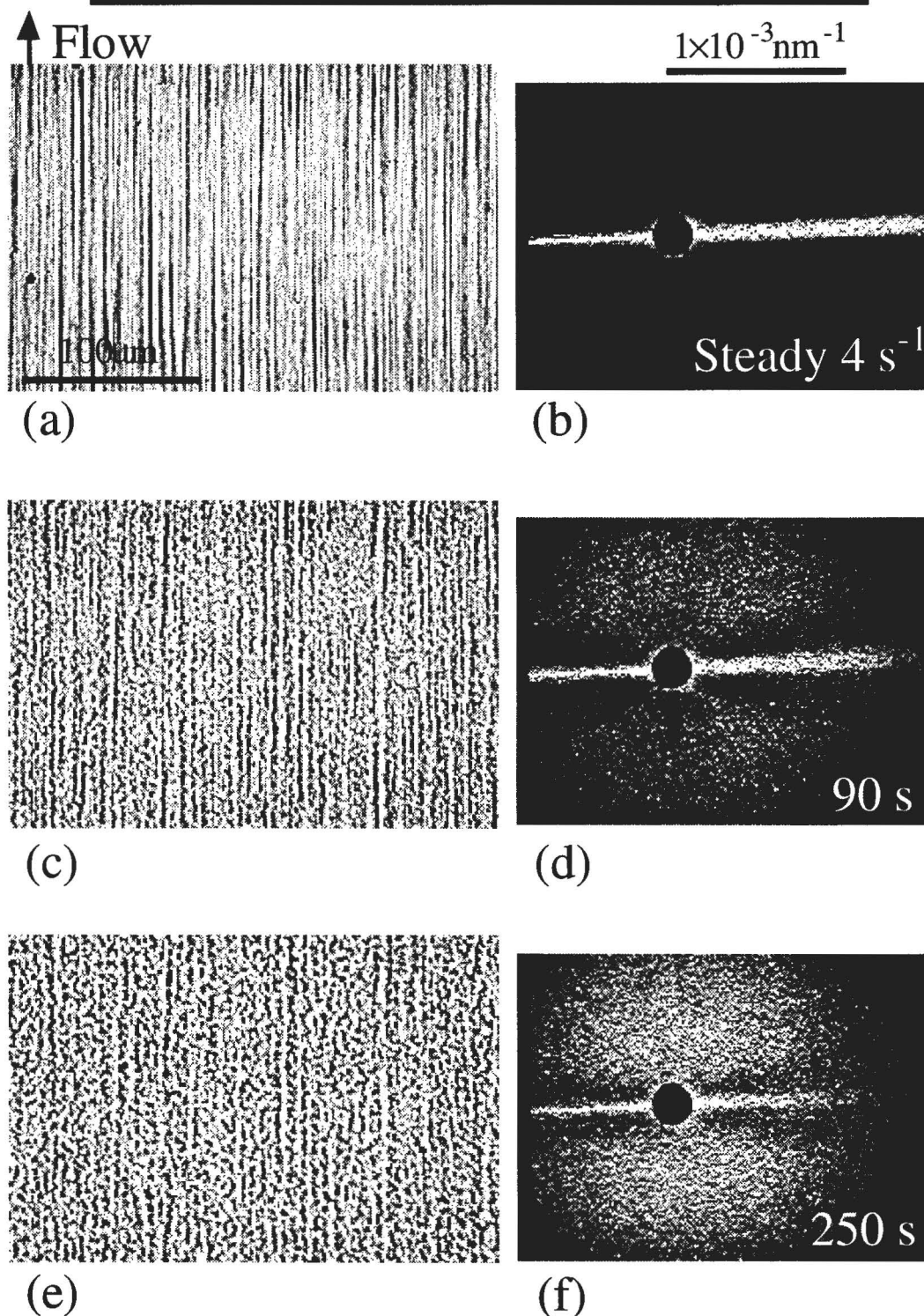


Figure 5-9 Microscopic images (a, c, e) and corresponding light scattering patterns (b, d, f) for the PS/PB(80:20)/DOP 3.3 wt% solution at $\Delta T = 14^\circ\text{C}$. (a) and (b) were obtained under steady state shear flow at 4 s^{-1} . (c) to (f) were obtained after cessation of shear.

This solution was shown²⁵ to form highly elongated strings along flow (Figure 5-9a) and thus to exhibit a very sharp streak-like scattering pattern normal to it (Figure 5-9b) under steady shear flow. The strings are rich in PB and dispersed in a matrix rich in PS. DOP is a neutral solvent for both phases. In this system the strings have a uniform polymer concentration along their axes and hence do not exhibit the butterfly pattern in steady state as in the case of PS/DOP system. This is because the strong shear flow stabilizes the strings against their intrinsic surface tension instabilities.^{26,27}

However, when the shear flow is ceased, surface tension instabilities occur, and the strings are broken into a series of droplets rich in PB in a matrix rich in PS (as seen Figure 5-9c). The droplets keep a memory of the string so that they have a one-dimensional spatial correlation along the string, just like a series of droplets A in the matrix M as schematized in Figure 5-8. This nematic alignment of the droplets gives rise to both the horizontal sharp streak-like scattering and the diffuse butterfly-type scattering oriented along flow as shown in Figure 5-9d. The butterfly pattern is a consequence of the concentration fluctuations of PB along the original string with a characteristic wavelength of the order of interdroplet distance, Λ (see Figure 5-8) and the streak pattern is a result of the spatial correlation of the concentration fluctuations with correlation length, L (see Figure 5-8).

As time elapses after cessation of flow, the droplets grow as a consequence of diffusion-coalescence processes and hence Λ is expected to increase. At the same time the nematic alignment of the droplets tends to be destroyed, giving rise to a decrease of L with time. The former would shift the butterfly pattern toward smaller scattering angles and increase its scattered intensity

with time as seen in Figures 5-9d and 5-9f. The latter would suppress the intensity of the butterfly pattern and make the lateral spread of the streak smaller with time as seen again in Figures 5-9d and 5-9f. The pattern in Figure 5-9f is quite analogous to the pattern observed for the PS/DOP system under steady shear. Thus the real-space structure of the PS/DOP system is expected to be analogous to that shown in Figure 5-9e. Although the structure in Figure 5-9e was obtained after cessation of shear in the PS/PB/DOP system, it exists in a steady state under strong shear flow of $\dot{\gamma} > \dot{\gamma}_a$ in the PS/DOP system.

5-5. Summary

The self-assembly of the PS/DOP systems under steady shear flow is summarized in Figure 5-10 in which the change of the light scattering pattern and real-space structure with $\dot{\gamma}$ are schematically illustrated in the upper and lower halves, respectively. Upon imposing shear flow on the single-phase PS/DOP solutions in the quiescent state (Figure 5-10a) strong concentration fluctuations are induced at $\dot{\gamma} > \dot{\gamma}_c$, as shown in Figure 5-10b to 10d in the order of increasing $\dot{\gamma}$. At $\dot{\gamma} < \dot{\gamma}_c$ (in Regime I) the solution remains homogeneous presumably, because $\dot{\gamma}_c$ is smaller than the relaxation rate for the reptation process.²⁸ Under this condition shear does not strongly affect molecular orientation and hence the elastic effect^{5-7,9,29} is not significant. At $\dot{\gamma} > \dot{\gamma}_c$, however, the elastic effect is significant, which enhances the concentration fluctuations along flow.^{8,12} The shear-enhanced concentration fluctuations may be expressed by a superposition of Fourier modes with wave vectors $\mathbf{k}$

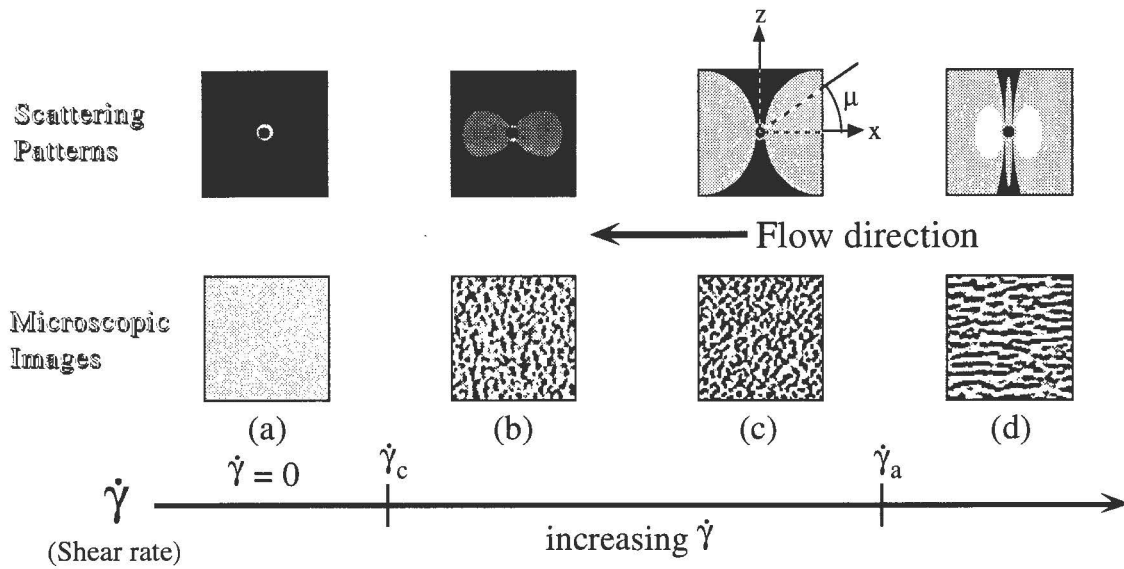


Figure 5-10 Schematic representation of the small-angle light scattering patterns (upper halves) and concentration fluctuations observed under shear-microscopy (lower halves) at quiescent state and under steady shear flow.

(See Figure 4-1).

At relatively small $\dot{\gamma}$ above $\dot{\gamma}_c$ (i.e., in Regime II) the wave vectors $\mathbf{k}$ spread over a narrow angular range around the flow direction (i.e., the fluctuations are enhanced along flow) and hence the scattering pattern spreads over a narrow azimuthal angle, μ , around $\mu = 0^\circ$ (i.e., the wing of the butterfly is narrow) as shown in Figure 5-10b. See Figure 5-1 for the definition of μ . Upon further increasing $\dot{\gamma}$ (in Regime III), the wave vectors $\mathbf{k}$ spread over a wider angular range around the flow direction and hence the butterfly wings became wider, giving rise to a thinner dark streak normal to flow as shown in Figure 5-10c.

With increasing $\dot{\gamma}$ from Regime III to IV the wave vectors $\mathbf{k}$ spread even to the direction normal to flow and a remarkable change in self-assembly

must occur to result in formation of the string phase at $\dot{\gamma} > \dot{\gamma}_a$ in Regime IV. The region rich in polymers (arrays of higher concentration blobs, A, in Figure 5-8) become more and more rich in polymer with increasing $\dot{\gamma}$ from Region III to IV, through the effect of polymer chains being squeezed from polymer-poor regions (region M in Figure 5-8) to polymer-rich regions, due to the elastic effect.^{6,7,29} At $\dot{\gamma} > \dot{\gamma}_a$, the blobs, A, are interconnected to form strings. This string formation should be responsible for shear thickening as observed in Figure 5-2.

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Chapter 6

Time Evolution of Shear-Induced Structures in Semidilute Polystyrene Solutions

6-1. Introduction

Effects of flow on miscibility and structures in polymeric systems have attracted a great deal of attention in recent years. Even for studies concerning semidilute polymer solutions only, many experimental and theoretical studies have been carried out.¹⁻²⁶ As far as our studies are concerned, we have been investigating the steady state behavior of semidilute solution of polystyrene (PS) with dioctyl phthalate (DOP) as a solvent (PS/DOP).^{9,15,21,23,27} In this chapter, a transient behavior of the PS/DOP systems, i.e., time evolution of the structure and stress developed after imposing simple shear flow to the solutions is focused on, as observed by shear-light scattering and rheology.

For homogeneous semidilute solutions or melts in which polymer molecules are well entangled with each other, many rheological investigations have been reported. Stress developments in such systems after onset of shear flow have been studied minutely in the context of nonlinear viscoelasticity.²⁸⁻³⁴ Upon imposing a high shear rate to such systems, a transient overshoot was observed in the shear and normal stress values. This phenomenon reflects the transient deformation of polymer chains and their subsequent relaxations

within the “tubes”, as proposed by Osaki et al.³⁰ and Doi-Edwards.³²

In a recent rheological investigation, Magda et al.³⁵ reported the transient rheological properties in DOP solutions of high molecular weight PS. They showed that at a high shear rate the transient stress value exhibits two overshoots before reaching steady state. They suggested that the first and second overshoots are, respectively, due to chain stretching and shear-induced demixing. In this chapter it is an aim to confirm the rheological behavior observed by Magda et al. for our samples and to directly investigate the transient structure formed under shear flow by using time-resolved light scattering.

6-2. Experimental Section

6-2-1. Samples

The three polymer solutions used in this chapter consist of high molecular weight polystyrene (PS) dissolved in dioctyl phthalate (DOP). DOP is a θ solvent for PS, and its θ temperature (T_θ) is 22 °C.³⁶ Characterizations of the PS and their solutions are listed in Table 6-1. Concentrations of the solutions are in the semidilute regime. The methods used to prepare them are same as those used in previous experiments.^{9,15,21,23,27}

The PS/DOP system has a phase diagram of the UCST-type. Figures 6-1 and 6-2 show, respectively, the cloud point curves of the PS548/DOP and the PS288/DOP systems used in this experiment. Crosses in the figures indicate the temperatures at which the experiments were carried out. Clearly

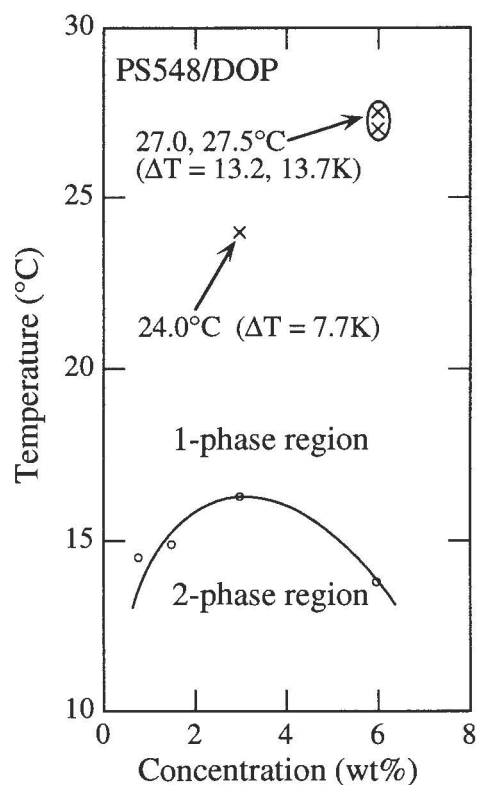


Figure 6-1 Cloud point curve of PS548/DOP. Crosses in the figure indicate the temperature and concentration at which experiments with shear-light scattering and rheometry were carried out.

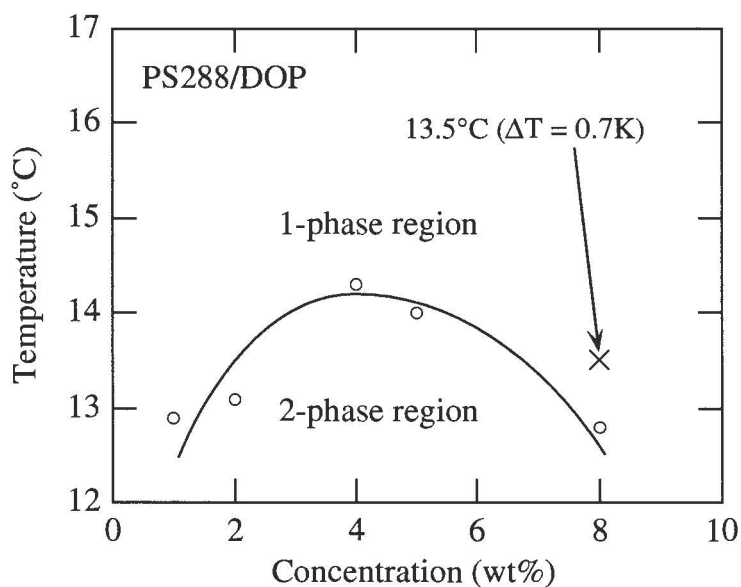


Figure 6-2 Cloud point curve of PS288/DOP. A cross in the figure indicates the temperature and concentration at which experiments with shear-light scattering and rheometry were carried out.

