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Effect of Unidirectional Shear on the Structure of Triblock Copolymers. 1. Polystyrene–Polybutadiene–Polystyrene

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ABSTRACT: Flow severely affects the morphological and rheological properties of microphase-separated block copolymers as shown here with a polystyrene–polybutadiene–polystyrene triblock copolymer. Small-angle X-ray scattering (SAXS) and form birefringence show that cylindrical polystyrene domains orient in the flow direction reaching a saturated orientation after approximately 30 shear units in a constant-stress experiment. The size and shape of the domains are unaffected by the flow as measured by SAXS and transmission electron microscopy (TEM). Shift factors a_T used to obtain master curves from small-strain dynamic measurements also do not change with shear. The master curves of samples sheared at 160 °C first drop at all frequencies, ω, with increasing strain and then recover at high ω for the highest strains. Samples sheared at 180 °C behave similarly but recover completely to the initial rheological state even though the domains in the samples are highly oriented. A flow mechanism is proposed to describe these results.

Introduction

Microphase-separated block copolymers are used for an increasing number of applications in a great variety of formulations. Particularly useful materials are block copolymers which behave as thermoplastic elastomers or rubber modified glassy materials at use temperatures between the glass transition temperatures, T_g's, of the blocks. The performance of these materials is critically dependent on their flow properties and resultant morphologies. These flow properties have been studied extensively and are often found to be anomalous compared with the properties of homopolymers due to the presence of microphase-separated domains in the melt.[1,2] Although many proposals have been made, the precise flow mechanism of these block copolymers is still unknown. Our present goal is to investigate structure development in order to understand the flow mechanism of microphase-separated triblock copolymers.

We have examined the evolution of structure in a polystyrene–polybutadiene–polystyrene (SBS) block copolymer by imposing measured and well-controlled levels of strain in a constant-stress experiment. The resulting orientation has been characterized in quenched samples with small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Small-amplitude oscillatory shear (G', G'') has been used to measure strain-induced changes in the material's relaxation behavior. A flow mechanism based on previous work in oscillatory shear with the same copolymer[3] was that polystyrene grains of oriented polystyrene (PS) domains remain intact throughout flow; this hypothesis is examined with respect to the present observations.

Experimental Study

The material used was a commercial SBS triblock, Shell Kraton 1102, and is designated SBS81 in the following. The composition of the polymer is listed in Table I.[4] Kraton 1102 contains about 15% diblock polystyrene–polybutadiene copolymer of molecular weight PS(10 600)–PB(31 050). Harpell and Wilkes[5] found that the presence of the precursor diblock does not influence the morphology of a triblock copolymer, and the presence of diblock has not been considered in this study. Some of the important physical properties of the two constituent homopolymers of SBS81 are listed in Table II.[6] The center polybutadiene block of SBS81 is far above its critical molecular weight for entanglement, M_c. The molecular weight of the end blocks is below the M_c of polystyrene, 37 400. Also, no separation temperature is observed below degradation at approximately 220 °C; this indicates that we are far from $(\chi N)_{\text{critical}}$, where χ is the Flory interaction parameter and N is the degree of polymerization. $(\chi N)_{\text{critical}}$ is the value of χN on the spinodal curve for the system at equilibrium. This can be calculated for SBS81 from Leibler's theory[7] to be $(\chi N)_{\text{critical}} \approx 17$.

Table I
Material Parameters for SBS81

χN	wt % PS	vol % PS	M_n	M_n(PS)	M_n(PB)	M_n/M_c
39 (160 °C) 35 (180 °C)	26	0.245	81 300	10 600	60 100	17

Table II
Material Parameters for the Constituent Homopolymers (χ_{SB}) Estimated from Reference 6

polymer	M_c	T_g, °C	ρ, g/cm^3	χ_{SB}
PB	3600	−67	0.895	0.07 (160 °C)
PS	37 400	100	0.970	0.06 (180 °C)

SBS81 as received contained processing oils; these were removed from the polymer by twice precipitating a 10% toluene solution into 2-propanol. Films 1 mm thick were cast over 24–48 h at room temperature from a 10 wt % toluene solution with 0.5 wt % Irganox 1010 (Ciba-Geigy) as an antioxidant. The films were then annealed in vacuum at 150 °C for 24 h. Samples were subjected to various amounts of strain at constant shear stress, $\tau = 2000$ Pa, in the cone-and-plate geometry in a Rheometrics stress rheometer (RSR). The stress value was chosen to correspond to a low shear rate—a condition which has been shown to yield macroscopic order in previous studies on block copolymers.[3,8] Nitrogen atmosphere was used in all cases. When the desired strain was reached, the samples were quenched rapidly (in less than 1 min) to room temperature.

To measure linear viscoelastic properties of the strained samples, the quenched specimens were transferred to the Rheometrics dynamic spectrometer (RDS). A typical sample temperature history is portrayed schematically in Figure 1. After straining at, for example, 160 °C, the sample was quenched in situ with cold air, passing through the T_g of polystyrene within about 25 s and reaching room temperature in about a minute. The samples were then stored at room temperature for varying amounts of time before insertion into preheated RDS fixtures. The samples rapidly heated and equilibrated at the test temperature; the maximum measurement temperature was that at which the sample had originally been sheared, in this example 160 °C. The reheating process typically took 5 min. G' and G'' were measured at a frequency of 1 rad/s on a sample which underwent a strain of 5.0 at $\tau = 2000$ Pa, $T = 160$ °C, in the RSR before transfer to the RDS (Figure 2). Zero on this figure corresponds approxi-

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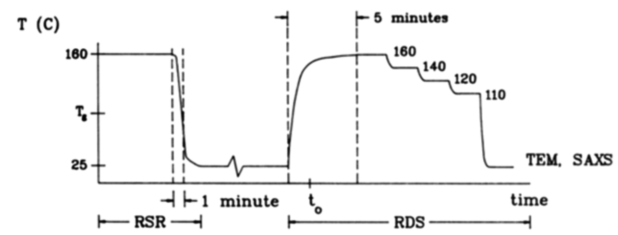

Figure 1. Time line of thermal history of the samples.

