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Phase Behavior under Shear Flow in PMMA/SAN Blends: Effects of Molecular Weight and Viscosity

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ABSTRACT: The effect of simple shear flow on the phase behavior of blends in styrene−acrylonitrile random copolymer with 29.5 wt % acrylonitrile content (SAN-29.5) and poly(methyl methacrylate) (PMMA) of different molecular weights ranging from 7000 to 396 000 g/mol has been investigated as functions of shear rate, sample composition, molecular weight, and rotation speeds of parallel plate by using a shear apparatus. Only shear-induced mixing was observed for all of the measured samples, and the shear effect was found to be composition and molecular weight dependent. The shear range was also extended by using different rotation speeds of plate ranging from 0.5 to 5.0 rad/s under constant sample thickness, and at first the cloud points increase monotonically with shear rate and then become almost constant regardless of the applied shear rate values. The normalized shift of cloud point $\Delta T(\dot{\gamma})/T(0) = \{T(\dot{\gamma}) - T(0)\}/T(0)$ depended on the molecular weight of PMMA remarkably. From the measurement of the complex dynamic viscosity (η^*), the viscosity ratio of PMMA/SAN blends (η_{PMMA}/η_{SAN}) was estimated, and it was shown that the molecular weight dependence of the normalized shift of cloud point was due to the values of viscosity ratio between pure polymers. A maximum elevation in the normalized shift of the cloud points took place when the viscosity ratio is close to unity.

Introduction

In the recent literature there has been a considerable interest concerning the effect of an applied flow field on the phase behavior of polymer mixtures and polymer solutions.[1−15] This is because the liquid−liquid phase separation is very sensitive to the application of relatively small external forces. Thus, the behavior of polymer blends in an external field is of a fundamental interest and is also technologically important, since deformation and related stress are unavoidable in many processing steps.

Both flow-induced mixing and demixing in polymer blends have been observed, but the former phenomenon greatly outweighs the latter in its frequency of occurrence. In the early studies on this field, a ternary system of polystyrene (PS)/ethylcellulose/benzene with UCST (upper critical solution temperature) behavior has been investigated by Silberberg et al.[16] They found that the shear-induced depression of the critical point and the difference between the apparent and the equilibrium coexistence temperature was as large as 13 K at shear rates up to 270 s^{-1}. An increase in the cloud point temperature as large as 28 K for a solutions of polystyrene in dioctyl phthalate (DOP) at shear rate up to 1360 s^{-1} has been observed by Rangel-Nafail et al.[17] Shear rates of up to 5000 s^{-1} decreased the UCST of polystyrene in *trans*-decalin, as reported by Wolf et al.[18,19] They also found that the shape of the coexistence curve was strongly influence by flow. It should also be realized that the effects produced by shear have been different in perpendicular and parallel to the flow direction of PS/polybutadiene (PB)/DOP.[20] The scattering intensity parallel to the flow was found to be weaker than that perpendicular to the flow. This means that the concentration fluctuations parallel to the flow are much more suppressed by shear than that perpendicular to the flow.

There are also a number of studies of binary polymer blends. Lynaae-Jorgensen et al.[6,7] observed phase transitions induced by shear flow in a blend of styrene−acrylonitrile random copolymer (SAN) with poly(methyl methacrylate) (PMMA) in a cone−plate rheometer using two-dimensional light scattering. A two-phase blend of SAN and PMMA if subjected to high enough shear stress forms a homogeneous phase (light scattering cannot be detected). But the results did not contain any data concerning the phase diagram of the blend as a function of shear rate. The influence of shear flow on the cloud point curves for three different binary polymer blends of PS/poly(vinyl methyl ether) (PVME), poly(ethylene-*co*-vinyl acetate)/solution chlorinated polyethylene (EVA/SCPE), and SCPE/poly(butyl acrylate) (PBA), which have an LCST (lower critical solution temperature) behavior, has been studied by Hindawi et al.[21] They observed depression and then raising of the cloud points under small and high values of shear rate, respectively, for each blend by using light scattering.