Table 6-1. Polymer solutions used in this chapter

polymer code	$M_w^{1)}$ ($\times 10^{-6}$)	$M_w/M_n^{1)}$	concentration (wt%)	$c/c^{*2)}$	cloud point ³⁾ (°C)	$\tau_R(s)^{4)}$
PS548	5.48	1.15	3.0	20	16.3	5
PS548	5.48	1.15	6.0	40	13.8	50
PS288	2.89	1.09	8.0	40	12.8	140

1) M_w and M_n are weight-average molecular weight and number-average molecular weight, respectively.

2) c^* : overlap concentration

3) The cloud points of the solutions were determined by the same method as described elsewhere.⁹

4) The longest stress relaxation time measured from $\log \eta$ vs. $\log \dot{\gamma}$ at the experimental temperature specified in the text.

all the samples are in one phase region in the quiescent state.

6-2-2. Shear-Light Scattering

Light scattering measurements under shear flow (shear-light scattering) are carried out with the two rheo-optical apparatuses^{23,37} constructed in our laboratory. One has a photodiode array as a one-dimensional detector for quantitative scattering measurements.³⁷ (See Sec. 1-2.) Another has a screen and CCD camera as shown in Figure 6-3. (See Chapter 2 in detail.) A He-Ne CW gas laser ($\lambda_0 = 632.8$ nm, 15 mW) is used as an incident beam source. The scattering pattern on the screen is captured by the CCD camera, and its NTSC video signal is transferred to a personal computer (Macintosh with

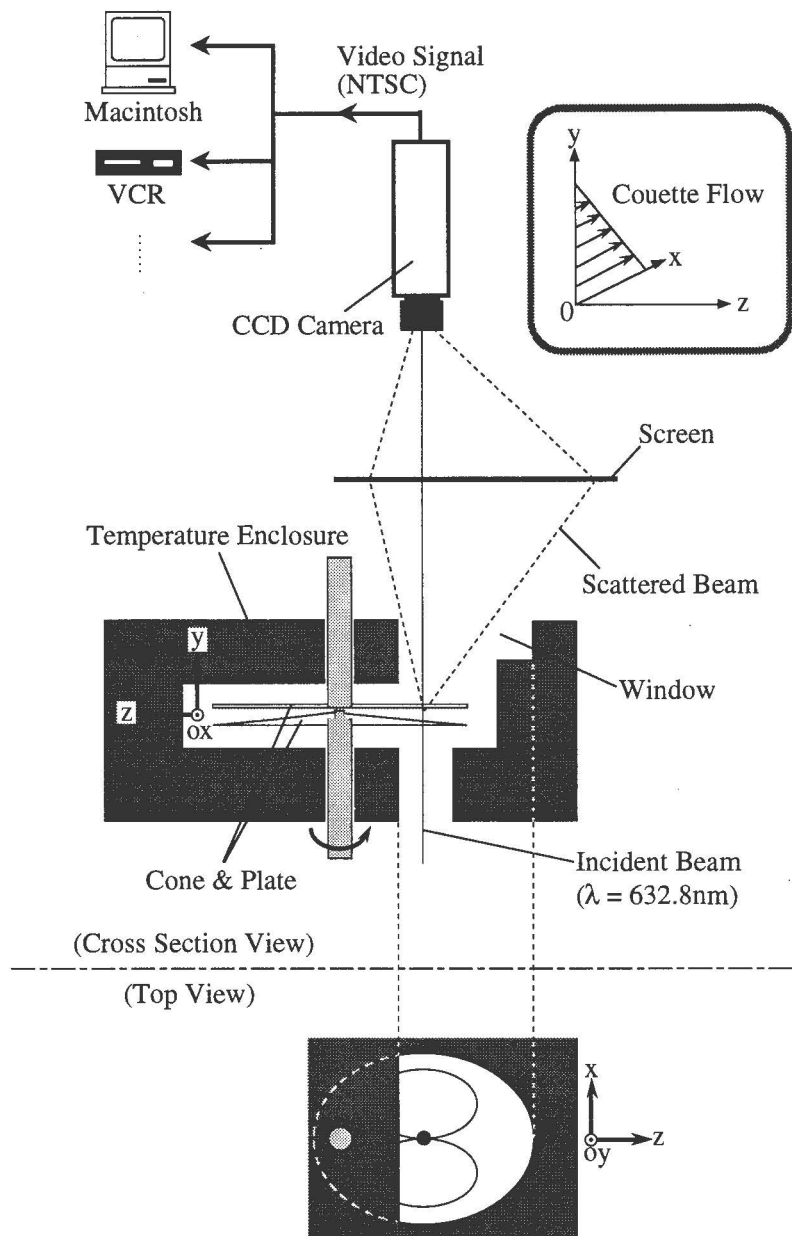


Figure 6-3 Schematic diagram of the experimental setup: CCD camera with image capturing system, temperature enclosure, cone-and-plate type shear cell to generate Couette flow, and coordinate system used in this chapter. Note that the coordinate system used here is identical to that commonly used in this field but is different from the one we used in our earlier work,^{8,9,15,21,23} which is based on a tradition in the field of scattering. A top view of the temperature enclosure indicates that a window for the scattered beam side screens the butterfly pattern partially, causing asymmetrical appearance of the butterfly patterns in Figures 6-5, 6-7, 6-8, and 6-11.

frame grabber board), VCR, and so forth.²³ Although the scattering intensity data obtained by the CCD camera system are qualitative, the system gives two-dimensional scattering profiles at short time intervals. The shear cell used is the same for both apparatuses, a transparent cone-and-plate type shear cell made of quartz with 80 mm diameter and 1 ° cone angle. The optical setup and coordinate system used in this chapter are the same as those previously used²⁷ and shown in Figure 6-3. The velocity gradient exists in the plane Oxy , where Ox is the flow direction. The incident beam is sent along the Oy axis, and the scattering profiles are detected in the plane Oxz .

The shear cell is covered by a temperature enclosure in both apparatuses in order to precisely control the sample temperature. The temperature enclosure has a double-chamber construction into which temperature-controlled air is fed, as shown in Figure 2-3 (see also Sec. 2-2). In the present experimental study, the sample temperature was controlled with accuracy of ± 0.3 °C at the incident beam spot and within 1 °C variation along the radial direction. As shown in Figures 6-3 and 2-3, a window of the temperature enclosure for a scattered beam side has the shape of truncated circle in the side of the shaft attached to the plate. Therefore scattering patterns are partially screened by the window, and their second and third quadrants on the detector plane are partially truncated (see the top view of the temperature enclosure in Figure 6-3) as seen in the patterns shown in Figures 6-5, 6-7, 6-8, and 6-11. For low-temperature experiments of PS288/DOP systems, dried cold air was fed to a temperature enclosure through an air-cooler set between the air compressor and the temperature enclosure.

6-2-3. Rheology

Rheological behavior was measured with a Rheometrics® RMS800 mechanical spectrometer and RDA-II dynamic analyzer at almost the same temperature as in the shear-light scattering measurements. The rheological time τ_R (the longest stress relaxation time or the reptation time) was estimated for each solution used in this experiment (PS548/DOP 6.0 wt% at 27 °C, PS548/DOP 3.0 wt% at 25 °C, and PS288/DOP 8.0 wt% at 13.5 °C) from the shear rate $\dot{\gamma}_{c,rheo}$ at the intercept of two straight lines, one in the low-shear-rate Newtonian regime and the other in the high-shear-rate shear thinning regime, on a double logarithmic plot of steady state shear viscosity and shear rate ($\tau_R \equiv 1/\dot{\gamma}_{c,rheo}$). The results are summarized in Table 6-1.

6-3. Results

6-3-1. PS548/DOP Systems

Figure 6-4 shows the transient rheological properties of the PS548/DOP 6.0 wt% solution at 27.5 °C after the onset of shear flow of a constant shear rate $\dot{\gamma} = 14.3 \text{ s}^{-1}$. Both normal and shear stresses (N_1 and σ , respectively) showed two overshoots on its approach toward steady state. The second overshoot in normal stress is very conspicuous. These trends are completely the same as those reported by Magda et al.³⁵ The first overshoot in shear stress appears to occur prior to that in normal stress.

In order to investigate structural origin of this intriguing rheological

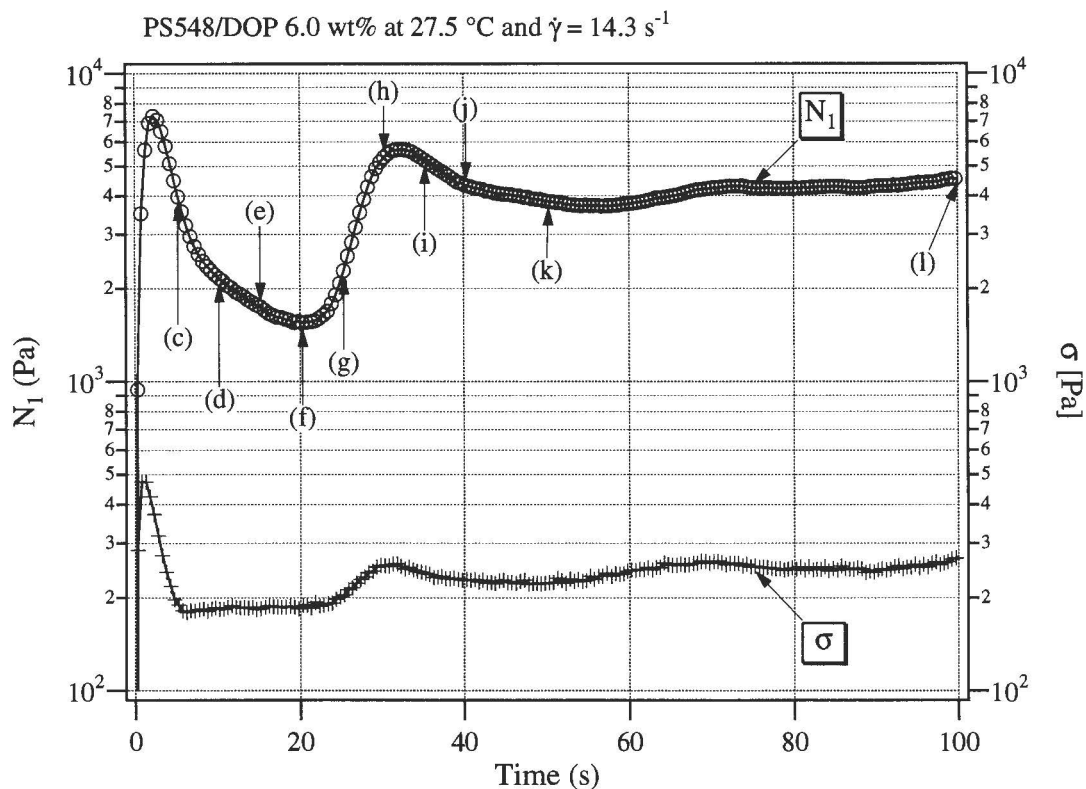


Figure 6-4 Plots of transient normal (N_1) and shear stresses (σ) of the PS548/DOP 6.0 wt% solution at 27.5 °C after the onset of the shear flow of $\dot{\gamma} = 14.3 \text{ s}^{-1}$.

behavior, the two-dimensional scattering experiments were carried out using the shear-light scattering apparatus with CCD camera described in Figure 6-3, under almost the same conditions as that used for the rheological measurements in Figure 6-4. Figure 6-5 shows the time evolution of the scattering pattern after the onset of shear flow of $\dot{\gamma} = 14.3 \text{ s}^{-1}$ for the PS548/DOP 6.0 wt% solution at 27.0 °C. The flow direction (the Ox axis in Figure 6-3) is horizontal in the figure. Here, annotations (c) - (l) with arrows in Figure 6-4 correspond to those in Figure 6-5 and indicate the time when two-dimensional scattering patterns in Figure 6-5 were taken. In order to investigate in detail the development of scattering patterns after the onset of shear flow, contour patterns showing the iso-intensity levels for the scattering patterns

PS548/DOP 6.0 wt% at 27.0 °C and $\dot{\gamma} = 14.3 \text{ s}^{-1}$

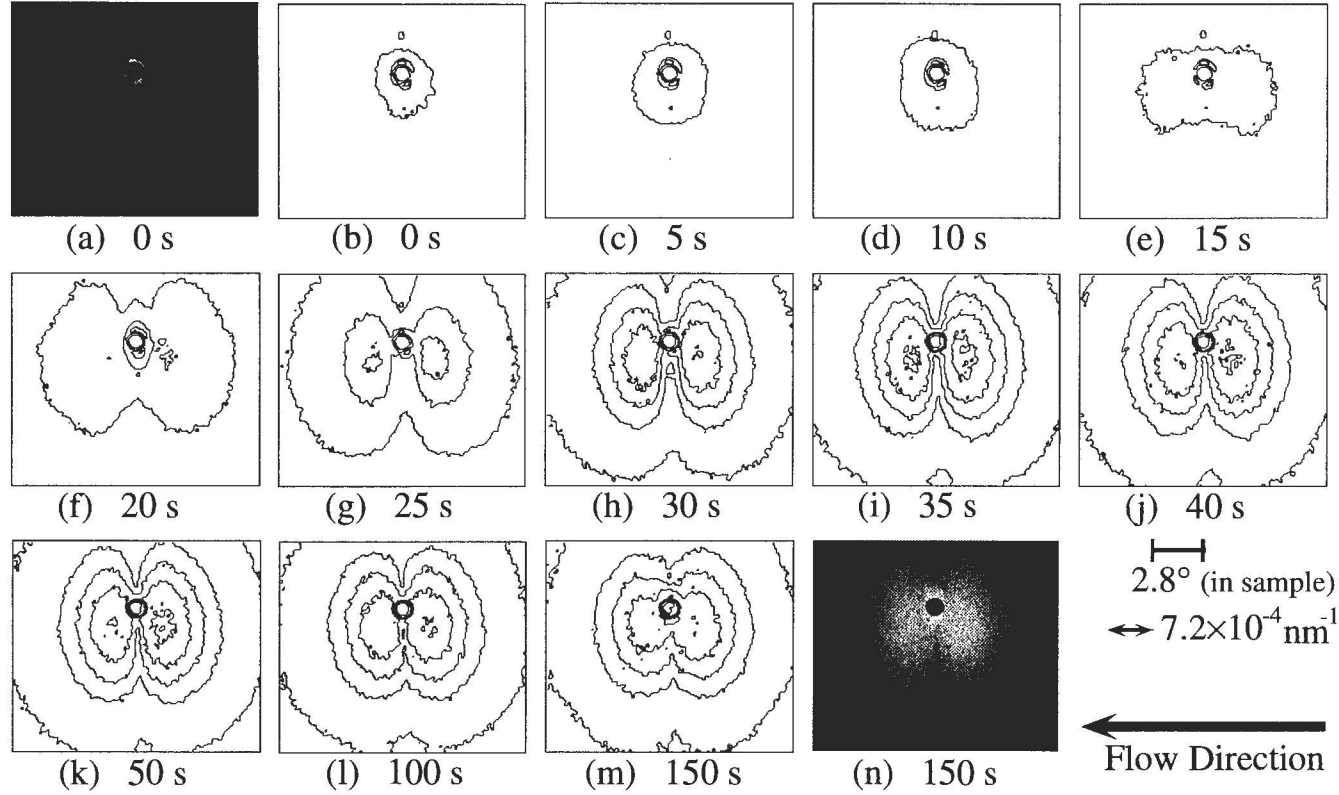


Figure 6-5 Time evolution of the scattering pattern of the PS548/DOP 6.0 wt% solution at 27 °C after the onset of the shear flow of $\dot{\gamma} = 14.3 \text{ s}^{-1}$. Images (a) and (n) are original scattering patterns, while others are contour plots of the scattered intensity distribution calculated from original scattering patterns. The asymmetry of the patterns with respect to the horizontal axis is due to an artifact induced by the window of the temperature enclosure as described in Sec. 6-2-2.

were constructed. In the construction, first the intensity fluctuations in the original scattering patterns which arise from the speckles in the patterns were smoothed. Images (b) - (m) are the contour patterns obtained up to 150 s after the onset of shear flow. For comparison between the contour patterns and the original scattering patterns, real patterns (a) and (n) are shown, corresponding to contour patterns (b) and (m), respectively.

