The Effects of Flow on Miscibility in a Blend of Polystyrene and Poly(Vinyl Methyl Ether)

J. D. KATSAROS*, M. F. MALONE, *and* H. H. WINTER

*Department of Chemical Engineering
University of Massachusetts
Amherst, Massachusetts 01003*

Shear and extensional flows can have a significant effect on the miscibility for a blend of polystyrene with poly(vinyl methyl ether). The cloud point temperature in a planar stagnation flow is elevated by as much as 12 K; the magnitude depends on the extension rate, the strain, and the blend composition. Flow-induced miscibility is also observed in the shear flow between parallel plates which has been used to test smaller samples and to prepare solid samples for further characterization. At lower temperatures, as much as 30 K below the coexistence temperature, flow-induced phase separation occurs in both shear flow and extensional flows. The stress, rather than deformation rate, appears to be the most important parameter in flow-induced phase separation.

INTRODUCTION

Polymer blend miscibility typically occurs in a limited range of temperature and composition. The miscibility is determined by a delicate balance of enthalpic and entropic interactions and the liquid-liquid phase behavior may, therefore, be sensitive to the application of relatively small external forces. Thus, the behavior of blends in external fields is of fundamental interest and is also technologically important since deformations and the related stresses are unavoidable in many processing steps. There are relatively few studies of the effects of flow on the liquid-liquid miscibility of polymer blends, partly because a significant number of miscibility blend systems and their equilibrium properties were not well-known until recently. In contrast, deformation-induced phase transitions in polymer solutions have been known for some time.

Here, we describe studies of the phase behavior for a binary blend of polystyrene and poly(vinyl methyl ether) in two different flows. It is useful to review previous studies of deformation-induced miscibility changes in polymeric liquids in the next section. Following this, we describe the materials, the blend preparation, and the flow devices that were used in this work. The results and discussion, in the next section, focus primarily on our observations of changes in the apparent coexistence temperature, followed by a brief qualitative interpretation.

BACKGROUND

In an early study, Silberberg and Kuhn, (1) described shear-induced miscibility in biphasic ternary solutions of polystyrene and ethyl cellulose in benzene. The difference between the apparent and the equilibrium coexistence temperature was as large as 13 K at shear rates up to 270 s^{-1}. Ver Strate and Philippoff (2) found that polystyrene solutions in di(2-ethyl hexyl) phthalate or in a mixture of cis- and trans-decalin demixed (became turbid) in the converging flow from a reservoir into a capillary tube. Contrary to the observations of Silberberg and Kuhn (1), they found that an increase in the deformation rate *raised* the upper critical solution temperature (UCST) and thus decreased the size of the miscibility region. In both of these studies, an increase in the cloud point temperature of the polymer solutions was used as an indication of phase separation.

Rangel-Nafaile, Metzner, and Wissbrun (3) reported increases in the cloud point temperature as large as 28 K for sheared solutions of polystyrene in dioctyl phthalate at shear rates from 1.7 to 1360 s^{-1}. Wolf and Kramer (4) and Wolf (5) reported that shear rates up to 5000 s^{-1} decreased the UCST of polystyrene in trans-decalin and that the shape of the coexistence curve was strongly influenced by flow. Koningsveld and Kleintjens (6) also found that shear rates of ~4000 s^{-1} decreased the cloud point temperature of a solution of polystyrene in cyclohexane by approximately 1 K.

Wolf (5) developed a model for the size of droplets formed in a phase-separated system as a function of the shear rate and used this description to explain the induction of miscibility by estimating the shear rate required to decrease the drop size to the radius

of gyration of the polymer molecules. Wolf's results and interpretation appear to be fundamentally different than those from the cloud point studies of Ver Strate and Phillipoff (2) and Rangel-Nafaile, Metzner, and Wissbrun (3), but they are not necessarily contradictory. However, reports of demixing in polymer solutions upon the application of a shear field significantly outnumber findings of induced miscibility (see the more detailed discussion in *Ref 3*).

In several studies, (2, 3, 5) the effect of flow on the coexistence temperature has been quantified by adding a term to the free energy of mixing to account for the effects of a deformation. In this approach, the "free energy elevation" due to flow is related to the stress using a mechanical model (7) where changes in the free energy are attributed exclusively to a loss in entropy. Enthalpic changes have not been considered, but it is notable that an effect has been seen only in poor solvents and that Ver Strate and Phillipoff (2) found no effect of shear on the miscibility of polystyrene in toluene at temperatures where it is a good solvent.

While there are a number of studies of flow-induced phase transitions in solutions, we know of only three studies of this sort for polymer blends. Mazich and Carr (8) studied a blend of polystyrene (PS) with poly(vinyl methyl ether) (PVME) in steady shear flow using a cone-and-plate geometry. The viscosity was measured using a Rheometrics Mechanical Spectrometer operated at constant shear stress. Mazich and Carr reported no measurements of turbidity, but an abrupt change in the slope of the viscosity versus temperature curve was interpreted as an indication of a phase transition. The temperatures where the change in slope was observed ranged from 2 to 7 K higher than the equilibrium lower critical solution temperature (LCST). Furthermore, these changes correspond to relatively mild shear rates of 0.14 to 24 s^{-1}. Katsaros, Malone, and Winter (9) also reported an increase in the apparent LCST for a PS/PVME blend in an extensional flow where the temperature elevation was as large as 12 K.

Lyngaae-Jorgensen and Sondergaard (10) observed phase transitions induced by shear flow in a blend of a styrene-acrylonitrile copolymer (SAN) with poly(methyl methacrylate) and when the samples were quenched below the glass transition temperature after shearing, no structure could be detected with transmission electron microscopy. A model based on the theoretical results of Marrucci (7) was used to estimate a critical stress for the apparent phase transition.