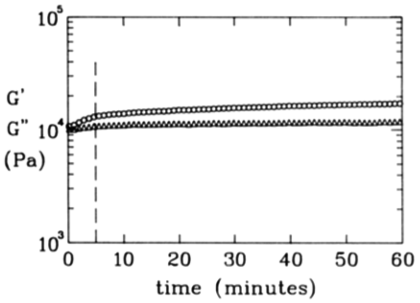

Figure 2. Efect of annealing at 160 °C on G' and G'' measured at $\omega = 1$ rad/s; sample was sheared at $\tau = 2000$ Pa, $T = 160$ °C, to $\gamma = 5$, (○) G' and (△) G''.

mately to the point labeled to in Figure 1. When the sample reaches the test temperature, the signal is very stable. Three pairs of samples subjected to identical treatments yielded identical measurements within experimental error, confirming that the state of the system after a given amount of strain is stable and reproducible. We do not measure the initial changes in the material, but we do measure the permanent changes which remain after the short-time relaxation processes have occurred.

The dynamic moduli measured have been reduced to master curves by time–temperature superposition. The time–temperature superposition principle as it is classically applied to simple fluids assumes that the changes in temperature affect all relaxation times λ_i in the same way:[9]

$$\lambda_i(T)/\lambda_i(T_{ref}) = a_T$$

For ordered systems such as microphase-separated block copolymers, this may not be the case. Fesko and Tschoegl[10] have used a simple series coupling model to predict the shift factors for SBS over wide ranges of temperature and frequency based on the properties of the constituent homopolymers. In their treatment, they allowed a_T to be time or frequency dependent, and their calculations produced master curves for an SBS copolymer with good agreement over 24 decades of frequency. Their results showed that empirical shifts of viscoelastic functions for SBS copolymers produce valid master curves only above and below the T_g's of both blocks. In this study master curves were produced for moduli measured in the range $110 \leq T \leq 195$ °C, above both T_g's.

SAXS measurements were performed at the National Bureau of Standards at Gaithersburg, MD, with the help of Dr. John Barnes. The camera uses pinhole geometry and a 2-D electronic detector with a sample-to-detector distance of 5.2 m. Thin sections were prepared for transmission electron microscopy with an AO/Reichert FC 4 cryomicrotome at −110 °C, using a diamond knife. These were stained with osmium tetroxide and viewed with a JEOL 100 kV electron microscope.

Results

Initial Morphology. The initial structure of the cast films consists of cylindrical microdomains of polystyrene (PS) in a matrix of polybutadiene (PB) as can be seen from TEM (Figure 3). The cylinder radius from the micrographs is between 60 and 80 Å. The cylinders align locally in a hexagonal array to form grains with a common director, but the director varies randomly from grain to grain resulting in a macroscopically random structure. This lack of orientation is confirmed by complete extinction when viewing the cast films through crossed polarizers.

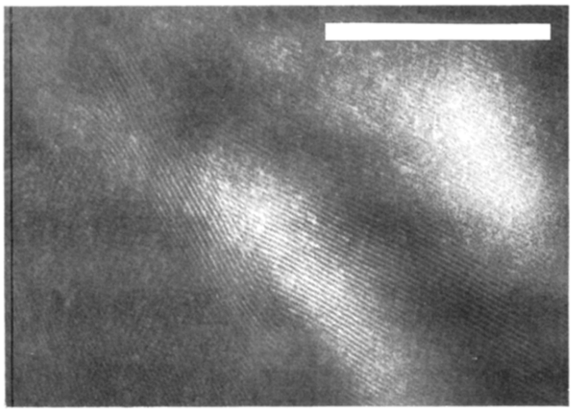

Figure 3. TEM of cast film. Bar indicates 1 μm.

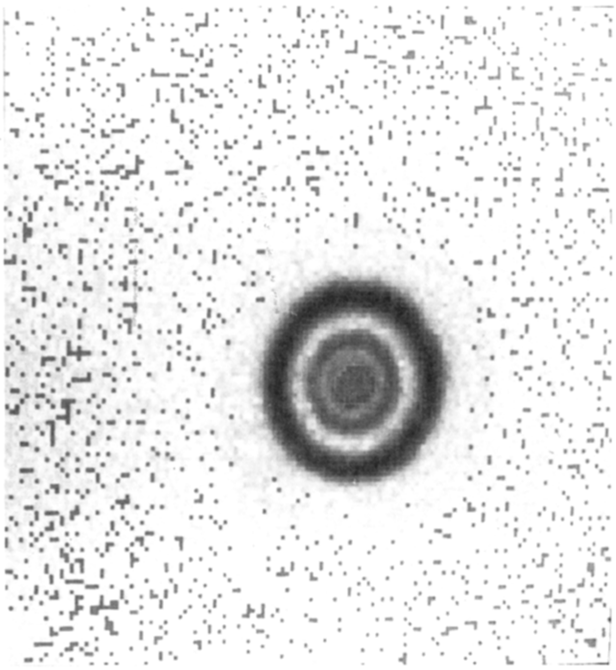

Figure 4. SAXS pattern of cast film.