The scattering intensity along the flow started to increase at about 15 s (pattern (e)) , and then the butterfly pattern was clearly developed: its intensity parallel to the flow direction increases and the “dark streak” perpendicular to flow direction narrows. The dark streak results from the fact that the scattered intensity normal to the flow direction stays weak, almost at the same intensity level as that in the homogeneous solutions. After 50 s (patterns (k)-(m)), the

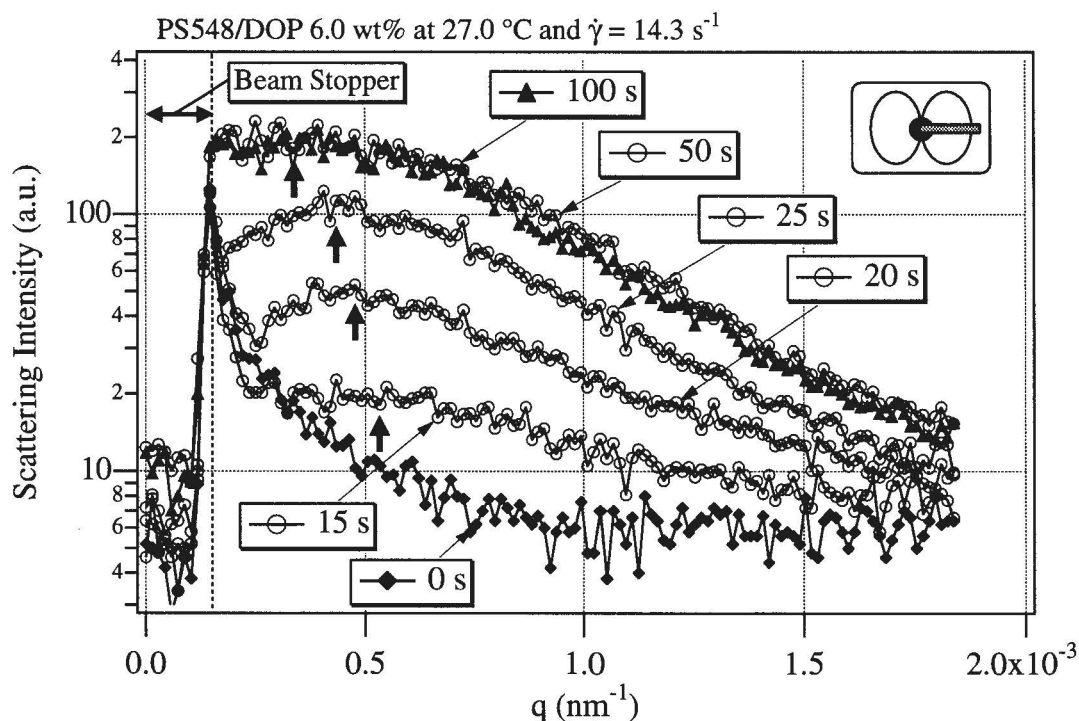


Figure 6-6 Time evolution of the scattering profiles along the flow direction which were calculated from the 2D scattering patterns shown in Figure 6-5.

butterfly did not change much with time, which indicates achievement of a steady state.

To investigate the time evolution of the butterfly pattern more quantitatively, the scattering profiles parallel to the flow direction were evaluated (Figure 6-6). They are a part of the scattered intensity in the two-dimensional scattering patterns which falls onto the shaded area, as schematically illustrated in the inset at top right-hand corner of Figure 6-6. The scattering intensity profiles shown are raw data subjected to no corrections, and hence these profiles are considered to be semi-quantitative. The intensity at $q \leq 1.5 \times 10^{-4} \text{ nm}^{-1}$ is very low, because a beam stop was set there. From right after the onset of shear flow (0 s) to 50 s, the scattered intensity increased by more than 1 order of magnitude, the scattering peak appeared, and its peak position moved to a smaller q with time. The scattering profile at 50 s was almost same as that of 100 s. Therefore the butterfly pattern reached a steady state pattern after 50 s.

Figure 6-7 shows the plots of the transient normal (N_1) stress of the PS548/DOP 3.0 wt% solution at 24 °C after the onset of shear flow of $\dot{\gamma} = 89.1 \text{ s}^{-1}$. Note that the stress level developed here is much higher than that in Figure 6-4, because of a higher $\dot{\gamma}$ and a lower temperature than the corresponding values in Figure 6-4. Only the normal stress data were shown, because the second overshoot in normal stress was observed more clearly than that in shear stress. The development of scattering patterns in terms of the contour patterns was also included in Figure 6-7. These contour patterns were constructed in the same manner as in Figure 6-5 from the original scattering patterns taken at the time indicated by the arrow on the data line of

normal stress. The shear rate of 89.1 s^{-1} chosen is high enough that it belongs to Regime IV^{15,27} showing the anomalous rheological and scattering behavior (see Figure 5-2 in Chapter 5 for the same solution with the same concentration or Figure 6-10, shown later, for the same solution with a higher concentration). The anomaly in Regime IV will be discussed later in Sec. 6-4-1. Because of the large $\dot{\gamma}$ (89.1 s^{-1}) imposed to the system, the normal stress was so large that their values at the first and second overshoots could not be properly

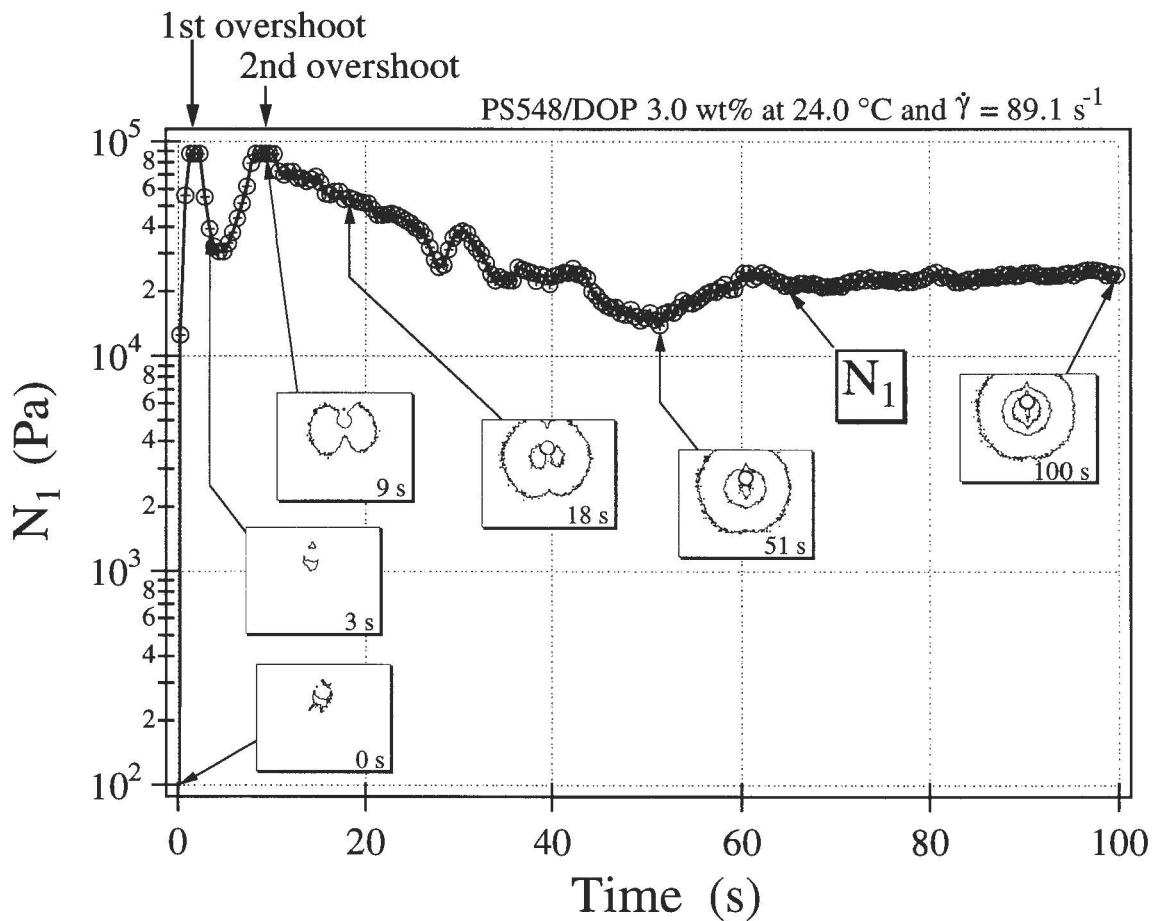


Figure 6-7 Time evolution of the scattering pattern and the normal stress (N_1) of the PS548/DOP 3.0 wt% solution at 24 °C after the onset of the shear flow of $\dot{\gamma} = 89.1 \text{ s}^{-1}$. This $\dot{\gamma}$ is much greater than $\dot{\gamma}_a$. The asymmetry in the contour patterns is due to the same reason as that in Figure 6-5.

detected: they were saturated. At 3 s after imposing shear flow at which the first stress overshoot was observed, no strong scattering yet appeared and the intensity level was the same as that in the quiescent homogeneous solution. At around the time at which the second overshoot occurred, a butterfly-like anisotropic scattering pattern developed. Then the scattering intensity increased with a further elapse of time, and a streak-like pattern perpendicular to the flow direction appeared at ca. 50 s after the onset of the flow. At this shear rate (89.1 s^{-1}) the steady state scattering pattern is a strong streak-like pattern developed perpendicular to the flow direction which is superposed on the butterfly pattern appeared at larger angles, as shown in the contour pattern at 100 s.²⁷ Comparison of the scattering patterns taken at a much later time (though not shown in Figure 6-7) revealed that this pattern at 100 s is the steady state pattern.

6-3-2. PS288/DOP Systems

In order to investigate the time evolution of the butterfly pattern more quantitatively, the scattering and rheological experiments for the PS288/DOP 8.0 wt% solution at $13.5 \text{ }^{\circ}\text{C}$ ($\Delta T = +0.7 \text{ }^{\circ}\text{C}$, $\Delta T = T - T_{cl}$), i.e., at much lower temperature than those for the PS548/DOP systems, were carried out as shown in Figure 6-2. Because of small ΔT , the critical shear rate, $\dot{\gamma}_c$, for the butterfly formation is also very low.⁹ Therefore, it was able to observe the phase-separation process under shear flow at a much lower shear rate than the previous cases shown in Figures 6-4 to 6-7. In the case of the lower shear rate, the time evolution of the scattering profile and the shear-induced structure

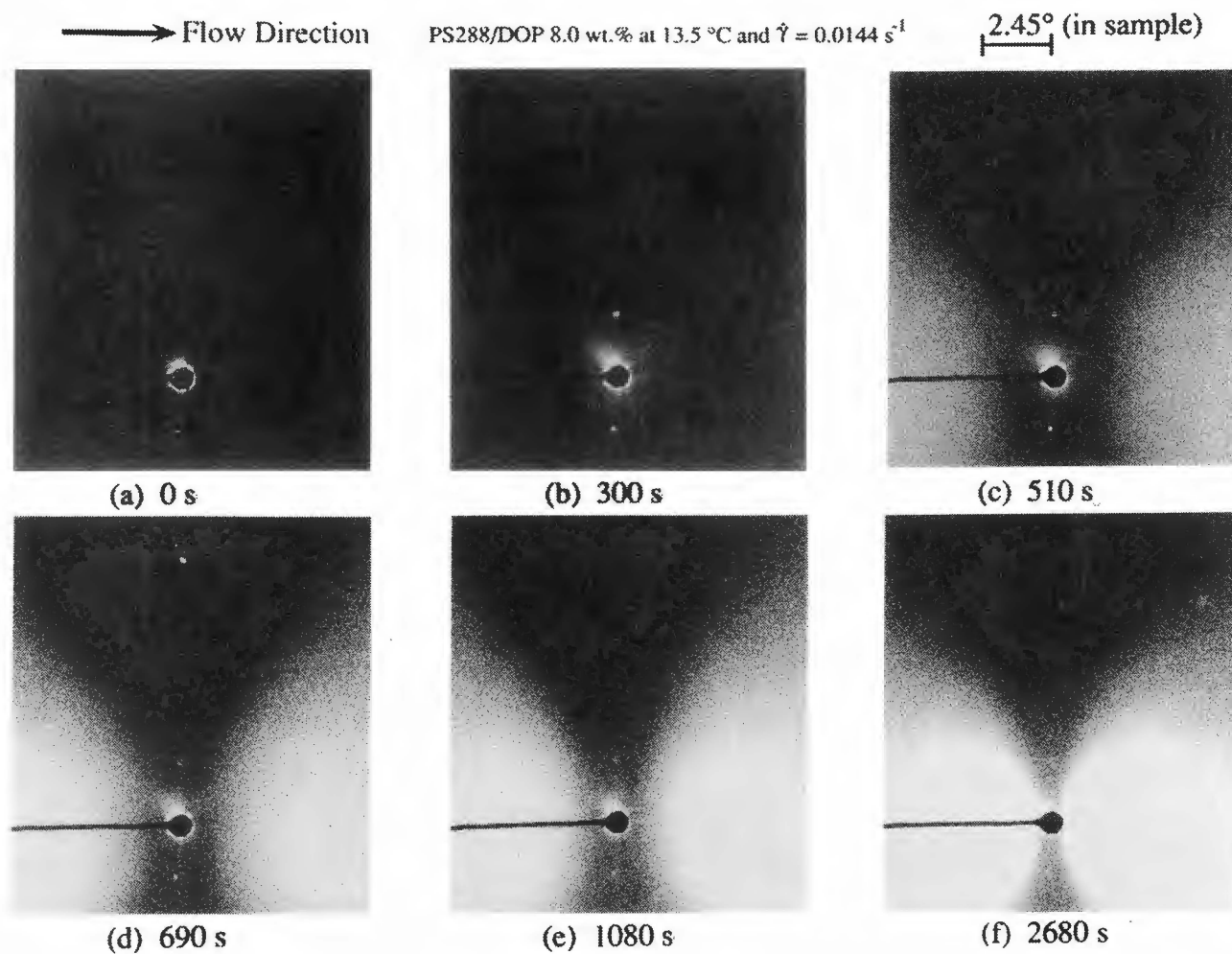


Figure 6-8 Time evolution of the scattering pattern of the PS288/DOP 8.0 wt% solution at 13.5 °C after the onset of the shear flow of $\dot{\gamma} = 0.0144 \text{ s}^{-1}$. These scattering patterns were taken by photographic films.

formation are expected to occur more slowly, which facilitates a quantitative study on the shear-induced ordering processes.

