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Shear-rate dependence of first normal stress difference of poly(isoprene-b-styrene) in solution near the order–disorder transition temperature

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Viscoelastic properties of poly(isoprene-b-styrene) in dioctylphthalate under steady shear flow were measured near the order–disorder transition temperature. In ordered states, first normal stress difference N_1 is proportional to shear rate $\dot{\gamma}$ at low $\dot{\gamma}$ region, but becomes proportional to $\dot{\gamma}^2$ at the high $\dot{\gamma}$ region, similar to the N_1 behaviour of polymer blends undergoing shear-induced homogenization. Because the existence of microdomains was confirmed at the high $\dot{\gamma}$ region by the flow birefringence method, it is concluded that the above N_1 behaviour is not caused by shear-induced homogenization, but is probably caused by the shear-induced alignment of the microdomain structure. Copyright © 1996 Elsevier Science Ltd.

(Keywords: block copolymer; first normal stress difference; shear-induced alignment)

Introduction

Effects of shear flows on phase transition and domain structures of polymeric materials have been studied extensively and both shear-induced homogenization and phase separation, and also structural changes have been reported (as recently reviewed by Larson[1]).

In a previous paper[2], we studied viscoelastic properties of polystyrene/poly(vinyl methyl ether) blends under steady shear flow in phase-separated states near the phase-separation temperature and found that shear rate ($\dot{\gamma}$) dependence on first normal stress difference, N_1, changes from first order for textured materials[3–5] at low $\dot{\gamma}$ region to second order for homogeneous polymers[6] owing to shear-induced homogenization at high $\dot{\gamma}$ region. The similar change of shear-rate dependence of N_1 can be expected for other polymeric systems which assume phase transition, such as block copolymers.

The shear-induced alignment of microdomain structures and phase transition have been reported for block copolymers[1]; most of the studies were carried out under large-amplitude oscillatory flow. Although a few other studies have been performed under steady shear flow[1–7], the shear rate dependence of N_1 of block copolymers near the order–disorder transition (ODT) temperature has not yet been elucidated. In this paper, we report preliminary results of the shear rate dependence of N_1 of a diblock copolymer in solutions measured near to ODT temperature. The existence of microdomain under the flow was examined by the birefringence method.

Experimental

A diblock copolymer sample used was poly(isoprene-b-styrene) prepared by anionic polymerization[8], kindly supplied by Professor Matsushita of ISSP, The University of Tokyo. Number average molecular weight M_n of polyisoprene precursor and the block copolymer, determined by osmotic pressure measurements are 37 K and 84 K, respectively, and M_w/M_n of the sample measured by g.p.c. is 1.08. The volume ratio of each block is 1 : 1, which means that this sample assumes lamellar structure in bulk.

The solvent used was dioctylphthalate which is a common solvent for both polymer components and the concentrations were varied between 25 and 35 wt%. The ODT temperature of each solution was determined by both birefringence method and dynamic mechanical analysis (d.m.a.)[9]. In the birefringence method, the sample solution in a quartz cell was inserted in a heater block placed between two crossed polarizers and the transmitted intensity I of the He–Ne laser was measured with a photocell at several different heating and cooling rates.

A homemade rheometer equipped with parallel plates made of quartz was used for birefringence measurements under steady shear flow. The optical systems are the same as in the static measurements, but the incident laser beam was applied vertically from the top of quartz plate.

Viscoelastic measurements of sample solutions under oscillatory flow (d.m.a.) and steady shear flow were carried out with a Mechanical spectrometer RMS800 (Rheometric Scientific Inc.). A parallel-plate geometry with 5 cm diameter was used for d.m.a., while a cone-plate geometry with 5 cm diameter and 0.04 rad cone angle was used for steady shear flow measurements.

Results and discussion

Order–disorder transition. Figure 1a shows an example of plots of transmitted intensity, I, against temperature, T, obtained by birefringence measurements. It is clear that I is almost constant at low T and rapidly decreases to be nearly equal to zero in a narrow temperature range with increase of T. In *Figure 1* the high values of I at the low T region indicate that microphase-separated structures exist in the solutions, whereas the almost zero values at the high T region

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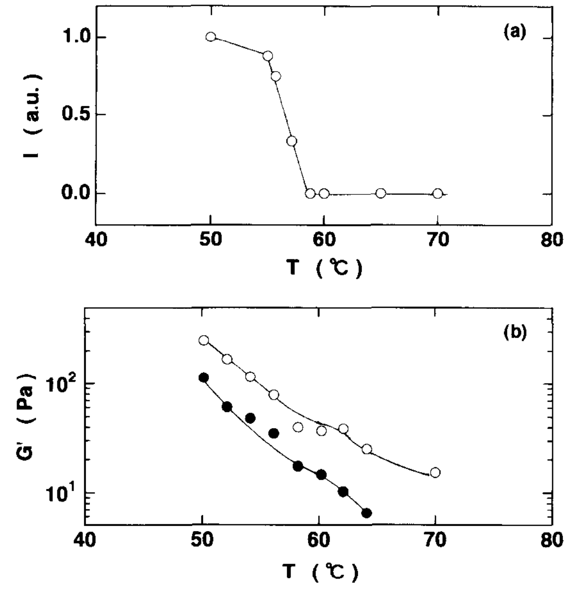

