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Chain degradation in rheological measurements and effects of molecular weight distributions on rheological data for polymer solutions undergoing flow-induced phase separation

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We examined chain degradation in rheological measurements and the effects of molecular weight distributions (MWDs) on rheological data at steady states for polystyrenes in dioctyl phthalate undergoing flow-induced phase separation. The chain degradation occurred when we observed a strong overshoot in transient stresses. The suppression of overshoot by lowering the concentration and the molecular weights of the samples, and/or by making a step increase in the shear rate, was effective in preventing the degradation. The most significant difference between the rheological data for samples with broad and narrow MWDs is the existence of plateau in the first normal stress difference in the former. Shear rate dependences of the stresses of broad MWD samples in the shear rate range before the plateau are somewhat steeper than those of narrow MWD samples. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

In the past decade, the flow-induced phase transition in polymeric materials, which was first reported more than 30 years ago, has attracted many theoretical and experimental researchers in the fields of polymer physics and critical phenomena[1–3]. Scattering (light, X-ray and neutron) and rheological measurements under flow have been performed in order to study the flow-induced phase transition of polymer blends, such as polystyrene/poly(vinyl methyl ether) (PS/PVME), and polymers in Θ solvents, such as PS in dioctyl phthalate (DOP). Recently[4–7], studies which include the first normal stress difference N_1 have increased after new theories[2,3] predicted that N_1 plays an important roll in the flow-induced phase transition. For simplicity, hereafter flow-induced homogenization and flow-induced phase separation are termed shear mixing and shear demixing, respectively.

In polymer blends, shear mixing and demixing can be observed for low molecular weight samples at relatively low shear rates, so that it is not difficult to measure N_1 of these samples. Actually, we have already reported viscoelastic properties of polymer blends in an homogeneous region[8], phase-separated regions at shallow[9] and deep quenching[10], and completely immiscible states[11,12]. For PS/PVME blends at shallow quenching[9], the shear rate ($\dot{\gamma}$) dependence of N_1 changed from first order for textured materials[11–14] in the low $\dot{\gamma}$ range to second order for homogeneous polymers[15] in the high $\dot{\gamma}$ range, indicating shear mixing.

The change in the $\dot{\gamma}$ dependence of N_1 is also expected for polymer solutions undergoing shear mixing and demixing. In polymer solutions[16], shear mixing was generally observed for low molecular weight samples, so N_1 could not be measured because of the low stress level. On the other hand, shear demixing was reported for high molecular weight samples at relatively low concentrations and high shear rates, so the stresses are strong enough to be measured. In such measurements, however, flow-induced chain degradation[17] may occur, changing the molecular weights and their distributions (MWDs) in the samples, which in turn affect the rheological data. Nevertheless, no study has been performed in order to clarify the effects of chain degradation in rheological measurements. In this work, we study chain degradation in rheological measurements of PS in DOP undergoing shear demixing, and the effects of MWDs of the sample on the rheological data at the steady state.

EXPERIMENTAL

The samples used were four polystyrenes, PS-1 and PS-2 having slightly broad MWDs, and F128 and F80 having narrow MWDs purchased from Tosoh Co. Ltd. PS-1 and PS-2 were mainly used to examine the experimental conditions described later. Molecular characteristics of the samples are listed in *Table 1*.

The solvents used were DOP, a Θ solvent (Θ = 22°C) for PS, and benzyl *n*-butyl phthalate (BBP), a good solvent for PS. Physical properties of these solvents were reported previously[18–20]. BBP was used for the PS-1 solution only to obtain reference data. The concentrations of the sample solutions, the measurement temperature, and the cloud

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Table 1 Molecular characteristics of polystyrenes and experimental conditions

Code	$10^{-6} M_w$	M_w/M_n	Concentration (wt%)	T_c (°C)	T (°C)
PS-1	1.45	1.51	5.4	10	27
			3.0	12	27
PS-2	1.07	1.18	6.0	9	27
F128	1.09	1.08	6.0	9	13.4
F80	0.71	1.05	6.0	9	13.4

Table 2 Molecular weights and the distributions after flow

Code	Concentration (wt%)	$\dot\gamma$	$10^5 M_w$	M_w/M_n
PS-1	5.4	2500	4.3	1.44
	3.0	380	1.42	1.58
PS-2	6.0	370	10.0	1.22
		800	7.8	1.33
		1000[a]	7.3	1.34
F128	6.0	1.11	10.8	1.11

[a]Steady values of σ and N_1 were not obtained for this shear rate because of fracture of the sample surface

points (T_c) (determination method given below) are also tabulated in *Table 1*.