In a previous work,[22] we studied the effect of shear flow on the phase behavior of PS/PVME blend with an LCST-type phase diagram. We found that the shear effect was composition-dependent, and the values of the cloud points corresponding to shear-induced mixing or demixing were greatly affected by rotation speed. At the same time, the sample thickness was found to have a pronounced effect on the cloud points under constant rotation speed, where the immiscibility region seems broader with increasing sample thickness.

Here we study the phase behavior for binary blends of SAN with 29.5 wt % acrylonitrile content (SAN-29.5) and PMMA with different molecular weight under simple shear flow applied by parallel plates. The blends show an LCST-type phase diagram. The variation of PMMA molecular weight enables the study of the relationship between the phase behavior of the blend under shear and viscoelastic properties. It is expected

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Table 1. Characteristics of Polymers

polymer	M_w	M_w/M_n	η^* (Pa s)[c]
SAN-29.5[a]	40 000	1.2	90 110
PMMA-7K[b]	7 000	2.2	2 100
PMMA-26K[b]	26 000	2.0	66 810
PMMA-71K[b]	71 000	1.8	101 000
PMMA-151K	151 000	2.1	167 400
PMMA-396K[b]	396 000	2.4	421 100

[a] Number means wt % acrylonitrile in SAN. [b] Number means M_w of PMMA (K means 1000). [c] 200 °C, $\dot{\gamma} = 10$ s^{-1}.

that the change of the phase behavior of blend under shear could be dependent on the molecular weight and viscosity ratio between both components. In addition, the effect of shear rate was investigated by using different rotation speeds of plate ranging from 0.5 to 5 rad/s in order to cover a wide range of shear rate of 0−180 s^{-1} compared with the small shear rate measured by Kammer et al.[23] (0−4 s^{-1}), who studied the effect of simple shear flow on the phase behavior of PMMA/SAN-31.5 blend by light scattering. Accordingly, our measurements are extended to a condition slightly closer to those encountered in processing devices such as extruders and injection molding machines, but it is a much higher shear rate than the one of Kammer et al.[23] and Hindawi et al.[21]

Experimental Section

Materials. Table 1 shows the molecular weight data of the samples used in this work. The SAN sample contains 29.5 wt % acrylonitrile and was supplied by Mitsubishi Monsanto Co., Japan. The samples of PMMA were supplied by Sumitomo Chemical Co., Japan, and chosen in order to cover the viscosity range from smaller to larger than that of SAN used in this work (see Table 1).

The blends of PMMA and SAN-29.5 were prepared by dissolving the corresponding weight of the two polymer components in tetrahydrofuran. The blend solutions were then cast onto a Petri dish and left to dry at room temperature for about 3 days and, after that, complete drying of the blends until a constant weight was accomplished under vacuum for another 3 days at 90 °C. About 1 g of the blend was taken and pressed at temperature lower than the cloud points of the corresponding compositions to prepare a film specimens of 1 mm thickness and 40 mm diameter for the shear measurements. Other specimens of 1 mm thickness and 25 mm diameter were prepared for the viscoelastic measurements.

Shear Apparatus. A schematic illustration of the shear apparatus is represented in Figure 1. The sample is located between two parallel silica glass plates (Figure 1b); the top one is fixed, and the bottom one is rotated at different rotation speeds. The lower rotating glass plate is restricted inside a copper ring attached to driving gear, and the upper glass plate is fixed inside a copper cylinder (Figure 1a). The copper cylinder and the copper ring can be taken out from the hot chamber. The temperature in the hot chamber is measured by a highly accurate platinum thermocouple whose resolution is ±0.1 °C. The thermocouple is set very close to the sample though it does not contact directly with sample and glass plate. Heat was supplied by four iron heater blocks mounted in hot chamber walls. To homogenize the inside temperature of chamber, four rotating motor fans are used inside chamber. The copper cylinder and ring which fix glass plates have many holes in order to obtain good thermal conduction for the glass plates and sample. The temperature was controlled using a digital program temperature controller REX F900 series RKC with accuracy of ±0.1 °C between room temperature and 400 °C. Simple shear flow was generated by applying constant rotation speeds to the sample, which was preheated to a temperature lower than the quiescent cloud point by about 20 °C. After this pretreatment, the sample is heated at constant heating rate (0.5 or 1 °C/min) with a constant rotation speed. Under this condition the phase separation of the sample takes place at different radii and different temperatures according to the values of the applied shear rate. The shear apparatus was designed to observe the sample under the shear flow by two methods: the first by directly seeing the sample from the upper window of the shear apparatus and the second by viewing with a video recording camera through a mirror fixed below the lower window of the shear apparatus.