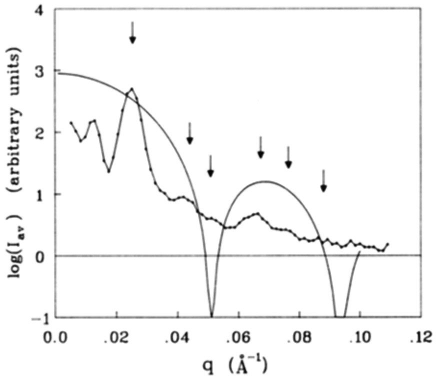

Figure 5. Circular average over all azimuthal angles of the SAXS pattern of the cast film (●). The locations of the maxima in an hexagonal lattice scattering pattern for $a = 284$ Å are indicated with arrows. Also shown (—) is the calculated form factor scattering for infinite cylinders of diameter 150 Å.

Small-angle X-ray scattering is used to determine the lattice parameter and the degree of lattice ordering. Figure 4 is a digital representation of the 2-D SAXS pattern of the as-cast film at 25 °C. The symmetric pattern is similar to crystal powder patterns and attests to the isotropic nature of these films. The first, strong maximum occurs

Table III
Lattice Spacings and Parameters for SBS81

	(q_{10}/q_{hk})	
lattice plane (*hk*)	hexagonal lattice	SBS81
10	1	1
11	0.577	0.587
20	0.500	
21	0.378	0.378
a, Å		284
R_0, Å		75

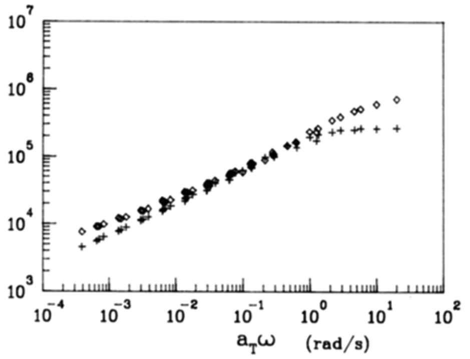

Figure 6. Master curves of G' (◇) and G'' (+) for the cast film; T_{ref} = 110 °C.

at $q = 0.0261$ Å^{-1} where q is the magnitude of the scattering vector, $q = (4\pi/\lambda)\sin(\theta)$ for a scattering angle of 2θ. The radial average of the scattering pattern of unoriented SBS81 as a function of q is shown in Figure 5, and the positions of the maxima are listed in Table III. The maxima for a perfect hexagonal lattice with lattice parameter $a = 284$ Å are also listed in Table III. The missing third reflection occurs at a q value which corresponds to a minimum in the form factor for cylinders of radius 75 Å. This minimum is not observed due to peak broadening from disorder in the system and due to the weakness of the scattering at this vector. The cylinder radius can also be calculated from the lattice parameter and the volume fraction of PS ($\phi_{PS} = 0.245$; Table I):

$$R = a/2\{2\phi_{PS}3^{1/2}/\pi\}^{1/2} = 74 \text{ Å}$$

This radius is consistent with the observations from TEM.

The samples were characterized in small-amplitude oscillatory shear at a strain amplitude, γ_{max}, of 0.03 and in the frequency range of $0.1 < \omega < 20$ rad/s. The strain is well below the linear viscoelastic limit of $\gamma_{max} = 0.7$. A master curve of data above T_g(PS) is shown in Figure 6. The required shift factors are plotted in an Arrhenius fashion (Figure 7); they do not fall on a straight line but follow a WLF relation (solid line; $C_1 = 0.21$, $C_2 = 80.4$ K).[9]

The dynamic moduli of the cast polymer reflect the microphase-separated domain structure in the melt. At low frequencies the flow is highly constrained due to the thermodynamic incompatibility of the two blocks. The moduli log (G') and log (G'') do not reach terminal slopes of 2 and 1; the storage modulus even seems to approach a low-ω plateau, indicating a kind of network behavior. At high frequencies, G' is very high and approaches a plateau comparable to the entanglement plateau of homopolybutadiene (on the order of 10^6 Pa).

Effect of Shear Strain. Figure 8 shows the whole-field birefringence of a sample strained to $\gamma = 28.6$ at $\tau = 2000$ Pa, 160 °C. All post-shearing measurements were recorded for samples which have been quenched after flow as portrayed in Figure 1. The Maltese cross image attests to the high orientation of the PS domains in the flow direction (circumferentially). The SAXS patterns of SBS81 after shearing to various strains at 160 °C, $\tau = 2000$ Pa, are shown in Figure 9. The azimuthal angle is Ω; the principle axis of scattering is oriented perpendicular to the domain axes and is called the equator ($\Omega = 0$). $\Omega = \pi/2$ is denoted the meridian. As strain increases, scattering intensity concentrates along the equator, and higher order maxima become more prominent. However, the lattice parameter does not change with shearing. This indicates that the shape and radii of the domains measured on the quenched films do not change as a result of the flow. Figure 10 shows the SAXS patterns for the samples sheared at 180 °C.

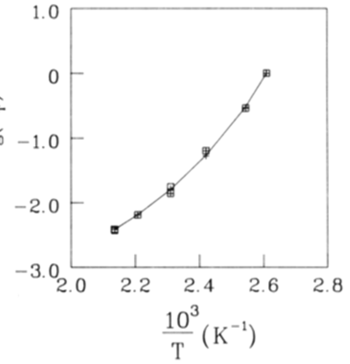

Figure 7. Empirical shift factors, a_T, versus inverse temperature for the cast film, T_{ref} = 110 °C (□, +). Also shown is the fit to the WLF equation (—).

