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Influence of Defect Density on the Rheology of Ordered Block Copolymers

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ABSTRACT: Quiescently ordered block copolymer materials contain randomly oriented grains with concomitant defects and grain boundaries. Current theories suggest that the anomalous rheological properties of block copolymers are related to the average grain size, i.e. defect density. We present rheological data from a concentrated solution of a polystyrene−polyisoprene diblock copolymer in dioctyl phthalate (70 wt % polymer). The sample has a cylindrical morphology in the ordered state. The average grain size was changed by over an order of magnitude (0.4 to 7.4 μm) by adjusting thermal history. The viscoelastic moduli of this material in the frequency range 10^{-2}−10^{2} rad/s were, however, not significantly affected by this change.

Introduction

The ability of ordered block copolymers to function as thermoplastic elastomers and adhesives is directly related to their mechanical properties in the ordered state. This state is characterized by relatively large shear moduli (G' and G'', the storage and loss moduli, respectively) and slow relaxation mechanisms which lead to a weak dependence of the moduli on frequency (ω).[1−7] In polyolefin diblock copolymers with a lamellar microstructure, G' is proportional to $\omega^{1/2}$ on time scales much longer than that required for the relaxation of individual chains.[3,4] In lamellar polystyrene−polyisoprene diblock copolymers, the ω dependence of G' is much weaker and it appears to approach a low-frequency plateau.[5] Solutions of polystyrene−polybutadiene diblock copolymers in *n*-tetradecane with spherical polystyrene domains exhibit a well-defined plateau at low frequency, indicating elastic behavior.[6] Experiments on ordered solutions of polystyrene−polybutadiene block copolymers in diethyl phthalate and dioctyl phthalate also revealed slow relaxation processes.[7]

In quiescently ordered block copolymers, coherent order is interrupted by numerous defects (lines) and grain boundaries (walls).[8] We define a "grain" to be a region in the sample within which coherent order prevails. There are thus three levels of structural organization: (1) the connectivity of monomers in a block copolymer chain, (2) the assembly of these chains into mesophases such as lamellae and cylinders, and (3) the assembly of mesophases into grains. Which of these structural features are responsible for the observed stresses at low frequencies remains to be elucidated.

Experiments indicate that the application of large-amplitude, oscillatory shear on lamellar and cylindrical systems results in an oriented sample with low defect density.[4,5,9] It is also found that the modulus of shear-oriented samples (with so-called parallel and perpendicular orientation) is lower than that of quiescently ordered materials comprising a random grain structure.[4,5] These facts naturally indicate that the anomalously high moduli obtained from unoriented lamellar and cylindrical samples is due to the presence of defects and grain boundaries. The theory of Kawasaki and Onuki indicates that the rheology of unoriented block copolymers is related to the characteristic grain size, L.[10] Rubenstein and Obukov,[11] based on independent theoretical considerations, concluded that in unentangled systems (low molecular weight block copolymers), the redistribution of defects is the only source of unusual viscoelastic response. A systematic study of the effect of grain size (or defect density) on block copolymer rheology is thus predicated by experiments as well as theory.

There has been some progress in recent years in our understanding of granular organization in block copolymers. Thomas and co-workers have used electron microscopy to characterize the local morphology of defects and grain boundaries.[8] On the other hand, it has been shown that statistical properties of granular block copolymer materials, such as the average grain size, are related to their optical properties.[12−16] In this paper, we have studied the effect of grain size on the shear moduli of a block copolymer material by a combination of optical and rheological experiments.

Experimental Results

A polystyrene-*block*-polyisoprene copolymer was synthesized by anionic polymerization under high vacuum. The molecular weights of the polystyrene and polyisoprene blocks were determined to be 8 and 20 kg/mol, respectively, and we refer to this polymer as SI(8−20). Rheological and optical experiments were conducted on a 70 wt % solution of SI(8−20) in distilled dioctyl phthalate (DOP). We expect this material to have a cylindrical polystyrene domain in the ordered state with a *d*-spacing of 20 nm, based on our previous data on a similar (but not identical) SI/DOP solution.[14] The order−disorder transition temperature (T_{ODT}) was determined by the local birefringence method[15,16] and found to be 34 ± 1 °C.