The cloud points of PS in DOP were determined by measuring the transmitted intensity of an He–Ne laser beam through the sample solutions in a test tube, 8 mm in diameter, immersed in a water bath with a photocell. The transmitted laser beam intensity was continuously recorded along with the temperature of the water bath. The cloud points were determined by extrapolating the apparent cloud points at different cooling rates, obtained as the temperatures at which the light intensity dropped, to zero cooling rate.

Viscoelastic measurements were performed with a Rheometrics mechanical spectrometer type RMS 800. A cone-plate geometry with 0.04 rad cone angle and 5 cm diameter was used. As a preliminary test, transient stress development after the onset of steady shear flow was observed for a 5.4 wt% PS-1 solution at several shear rates including higher ones (in the order of hundreds), around which shear demixing was expected to be observed. At low shear rates ($\dot\gamma < 150\,\mathrm{s}^{-1}$), the transient behaviour is practically the same as that reported for homogeneous polymer solutions; a monotonic increase at low shear rates and a small overshoot at higher shear rates. On the other hand, at a high shear rate ($\dot\gamma = 300\,\mathrm{s}^{-1}$), the overshoot was so strong that the instrument shut down due to overload. To avoid this, therefore, we used the transient mode with four successive increases in shear rate ($\dot\gamma_1$ to $\dot\gamma_4$) in all the measurements, which was effective in reducing the overshoot peaks.

For the PS-1 and PS-2 solutions, no temperature chamber was used to visually observe the turbidity. In these cases, the room temperature (27°C) was kept almost constant so the measuring temperature monitored in the cone plate was 27.0 ± 0.5°C. For the F128 and F80 solutions, the measuring temperature was regulated at 13.4 ± 0.1°C with a home-made water jacket.

Weight-average molecular weights, M_w, and molecular weight distribution indices, M_w/M_n, were determined by g.p.c. (resolution columns from Tosoh Co. Ltd, GMHXL × 2; eluent, THF) and are listed in *Table 2*, together with the highest shear rate used in the rheological

measurements which were performed just before the g.p.c. measurements.

RESULTS AND DISCUSSION

Figure 1a shows examples of the transient shear stress $\sigma(t)$ and the transient first normal stress difference $N_1(t)$ observed after a step increase in the shear rate (only for the first two shear rates) for the fresh 5.4% PS-1 solution (first run). The transient behaviour after the onset of steady shear flow with $\dot\gamma = 100\,\mathrm{s}^{-1}$ (left-side end) is normal, as is already mentioned in the experimental section, but the overshoot peaks of both $\sigma(t)$ and $N_1(t)$ after a step increase to $\dot\gamma = 360\,\mathrm{s}^{-1}$ are very high, showing stress vibrations, and it took a very long time to reach the steady state. At this shear rate, the solution became remarkably turbid.

Recent studies[4–7] on shear demixing reported the existence of a second overshoot, which was not observed in our experiments. In the case of polymer solutions, a second overshoot was clearly observed for extremely high molecular weight samples close to the cloud point, but not for lower molecular weight samples and/or at higher temperatures. Since our experimental temperature is not so close to the cloud point, it may be reasonable that there is no apparent second overshoot in our data. It might be located somewhere in the long tail of the strong overshoot, as reported by Migler et al.[6].