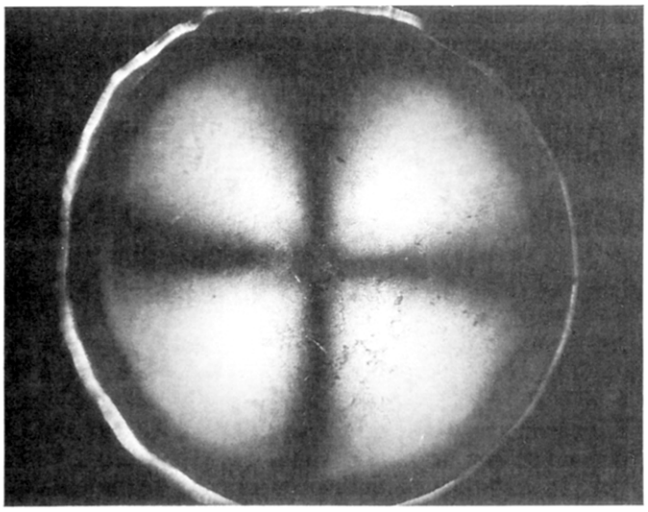

Figure 8. Birefringence of sample strained at $\tau = 2000$ Pa, T = 160 °C, to a strain of 32.

Transmission electron micrographs for samples strained to $\gamma = 0.8$ and 44.9 at 160 °C are shown in Figure 11. The samples were cut so that the view is in the direction of the shear flow. The effect of a small amount of flow is to reduce the size of the grains (Figure 11A); there still appears to be a pattern of domains aligned in grains, but the size of the grains has been reduced from ≃1 μm to 0.2–0.4 μm. With higher amounts of strain, well-aligned domains are observed (Figure 11B; circular cross section as viewed in the direction of flow), but the grain texture is no longer visible. Also, the domain surfaces seem less well-defined, suggesting that the degree of phase separation may have decreased for this sample.

To quantify the domain orientation in the flow direction, the ratio of the equatorial and meridional intensities, I_e/I_m, at $q = 0.0261$ Å^{-1} was used. The Hermans orientation function,[11] a standard measure of orientation, requires fiber symmetry, i.e., preferential orientation in the flow direction and random orientation in the plane perpendicular to this. SAXS measurements in the flow direction on SBS81 yield

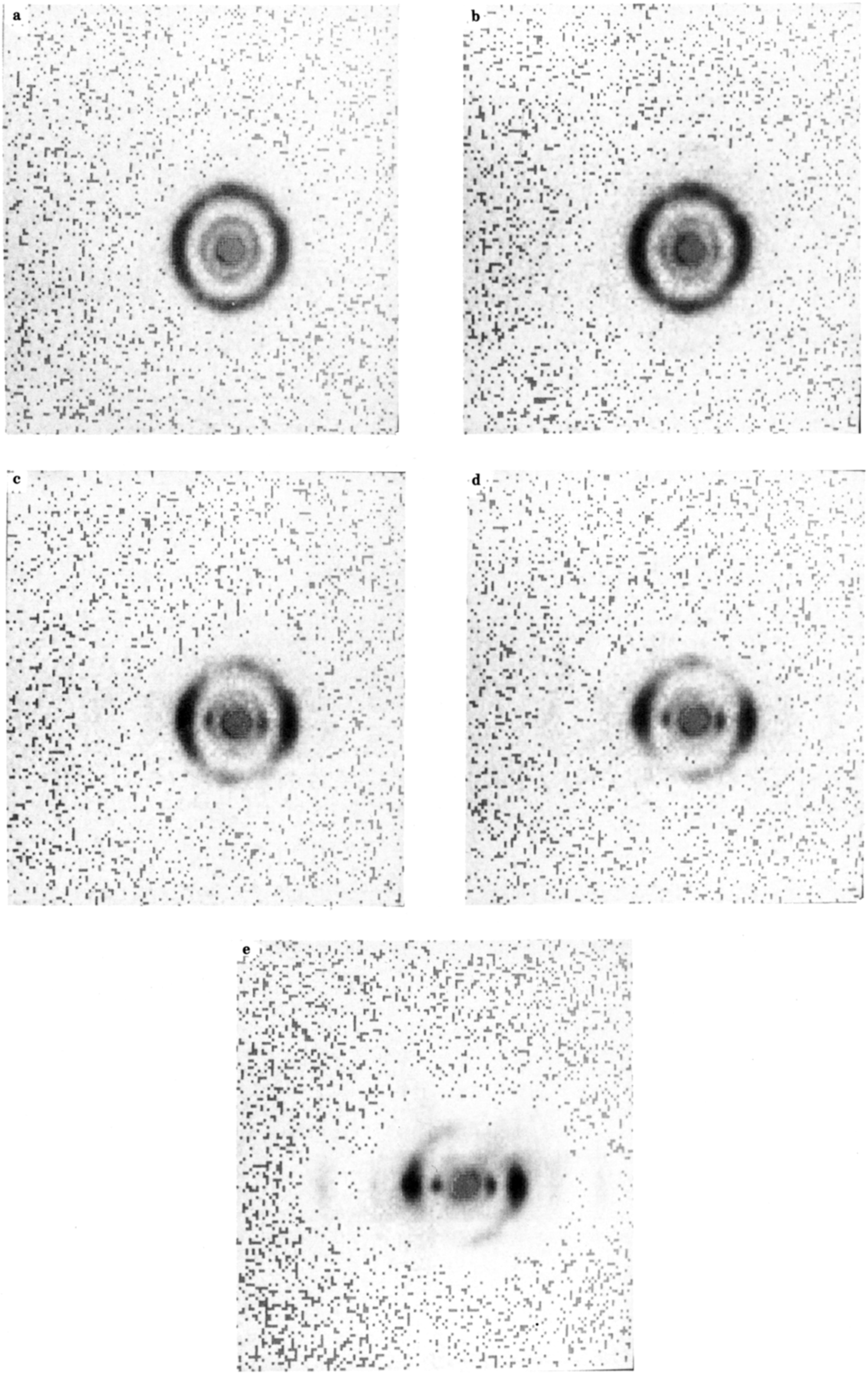

Figure 9. SAXS patterns of samples strained at τ = 2000 Pa, T = 160 °C, to strains of (a) 0.8, (b) 2.0, (c) 5.0, (d) 11.4, and (e) 44.9.