Figure 6-8 qualitatively shows the time evolution of the butterfly pattern for the PS288/DOP 8.0 wt% solution at 13.5 °C after the onset of the flow of

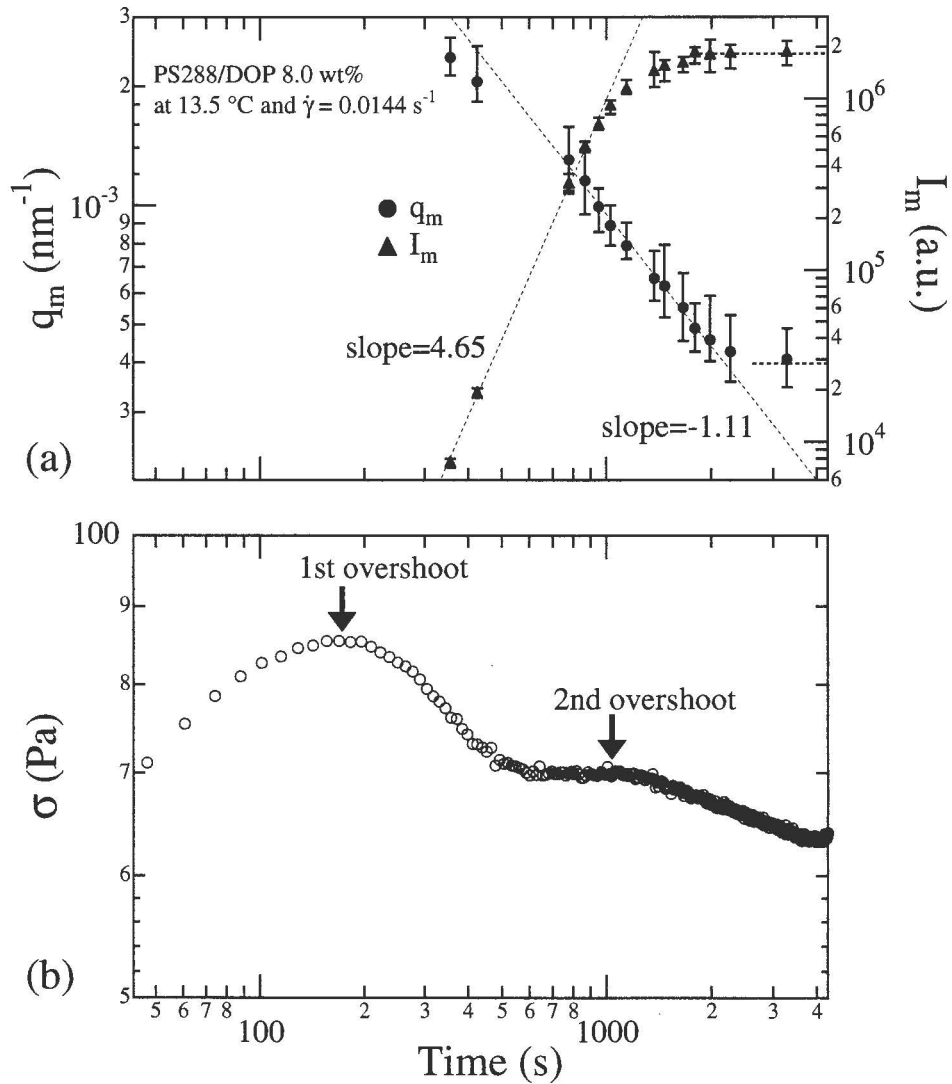


Figure 6-9 (a) Time changes in peak scattering vector q_m and peak scattering intensity I_m of the PS288/DOP 8.0 wt% solution at 13.5 °C after the onset of shear flow of $\dot{\gamma} = 0.0144 \text{ s}^{-1}$. The values q_m and I_m were quantitatively measured with a photodiode array detector. (b) Plot of transient shear stress (σ) of the same sample under the same conditions as in (a).

$\dot{\gamma} = 0.0144 \text{ s}^{-1}$, where the flow direction is horizontal. These scattering patterns were taken with photographic films. This development of the butterfly pattern is similar to that of PS548/DOP 6.0 wt% solution at 27 °C (Figure 6-5). However the shift of the peak position and the spreading of the butterfly wings with time can be more clearly observed in Figure 6-8.

For quantitative studies of the time evolution of scattering profiles, the shear-light scattering apparatus with a 35-elements photodiode array as a one-dimensional detector was used. Using this apparatus the time-evolution of the scattering profiles parallel to the flow direction was measured, which enabled us to quantitatively determine the time changes in the peak scattering vector q_m and the peak scattering intensity I_m parallel to flow. Figure 6-9a shows the time changes in q_m and I_m of the PS288/DOP 8.0 wt% solution at 13.5 °C after the onset of shear flow of $\dot{\gamma} = 0.0144 \text{ s}^{-1}$, the data of which were obtained simultaneously with the experiment shown in Figure 6-8. Figure 6-9b shows the results of transient rheological experiments on this sample under the same conditions as the scattering experiments. In this rheological experiment, the shear rate imposed (0.0144 s^{-1}) was so low that the first normal stress was too small to be detected with sufficient accuracy. On the other hand, the shear stress (σ) could be accurately detected, showing the two overshoots as indicated by the arrows in Figure 6-9b.

6-4. Discussion

6-4-1. Steady state Structures and Properties as a Function of $\dot{\gamma}$

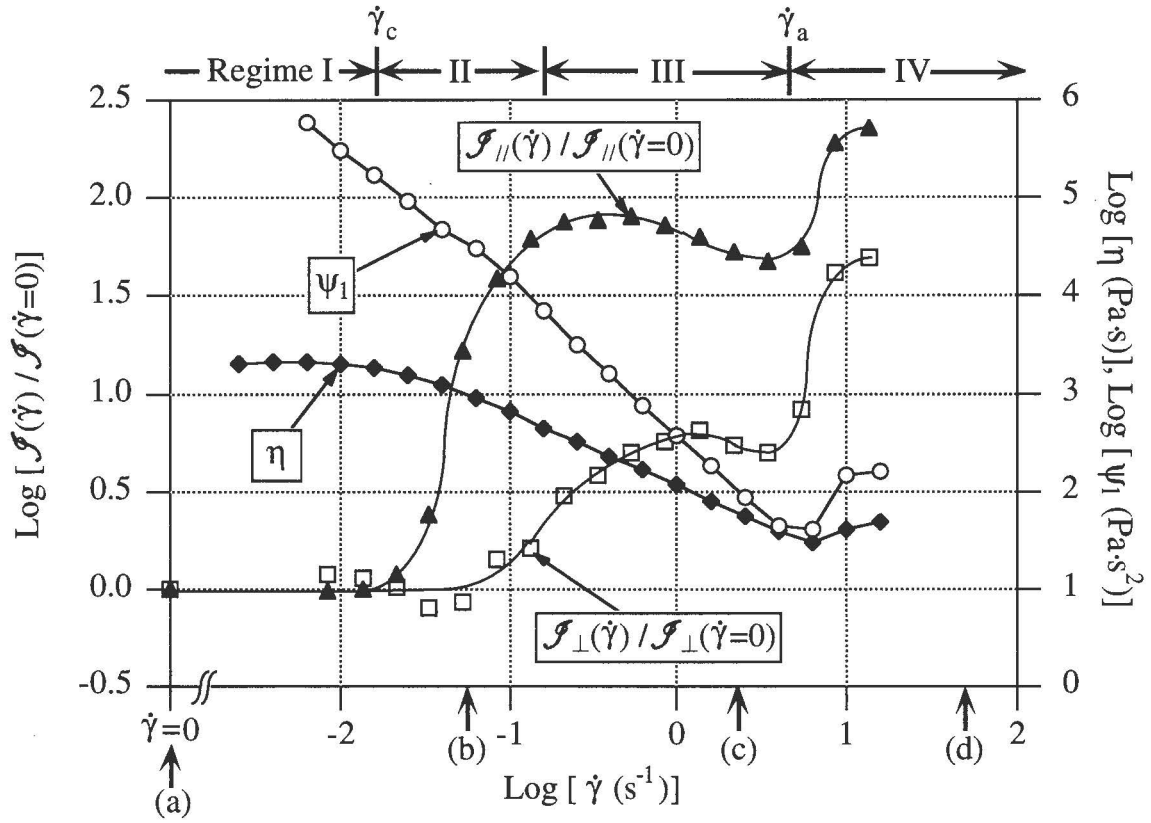


Figure 6-10 Shear viscosity, η , coefficient of the first normal stress difference, ψ_1 , normalized integrated scattered intensity parallel and perpendicular to flow, $\mathcal{I}_{||}(\dot{\gamma})/\mathcal{I}_{||}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma})/\mathcal{I}_{\perp}(\dot{\gamma}=0)$ for the PS548/DOP 6.0 wt% solution in steady state shear flow at 27°C. $\dot{\gamma}_c$ and $\dot{\gamma}_a$ are the critical shear rates for the onset of the shear-enhanced concentration fluctuations and of the anomalies in the rheological and scattering behavior, respectively.

Before the transient structures and properties are discussed, it would be useful to briefly review steady state structures and properties.^{15,21,27} Figure 6-10 shows the steady state scattering and rheological properties of the PS548/DOP 6.0 wt% solution at 27 °C as a function of shear rate. $\mathcal{I}_{||}(\dot{\gamma})/\mathcal{I}_{||}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma})/\mathcal{I}_{\perp}(\dot{\gamma}=0)$ are, respectively, the integrated scattered intensity at a given $\dot{\gamma}$, normalized with respect to the integrated intensity of the quiescent solution,

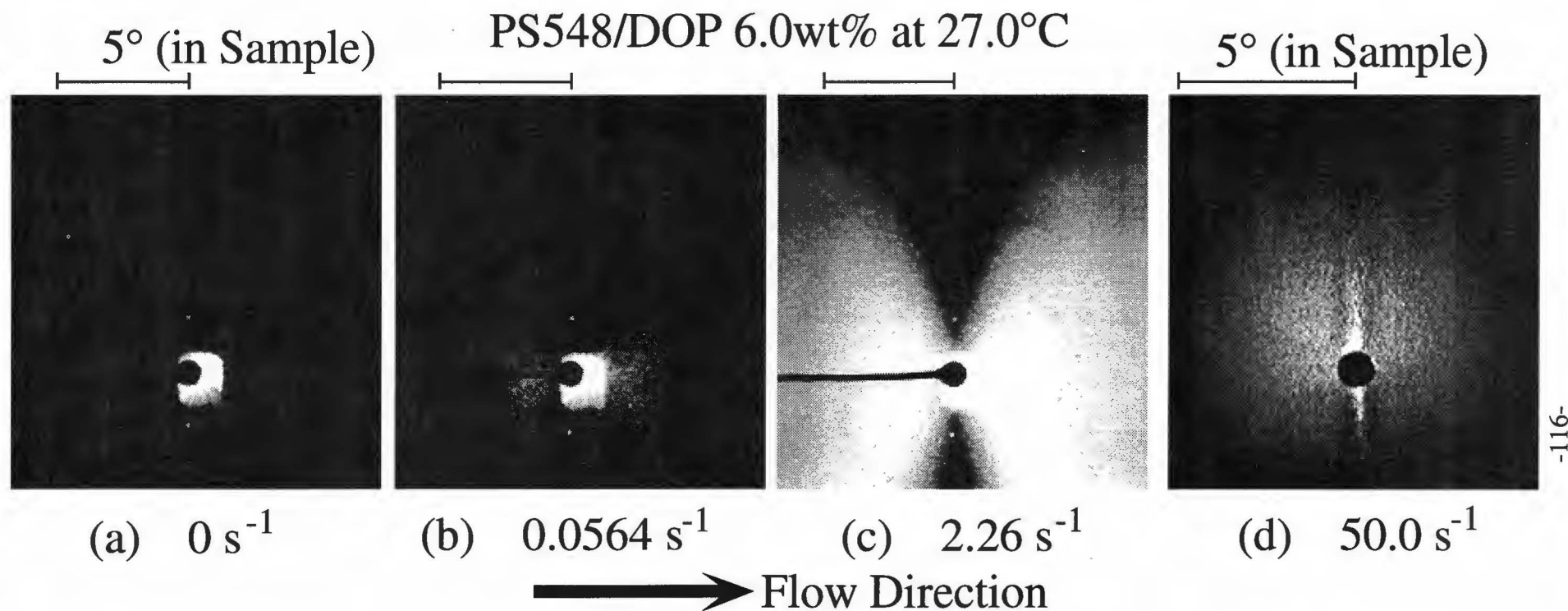


Figure 6-11 Steady state scattering patterns at various shear rates for the same solution as in Figure 6-10. Pattern (d) was taken with a shorter exposure time than the other patterns. The asymmetry of the LS patterns is due to the same origin as that in Figure 6-5.

parallel and perpendicular to the flow direction. The definition of integrated intensity was given in previous papers.^{9,27} (See also Sec. 5-3.) η and ψ_1 are the shear viscosity and the coefficient of the first normal stress difference, respectively. Figure 6-11 shows a characteristic change in the steady state scattering pattern with $\dot{\gamma}$, corresponding to the changes shown in Figure 6-10. Patterns (a) - (d) of Figure 6-11 were obtained at $\dot{\gamma}$ marked (a) - (d) in Figure 6-10, and the flow direction is horizontal. The steady state structure and anisotropic concentration fluctuations in the PS/DOP solutions under shear flow by a direct visualization with shear microscopy, i.e., by *in situ* observation with optical microscopy were reported previously.^{21,23} The observed changes in the light scattering patterns and real-space structures with $\dot{\gamma}$ were summarized in Figure 5-10 in Chapter 5.

The shear-rate dependence of the scattering and rheological behavior can be classified into four regimes, as shown in the top margin of Figure 6-10; Regime I at $\dot{\gamma} < \dot{\gamma}_c$, where $\dot{\gamma}_c$ is the critical shear rate for the *shear-enhanced concentration fluctuations* or *phase-separation*, and Regimes II - IV at $\dot{\gamma} > \dot{\gamma}_c$. In Regime I, the scattering and concentration fluctuations are essentially identical to those of homogeneous semidilute solutions, and rheological behavior is almost that of Newtonian fluid. In Regime II, a unique butterfly-type scattering pattern appears with a dark streak perpendicular to the flow direction. The scattered intensity $\mathcal{I}_{//}$ is increased by about 2 orders of magnitude, but $\mathcal{I}_{\perp}$ is still weak. In Regime III, $\mathcal{I}_{//}$ reaches nearly a steady value but $\mathcal{I}_{\perp}$ still increases. Thus the butterfly pattern changes in such a way that its wings open and the dark streak narrows. In Regimes II and III, η and ψ_1 decrease with increasing $\dot{\gamma}$, i.e., shear thinning occurs.

In Regime IV (at $\dot{\gamma} > \dot{\gamma}_a$, where $\dot{\gamma}_a$ is the second critical shear rate or the critical shear rate for the onset of the anomalous behavior), the intensities $\mathcal{I}_{//}$ and $\mathcal{I}_{\perp}$ further increase and the butterfly pattern changes into the two-point pattern elongated normal to the flow (the tendency being especially remarkable in PS548/DOP 6.0 wt%) with a broad intensity maximum along the flow. Then at much higher shear rate in Regime IV, a strong bright streak-like pattern oriented perpendicular to the flow appears at small-angle regions as seen in Figure 6-11d. This streak-like pattern is superposed on the two-point pattern at large q regions. These anomalies in the change of the scattering pattern with $\dot{\gamma}$ are closely related to anomalies in rheological behavior: Both η and ψ_1 turn and begin to increase in Regime IV. In a previous report¹⁵ for the PS548/DOP 6.0 wt% solution, it was stated that there is no anomaly in η even in Regime IV (though there is a definite anomaly in ψ_1), because the first overshoot of shear stress decays to the level expected from the $\dot{\gamma}$ -dependence of η in the lower $\dot{\gamma}$ regime, if the solution is kept under shear. However it was found that this solution exhibits further the second overshoot on its approach toward steady state, if the solution is kept under shear even longer, and that the steady values are larger than those reported previously. Therefore this solution was found to exhibit the anomaly in both η and ψ_1 , as shown in Figure 6-10 and Yanase et al.¹²

6-4-2. Transient Behavior in PS548/DOP Systems

Figure 6-5 indicates that the butterfly pattern starts to grow at ca. 15 s after the onset of shear flow of $\dot{\gamma} = 14.3 \text{ s}^{-1}$ for the 6.0 wt % solution.