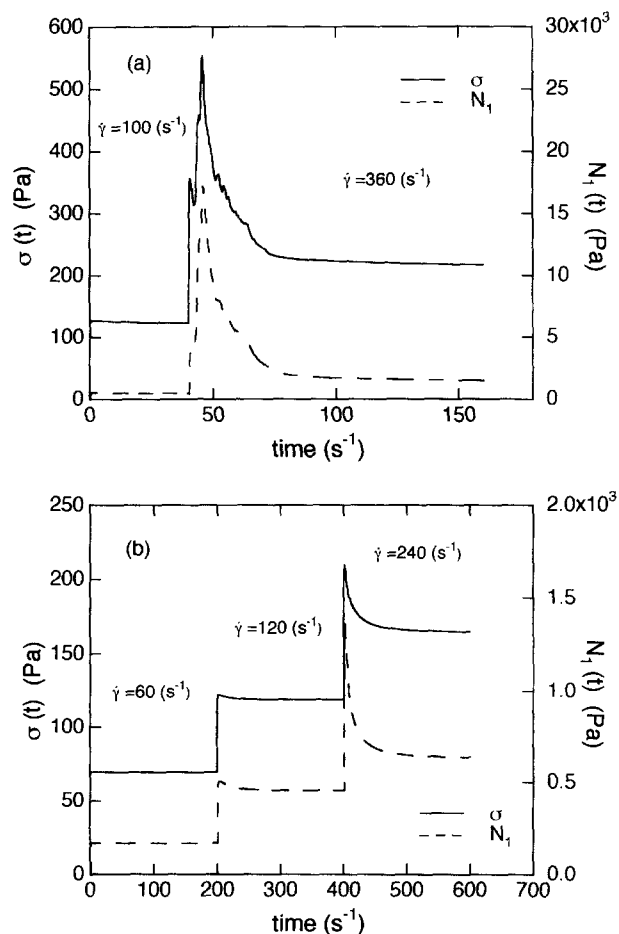The steady shear stress σ and the steady first normal stress

Figure 1 Plots of transient stresses observed after the start-up of flow and step increase of shear rates against time for (a) 5.4% PS-1 solution and (b) 3% PS-1 solution. Shear rates are indicated in the figure

difference N_1 of the 5.4% PS-1 solution were evaluated as average values at the long-time end of each shear rate in the transient mode experiments described above (the first run). *Figure 2* shows double logarithmic plots of σ and N_1 against $\dot{\gamma}$ thus obtained, together with the data for PS in BBP for comparison. Although the shear rate dependence of σ changes more significantly for the DOP solution than for the BBP solution, the shear rate dependences of both solutions seem to show ordinary non-Newtonian behaviour[15]. On the other hand, a plateau is observed for N_1 of the DOP solution at shear rates where the turbidity becomes remarkable.

Gel permeation chromatographic elution curves for PS-1 obtained before and after the first run are shown in *Figure 3a* and *b*, respectively. As shown in *Figure 3b* and *Table 2*, PS-1 in the DOP solution was seriously degraded, while PS-1 in the BBP solution was not degraded (the g.p.c. elution curve is not shown). Since the highest stresses at the steady state were not very different for both solutions but the stress overshoot was small even at the highest shear rate for the BBP solution, we can speculate that the degradation occurred during the strong stress overshoot for the DOP solution. Thus we performed a few more transient measurements combined with g.p.c. measurements for fresh 5.4% PS-1 solutions and found that chain degradation occurred when we observed a strong stress overshoot, as shown in *Figure 1a*.