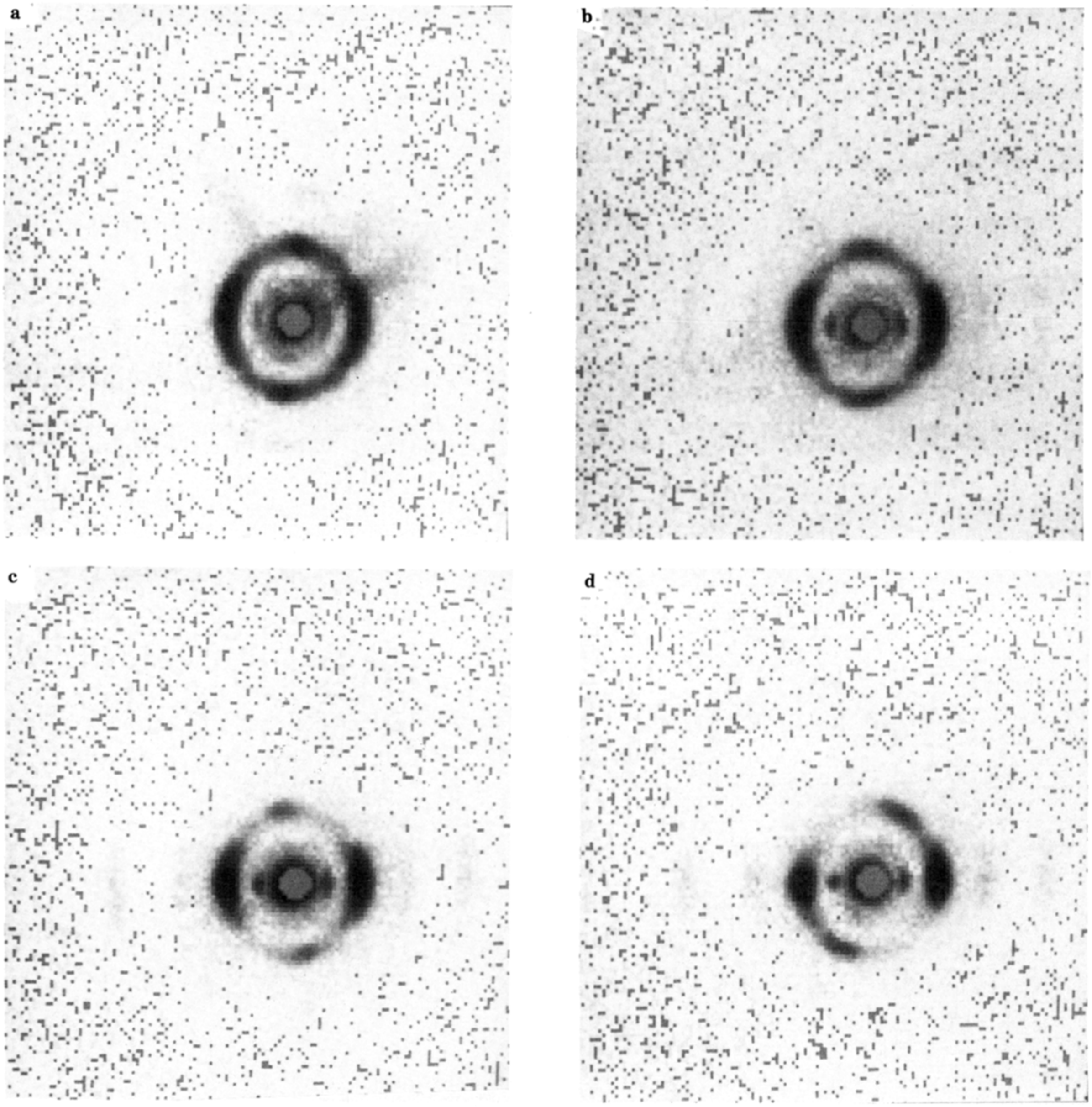

Figure 10. SAXS of samples strained at τ = 2000 Pa, T = 180 °C, to strains of (a) 3.0, (b) 5.0, (c) 11.5, and (d) 28.6.

a six-spot hexagonal pattern, implying single-crystal-type orientation rather than fiber type; thus the Hermans function could not be used. The effect of strain on orientation is shown in Figure 12 for both test temperatures. The domain orientation increases quickly at first but slows and ultimately saturates at high strains regardless of the test temperature.

G' and G'' are lower at all frequencies for the sheared samples. For $\gamma < 5.0$ the moduli drop at all frequencies (Figure 13). The effect of strains greater than 5.0 is shown in Figure 14. As larger and larger strains are imposed, the modulus increases, i.e., the material becomes stronger. This strengthening occurs preferentially at high frequencies. Another interesting feature of this trend is that between strains of 28.6 and 44.4 there is no change in moduli, mimicking the saturation observed with SAXS.

When the samples were strained at a higher temperature, T = 180 °C, the results were similar but with an important difference (Figure 15). G' dropped at low strains and recovered at higher strains as was observed for shearing at 160 °C. The recovery at high strain, however, occurs over the entire frequency range. At the highest strain measured, γ = 28.6, the modulus is indistinguishable from that of the initial material. Thus, by varying strain, we have gone through a regime of measurable change in the modulus of the material and returned to a rheologically indistinguishable state. This is a very surprising result since for most materials small changes in structure result in drastic changes in rheology. For the five decades of frequency covered by these time–temperature superposed data, it does not matter whether the domain structure is isotropic or anisotropic—in both cases the molecules exhibit the same relaxation modes.

A brief study was also made of the effect of stress, but only a narrow range of stresses was accessible due to the stiffness of the samples. Over the available range, the effect of stress was small, although orientation increased and moduli decreased with increasing stress, much in the same manner as with increasing strain.