Figure 1 (a) An examle of plots of *I versus T* measured at a heating rate of 2/8C min^{-1}. Concentration of the sample solution is 29.0 wt%. (b) Examples of plots of *G' versus T* for 29.0 wt% solution. Open and filled circles denote the data measured at 20 and 10 rad s^{-1}, respectively

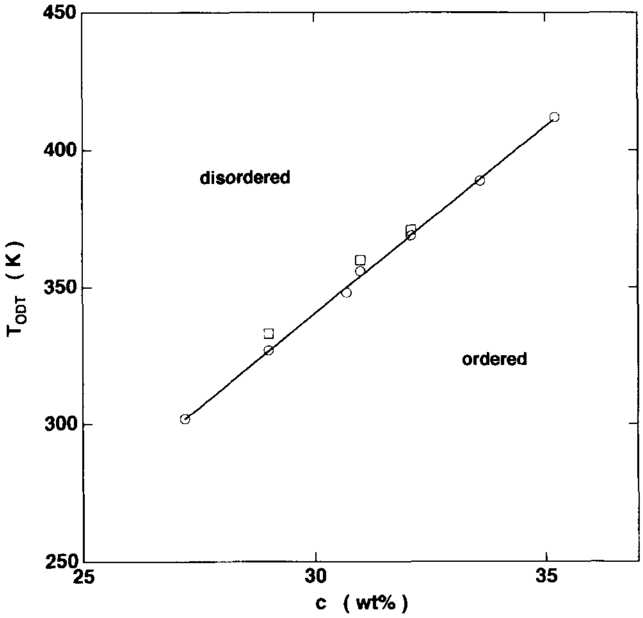

Figure 2 Plots of T_{ODT} *versus* block copolymer concentration in solution. Squares and circles denote the data measured by dynamic mechanical analysis and birefringence method, respectively

indicate that the solutions are homogeneous[9]. The ODT temperature T_{ODT} for each solution was determined by extrapolating the apparent ODT temperatures evaluated from the inflection points at various heating (or cooling) rates, to zero heating (or cooling) rate.

Figure 1b shows examples of semilogrithmic plots of storage modulus G' at fixed frequencies ω against T, obtained by d.m.a. In this analysis, the ω dependence of G' and G'' (loss moduli) at several temperatures were measured and the T dependence of G' and G'' at a few frequencies in the terminal region were examined. Although these dependences are not as sharp as the plots of I *versus* T, the change in the T dependence of G' can be observed, as shown in the figure[9]. Similar behaviour was also observed for G''. T_{ODT} for each solution was determined as a simple average of apparent ODT temperatures evaluated from the inflection points of G' and G'' at different frequencies.

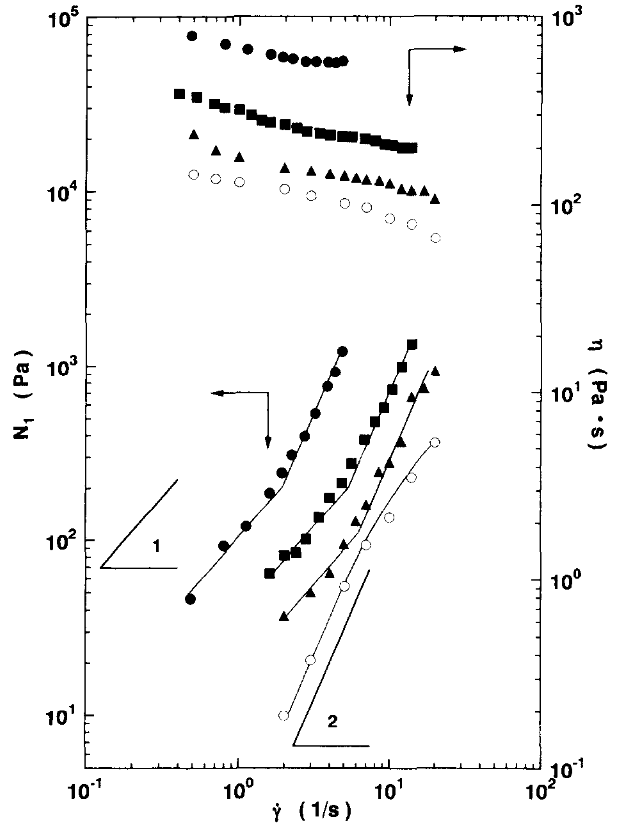

Figure 3 Shear rate dependences of shear viscosity η and first normal stress difference N_1 in ordered (filled symbols) and in disordered (open symbols) states at quiescence at 25°C. Concentrations are (from top to bottom) 31.0, 30.7, 27.2 and 25.0 wt%

Figure 2 shows plots of T_{ODT} against concentration C of block copolymer in solution. It is clear that T_{ODT} values determined from birefringence measurements and d.m.a. coincide with each other[9]. In this paper, we will not discuss ODT further and instead concentrate our discussion on the viscoelastic properties measured under steady shear flow in both ordered and disordered states near the T_{ODT} shown in this figure.