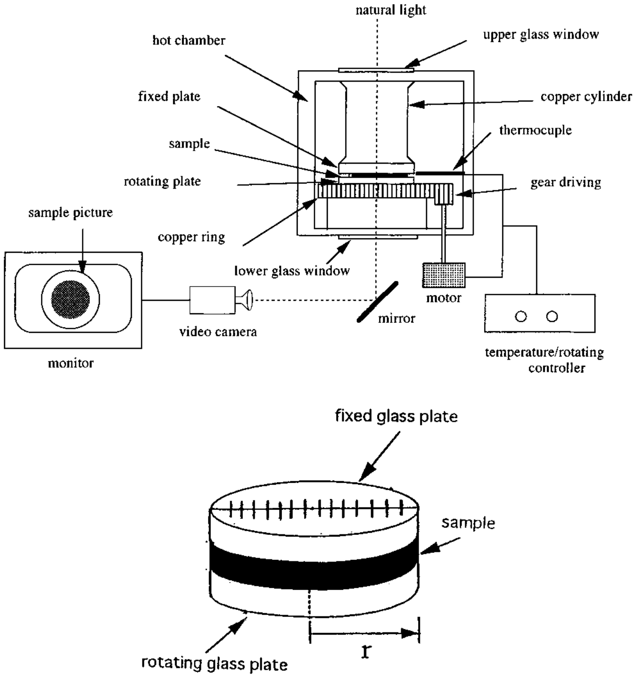

Figure 1. (a, top) Schematic representation of the shear apparatus used in this work. (b, bottom) Schematic representation of the sample inside the two parallel glass plates.

For the parallel plate measurements, the shear rate is a linear function of the radius

$$\dot{\gamma} = \Omega r/h \qquad (1)$$

where h is the sample thickness, r is the radius, and Ω is the rotational speed (rad/s). The shear rate is a maximum at the outer edge of the disk and decreases to zero at the center of the disk.

Viscoelastic Measurements. The complex dynamic viscosity (η^*) was measured by a Rheometrics dynamic mechanical spectrometer using 25 mm parallel plates with strain amplitude less than 10%, to stay in the linear viscoelastic regime. The measurements were carried out at frequencies from 0.1 to 100 rad/s at 170 °C.

Results and Discussion

Figure 2 shows the quiescent cloud points curves for four blends of PMMA/SAN measured at constant heating rate of 1 °C/min, which is identical to the experimental condition under shear.[24] These blends show a typical LCST-type phase diagram. As the molecular weight of PMMA increases, the two-phase region increases and the phase boundary shifts to lower temperature. This is expected since the combinatorial entropy term in the free energy of mixing increases monotonically as the molecular weight of either component increases.[25]

Figure 3 shows schematic representations of change of the cloud region in PMMA-26K/SAN = 75/25 under constant rotation speed (0.5 rad/s) started by a heating rate of 1 °C/min from 145 to 186 °C, which correspond to 20 °C below and 21 °C above its quiescent cloud point, respectively.[26] It is apparent that no shear-induced

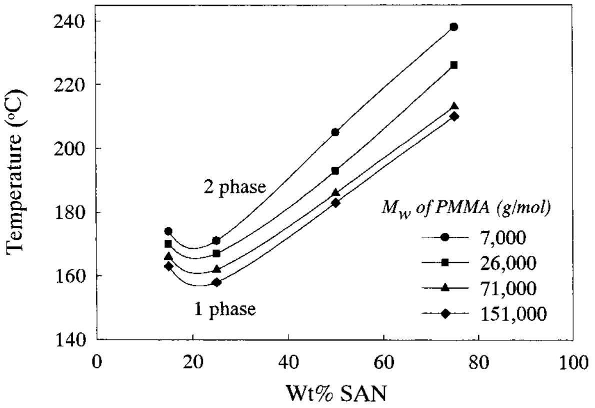

Figure 2. Quiescent cloud points curves for blends of SAN and PMMA with different molecular weight.