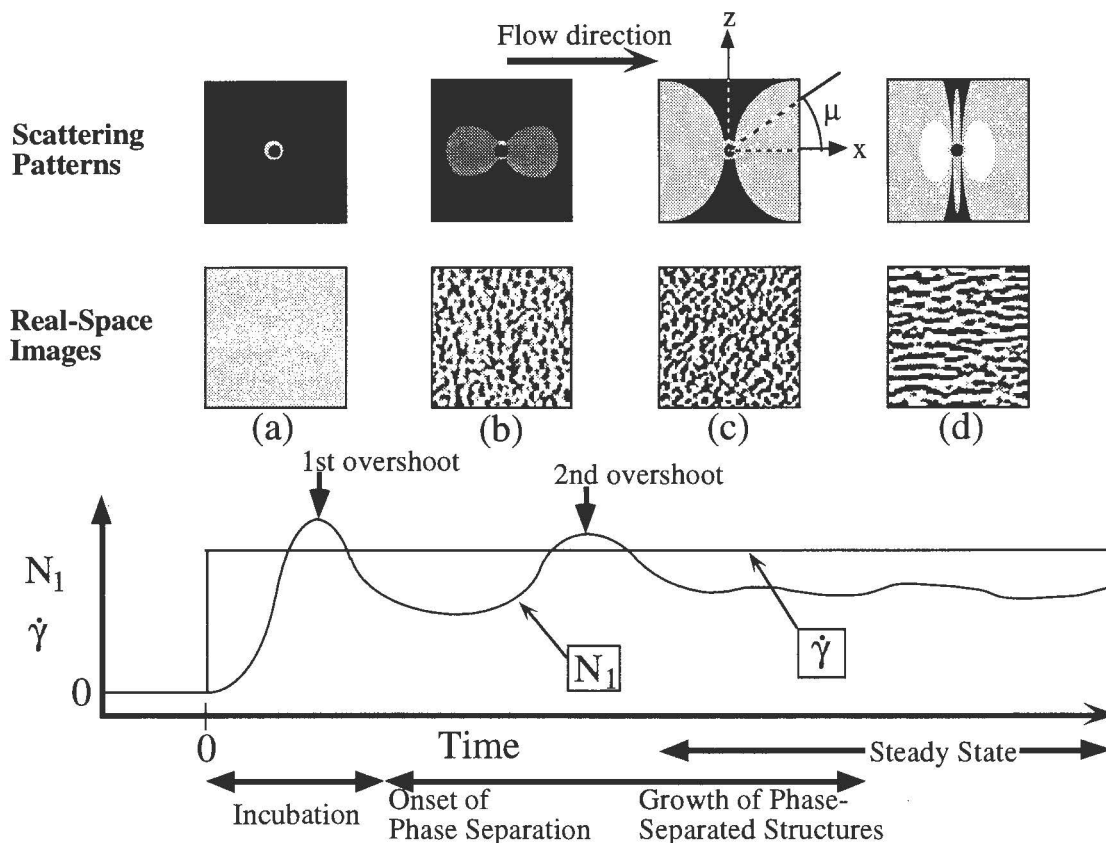


Figure 6-12 Schematic representation of transient changes in the butterfly-type light scattering pattern, the microscopic (real-space) image for the concentration fluctuations, and the normal stress after the onset of the flow at a constant shear rate $\dot{\gamma}$. The dark and bright regions in the microscopic images correspond to polymer-rich and polymer-poor regions, respectively. The angle μ on the scattering pattern indicates azimuthal angle. Parts a and b represent the incubation state and the early stage of the shear-induced phase separation. In the case of a low imposed shear rate satisfying $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$, the steady state is represented by part c and the change from parts a and c corresponds to a growth of the phase-separated structures. In the case of a high imposed shear rate, the steady state is represented by part d, while the growth of the structures by the change from part b to c and finally to d.

Furthermore, from Figure 6-4 it was found that this change occurred after the first stress overshoot and near the minimum in N_1 in the plot of $\log N_1$ vs t . Further comparison of Figures 6-5 and 6-6 with Figure 6-4 shows that the butterfly pattern reached almost steady state after the second stress overshoot, i.e., at > 50 s.

The trends found above are schematically summarized in Figure 6-12 where the changes in the light scattering patterns, the real-space structures, and the normal stress with time after the onset of a constant shear rate are schematically shown and classified into three regions. First, some incubation time exists from the onset of shear flow to evolution of the butterfly pattern for the q window covered in the light scattering experiments (part a). Note that the structure development occurs at around a time at which N_1 becomes minimum after the first stress overshoot (part b). Furthermore the system reaches steady state after the second overshoot. The steady state scattering pattern and structures at this shear rate of $\dot{\gamma} = 14.3 \text{ s}^{-1}$ are shown in part c. Note that part d refers to the case in which the imposed shear rate $\dot{\gamma}$ is much higher than $\dot{\gamma}_a$ (e.g., 50.0 s^{-1} in Figure 6-11d). As the steady state is approached (from (b) to (c) in Figure 6-12), the butterfly wings become wider, giving rise to a thinner dark streak normal to flow. The corresponding schematic real-space images, i.e., real structures of the sample under flow, are shown beneath the scattering patterns. The dark and bright regions correspond to polymer-rich and polymer-poor regions, respectively. Right after the onset of the evolution of the butterfly pattern, the wave vectors $\mathbf{k}$ for the Fourier modes of the shear-enhanced concentration fluctuations are spread over a narrow range of orientation angles around the flow direction; that is, the fluctuations are

enhanced primarily only along flow. Therefore the scattering pattern spreads over a narrow azimuthal angle, μ , around $\mu = 0^\circ$. As time elapses the wave vectors k spread over a wider angular range around the flow direction, and hence the butterfly wings become wider.

Figure 6-7 for the case of a high imposed shear rate of $\dot{\gamma} > \dot{\gamma}_a$ also indicates that the scattering pattern starts to grow after the first stress overshoot. In the beginning of the development of the scattering pattern, the shape of anisotropic scattering pattern is butterfly-type. However, the steady state scattering pattern is the strong streak-like pattern at small q regions superposed on the two-point pattern at large q regions. These developments of scattering patterns are very similar to those under steady shear flow with increasing $\dot{\gamma}$ as shown in Figure 5-10 in Chapter 5. The development of the transient scattering and structure at the high shear rate is also represented schematically by Figure 6-12. However, it should be noted that at this high shear rate the steady state scattering pattern and structures are given by part d instead of part c. Although the steady state is different, the time evolution is also classified into three regions, i.e., incubation, evolution, and steady state regions. The early stage of the structure development at the high shear rates ($\dot{\gamma} > \dot{\gamma}_a$) (whose steady state pattern and structure are given by Figure 6-12d) is same as that at the low shear rates ($\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$) (whose steady state is given by Figure 6-12c). It occurs after the first stress overshoot and around a time at which the stress becomes minimum (part b). The structure growth and evolution of the butterfly patterns after the onset of the phase separation are shown in parts b and c. As shown in Figure 6-12d, however, the steady state structure has long strings aligned parallel to the flow (part d). It is believed that these strings themselves

have internal concentration fluctuations along their axes. The strings give rise to the strong streak-like pattern at small q regions and the internal concentration fluctuations are responsible for the two-point pattern at large q regions.²⁷

6-4-3. Transient Behavior in PS288/DOP Systems

Figures 6-8 and 6-9 indicate that the scattering intensity of the butterfly patterns started to increase after 300 s, shortly after the first overshoot at ca. 170 s (see arrow in Figure 6-9b). After that, $\log I_m$ increased and $\log q_m$ decreased almost linearly with increasing $\log t$ (see Figure 6-9a). This behavior in the time evolution of I_m and q_m suggests a slow ordering process of the structures in the solution after the onset of constant shear flow. This ordering process is very similar to that in spinodal decomposition in thermodynamically unstable solution without shear flow, except for the fact that the slopes in $\log I_m$ and $\log q_m$ versus $\log t$ are larger than those in the spinodal decomposition in quiescent solution. This result may strongly suggest that the butterfly patterns reflect the structure formation as a consequence of “shear-induced phase separation” rather than the shear-enhanced concentration fluctuations in single phase. The evolution of I_m and q_m stopped, and thus the system has reached the steady state at ca. 2000 s. During the phase separation and the structure-ordering process, the shear stress decays after the first overshoot and the second overshoot (see the arrow in Figure 6-9b) appears before the formation of the shear-induced steady state structures. The steady state is achieved, because structures above a certain size would be broken under shear

flow and the broken structures tend to grow due to the shear-induced thermodynamic instability of the solutions.

6-4-4. Comparison of the Transient Behavior in PS548/DOP and PS288/DOP Systems

The scattering and rheological behaviors in the PS288/DOP system are essentially same as those of the PS548/DOP systems. However the transient behavior is more clearly resolved in the former than in the latter, because of the slower evolution of the structure and properties in the former. From the onset of shear flow to near the first overshoot, the scattering intensity was found to hardly increase with time; therefore the shear-flow-induced structures are not expected to be developed. Furthermore the strain value $\gamma (= \dot{\gamma}t)$ at the maximum of the first overshoot in the PS288/DOP system (Figure 6-9b) is ca. 2.5. The corresponding strain values in the well-entangled homogeneous polymer solutions or polymer melts were reported to be typically in the range of 2-3.^{28,32,34} Thus it is clear that the first overshoot is not necessarily due to the phase-separated structure. The origin of the first overshoot is probably same as that encountered in normal, well-entangled homogeneous polymer solutions or melts subjected to large shear deformation and may be ascribed to the transient stretching of polymer chains and their relaxations within the tubes.^{30,32}

The transient stretching of polymer chains may be more or less uniform, thus giving rise to no remarkable concentration fluctuations and hence scattering patterns. The overstretched chains tend to be relaxed through

slippage of the entanglement couplings, which causes the decay of the first stress overshoot. This process is accompanied by the shear-induced concentration fluctuations due to the coupling of stress and the concentration fluctuations as postulated theoretically (the so-called elastic effect⁵⁻⁷) and as proposed experimentally (the so-called onset of the butterfly formation^{3,9,11,12}). The concentration fluctuations further grow at a certain time after the onset of flow as shown in the changes in the butterfly patterns (Figures 6-5, 6-7, 6-8, and 6-12) and in the scattered intensity profiles parallel to flow (Figure 6-6). This structure growth may be responsible for the second overshoot. The overgrown structures will be burst by shear, but broken structures will grow due to the shear-induced thermodynamic instability of solutions. The burst and growth eventually give rise to steady state structures and stress. However an initial growth-burst process may give rise to a big effect on rheological properties, resulting in the observed second overshoots in shear and normal stresses.

6-4-5. Comparison with Earlier Reports

In this chapter the postulate proposed for the rheological studies of Magda et al.³⁵ was confirmed directly by means of the shear-light scattering studies. Thus it is concluded that first and second overshoots are due to the chain stretching followed by relaxation and the shear-induced demixing, respectively.

Very recently the report by Migler et al.²⁶ appeared, which was concerned with the transient rheology and shear-light scattering experiments very similar to those in this chapter. They observed a very weak second overshoot in

shear stress only at the highest shear rate ($\dot{\gamma} = 120 \text{ s}^{-1}$) employed in their experiment. The overshoot is so weak that a minimum of shear stress is only weakly discernible at ca. 8 s (see Figure 2a²⁶). The weak overshoot is due to low molecular weight of PS ($M_w = 1.03 \times 10^6$) and low concentration (4 wt% DOP solution) compared with the experiment of this chapter. Though in the case of this chapter the scattered intensity increased continuously with time as shown in Figures 6-6 and 6-9a, they found that the intensity at particular scattering vector gave an overshoot at ca. 8 s for $\dot{\gamma} = 120 \text{ s}^{-1}$ (see Figure 7a and Table 1)²⁶. The difference may be attributed to that in the plane of light scattering observation, i.e., xz (the velocity-neutral axis) plane in the case of this chapter and xy (the velocity-velocity gradient) in their case. The fact that the scattered intensity becomes strong at the minimum in the shear stress vs time may be consistent with the result of this chapter. The conclusion about the origin of the first and second overshoots agrees with theirs.

6-5. Summary

The time evolution of the butterfly pattern and the concentration fluctuations or phase-separated structures in the sheared solutions can be classified into three time regions. There is an incubation time between the onset of shear flow and the development of the butterfly pattern. During this incubation period, the first stress overshoot was observed, probably due to the instantaneous, more or less uniform deformation of entangled polymer chains and their relaxations within the tubes as proposed by Osaki et al.³⁰ and Doi-Edwards.³² In the PS/DOP system the relaxations involve enhanced

concentration fluctuations. Therefore the first overshoot ends with the onset of the butterfly pattern: the butterfly pattern appears at about the time when the stress reaches a minimum value after the first stress overshoot. It changes with time due to a further growth of concentration fluctuations or the shear-induced structures. This structure growth is responsible for the second stress overshoot. Finally the system attains the shear-rate dependent steady state structures after the second overshoot, due to a dynamical equilibrium between the growth of the structures driven by the shear-induced instability of the system and the burst of the overgrown structures driven by shear.

The first overshoot in the PS/DOP system is probably associated with the same mechanism as that proposed by Osaki et al. and Doi-Edwards for homogeneous semidilute polymer solutions or polymer melts subjected to a large deformation. The second overshoot in the PS/DOP system is confirmed to be due to growth of the phase-separated structures, before reaching shear-rate dependent steady state structures.

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Chapter 7

Rheo-Optical Studies of Shear-Induced Structures in Semidilute Polystyrene Solutions

7-1. Introduction

In recent years the shear-induced structure formation in polymeric systems have attracted a great deal of attention, and many experimental and theoretical studies of shear-induced concentration fluctuations or phase separation in semidilute polymer solutions have been reported¹⁻³³. In order to investigate this phenomenon, several experimental methods, such as rheology,^{12,13,15,24-27,29,31-33} transmitted light intensity,^{2-4,19} shear-dichroism,^{12,17,19,20,24,26,32} shear-small-angle light scattering,^{8,9,11,12,15-21,23-31,33} shear-small-angle neutron scattering,²² and shear-optical microscopy^{21,25,27-30,33} have been used.

The previous studies^{9,15,21,23,27,33} revealed that the effects of shear on the semidilute polymer solutions could be classified into some regimes with respect to shear rate $\dot{\gamma}$: Homogenous solution at $\dot{\gamma} < \dot{\gamma}_c$; Shear-induced concentration fluctuations at $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$ which cause the strong butterfly-type light scattering pattern; The anomalies in the rheological and scattering behaviors at $\dot{\gamma} > \dot{\gamma}_a$ which are related to streak-like scattering pattern and string phase in microscopic images. Here $\dot{\gamma}_c$ and $\dot{\gamma}_a$ are the critical shear rates for the

onset of the shear-enhanced concentration fluctuations and for the onset of the anomalies in the rheological and scattering behaviors, respectively. The basic concept which explains the origin of the butterfly patterns has been well developed by recent theories^{5-7,10,13,14} based on the non-equilibrium statistical mechanics: The butterfly patterns or anisotropic concentration fluctuations are induced by a coupling between concentration fluctuations and stress existing in the system as a result of the concentration dependence of viscosity and normal stress coefficients (so called the elastic effects). Important future studies would involve quantitative interpretations of experimental results with the theories. On the other hand, the transition of scattering pattern from the butterfly pattern to the streak-like pattern at $\dot{\gamma}_a$ has not been accounted for at all by the present theories.

The focus of this chapter is the construction of a more complete picture of the shear-induced phase separation and structure formation by systematically

Table 7-1. Polymer solutions used in this chapter

polymer code	$M_w^{1)}$ ($\times 10^{-6}$)	$M_w/M_n^{1)}$	concentration (wt%)	$c/c^{*2)}$	cloud point ³⁾ (°C)
PS548	5.48	1.15	3.0	≈ 20	16.3
PS548	5.48	1.15	6.0	≈ 40	13.8
PS384	3.84	1.06	6.0	≈ 30	10

1) M_w and M_n are weight-average molecular weight and number-average molecular weight, respectively.

2) c^* : overlap concentration

3) The cloud points of the PS548 and PS384 solutions were determined by the same method as described elsewhere.^{8,9,15}

comparing the results from a wide range of techniques on the same polymer solutions: rheological experiments, form dichroism, birefringence, light scattering and optical microscopy. This is in contrast to previous reports using a limited number of rheo-optical techniques used separately for different systems.