At temperatures well above 34 °C, the solution rheology will depend on whether or not the SI(8−20) chains are entangled. As a crude approximation, we consider the SI(8−20)/DOP solution to be equivalent to a polyisoprene homopolymer with a "reduced" molecular weight, $c_{\mathrm{SI}}M_{\mathrm{SI}} = 19.6$ kg/mol, where c_{SI} is the concentra-

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Table 1. Grain Growth Characteristics of SI(8−20)/DOP

tempering temp (°C)	induction regime		growth regime		saturation regime		
	range (min)[a]	d*L*/d*t* (μm/min)[b]	range (min)[a]	d*L*/d*t* (μm/min)	range (min)[a]	d*L*/d*t* (μm/min)	*L* (μm)[c]
20	0−50	~0	60−100	1.4×10^{-3}	>200	1.2×10^{-4}	0.4[d]
25	0−60	~0	100−180	2.0×10^{-2}	>400	2.5×10^{-4}	2.2
29	0−80	~0	200−350	2.4×10^{-2}	>500	2.6×10^{-3}	7.4

[a] Range over which d*L*/d*t* is approximately constant. [b] Small positive and negative slopes are obtained by least squares fit. [c] The average grain size at the beginning of the saturation regime. The rheological measurements were started at this time and were completed in 1 h. The change in *L* during this time is about 1%. [d] When *L* is smaller than λ, diffraction effects become important, and the reported value of *L* is obtained after correcting for these effects.[12] The uncorrected value of *L* is 0.2 μm.

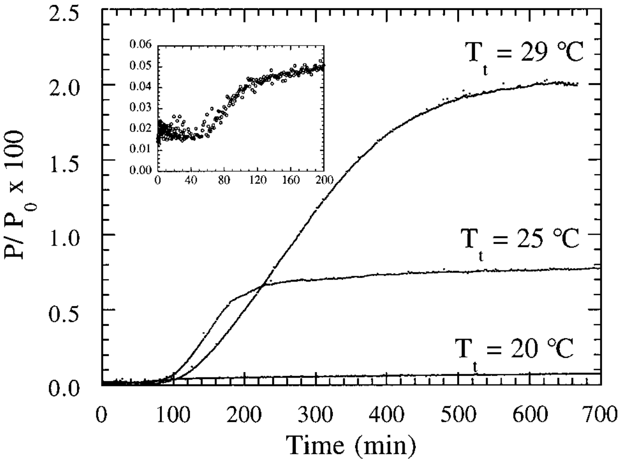

Figure 1. Plot of P/P_0 versus time for three different tempering temperatures. Inset: Data obtained while tempering at 20 °C shown on an expanded scale ($P/P_0 \times 100$ versus tempering time in minutes), for the sake of clarity.