Discussion

Researchers have previously put forward several pictures of flowing microphase-separated systems. When the end blocks of a triblock copolymer form isolated domains, Kraus et al.[12] proposed that the domains must be disrupted during steady-state flow. The disruption of domains would

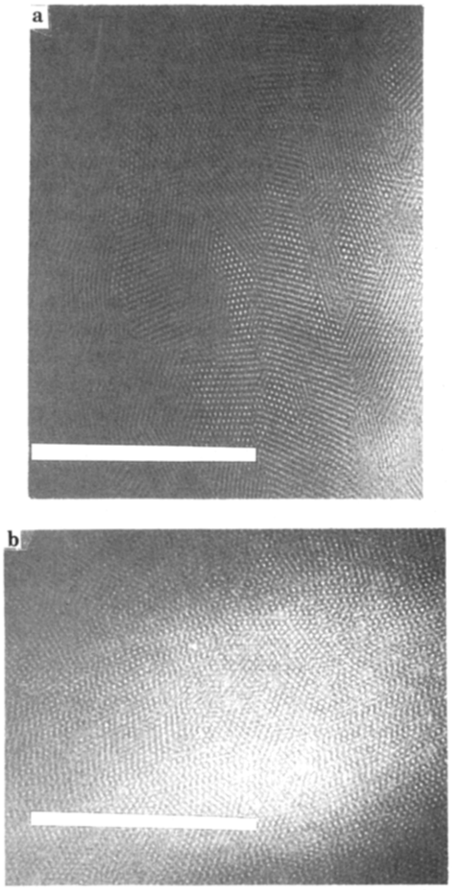

Figure 11. TEM of samples sheared at τ = 2000 Pa, T = 160 °C, to strains of (A) 0.8 and (B) 44.9; bar indicates 1 μm.

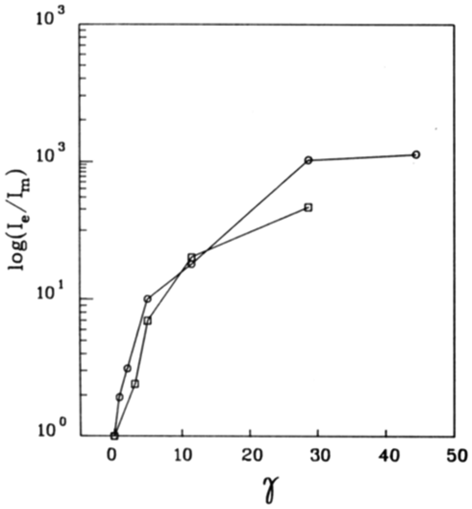

Figure 12. log of the ratio of equatorial, I_e, to meridional, I_m, scattering at the first maximum, q = 0.0261 Å, versus shear strain. Sheared at τ = 2000 Pa at T = (○) 160 °C and (□) 180 °C.

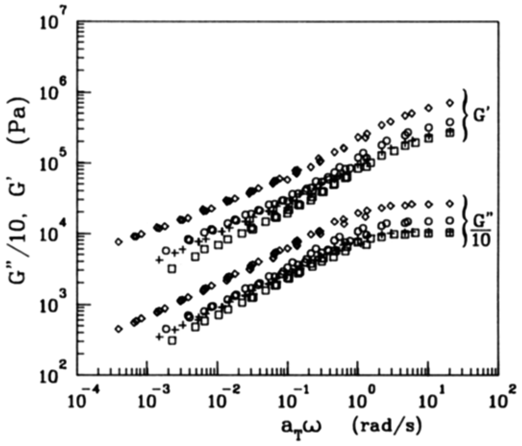

Figure 13. Master curves of G' and $G''/10$ for samples sheared at τ = 2000 Pa, T = 160 °C, to γ = (◇) 0, (○) 0.8, (+) 2.0, and (□) 5.0; T_{ref} = 110 °C.

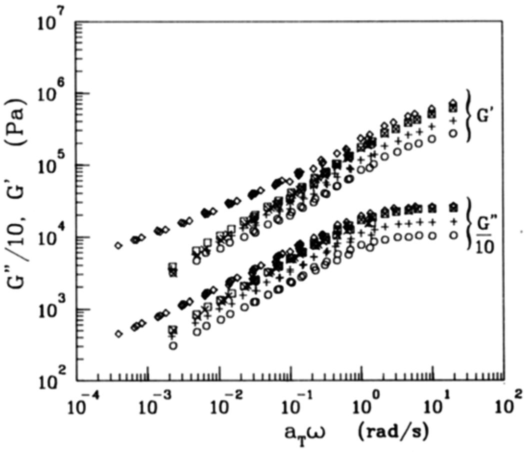

Figure 14. Master curves of G' and $G''/10$ for samples sheared at τ = 2000 Pa, T = 160 °C, to γ = (◇) 0, (○) 5.0, (+) 11.4, (□) 28.6, and (×) 44.9; T_{ref} = 110 °C.

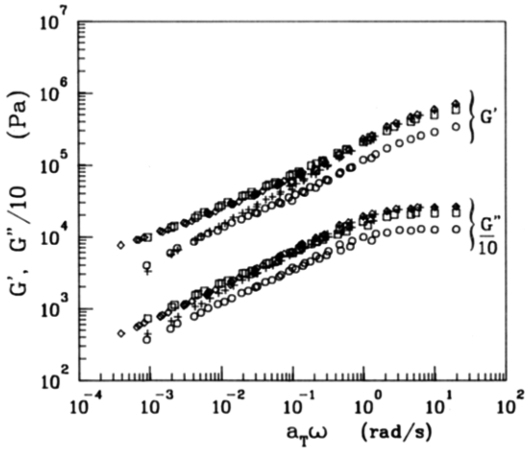

Figure 15. Master curves of G' and $G''/10$ for samples sheared at τ = 2000 Pa, T = 180 °C, to γ = (◇) 0, (○) 5.0, (+) 11.5, and (□) 28.6; T_{ref} = 110 °C.

not occur during dynamic tests at small amplitudes and hence the dynamic viscosity, $\eta' = G''/\omega$, is higher than the steady-state shear viscosity, as observed. A mechanism of flow of intact domains was proposed for the case of microdomains formed of center-block material.