7-2. Experimental Section

7-2-1. Samples

The three polymer solutions used in this chapter consist of high molecular weight polystyrene (PS) dissolved in dioctyl phthalate (DOP). DOP is a θ solvent for PS, and its θ temperature (T_θ) is 22 °C.³⁴ Characterizations of the PS and their solutions are listed in Table 7-1. Concentrations of the solutions are in the semidilute regime. The methods used to prepare them are same as those used in previous experiments.^{8,9,15,21,27}

The PS/DOP system has a phase diagram of the UCST-type. Cloud points of three samples exist at the temperature range of 10-16.3 °C. All the samples are in one phase region in the quiescent state at experimental temperature (PS548/DOP: 22 °C, PS384/DOP: 21 °C).

7-2-2. Shear-Dichroism, Birefringence, and Rheology

Figure 7-1 shows the experimental system to measure the dichroism and birefringence of the solutions under shear flow. A Rheometrics® Dynamic

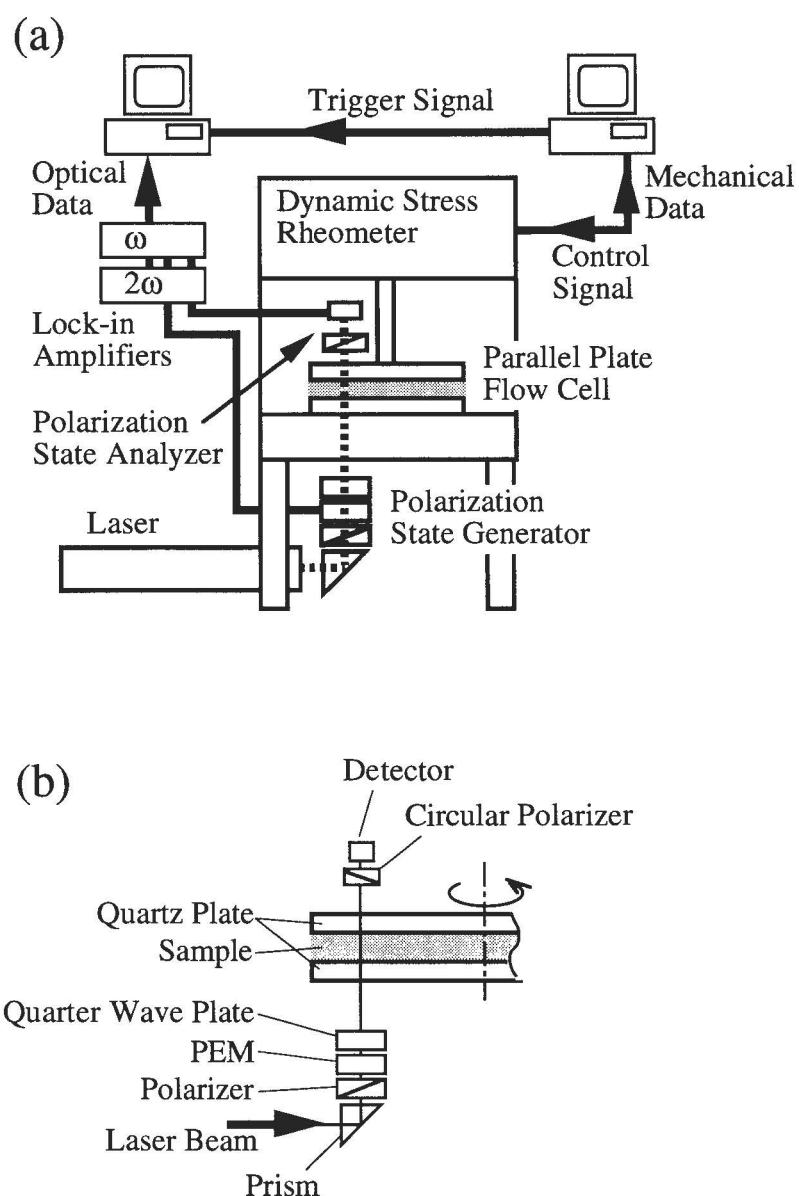


Figure 7-1 Schematic diagram of the experimental setup for shear-dichroism, shear-birefringence and rheology. (a) Schematic diagram of the combined mechanical rheometer and optical train. (b) Shear cell and optical train.

Stress Rheometer (DSR) serves as the mechanical platform. The sample is contained between two quartz disks that form a parallel plate shear cell. The upper plate is rotated to induce shear. The optical train is situated below the rheometer and light is directed through the sample at normal incidence. The optical train below the shear cell consists of a He-Ne laser, followed by a prism, a photo-elastic modulator and a quarter-wave plate. The transmitted light is received by a detector either directly (for dichroism measurements), or after passing through a circular polarizer (for birefringence measurements). Details of this measurement technique was reported in elsewhere.^{24,32}

7-2-3. Shear-Light Scattering

Small-angle light scattering measurements under the shear flow (shear-small-angle light Scattering, shear-SALS) are carried out in the same way as those performed previously^{9,15,27,29,33} with the rheo-optical apparatus described in detail elsewhere.³⁵ Figure 7-2 shows a schematic diagram for the optical setup and the coordinate system used in this chapter. The sample cell is a transparent cone-and-plate type shear cell, and made of quartz with 80 mm diameter and 1 ° cone angle.

A He-Ne CW gas laser ($\lambda_0 = 632.8$ nm, 15 mW) and a 35-elements photodiode array are used as an incident beam source and a one-dimensional detector, respectively, for quantitative measurements of the scattered intensity distributions from the sheared solutions.

The light scattering intensity profile $I(q_x, q_z)$ was measured in the plane Oxz , where q_x and q_z are the x and z components (i.e., $\mu = 0$ and 90° ,

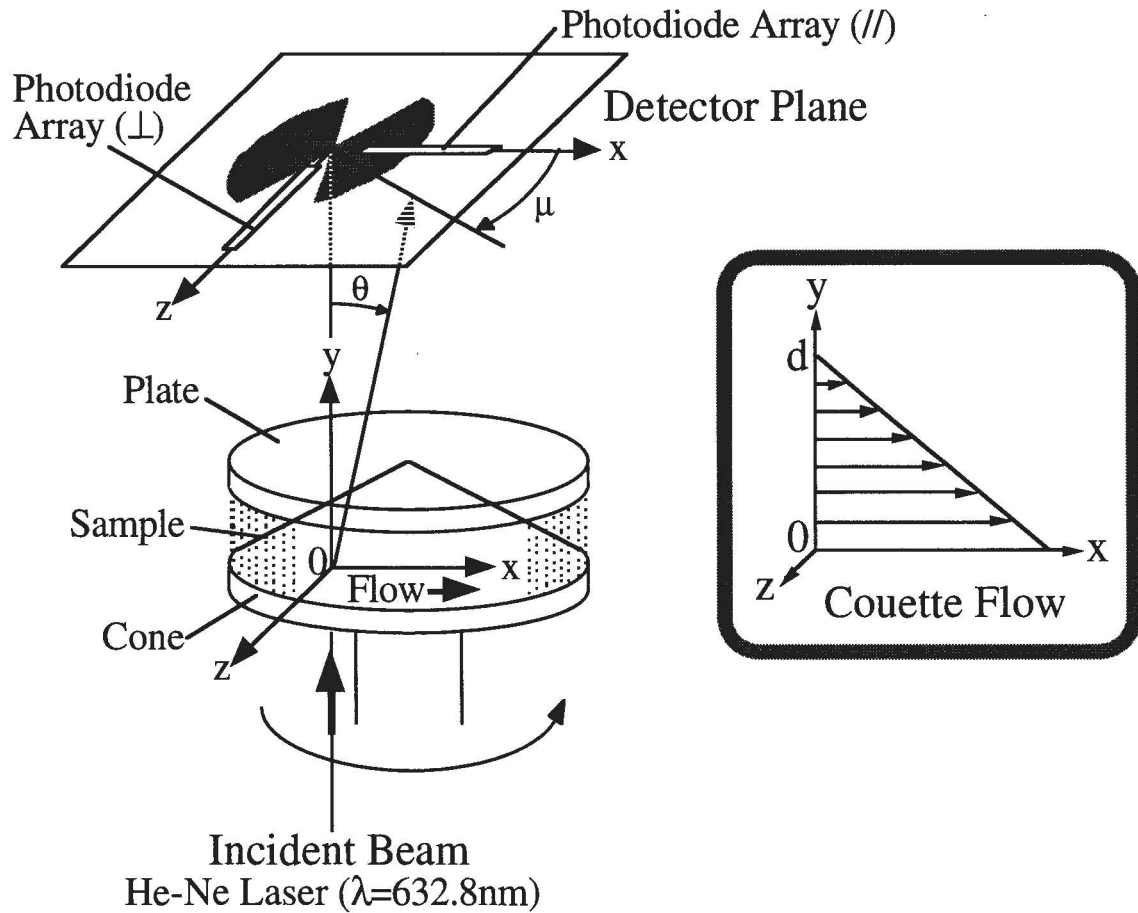


Figure 7-2 Schematic diagram of the experimental setup for shear-light scattering: one-dimensional detector (photodiode array), cone-and-plate type shear cell to generate Couette flow, and coordinate system used in this study. Note that the coordinate system used here is identical to that commonly used in this field but is different from the one we used in our earlier work,^{8,9,15,21,25,34} which is based on a tradition in the field of scattering.

respectively) of the scattering vector $\mathbf{q}$ whose magnitude q is related to the wavelength λ of the incident beam and the scattering angle θ in the solution by

$$q = (4\pi / \lambda) \sin(\theta/2). \quad (7-1)$$

Furthermore, the shear-induced phase separation was investigated by measuring integrated scattering intensities, $\mathcal{J}_{//}(\dot{\gamma})$ and $\mathcal{J}_{\perp}(\dot{\gamma})$, parallel and perpendicular to the flow direction, respectively, as a function of shear rate $\dot{\gamma}$. They are defined by

$$\mathcal{J}_{//} = \int_{a_2}^{a_1} dq_x \int_{-\delta}^{\delta} dq_z I(q_x, q_z) \quad (7-2)$$

and

$$\mathcal{J}_{\perp} = \int_{a_2}^{a_1} dq_z \int_{-\delta}^{\delta} dq_x I(q_x, q_z) \quad (7-3)$$

The quantity δ is the magnitude of the scattering vector ($3.4 \times 10^{-5} \text{ nm}^{-1}$) which is subtended by the height of the slit placed in front of the photodiode array, and a_1 and a_2 were set at $6.2 \times 10^{-4} \text{ nm}^{-1}$, and $2.7 \times 10^{-3} \text{ nm}^{-1}$, respectively. Furthermore photographic films, which were set in the plane Oxz , were used for observation of qualitative two-dimensional light scattering patterns.

The modified DSR does not have temperature-control system. On the other hand the shear-light scattering apparatus has a double-chambered temperature enclosure (See Sec. 1-2 and 2-2).³³ Thus in this chapter, the sample temperature was controlled at the temperature where the experiments with the modified DSR apparatus were conducted (e.g. 21 °C or 22 °C) with accuracy of ± 0.2 °C at the incident beam spot.

7-3. Results

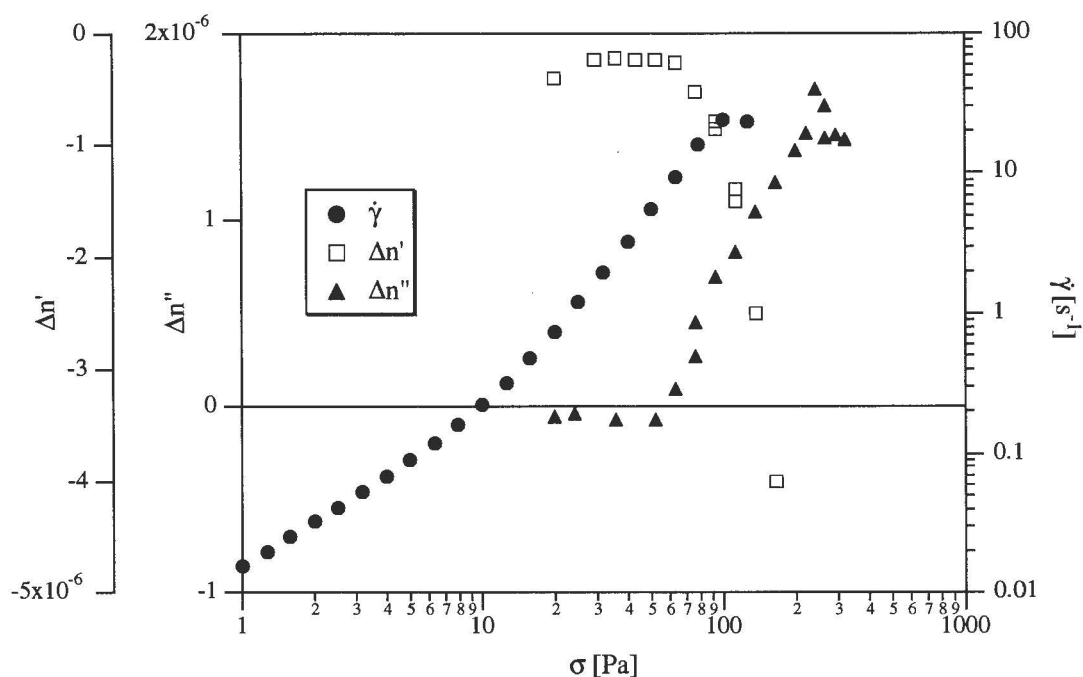


Figure 7-3 Plots of shear rate ($\dot{\gamma}$), birefringence ($\Delta n'$), and dichroism ($\Delta n''$) for the PS548/DOP 3.0 wt% solution at RT (22°C) as a function of shear stress (σ).

Figure 7-3 shows the plots of shear rate ($\dot{\gamma}$), birefringence ($\Delta n'$), and dichroism ($\Delta n''$) values for the PS548/DOP 3.0 wt% solution as a function of shear stress (σ) measured by using the modified DSR. These three measurements were separately carried out. The DSR is a stress-controlled type rheometer, thus the modified DSR can measure these data under the steady shear flow at a given shear stress. These measurements were also carried out similarly for other two solutions. However, the shear-light scattering data were measured as a function of shear rate as described in the pervious study (See Chapters 3 and 5).^{9,15,27,29,33} Therefore birefringence and dichroism data were replotted as a function of shear rate in parts a of Figures 7-4, 7-5 and 7-6 in comparison with light scattering data. Furthermore shear viscosity (η) data, as estimated by

$$\eta = \sigma / \dot{\gamma}, \quad (7-4)$$

were also included in these figures.

Figures 7-4, 7-5 and 7-6 show the results of the PS548/DOP 3.0 wt% solution, the PS548/DOP 6.0 wt% solution, and the PS384/DOP 6.0 wt% solution, respectively. Parts a of these figures are the plots of η , $\Delta n'$ and $\Delta n''$ of each solution as a function of shear rate ($\dot{\gamma}$). Parts b of them are plots of $\mathcal{I}_{||}(\dot{\gamma})/\mathcal{I}_{||}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma})/\mathcal{I}_{\perp}(\dot{\gamma}=0)$, integrated scattered intensity parallel and perpendicular to the flow direction, respectively, at a given $\dot{\gamma}$, normalized with respect to the integrated intensity of the quiescent solution. Furthermore Figure 7-7 shows the small-angle light scattering patterns of the PS384/DOP 6.0 wt% solution at 21 °C, which were simultaneously taken with the experiments of Figure 7-6. These patterns represent contour plots showing the iso-intensity levels. In the construction of the contour patterns, first the scattered intensity recorded on photographic films was scanned with an intensity scanner, and then the intensity fluctuations in the original scattering patterns were smoothed, which arise from the speckled patterns.