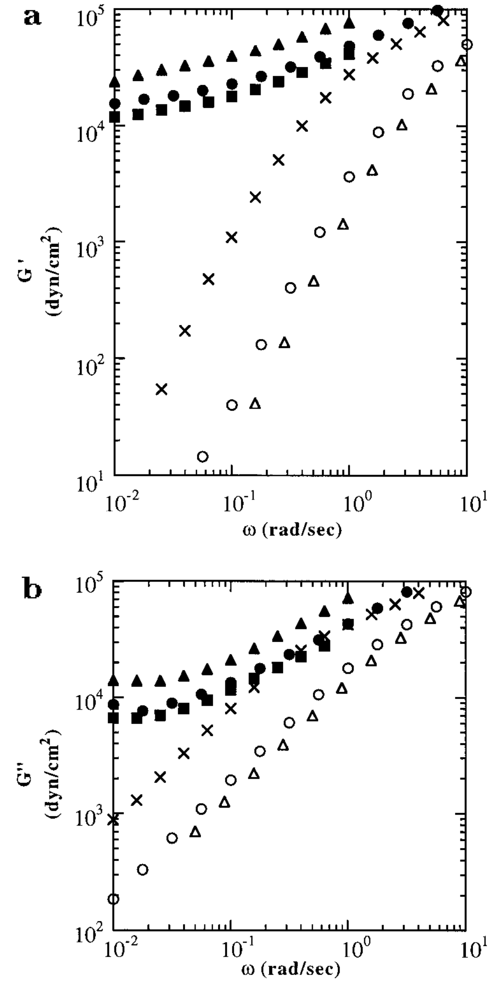

Figure 2. Changes in the frequency dependence of (a) G' and (b) G'' for SI(8−20)/DOP with temperature. Measurements were made at the tempering temperature, T_t. Unfilled symbols: disordered state (triangles, 38 °C; circles, 36 °C). Filled symbols: ordered state with saturated grain structure (squares, 29 °C; circles, 25 °C; triangles, 20 °C). Crosses: data taken at 29 °C ($<T_{ODT}$) in the induction regime.

tion (mass per unit volume) and M_{SI} is the molecular weight of the copolymer. This reduced molecular weight is larger than $M_c = 10$ kg/mol but smaller than $M_c' = 60$ kg/mol, where M_c and M_c' are the characteristic molecular weights for the appearance of entanglement effects for zero-shear viscosity and steady-state compliance, respectively, in bulk PI.[17] Thus at temperatures well above 34 °C (T_{ODT}), wherein fluctuation effects on rheology[9,18] are negligible, the SI(8−20)/DOP solution is expected to behave like a lightly entangled homopolymer melt.

The effect of thermal history on grain structure of the SI/DOP solution was studied using an apparatus described in refs 12. The frequency dependence of G' and G'' was measured on a Rheometrics RMS 605 equipped with cone-and-plate fixtures (50 mm diameter, 0.1 rad), using 5% strain. Some measurements were repeated at 3% and 1% strain to ensure that the measured response was in the linear viscoelastic regime. Both rheological and optical experiments were carried out on the same sample with nearly identical thermal histories. The sample history was "erased" between the runs by heating to 55 °C. The sample was then cooled to a predetermined temperature, usually in the ordered state. We refer to this temperature as the tempering temperature, T_t. The time required for the sample temperature to change from 55 °C to T_t was about 15 min in all the experiments.

The time dependence of the optical power transmitted through the SI(8−20)/DOP solution (0.74 cm in thickness) held between crossed polarizers is shown in Figure 1 for tempering temperatures of 29, 25, and 20 °C. Time zero is defined as the time at which the change in sample temperature from 55 °C to T_t was initiated. The ordinate in Figure 1, P/P_0, is the ratio of transmitted to incident power. For random grains, P/P_0 is proportional to the average grain size.[12,19] The growth of the ordered phase occurs in three distinct regimes: an induction regime in which no grain growth is evident (transmitted power is below the detection limit), a growth regime in which a rapid increase in P/P_0 is observed, followed by a saturation regime in which P/P_0 changes very slowly with time. In Table 1 we summarize the characteristics of the three regimes by computing d*L*/d*t*.[20] The average grain size in the saturation regime increases by a factor of 20 when T_t is increased from 20 to 29 °C.

The SI(8−20)/DOP solution was tempered in the rheometer at temperatures ranging from 20 to 38 °C after which rheological measurements were commenced. The results are shown in Figures 2a and 2b where G' and G'' are plotted as a function of ω. The unfilled symbols represent data in the disordered state ($T_t > T_{ODT}$), which were independent of tempering time. The filled symbols represent data in the ordered state ($T_t < T_{ODT}$) with a saturated grain structure (i.e., long tempering times). The results of the local birefringence experiments were used to determine the tempering time in the rheometer and it varied from 120 min at 20 °C to 500 min at 29 °C. The crosses represent data at 29 °C before the development of granular organization. These measurements were started at $t = 20$ min and completed at $t = 80$ min; the induction time at 29 °C is 80 min (see Figure 1).