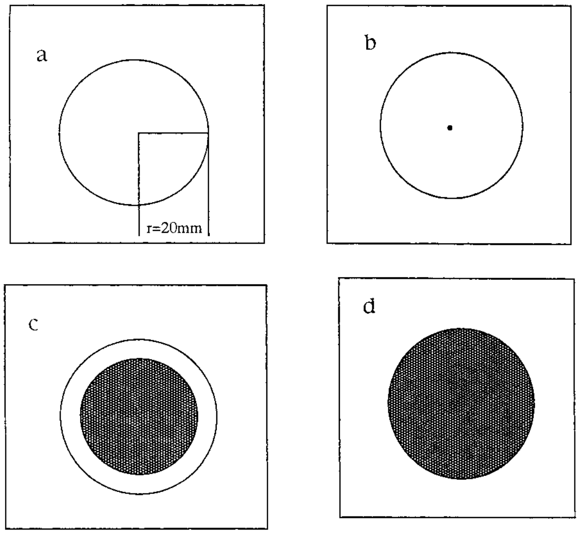

Figure 3. Schematic representations of the blend behavior in PMMA-26K/SAN = 75/25 between two parallel plates under shear (0.5 rad/s). The shadow region is opaque. (a) 145 °C (20 °C below the quiescent cloud point). (b) 170 °C (5 °C above the quiescent cloud point). (c) 180 °C (15 °C above the quiescent cloud point). (d) 186 °C (21 °C above the quiescent cloud point).

demixing can be observed at 145 °C (20 °C below its quiescent cloud point) as shown in Figure 3a. Figure 3b represents the sample at 170 °C (5 °C above the quiescent cloud point). The sample is still transparent except for a quite small region near the center ($\dot{\gamma} \approx 0$ s^{-1}). This means that shear-induced mixing occurs. At a temperature higher than the quiescent cloud point by 15 °C (180 °C), the cloud area increases gradually as shown in Figure 3c. Finally, every region of the sample turns cloudy at 21 °C above its quiescent cloud point (186 °C) as shown in Figure 3d. From the radius at the boundary between transparent and opaque region, one can estimate the shear rate by eq 1.

Figure 4 shows the shear rate dependence of the cloud points for different compositions in PMMA-26K/SAN. One can see that the cloud point shifts to higher temperature; i.e., the shear suppresses the phase separation and enlarges the homogeneous region of the blend. The measurements are in good agreement with that of Kammer et al.,[23] who studied the effect of shear rate on the phase behavior of PMMA/SAN-31.5 blends (small shear rate values were used, $\dot{\gamma} \leq 4$ s^{-1}) by using light scattering measurements. They have found that the shear flow elevated the phase separation temperature. In Figure 4, the cloud points become almost constant regardless of shear rate at shear rates higher than 10 s^{-1}.

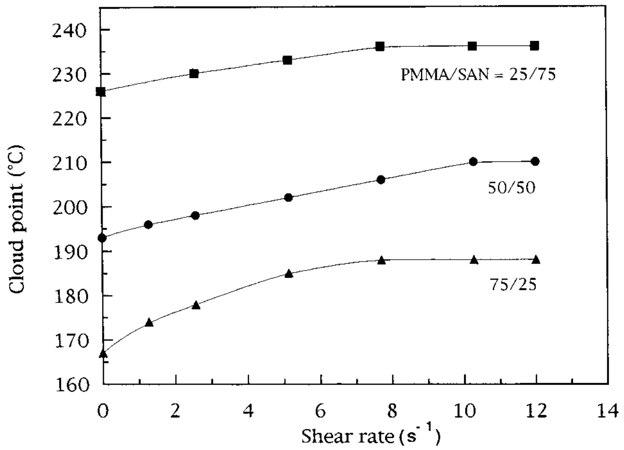

Figure 4. Shear rate dependence of the cloud point in PMMA-26K/SAN for different composition ratios.