The results on three solutions in Figure 7-4 to 7-6 showed the same tendency, except for the shifts of the critical shear rates $\dot{\gamma}_c$ and $\dot{\gamma}_a$ with varying concentrations and molecular weights of polystyrene. It is extremely important to note that similar results could be obtained on the solutions with different concentrations and molecular weights, because it suggests that these transitions under the shear flow are quite universal phenomena. First, parts b of Figures 7-4 to 7-6 indicate that shear-rate dependence of the integrated

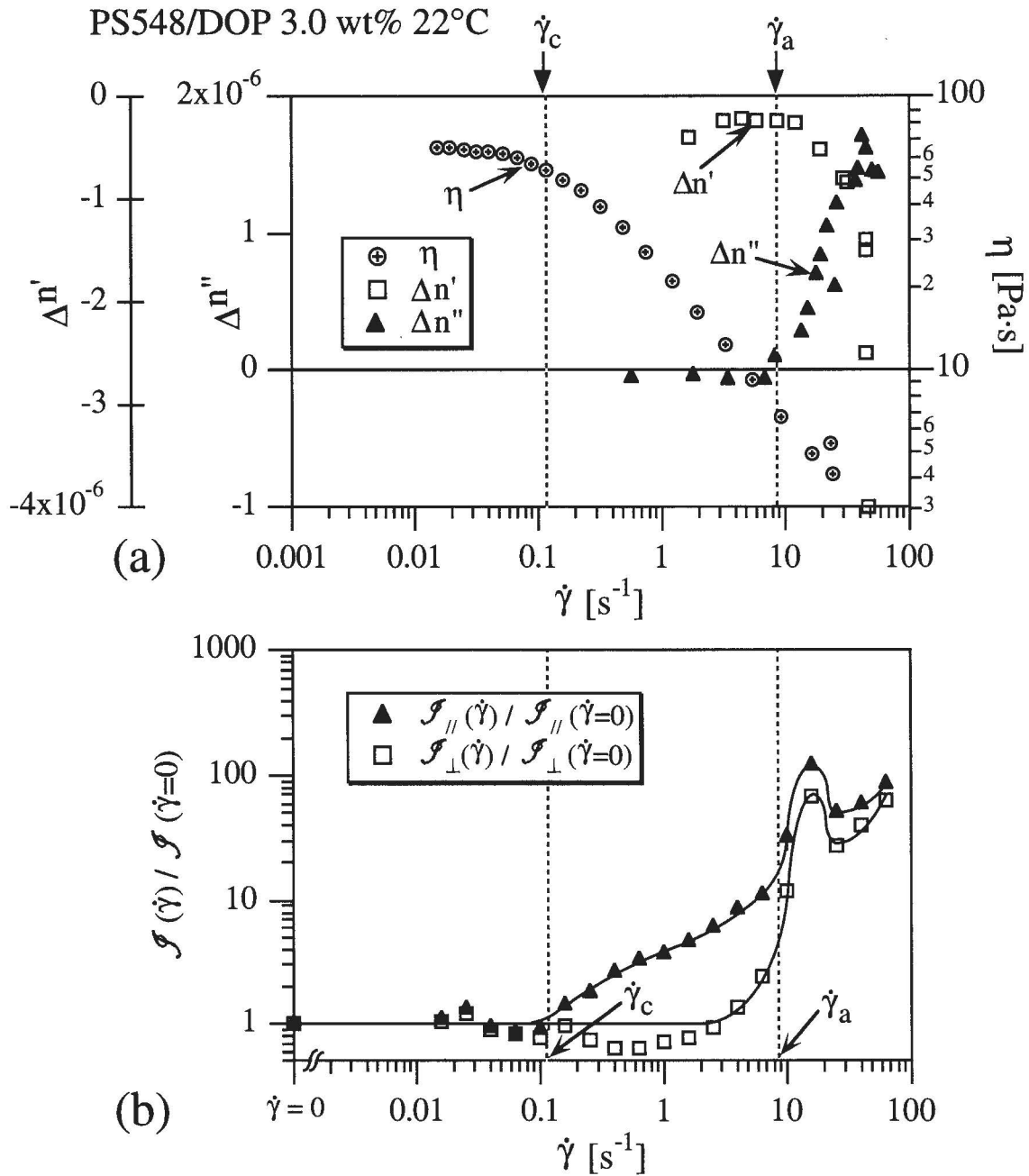


Figure 7-4 Sample solution used for this figure is PS548/DOP 3.0 wt% at 22°C. (a) The plots of shear viscosity (η), birefringence ($\Delta n'$), and dichroism ($\Delta n''$) of this solution as a function of shear rate ($\dot{\gamma}$), which were calculated from the data as shown in Figure 7-3. (b) The plots of $\mathcal{I}_{\parallel}(\dot{\gamma}) / \mathcal{I}_{\parallel}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma}) / \mathcal{I}_{\perp}(\dot{\gamma}=0)$, integrated scattered intensity at a given $\dot{\gamma}$, normalized with respect to the integrated intensity of the quiescent solution, parallel and perpendicular to the flow direction, respectively.

PS548/DOP 6.0 wt% 22°C

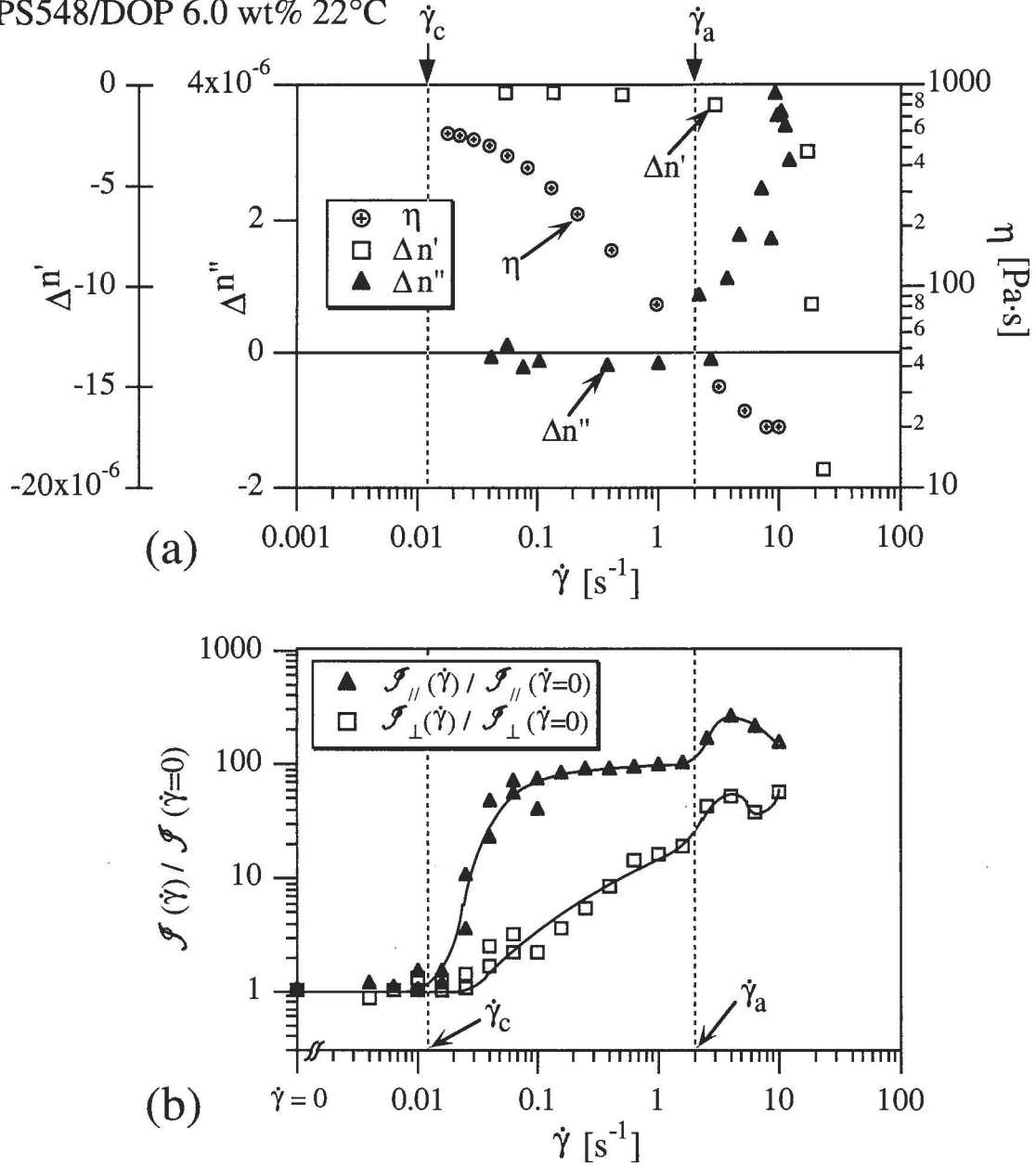


Figure 7-5 Sample solution used for this figure is PS548/DOP 6.0 wt% at 22°C. (a) The plots of shear viscosity (η), birefringence ($\Delta n'$), and dichroism ($\Delta n''$) of this solution as a function of shear rate ($\dot{\gamma}$). (b) The plots of $\mathcal{I}_{\parallel}(\dot{\gamma})/\mathcal{I}_{\parallel}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma})/\mathcal{I}_{\perp}(\dot{\gamma}=0)$, integrated scattered intensity at a given $\dot{\gamma}$, normalized with respect to the integrated intensity of the quiescent solution, parallel and perpendicular to the flow direction, respectively.

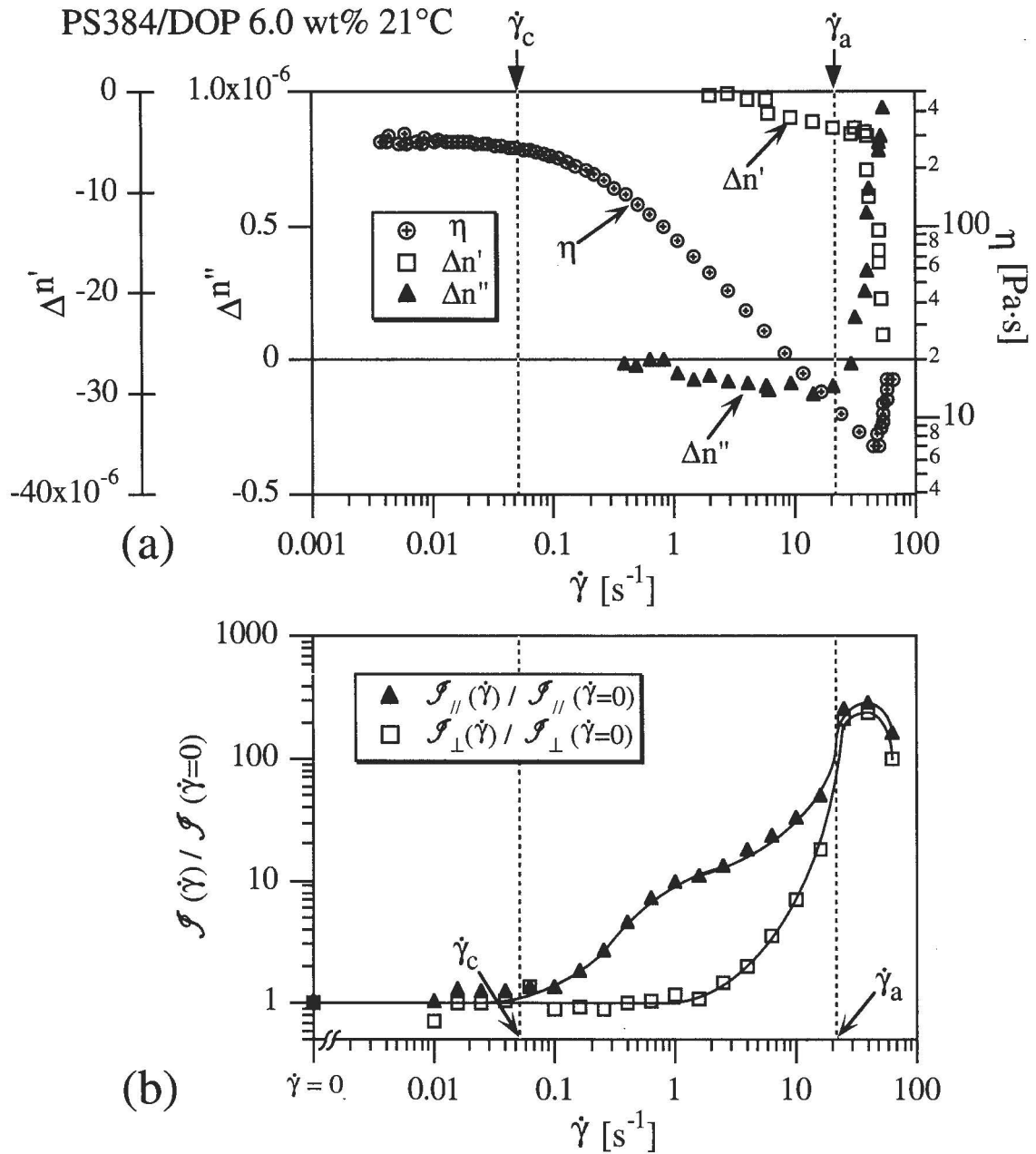


Figure 7-6 Sample solution used for this figure is PS384/DOP 6.0 wt% at 21°C. (a) The plots of shear viscosity (η), birefringence ($\Delta n'$), and dichroism ($\Delta n''$) of this solution as a function of shear rate ($\dot{\gamma}$). (b) The plots of $\mathcal{I}_{\parallel}(\dot{\gamma})/\mathcal{I}_{\parallel}(\dot{\gamma}=0)$ and $\mathcal{I}_{\perp}(\dot{\gamma})/\mathcal{I}_{\perp}(\dot{\gamma}=0)$, integrated scattered intensity at a given $\dot{\gamma}$, normalized with respect to the integrated intensity of the quiescent solution, parallel and perpendicular to the flow direction, respectively.

PS384/DOP 6.0 wt% at 21°C

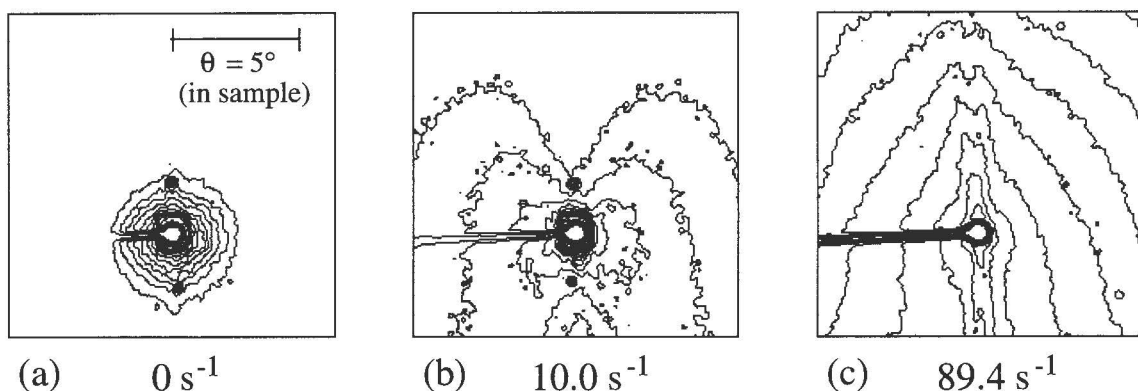


Figure 7-7 Contour plots of the scattered intensity distribution for steady state scattering patterns at various shear rates for the solution shown in Figure 7-6.

scattering intensity, especially along the flow ($\mathcal{I}_{//}(\dot{\gamma})/\mathcal{I}_{//}(\dot{\gamma}=0)$), can be classified into several regimes as those reported previously.^{15,27,29,33} (See also Chapters 3 and 5.) For each solution there are two critical shear rate, the critical shear rate for the shear-enhanced concentration fluctuations or phase separation ($\dot{\gamma}_c$) and the second critical shear rate or the critical shear rate for the onset of the anomalous behavior ($\dot{\gamma}_a$). Furthermore behavior of the shear viscosity in part a is also classified into the same regimes.