The microphase separation transition (MST) has been shown to greatly affect the linear viscoelastic properties of block copolymers. Gouinlock and Porter[13] and Chung and Gale[14] found that there were two branches to the low-ω dynamic viscosity curves: η' was much lower in the homogeneous region. It was proposed that the enhancement of dynamic viscosity below the microphase separation temperature, T_s, reflects the extra energy needed to disrupt the domains; above T_s the domains do not exist and the flow is more conventional, i.e., exhibits a zero-shear viscosity and shear thinning. Further evidence of the relationship between viscosity and degree of microphase separation was obtained by a study of the influence of the chemical structure of the center block on the rheological properties of styrene-terminated triblock copolymers.[15] This showed that the viscosity and the block interaction parameter could be correlated—viscosity increased with decreasing component compatibility, i.e., increasing χN. The high melt viscosity in these systems was postulated to be due to the extra energy required to mix the domains into the matrix.

To mix the system, the flow energy $\tau\gamma$ must overcome the phase-separation energy, ΔG_{mix}, which is given by the Flory–Huggins theory:

$$\Delta G_{\mathrm{mix}} = RT\left(\frac{\phi_{\mathrm{PS}} \ln \phi_{\mathrm{PS}}}{V_{\mathrm{PS}}} + \frac{\phi_{\mathrm{PB}} \ln \phi_{\mathrm{PB}}}{V_{\mathrm{PB}}} + \frac{\chi \phi_{\mathrm{PS}} \phi_{\mathrm{PB}}}{V_{\mathrm{ref}}}\right)$$

where ϕ_{PS} and ϕ_{PB} are the volume fractions of polystyrene and polybutadiene, R is the gas constant, T is temperature, V_{PS} and V_{PB} are the molar volumes of PS and PB, χ is the interaction parameter and V_{ref} is the reference volume for χ, which is taken to be $V_{\mathrm{ref}} = (V_{\mathrm{PS}}V_{\mathrm{PB}})^{1/2}$.[16,17] An estimate for SBS81 at 160 °C (433 K) gives a value $\Delta G_{\mathrm{mix}} = 5 \times 10^5$ J/m^3. The mechanical flow energy is given by $\tau\gamma$, or approximately (2000 Pa)(40) = 0.8×10^5 J/m^3, and the ratio of flow energy to energy of mixing is therefore estimated as $\gamma\tau/N\chi kT \simeq 0.2$. These rough calculations indicate that domain disruption may be possible at the stress–strain combinations that have been used but that complete homogenization is not necessarily achieved.

A thermodynamically phase mixed flow morphology is not adequate to explain our observations, however. A system made compatible by flow would recover to the same morphology as a system which is solution cast—an isotropic morphology. This does not explain the structure development which occurs, such as that evidenced by SAXS in this study (Figures 9 and 10) and that seen by Folkes et al.[18] and Hadziioannou et al.[8]

The alternative to domain dissolution is to postulate that the microphase separation energy is too high to be overcome by flow. Then two things are possible: the chains will move only within their respective phases in order to relieve the flow stresses, or whole sections of the material will flow intact. Of importance when considering the first of these two processes is the fact that although the PS blocks are not entangled, the PB blocks are far above their entanglement molecular weight. The PS segments will move quickly to relieve stress, but the rubbery blocks are constrained by entanglements and microphase separation. The rubber chains can stretch to accommodate the stress, but certainly not to $\gamma = 44$ without breaking. A flow in which large sections remain intact would provide a solution to this problem. If grains could deform and rotate as units, flow could occur without the domains having to dissolve. The grain boundaries are regions of discontinuity in the ordered structure, and these regions may be susceptible to domain disruption already at low stresses when the total energy of the system prevents dissolution. Granular flow cannot explain domain orientation, however; a flow of large rotating grains would result in an isotropic sample independent of the strain magnitude.

A mixture of phase disruption and granular flow is another possibility. Well placed grains, i.e., those nearly aligned in the flow direction, would be stretched and rotated into the flow direction, producing macroscopic orientation. Poorly aligned grains such as those initially perpendicular to the flow direction would rotate at low strain and then dissolve at high strain. Close examination of the SAXS patterns indicates that some preferential orientation of domains perpendicular to the flow direction persists at low strain; this is manifested by scattering on the meridian as seen in Figure 9c,d. At high strains (high flow energy $\tau\gamma$) these rotating grains are also disrupted, and the off-axis scattering disappears.

The small-amplitude oscillatory shear can be interpreted with this mixed mechanism in mind. Recall that the plateau at low frequencies is due to the microphase structure, and the value of the high-frequency plateau is attributed to the entanglement molecular weight. At low strains on the sample at 160 °C, the moduli drop at all frequencies, implying some microphase mixing as well as less entanglement. This is a nonequilibrium state produced as a result of domain disruption. It is a stable state, however, since microphase separation retards the system's ability to recover. At higher strains, the phase mixing remains, but the equilibrium level of entanglement is recovered. The more highly disrupted flow morphology at higher strains makes it possible to recover the equilibrium entanglement, although not the equilibrium degree of microphase separation. At higher temperature, 180 °C, again the moduli drop at all frequencies and the interpretation is the same, but at high strains both the microphase-separated structure and the degree of entanglement recover to that present in the cast sample due to greater molecular mobility and slightly reduced microphase separation energy at the higher temperature. An important test of the proposals made here is to do similar structuring experiments in the homogeneous state of a block copolymer. This aspect will be addressed in part 2 of this series.