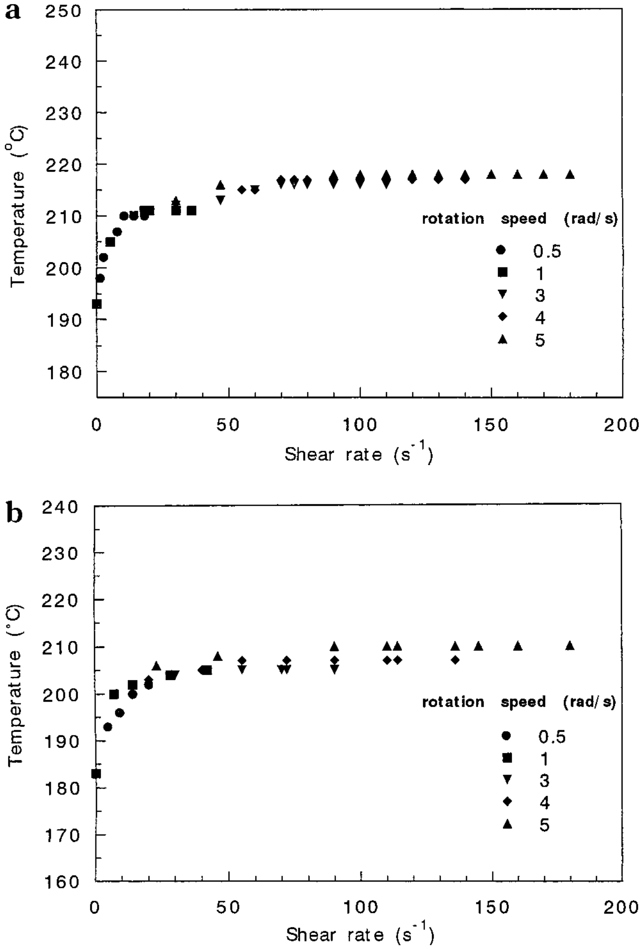

Figure 5. Change of the cloud points as a function of shear rate of PMMA/SAN = 50/50 blend under different rotation speeds: (a) PMMA-26K/SAN blend, (b) PMMA-151K/SAN blend.

Effect of Rotation Speeds. The above measurements have been studied at constant rotation speed and constant sample thickness (0.5 rad/s and 1 mm, respectively), and they covered only a shear rate up to 15 s^{-1}. Here we will extend our data to higher shear rate values by changing the rotation speed of the plate while keeping constant sample thickness (1 mm).