At temperatures above T_{ODT} (34 °C) we clearly observe a terminal flow regime where $G' \propto \omega^2$ and $G'' \propto \omega^1$ (see Figure 2). The measured steady-state compliance $J_e°$ $(=G'/G''^2)_{\omega\to 0}$ is 1.1×10^{-5} and 9.1×10^{-6} cm^2/dyn at $T = 36$ and 38 °C, respectively. It is important to note that $J_e°$ is sensitive to slow relaxation processes.[17] The measured values are considerably larger than calculated values for lightly entangled SI(8−20) chains in a completely homogeneous DOP solution with 70 wt % polymer, at temperatures between 36 and 38 °C: $J_e°(\text{calc}) = 6.2 \times 10^{-7}$ cm^2/dyn. [Since the reduced molecular weight, $c_{SI}M_{SI}$, for this system is much smaller than M_c', $J_e°$(calc) is evaluated from the Rouse equation, $J_e°(\text{calc}) = 0.4M/cRT$.] Thus the SI(8−20) chains at 36 and 38 °C exhibit a relaxation mode that is slower than the relaxation of individual chains. It is possible that this slow mode is due to disordered concentration fluctuations.[9,18]

It is evident from Figure 2 that the measured rheological properties, in the induction regime, at 29 °C (crosses) are qualitatively similar to those in the disordered state, in spite of the fact that the sample temperature is below T_{ODT}. This suggests that the small strain applied to the solution has little effect on the induction time for grain formation. The magnitude of the steady-state compliance at 29 °C ($J_e° = 1.7 \times 10^{-5}$ cm^2/dyn) suggests that the low-frequency viscoelastic behavior of the solution is dominated by the fluctuation mode. The ω dependence of G' and G'' changes drastically when the solution is ordered and in the saturation regime (filled symbols in Figure 2). Low-frequency tails, indicating the presence of extremely slow relaxation modes, are observed at 29, 25, and 20 °C. These data also demonstrate that the rheological properties are weak functions of defect density. The average grain size in the saturation regime at 29 °C is an order of magnitude larger than that at 20 °C. Yet, the corresponding change in G' and G'' is only a factor of 2.

From the results described thus far, it is not clear if the small differences in the ordered state rheology (filled symbols in Figure 2) are due to differences in grain structure or due to differences in temperature. Optical experiments indicated that the larger grains obtained in the saturation regime at 25 and 29 °C were stable to subsequent temperature changes. This allows us to compare different grain structures at the same temperature. For instance, by tempering the sample for 500 min at 29 °C and then cooling it to 20 °C, we can create large grains at 20 °C. By comparing the rheology of this sample with that obtained by tempering directly at 20 °C for 120 min, we could study the effect of changing grain size alone; the former procedure gave $L = 7.4$ μm while the latter gave $L = 0.4$ μm. Such comparisons are shown in Figure 3. It is evident that G' and G'' in the ω-window examined are insensitive to changes in grain size, L. Some minor differences exist, e.g. G'' at 20 °C (Figure 3a). However, these differences are small when one considers the large changes in L. The relaxation processes that depend on grain size are essentially outside our experimental window; i.e., the time scales are greater than 100 s. Thus, the small rheological changes observed in our ω-window in the ordered state in Figure 2 are mainly due to changing temperature, not changes in defect density.