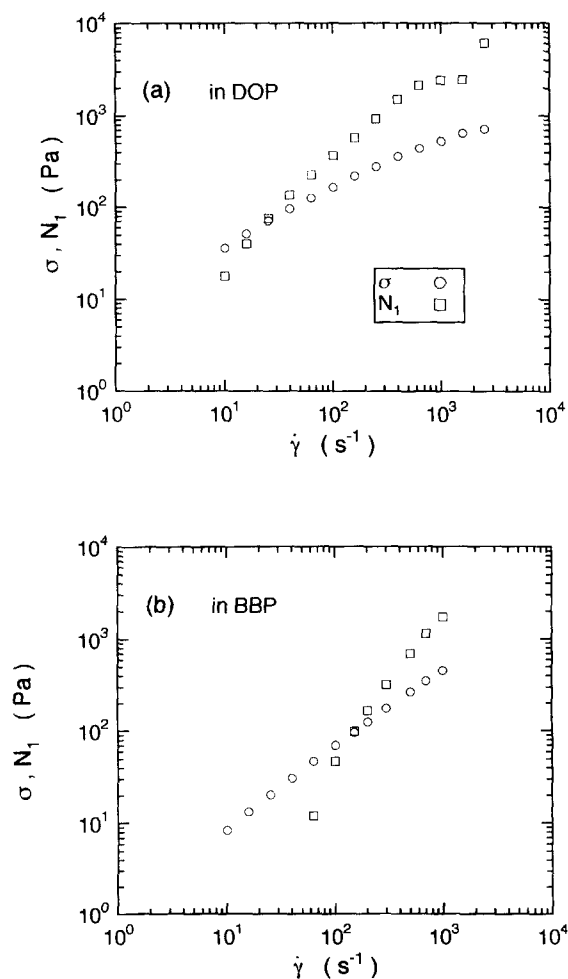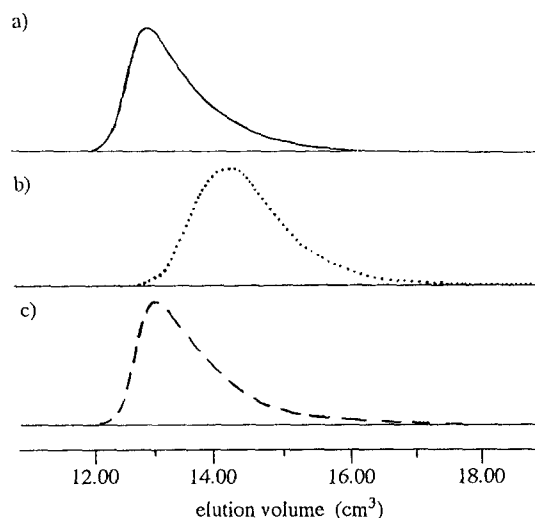To reduce the overshoot peak further at higher shear rates,

Figure 3 Gel permeation chromatographic elution curves for PS-1 (a) before the measurements; (b) after the first run (5.4% solution); and (c) after the second run (3% solution). The highest shear rates used in the measurements are shown in *Table 2*

the second and third runs were performed in the transient mode, with a smaller step increase of shear rate especially for the third and fourth runs in the high shear rate range. We employed a lower concentration (3.0 wt%) in the second run and a lower molecular weight sample (PS-2) in the third run than in the first run. Because of these changes, the differences between the measuring temperatures and T_c were also slightly changed (*Table 1*).

Examples of transient stresses for the 3% PS-1 solution thus measured are shown in *Figure 1b*. In these cases, the peak height of the overshoot is less than that observed in *Figure 1a* at all the shear rates. *Figure 4a* and *b* show double logarithmic plots of σ and N_1 against $\dot{\gamma}$ for the 3% PS-1 solution (second run) and 6% PS-2 solution (third run), respectively. The shear rate dependences of σ and N_1 are similar to those observed for the 5.4% PS-1 solution (first run), that is, a plateau was observed in N_1 at high shear rates for both solutions. In addition, a small shoulder was observed for σ in both solutions. The solutions became remarkably turbid around the shear rates of the plateau.

The g.p.c. elution curve for the 3% PS-1 solution after the flow is shown in *Figure 3c*. A comparison of the M_w and M_w/M_n values in *Tables 1* and *2* indicates that degradation hardly occurred for the 3% PS-1 solution (second run) and the 6% PS-2 solution (third run) up to $\dot{\gamma} = 370 \text{ s}^{-1}$. Degradation occurred in the 6% PS-2 solution at higher shear rates, but it was not as significant as in the 5.4% PS-1 solution (first run). Migler *et al.*[6] also reported a slight degradation in a PS sample ($M_w = 1.03 \times 10^{-6}$) used as a 4% DOP solution, detected by the decrease of the scattering intensity in measurements of light scattering under flow. For the same samples, they observed overshoots in the transient stress measurements, the peaks of which were lower than that shown in *Figure 1a*. In this work, severe flow-induced degradation was observed only after the strong overshoots in the first and third runs, as shown in *Figure 1a*.