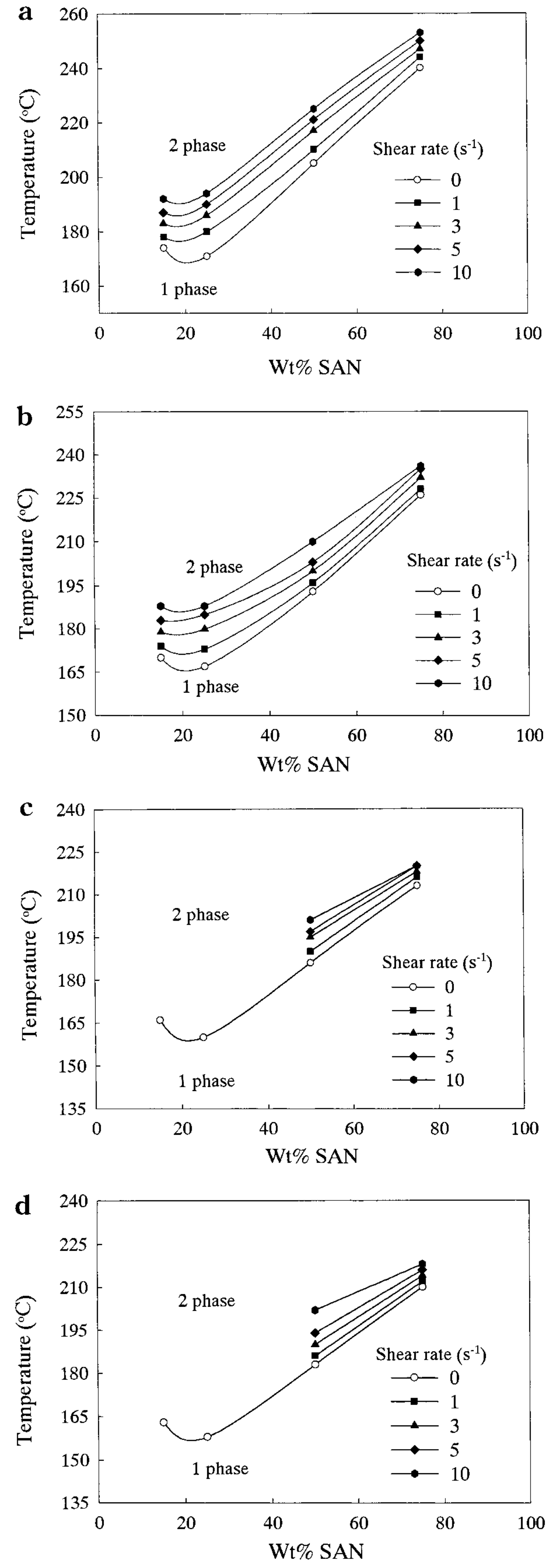

Figure 6. Comparison between the phase diagrams of PMMA/SAN blends under the different shear rates: (a) PMMA-7K/SAN, (b) PMMA-26K/SAN, (c) PMMA-71K/SAN, (d) PMMA-151K/SAN.

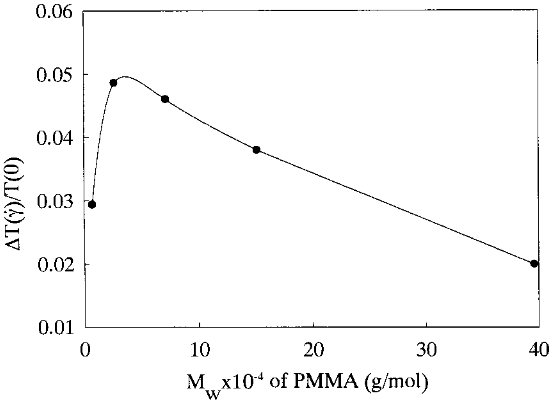

Figure 7. Molecular weight dependence of normalized shifts in the cloud points of PMMA/SAN = 25/75 blends at $\dot{\gamma}$ = 10 s^{-1}.

Parts a and b of Figure 5 show the shear rate dependence of the cloud points in PMMA-26K/SAN = 50/50 and PMMA-151K/SAN = 50/50, respectively. For all of the measurements in these figures the cloud points start to increase monotonically with small values of the applied shear rate and then become almost constant regardless of the shear rate value. These results can be plotted on one master curve regardless of rotation speed. This behavior is in contrast to that of PS/PVME blends which showed both shear-induced demixing and mixing. In our previous work,[22] it was found that the behavior of cloud point of PS/PVME = 30/70 blend was strongly affected by the rotation speed of the plate, and one could not draw one master curve. It can be considered that the only factor which dominates the shear-induced demixing behavior depends on the rotation speed, but the reason is not clear at present. Also, the reason why the cloud points become almost constant at high shear rate is not clear at present.

Effect of Molecular Weights. The phase diagrams of the blends of SAN-29.5 and PMMA of different molecular weight, 7000, 26 000, 71 000, and 151 000 g/mol, in some shear rates are shown in parts a–d of Figure 6, respectively. For the two blends of PMMA-71K/SAN and PMMA-151K/SAN we measured only the SAN-rich region due to the very high viscosity of the PMMA at the measuring temperatures. A similar behavior can be seen very clearly; the phase boundaries gradually increase with shear rate. In addition, the elevation of the cloud points under shear rate was found to be composition dependent. On the basis of the above results, it is apparent that shear flow could induce phase mixing as in the case of a simple liquid mixture.

The elevation of the cloud point with shear rate could depend on the molecular weight. To compare the effect of molecular weight for the elevation of phase boundary, we use the normalized shift of cloud point,[27,28]

$$\Delta T(\dot{\gamma})/T(0) = \{T(\dot{\gamma}) - T(0)\}/T(0) \qquad (2)$$

where $T(\dot{\gamma})$ is the cloud temperature at $\dot{\gamma}$. Figure 7 shows the PMMA molecular weight dependence of $\Delta T(\dot{\gamma})/T(0)$ in PMMA/SAN = 25/75 blends at constant shear rate ($\dot{\gamma}$ = 10 s^{-1}); this value was selected because the elevation of the cloud points at this value of shear rate nearly levels off for this composition. The normalized shift of the cloud points, at first, increases with molecular weight and then decreases, exhibiting a maximum. It is understood that the amount of the normalized shift in the cloud points of the blends under shear flow is remarkably affected by the PMMA molecular weight.