At $\dot{\gamma} < \dot{\gamma}_c$, the scattering intensity was essentially identical to those of homogeneous semidilute solutions as seen in Figure 7-7a, and shear viscosity is almost constant with $\dot{\gamma}$, i.e., the solution appears to be almost a Newtonian fluid. At $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$, the scattering intensity increased and the shear viscosity decreased with increasing shear rate. Moreover, in this regime it was possible to observe the unique butterfly-type scattering pattern^{15,21,25,27,29,33} as seen in Figure 7-7b. At $\dot{\gamma} > \dot{\gamma}_a$, the scattering intensity further increased and the butterfly

pattern changed into a strong streak-like pattern oriented perpendicular to the flow as seen in Figure 7-7c (the tendency being especially remarkable at high shear rates in this regime²⁷). This strong streak-like pattern appeared at small-angle regions, and it was superposed on the elongated two-point pattern at large q regions which appeared parallel to the flow, though the elongated two-point pattern is less distinct in Figure 7-7c than that in Figure 5-3g and of Chapter 5.²⁷ These anomalies in the change of the scattering pattern with

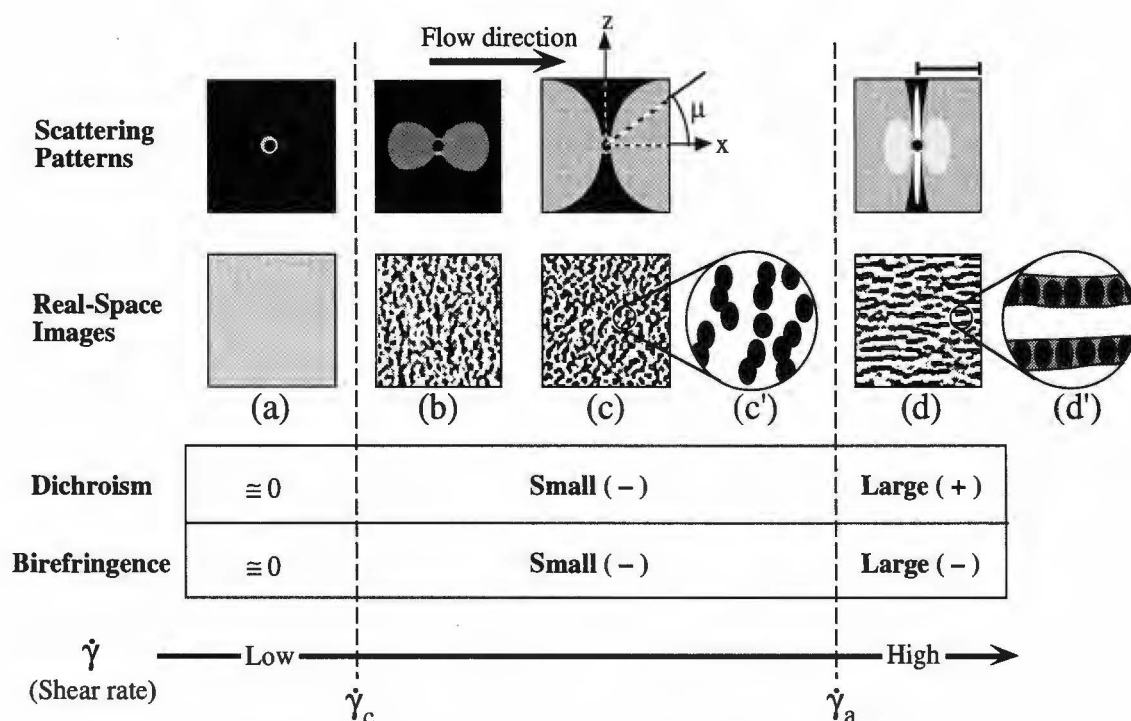


Figure 7-8 Schematic representation of the small-angle light scattering patterns and concentration fluctuations observed in real space, i.e., by using optical microscopy, and a table of behaviors in dichroism and birefringence under the steady shear flow at various shear rates. A scale bar on the top of part d indicates ca. 5° in the scattering angle, and length scale of the real-space images ca. $50 \mu\text{m}$. The critical shear rates, $\dot{\gamma}_c$ and $\dot{\gamma}_a$, should depend on concentration and molecular weight and be referred to Figure 7-4 to 7-6. Parts c' and d' are enlarged models in part c and d, respectively.

$\dot{\gamma}$ were closely related to anomalies in rheological behavior: shear viscosity began to increase in this regime.

Next, the birefringence ($\Delta n'$) and dichroism ($\Delta n''$) at $\dot{\gamma} < \dot{\gamma}_c$ were too small to be detected with enough accuracy for the DSR. All three solution indicated that the values of both the dichroism and the birefringence were negative and small at $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$, and that the dichroism changed sign with its value increasing with $\dot{\gamma}$ and the birefringence negatively increased drastically with $\dot{\gamma}$ at $\dot{\gamma} > \dot{\gamma}_a$.

7-4. Discussion

The scattering pattern and intensity change together with the previous *in situ* observation with the optical microscopy under the shear flow^{21,25,27,33} (See Chapters 2, 4, and 5) reveal that the structure formation or the enhancement of concentration fluctuations depends on the shear rate $\dot{\gamma}$ as summarized in Figure 7-8. At $\dot{\gamma} < \dot{\gamma}_c$, only weak thermal concentration fluctuations exist in the solution, which are essentially identical to those of homogeneous semidilute solutions in the quiescent state (Figure 7-8a). At $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$, the elastic effect is significant, which develops the concentration fluctuations enhanced along the flow and extended normal to the flow, as evidenced by the shear-microscopy result (Figures 7-8b and 7-8c) or as schematically shown in Figure 7-8c'.³⁶ This result is consistent with the development of the butterfly pattern and the negative form dichroism. The birefringence is small and negative, suggesting that polystyrene chains only weakly orient along the flow direction.

However, at $\dot{\gamma} > \dot{\gamma}_a$ the shear-microscopy showed formation of long string-like structures oriented along the flow (Figure 7-8d). This observation is consistent with the streak-like LS pattern oriented normal to the flow and the positive form dichroism. Namely, the structure transformation from the oblate-ellipsoidal structures with their axes preferentially oriented along the flow to the string-like structures with $\dot{\gamma}$ across $\dot{\gamma}_a$ causes the change of sign and absolute value of the form dichroism. The positive value of the dichroism increases with $\dot{\gamma}$, revealing that spatial correlation length of the strings along the flow increases with $\dot{\gamma}$.

Although the previous experimental methods did not clarify the molecular orientation, the shear-birefringence results (the large negative values) indicate that the polymer molecules oriented strongly with their end-to-end vectors parallel to the flow and therefore parallel to the strings at the high shear rate, $\dot{\gamma} > \dot{\gamma}_a$. The elongated two-point pattern at the large q region superposed on the streak pattern at the small q region suggests that the strings may have internal structures composed of domains rich in polymers (dark oblates) and poor in polymers (gray region) as schematically illustrated in Figure 7-8d' (an enlarged model of the strings in Figure 7-8d). At $\dot{\gamma} > \dot{\gamma}_a$ these domains are aligned in a row parallel to the flow axis, forming the strings, but they are not aligned in a row at $\dot{\gamma}_c < \dot{\gamma} < \dot{\gamma}_a$, as schematically shown in the enlarged model of Figure 7-8c (Figure 7-8c').

The PS used are not crystallizable polymers, and consequently they were not crystallized under the shear flow. This result suggests that the strings formed at high shear rates may eventually result in crystallization into row nuclei, when polymers are crystallizable, as those reported elsewhere.^{23,29}

7-5. Summary

The shear-rate dependence of dichroism and birefringence for the high molecular weight semidilute polystyrene solutions under the shear flow can be classified in the same manner as those of light scattering and rheological behavior in terms of the critical shear rate. It is believed that the change in the sign of the dichroism is due to the shear-induced formation of string-like structures oriented parallel to the flow and that the change of the birefringence associated with the string formation is due to the orientation PS chains in the strings with their end-to-end vectors parallel to the flow and axes of the strings.

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36. The structural characteristic was presented more clearly in Figure 11(d) of ref. 30.

Summary

In Chapter 1, the motivations and objectives of this thesis were discussed. The most important objectives are to clarify the effect of flow field on the concentration fluctuations in polymer solutions and discover the universal features in the flow field effects on the concentration fluctuations. I pointed out the universality of the butterfly patterns and reviewed the theoretical background of shear-induced phase separation or concentration fluctuations. The butterfly pattern is one of the most important key words of this thesis, which were observed in systems with concentration fluctuations, e.g., semidilute polymer solutions, colloidal dispersions, and swollen gels under flow or elongation fields. I also described the shear-small-angle light scattering (shear-SALS) apparatus previously developed in our laboratory, which were used in most of the experiments in this thesis.

In Chapter 2, the new apparatus developed in our laboratory were presented, which simultaneously provides information by using shear-small-angle light scattering (shear-SALS) and shear-optical microscopy (shear-microscopy). It was shown that the shear-microscopy technique enabled us to observe the concentration fluctuations and the structure formation induced by shear flow more directly and exactly than by using shear-SALS alone. This is because the scattering method is an indirect method, having the advantage of providing information that is a statistical average over the system as a whole. It is difficult, however, to get detailed features of the structures from shear-SALS alone. Thus both shear-SALS and shear-microscopy

techniques complementarily helped us to investigate the development of the supramolecular structures in polymeric systems under shear flow. Applications of this apparatus to two phenomena in polymeric systems were introduced, i.e., shear-induced phase separation in semidilute polymer solution (PS/DOP) and shear-induced homogenization in semidilute solutions of a polymer mixture (PS/PB/DOP), and merits of combination with shear-SALS and shear-microscopy were described .

In Chapter 3, the essential effects of simple shear flow on concentration fluctuations in semidilute solutions of high molecular weight polystyrene were investigated by using shear-SALS and rheological measurements. The shear-rate ($\dot{\gamma}$) dependence of scattering was found to fall into four regimes: Regime I at $\dot{\gamma} < \dot{\gamma}_c$ where the scattering is that of homogeneous semidilute solutions, and Regimes II to IV at $\dot{\gamma} > \dot{\gamma}_c$, where $\dot{\gamma}_c$ being the critical shear rate for the shear-enhanced concentration fluctuations. In Regime II, a unique butterfly-type scattering pattern with a dark streak perpendicular to the flow direction appears. The intensity parallel to the flow increases by about 100 times with increasing $\dot{\gamma}$, suggesting that the concentration fluctuations enhanced along the flow. In Regime III at higher shear rates, the increase in the intensity with $\dot{\gamma}$ tends to saturate, and finally in Regime IV at even higher shear rates ($\dot{\gamma} > \dot{\gamma}_a$), the intensity further increases and the butterfly pattern changes into a two-point pattern elongated perpendicular to the flow, with a broad intensity maximum along the flow. These scattering anomalies are believed to be related to those observed in rheological behavior.

In Chapter 4, concentration fluctuations in a semidilute polymer solution induced by shear flow were shown, which were directly visualized by using

shear-microscopy for the first time. Furthermore, by using a fast Fourier transform (FFT) it was demonstrated that the butterfly pattern arose from the concentration fluctuations and that their angular distribution depended on the shear rates. The concentration fluctuations have a time scale related to a shear rate $\dot{\gamma} \sim 1 \text{ s}^{-1}$ and periodicity $l \sim 10 \text{ }\mu\text{m}$, indicating a link to reptation processes.

In Chapter 5, the existence of the long string phase parallel to flow in semidilute solutions of polystyrenes at high enough shear rate, $\dot{\gamma} > \dot{\gamma}_a$, was revealed by using shear-microscopy. Furthermore, the streak-like scattering pattern at small scattering angles, which arises from the string phase, and the butterfly patterns at large scattering angles were observed by using shear-SALS in this shear rate regime. This shear-SALS result suggests that concentration fluctuations along the flow still exist in the string phase. This string formation should be responsible for shear thickening in the anomaly region (Regime IV), at $\dot{\gamma} > \dot{\gamma}_a$. These results enabled us to describe a more detailed model of self-assembly of the PS/DOP systems under steady shear flow.

In Chapter 6, transient behavior of shear-induced phase separation was investigated. The relationship between the time evolution of the scattering pattern and rheological change was confirmed. The time evolution of the butterfly pattern and the concentration fluctuations or phase-separated structures in the sheared solutions can be classified into three time regions: incubation time between the onset of shear flow and the development of the butterfly pattern; onset of phase separation and growth of phase-separated structures; steady state. Two stress overshoots were observed in rheological

measurements; the first and second stress overshoots occurred during the incubation time, and before the onset of steady state, respectively. The first overshoot in the PS/DOP system is probably associated with the same mechanism as that proposed by Osaki et al. and Doi-Edwards for homogeneous semidilute polymer solutions or polymer melts subjected to a large deformation. The second overshoot in our system was confirmed to be due to the growth of the phase-separated structures, before reaching shear-rate dependent steady state structures.

In Chapter 7, rheo-optical studies, including rheology, shear-dichroism, shear-birefringence, shear-small-angle light scattering (shear-SALS) and shear-microscopy, were carried out in order to get more detailed information about shear-induced phase separation. The shear-rate dependence of shear-dichroism and shear-birefringence was similar to that of shear-SALS and shear-microscopy. It is believed that the change in the sign of the dichroism is due to the shear-induced formation of string-like structures oriented parallel to flow and that the change of birefringence associated with the string formation is due to the orientation of PS chains in the strings with their end-to-end vectors parallel to the flow.

List of Publications

1. “‘Butterfly’ Light Scattering Pattern in Shear-Enhanced Concentration Fluctuations in Polymer Solutions and Anomaly at High Shear Rates”;
T. Hashimoto and T. Kume, *J. Phys. Soc. Japan* **61**, 1839 (1992).
(Chapter 3)
2. “Shear microscopy of the ‘butterfly pattern’ in polymer mixtures”;
E. Moses, T. Kume and T. Hashimoto, *Phys. Rev. Lett.* **72**, 2037 (1994).
(Chapter 4)
3. “Shear-Induced Phase Separation of Semidilute Polymer Solution”;
T. Kume, T. Hashimoto and E. Moses, *Proc. Am. Chem. Soc., Div. Polym. Mater. Sci. and Eng.*, **71**, 190 (1994).
(related to Chapter 2 and 3)
4. “Formation of String Phase in Phase-Separating Solutions of Polymer Mixtures under Shear Flow”;
T. Hashimoto, K. Matsuzaka, T. Kume and E. Moses, *Proc. Am. Chem. Soc., Div. Polym. Mater. Sci. and Eng.*, **71**, 111 (1994).
(related to Chapter 2)
5. “Flow-Induced Anisotropic SALS in Silica-Filled PDMS Liquids”;
J. V. DeGroot, C. W. Macosko, T. Kume and T. Hashimoto, *J. Colloid*

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(related to Chapter 1)

6. “A New Apparatus for Simultaneous Observation of Optical Microscopy and Small-Angle Light Scattering Measurements of Polymers under Shear Flow”;

T. Kume, K. Asakawa, E. Moses, K. Matsuzaka and T. Hashimoto, *Acta Polymer.* **46**, 79 (1995).

(Chapter 2)

7. “String Phase in Semidilute Polystyrene Solutions under Steady Shear Flow”;

T. Kume and T. Hashimoto, in *ACS Symposium Series 597, Flow-Induced Structure in Polymers*; A. I. Nakatani and M. D. Dadmun, Eds.; ACS: Washington, DC, p35 (1995).

(Chapter 5)

8. “Time Evolution of Shear-Induced Structures in Semidilute Polystyrene Solutions”;

T. Kume, T. Hattori and T. Hashimoto, *Macromolecules* **30**, 427 (1997).

(Chapter 6)

9. “Rheo-Optical Studies of Shear-Induced Structures in Semidilute Polystyrene Solutions”;

T. Kume, T. Hashimoto, T. Takahashi and G. G. Fuller, *Macromolecules*

in press.

(Chapter 7)

- 10.** “Shear-Induced Concentration Fluctuations in Ultrahigh Molecular Weight Polyethylene Solutions. 1. Observation above the Melting Point”; H. Murase, T. Kume, T. Hashimoto, Y. Ohta and T. Mizukami, *Macromolecules* **28**, 7724 (1995).

(not included in this dissertation)

- 11.** “Structure Development under Transient Shear Flow in Semidilute Polystyrene Solution”; H. Murase, T. Kume and T. Hashimoto, *Macromol. Symp.* **104**, 159 (1996).

(not included in this dissertation)

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