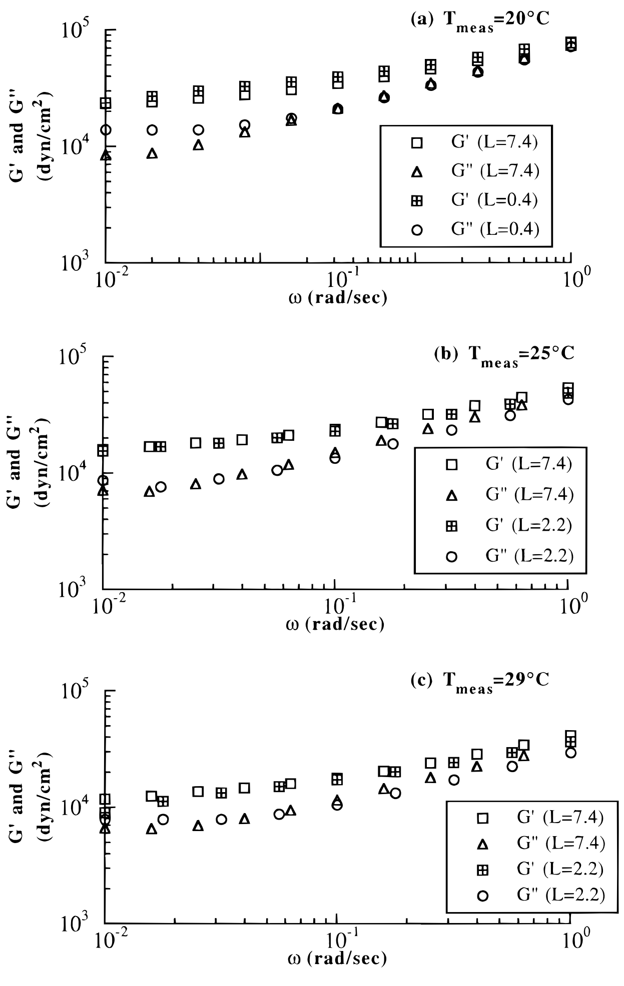

Figure 3. Demonstration of the insensitivity of rheology to the average grain size. G' and G'' versus ω from the saturated grain structures formed at T_t and measured at T_{meas}. (a) $T_{meas} = 20$ °C; (b) $T_{meas} = 25$ °C; (c) $T_{meas} = 29$ °C. The average grain size, L, corresponding to each measurement is indicated in the legend in μm. T_t for $L = 0.4$, 2.2, and 7.4 μm were 20, 25, and 29 °C, respectively.

Concluding Remarks

The rheological properties of an ordered SI(8−20)/DOP solution with a saturated grain structure, in the frequency range 10^{-2}–10^{2} rad/s, were not significantly affected by a change in the average grain size from 0.4 to 7.4 μm. The measured stresses are thus generated by either the block copolymer chains, the cylindrical mesophases, or subportions of grains smaller than 0.4 μm (20 times the d-spacing). Note that this is a relatively low-modulus material and the copolymer chains are only lightly entangled. In other materials with larger moduli and/or enhanced entanglements, the stress generating structures in this frequency window will have an even smaller characteristic length. Finally, the observed lack of sensitivity of rheology to grain size is pertinent to experiments wherein structural evolution of block copolymers is followed by measuring the time dependence of G'.[3]

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(19) A quarter-wave plate (compensator) was placed between the incident polarizer and the sample to ensure that the grains were randomly oriented (see refs 12 for details).
(20) Values of L and $\mathrm{d}L/\mathrm{d}t$ were calculated from eqs 15 and A2.1 in ref 12b, which apply to random, uncorrelated, space-filling grains. These equations are only approximate for cylindrical systems due to factors described in refs 12 and 13 and difficulties in obtaining fluctuation corrections to the free energy of low molecular weight block copolymers.[18] However, the relative changes in grain size are not affected by these factors. The value of Δn at 29 °C was calculated to be 2.36×10^{-4}.[12,18] Small changes in Δn with temperature were estimated on the basis of optical experiments; at 25 °C $\Delta n = 2.53 \times 10^{-4}$ and at 20 °C $\Delta n = 2.71 \times 10^{-4}$.

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