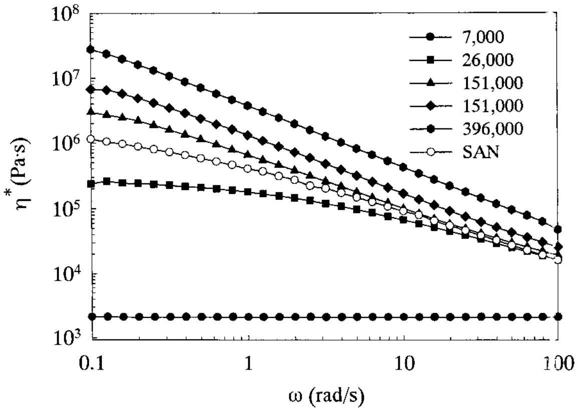

Figure 8. Complex dynamic viscosity (η^*) as a function of frequency of SAN and different PMMA molecular weights at 170 °C.

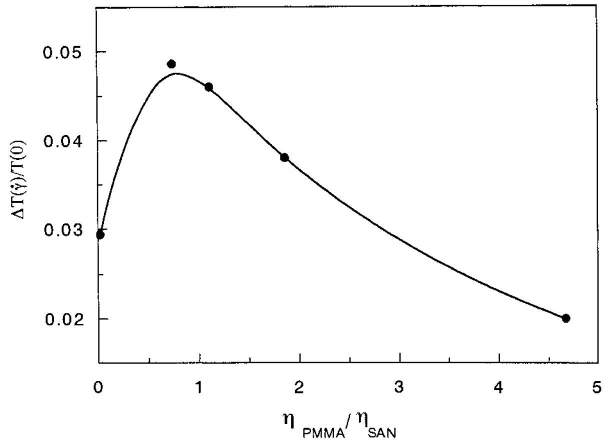

Figure 9. Viscosity ratio dependence of normalized shifts in the cloud points of PMMA/SAN = 25/75 blends at $\dot{\gamma} = 10\ s^{-1}$.

The interaction parameter χ of the blend may depend on the molecular weight for a very low molecular weight region, because the effect of end groups is large. However, it is well-known that the χ does not depend on molecular weight and is almost constant in this molecular weight region. Therefore, it is predicted that the result of Figure 7 is attributed to the difference of viscoelastic properties.

Effect of Viscosity Ratio. The complex viscosities (η^*) of pure SAN and five different molecular weight of PMMA are measured at 170 °C as a function of shear rate (0.1−100 rad/s). These results are shown in Figure 8. The value of η^* of SAN used in this work was always located between PMMA-26K and PMMA-71K in the measured range. The molecular weight with a maximum of $\Delta T(\dot{\gamma})/T(0)$ was located at the same range. So we replotted $\Delta T(\dot{\gamma})/T(0)$ as a function of the viscosity ratio of PMMA for SAN (η_{PMMA}/η_{SAN}) at $\dot{\gamma} = 10\ s^{-1}$, and the result is shown in Figure 9.[29] The different molecular weight of PMMA used in this work covers a viscosity ratio ranging from 0.02 to 4.6. The normalized shift of the cloud points increases with viscosity ratio and then decreases, and it is similar to the result of Figure 7. It is considered that the changing of molecular weight can be almost comparable to the changing of viscosity ratio between pure polymers as the factor affecting the normalized shift in the cloud points under shear. A maximum elevation of cloud point takes place at $\eta_{PMMA}/\eta_{SAN} \approx 1$. So it is considered that the mixing effect by shear is most effective at $\eta_{PMMA}/\eta_{SAN} \approx 1$.