From the above results, we speculate that chain degradation takes place when polymer chains are highly stretched during the occurrence of strong overshoot. However, we cannot specify the mechanism and timing of the chain degradation. Further work is needed to elucidate them. Here, we can conclude that the suppression of overshoot by
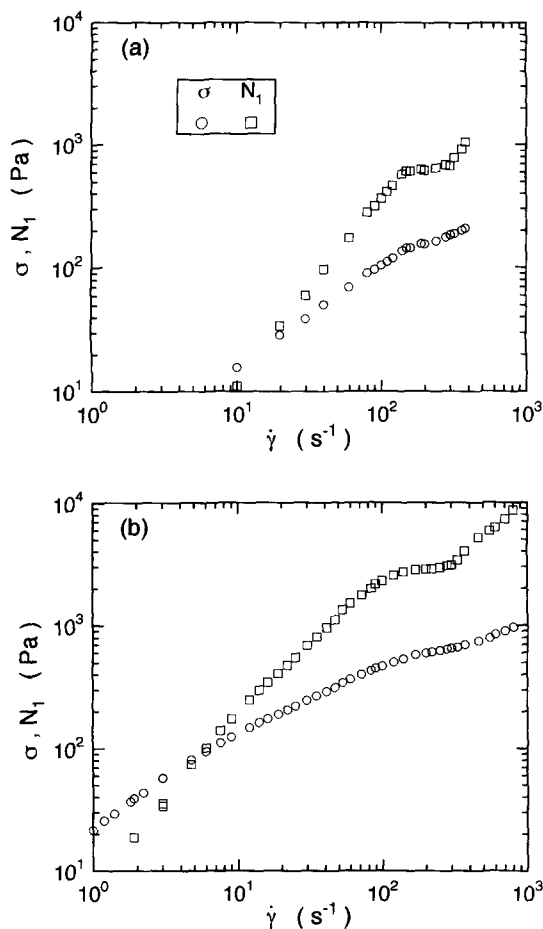

Figure 2 Double logarithmic plots of σ and N_1 against $\dot{\gamma}$ for (a) a 5.4% PS-1 solution and (b) a 6% PS-1/BBP solution. Symbols are identified in the figure

Figure 4 Double logarithmic plots of σ and N_1 against $\dot{\gamma}$ for (a) a 3% PS-1 solution (second run) and (b) a 6% PS-2 solution (third run). Symbols are identified in the figure

Figure 5 Double logarithmic plots of σ and N_1 against $\dot{\gamma}$ for (a) the F128 solution, and (b) the F80 solution. Symbols are identified in the figure

lowering the concentration and the molecular weight of samples, and/or by making step increases in the shear rate, is effective in preventing the flow-induced degradation of a polymer chain undergoing shear demixing.

The linear viscoelastic properties of PS in DOP near Θ, especially at temperatures lower than Θ, significantly change with temperature[20]. The critical shear rate for shear demixing seems to be strongly dependent on the difference between the measurement temperature and the cloud point, which changes with molecular weight and concentration of the sample. Moreover, the height of the overshoot peak may depend not only on the temperature difference but also on the shear rates used. Thus, it is not an easy matter to provide a general rule for avoiding the flow degradation of samples in solutions undergoing shear demixing.

In this work, therefore, we obtained rheological data for PS samples with narrow MWDs (F128 and F80) in DOP undergoing shear demixing without degradation by measuring stresses after step increases in the shear rate at a lower temperature (13.4°C) which lowers the stresses and shear rates inducing demixing. It should be noted that the molecular weights of F128 and F80 are almost the same as those of PS-2 before and after degradation in the third run, respectively, although the MWDs of F128 and F80 are narrower than those of PS-2 before and after the third run.