Viscoelastic properties. Figure 3 shows double logarithmic plots of shear viscosity η and N_1 against $\dot{\gamma}$ for the copolymer solutions with $C = 25.0$–31.0 wt% at 25°C. At the quiescent state, the 25 wt% solution is in disordered state while other solutions with high C are in the ordered state. It is clear that the $\dot{\gamma}$ dependences of η and N_1 of the disordered solution are practically the same as those observed in homogeneous polymer systems[6]; η gradually decreases with $\dot{\gamma}$ and N_1 is proportional to $\dot{\gamma}^2$ at low $\dot{\gamma}$, but the $\dot{\gamma}$ dependences decrease at high $\dot{\gamma}$.

For the solutions in ordered state at quiescent, however, η is almost constant in the middle range of $\dot{\gamma}$, but is somewhat enhanced in the low $\dot{\gamma}$ region and assumes shear thinning in the high $\dot{\gamma}$ region. More

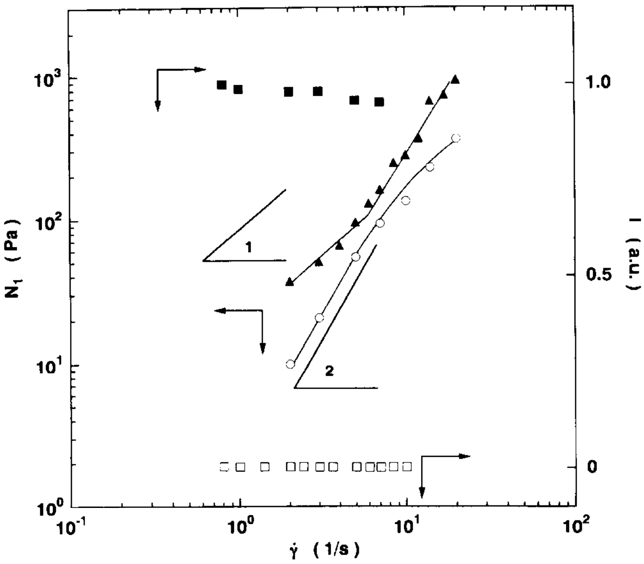

Figure 4 Shear rate dependences of N_1 (triangles and circles) and I (squares) in ordered (filled symbols) and disordered (open symbols) states at quiescence at 25°C. Concentrations are 27.2 and 25.0 wt% for ordered and disordered states, respectively

significant change is observed in the $\dot{\gamma}$ dependence of N_1; N_1 is proportional to $\dot{\gamma}$ at the low $\dot{\gamma}$ region, but it becomes proportional to $\dot{\gamma}^2$ at the high $\dot{\gamma}$ region. The change in the $\dot{\gamma}$ dependence occurs at a critical shear rate, $\dot{\gamma}^*$. It should be noted that the shear rate dependences of viscoelastic properties observed at $\dot{\gamma} < \dot{\gamma}^*$ are the same as those of binary immiscible fluid mixtures[10,11], so that block copolymer solutions in ordered states may be one type of textured material[4,5].

All the $\dot{\gamma}$ dependences of viscoelastic properties of block copolymers in ordered states are apparently the same as those observed for polymer blends in the phase-separated region near the phase transition temperature when the shear-induced homogenization occurs[2]. Moreover, the ω dependencies of G' and G'' in the terminal region measured just after cessation of steady shear flows at $\dot{\gamma} < \dot{\gamma}^*$ and $\dot{\gamma} > \dot{\gamma}^*$ were almost the same as those observed in ordered and disordered states at quiescence, respectively.

From the above results, one might expect shear-induced homogenization for block copolymer solution. However, it was reported that when the shear-induced alignment of microdomains occurs under large amplitude oscillatory flow, the ω dependences of G' and G'' in the terminal region measured by an ordinary method become almost the same as those in disordered states[12]. Therefore, there are two different possibilities, i.e., the shear-induced homogenization and shear-induced alignment of the structure, which cannot be distinguished from viscoelastic measurements alone. Hence, for the 27.2 wt% solution (in ordered states at quiescence) birefringence was measured under steady shear flow to examine whether the microdomains exist around the $\dot{\gamma}^*$ value. For comparison, the birefringence was measured under steady shear flow for the 25.0 wt% solution (in disordered state at quiescence).

Figure 4 shows the shear rate dependence of N_1 at 25°C for those solutions, together with the intensity I measured by birefringence method under steady shear flow. As shown in this figure, the I values for the 25.0 wt% solution (in disordered state at quiescence) remain almost zero, denoting that there is no domain structure in this solution in the range of $\dot{\gamma}$ examined. Conversely, the I values for 27.2 wt% solution (in ordered states at quiescent) are almost constant at high value even at $\dot{\gamma} > \dot{\gamma}^*$, showing that there still exists a microdomain structure at $\dot{\gamma} > \dot{\gamma}^*$. Therefore, for the solutions in the ordered state at quiescence, we conclude that the change in the shear rate dependence of their first normal stress difference is not caused by the shear-induced homogenization, but is probably caused by shear-induced alignment of the microdomain structure.

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