For phase-separated binary blends in which domains disperse in a matrix, Wu[30] proposed that the average size of dispersed phase was governed by the viscosity ratio, and he has found that a minimum of average domain size in a nylon/rubber system was obtained at $\eta_d/\eta_m \approx 1$. The number-average diameter of dispersed phase as functions of shear rate, temperature, interfacial tension, viscosity ratio, and concentration have been studied by Serpe et al.[31] They have also found that the smallest average sizes of particles are obtained when the viscosity ratio is about unity. From these results, it is considered that the shear effect for breakup of dispersed domains is the largest when $\eta_d/\eta_m \approx 1$. Therefore, it can be considered that this shear effect is very similar to one for the phase boundary shift in this study. However, one cannot compare simply the shear effect for the phase boundary shift with one for the breakup behavior of dispersed domains, because the breakup behavior was discussed for complete two-phase mixtures and the phase boundary shift is due to the suppression of the concentration fluctuation growth. Since the theoretical investigation about the shear effect for phase boundary shift is not enough at present, we do not discuss this matter in this paper.

Conclusions

Shear-induced mixing was observed for all of samples measured in blends of SAN-29.5 and PMMA of different molecular weight. The magnitudes of the elevation of the cloud points with shear rate were found to be molecular weight of PMMA dependent. The shear rate dependence of cloud point was also measured over a wide range of shear rate up to 180 s^{-1}, and the cloud point increased monotonically with shear rate and then leveled off. For this behavior, one could draw one master curve without rotation speed effect on the position of the cloud points under shear in a contrast to PS/PVME blends. The value of elevation of the cloud point in blends of PMMA/SAN = 25/75 depended on molecular weight of PMMA remarkably. The molecular weight of PMMA which showed a maximum elevation of cloud point was consistent with one at which the viscosity ratio of PMMA for SAN (η_{PMMA}/η_{SAN}) is almost unity. This means that the phase behavior of the polymer blend under shear is strongly affected by viscoelastic properties of constituent polymers. To obtain deeper insights into the phase behavior of polymer blends under shear, it is important to investigate the effects of viscoelastic properties on thermodynamics of polymer blends both qualitatively and quantitatively, and this work is ongoing.

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(24) Generally, the phase boundary in the cloud point measurement depends on heating rate. But the change of phase boundary is not so large in these mixtures if the heating rate is relatively slow. From the extrapolation of phase boundary temperature to 0 heating rate by measurements of some heating rates, the temperature difference of phase boundary between 0 and 1 °C/min was less than 5 °C in these mixtures. So we showed the results of the same heating rate (1 °C/min) as one of the shearing measurements here.

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(26) The measurements were also carried out at lower heating rates (0.5 °C/min) under the same rotation speed. The obtained result showed almost no difference between these two heating rates on the magnitudes of the elevation of the cloud points at constant shear rate. It is considered that the sample is not under steady state but under quasi-equilibrium state during the shear flow at the early stage of the measurements. Namely, if the phase separation takes place, the development of morphology may stop after a short time, and the coarsening behavior was suppressed by shear. Therefore, if it is slow enough such as 1 °C/min, the results were almost independent of heating rate. Generally, there is no any hysteresis in the cloud point curve for the quiescent state. It is also considered that there is no hysteresis under shear flow. However, there is a possibility that the phase boundary temperature from a down ramp measurement is different from one of an up ramp. This is because the kinetics of phase dissolution is different from one of phase separation. Generally the rate of phase dissolution is slower than one of phase separation. Especially for the case of a down ramp under shear in LCST systems, the phase dissolution rate is very slow. This is because the effect of viscosity difference between constituent polymers affects phase dissolution behavior, and its effect does not affect phase separation behavior so much. Therefore, the measurements in this paper were carried out only for an up ramp without a down ramp. This procedure was found to give reasonable reproducible results. The up ramp could be repeated without changing the results by more than 1−2 °C statistical error. So only the result of an up ramp of 1 °C/min was shown in this paper.

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(29) This phenomenon is consistent in all compositions at which the PMMA acts as minor component; however, an inversion of this phenomenon might be detected for the blends of higher contents of PMMA (PMMA is a matrix) due to the inversion of the viscosity ratio. But we could not verify the inversion of this phenomenon due to the high viscosity of PMMA-71K and PMMA-151K, which leads in turn to difficult measurement at the experimental temperatures.

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