Figure 5a and *b* show double logarithmic plots of σ and N_1 against $\dot{\gamma}$ for the F128 and F80 solutions, respectively. In these measurements, no detectable degradation of samples occurred, as shown in *Figure 6* (for F128) and *Table 2*. At
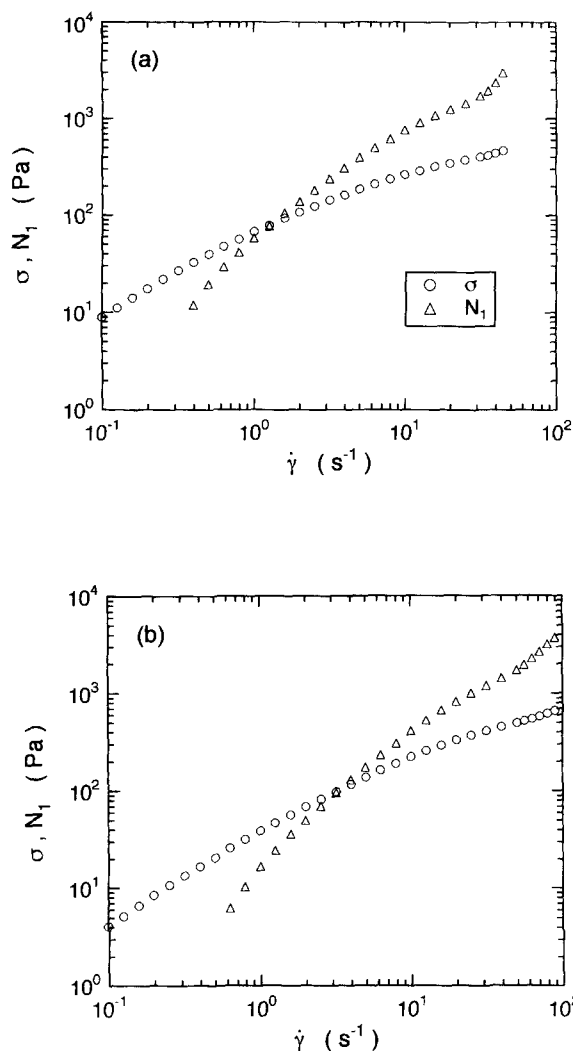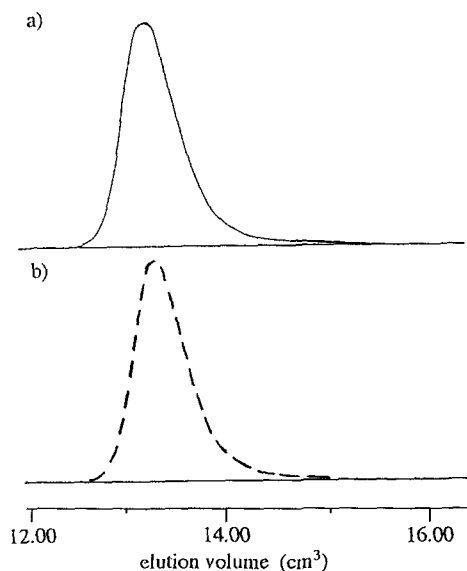

Figure 6 Gel permeation chromatographic elution curves for F128 (a) before and (b) after the rheological measurements

low shear rates, the shear rate dependences of σ and N_1 gradually decrease with increase in shear rate. These dependences are similar to the ordinary non-linear behaviour of homogeneous polymer solutions. At high shear rates, no apparent plateau is observed for N_1 of the F128 and F80 solutions, but both σ and N_1 for these solutions show a slight upturn at the high shear rate end. The solutions were remarkably turbid after the measurements. It should be noted that F80 is the lowest molecular weight sample that exhibits shear demixing behaviour, to our knowledge.

Finally, we compare rheological data at the steady state in order to examine the effect of the MWD. The most significant difference between the data for samples with broad and narrow MWDs is the existence of a plateau for N_1 in the former sample, as shown in *Figures 2a* and *4*. It should be noted that the plateau in N_1 is observed for broad MWD samples irrespective of the occurrence of flow degradation. Moreover, it can be pointed out that the $\dot\gamma$ dependences of σ and N_1, especially N_1 for broad MWD samples in the middle range of shear rates before the plateau, are somewhat steeper than those for narrow MWD samples, and the former can be approximated by straight lines with slopes between 1 and 2.

Since not only the critical shear rates of shear demixing but also the measurement temperatures were different for these samples with broad and narrow MWDs, we cannot discuss quantitatively the difference in the rheological data. In this work, we can only conclude that the rheological data for polymer solutions undergoing shear demixing are affected by the MWDs. Therefore, careful experiments, taking into account the flow degradation and the resulting MWDs of polymer samples are needed for a more quantitative study of flow-induced phase separation.

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