Conclusions

Experiments in undirectional shear in a cone-and-plate rheometer show that increasing shear strain has a profound effect on the morphology and mechanical behavior (G', G'') of an SBS block copolymer. Small-angle X-ray scattering and form birefringence show that the cylindrical microdomains orient preferentially in the flow direction, saturating in orientation after 30–40 shear units. The size and shape of the domains observed after the flow is quenched do not differ from those measured on as-cast samples. G' and G'' at first decrease at all frequencies when a strain is applied and with increasing strain the moduli recover, first at high frequencies, and then, if the temperature is high enough, at all frequencies. The flow mechanism is proposed to be a combination of domain dissolution and the flow of grains. Recovery from domain dissolution produces nonequilibrium structures which are nevertheless stable due to the restricted mobility imposed by microphase separation. The nonequilibrium structures are strongly reflected in the linear viscoelastic properties.

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Poly[(acylimino)alkylene] Block Copolymers Having Perfluoroalkyl Hydrophobic Blocks: Synthesis and Surfactant Properties

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ABSTRACT: The block cooligomer between 2-(perfluoroalkyl)-2-oxazoline and 2-methyl(or 2-ethyl)-2-oxazoline was prepared by the so-called "one-pot two-stage" polymerization. The copolymer consists of a hydrophobic and a hydrophilic block, which exhibits excellent properties of water-soluble surface active agents. The monomers of the first-stage polymerization were 2-(pentafluoroethyl)-2-oxazoline (**1a**), 2-(heptafluoro-*n*-propyl)-2-oxazoline (**1b**), and 2-(pentafluoroethyl)-5,6-dihydro-4*H*-1,3-oxazine (**2**), and methyl triflate was the initiator. 2-Methyl- (**3a**) and 2-ethyl-2-oxazoline (**3b**) were used in the second-stage polymerization. The surface activity was evaluated by surface tension (γ) of aqueous solutions. The block copolymer showed very low values of critical micelle concentration (cmc) and γ values. The γ value of a sample derived from **1a** and **3a** was as low as 15.0 dyn/cm at 0.1 wt %. It is worthy to note that even short perfluoroalkyl chains (C_2F_5 and C_3F_7 groups) are quite effective in reducing the surface tension value of aqueous solution when these chains are present in the pendant groups of homosequence units of a length (degree of polymerization) longer than 2.7.

Introduction

Hydrophilicity and lipophilicity (hydrophobicity) of cyclic imino ethers have successfully been controlled by changing the substituent at the 2-position of the imino ether ring of the monomer. For example, the polymers of 2-methyl- (**3a**) and 2-ethyl-2-oxazoline (**3b**) are hydrophilic and are easily soluble in water. On the other hand, the polymers of oxazolines having a longer alkyl substituent are hydrophobic.[1] This difference of property among the above polymer homologues has successfully been applied to the preparation of a novel type of nonionic surfactants which were AB- or ABA-type block copolymers between two different cyclic imino ethers, one giving rise to a hydrophobic block and the other to a hydrophilic block.[1,2]

In comparison to the values of ionic surfactants, the surface tension values of nonionic surfactants are influenced by electrolyte to a much less extent.[3] In addition, the critical micelle concentration (cmc) in aqueous solution is lower.

As described in the preceding paper,[4] the ring-opened polymers of 2-perfluoroalkyl-substituted cyclic imino ethers, i.e., 2-(pentafluoroethyl)-2-oxazoline (**1a**), 2-(heptafluoro-*n*-propyl)-2-oxazoline (**1b**), and 2-(pentafluoroethyl)-5,6-dihydro-4*H*-1,3-oxazine (**2**), are very hydrophobic in spite of the short chains of the perfluoroalkyl substituents. The surface energy of **1b** polymer film is similar to the value of poly(1,1-dihydroperfluorooctyl methacrylate), which is taken to be a representative fluorine-containing polymer with a low surface energy.[5]

The present paper describes the synthesis of block copolymers of perfluoroalkyl-substituted cyclic imino ethers with **3** by means of the so-called "one-pot two-stage copolymerization technique" based on the living character of the polymerization of cyclic imino ethers. Namely, a sequential polymerization of two monomers in a single pot of the polymerization system gives rise to the production of an AB-type block copolymer.

Perfluoroalkyl-containing surfactants are generally known to possess an excellent ability to reduce surface tension. However, for nonionic surfactants based on perfluoroalkyl groups, the hydrophilicity of the conventional hydrophilic component of poly(oxyethylene) is not enough to balance with the highly hydrophobic property of the perfluoroalkyl group.[6,7] For example, poly(oxyethylene) (DP = 8) with a perfluorooctyl end group is insoluble in water at room temperature,[6] and higher DPs of the poly(oxyethylene) block are required for water solubility. In the present study, highly hydrophilic oligomers of cyclic imino ethers have been combined with the corresponding oligomers having a perfluoroalkyl group, in order to explore a new type of nonionic surfactant of high performance. It is interesting that short perfluoroalkyl groups (C_2F_5 or C_3F_7 group) are hydrophobic enough to produce excellent surfactants when these groups are present in the homosequence of a block copolymer.

Results and Discussion

The block copolymer was easily prepared by a one-pot two-stage copolymerization of two different types of cyclic imino ethers. First, **1** or **2** was polymerized, and after the completion of the first-stage polymerization the second monomer **3** was added to the reaction mixture. The second-stage polymerization was initiated by the propagating end group of the A block of the first monomer to produce the B block (Scheme I).

As described before,[4] the polymerization of **1** with an alkyl triflate initiator proceeds via a reactive oxazolinium intermediate, whereas the polymerization with alkyl to-