Compressibility can also be important in LCST behavior. When a binary liquid mixture is subjected to a variation in pressure, the unlike compressibilities of the two components can cause a change in miscibility; small volume changes on mixing are also potentially important. Maeda, Karasz, and MacKnight (11) studied the effect of pressure on the LCST for a blend of poly(2,6-dimethyl-1,4-phenylene oxide) and poly (o-fluorostyrene-co-p-fluorostyrene) copoly-

mers. The LCST increased approximately 0.1 K/MPa up to 200 MPa, where it became independent of pressure. The increase in miscibility was attributed to a volume change on mixing that is initially negative and that decreases in magnitude with increasing pressure, approaching zero above 200 MPa; at higher pressures there is little or no effect on the miscibility.

Walsh and Rostami (12) found a 10 to 18 K increase in the LCST for blends of ethylene-vinyl acetate copolymer with chlorinated polyethylenes where the LCST increased by 0.14 K/MPa for pressures in the range of 1 to 80 MPa. In the same pressure range, an increase of 0.46 K/MPa was found for blends of polyether sulfone with poly(ethylene oxide). They also studied the effects of an isotropic pressure on the miscibility of several oligomeric mixtures exhibiting UCST behavior as well as for three polymer blends that show an LCST (13). The Flory equation of state was used to describe the binodal and spinodal curves for several oligomer-oligomer and polymer-polymer mixtures at various pressures and was in good agreement with their experimental results. They suggest that an increasing pressure *decreases* the miscibility for mixtures with positive heats of mixing, and *increases* the miscibility for mixtures with a negative heat of mixing. Based on these results and because blend miscibility is usually found when the heat of mixing is exothermic, the application of an isotropic pressure is expected to increase the miscibility region for a partially miscible blend.

In summary, both flow-induced miscibility and demixing occur in polymer solutions although there are more reports of induced demixing than of induced miscibility. Theoretical descriptions based on the deformation of droplets or on the free energy changes induced by the deformation have met with some success in the interpretation and correlation of the measured changes in the coexistence temperature. The latter has been based strictly on entropic contributions from the deformation; however, the effects of polymer-solvent interactions and enthalpic contributions to the free energy need to be studied. Limited studies of polymer blends have shown that a steady shear flow can enhance miscibility near the LCST and that the data can be correlated with a model that accounts for the entropic contributions of the deformation to the free energy. However, there is some doubt as to whether the basis for this model is valid for concentrated systems and there are additional effects that are probably important in blends.

EXPERIMENTAL

Materials

The blend used in this study was polystyrene (M_w = 348,000, polydispersity = 1.9) supplied by Monsanto (Lustrex 101) with poly(vinyl methyl ether) (M_w = 48,000, polydispersity = 1.9) supplied by Scientific Polymer Products.[1] The molecular weight distribu-

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[1] Monodisperse PVME samples could not be obtained and the polydispersities of PS and PVME were matched to minimize the effects of the molecular weight distribution on the equilibrium phase diagram.

tions were measured by gel permeation chromatography in toluene. The equilibrium phase behavior of this blend has been studied extensively (14–16).

Blends were prepared by solution casting. Each polymer was dissolved individually in toluene (~30–50% (wt) solutions) and the required amounts of the two solutions were mixed at room temperature in a Baker-Perkins planetary mixer for 12 hours. Each batch contained approximately 700 grams of solution. After mixing, the toluene was evaporated in a sealed oven at modest vacuum for approximately 10 days. The blend was then thoroughly dried to a constant weight (less than 0.1 gram weight change) under vacuum at approximately 70°C for about two weeks. The range of compositions used was 35 to 64% PS; compositions below 35% PS are very sticky and difficult to keep clean in large amounts, while blends containing more than 64% PS are hard, brittle, and difficult to purify and process since the glass transition temperature is much closer to the coexistence temperature.

The refractive indices of polystyrene and poly(vinyl methyl ether) at 20°C are 1.590 and 1.466, respectively (16). Thus, the phase separation of the PS/PVME blend can be accurately detected by the onset of turbidity due to the appearance of two phases with different refractive indices and the sharp cloud point. The cloud points were measured by observing the transparency of the blend in the die used for planar extensional flow experiments as it was heated at a rate of 1 K in order to give the best value of the equilibrium cloud point temperature under the conditions in the flow. The resulting equilibrium cloud point curve is shown in *Fig. 1*.

The glass transition temperature of the miscible blend (15) is substantially below the cloud point curve shown in *Fig. 1* at all of the compositions we studied. We note that lower values of the LCST are generally undesirable since the PS rich phase in a sample exhibiting a phase separation could vitrify at the temperature of the experiment, precluding the imposition of a well-defined deformation.

Stagnation Flow

Extensional flows are effective for stretching a molten polymer. For example, flow-induced crystallization was studied by Mackley and Keller (17) for high density polyethylene melts and by Frank, Keller, and Mackley (18) for polyethylene solutions in extensional flows. A review of some extensional flow-induced modifications of polymers is given by Keller and Odell (19).

Extensional flows are also important in many polymer processing applications and a planar stagnation flow is especially interesting since it contains an internal stagnation point. This results in very long residence times and a local planar extensional flow near the stagnation point; Winter, *et al.* (20), suggested the use of this flow as a rheometer. We are interested in using a similar device to study blend miscibility.

For a constant density fluid the kinematics of planar extensional flow are

$$\vec{v} = (\dot{\epsilon}x, -\dot{\epsilon}y, 0) \qquad (1)$$

where x, y, and z are the principal directions; the geometry of the planar stagnation flow die is shown in *Fig. 2*. In the ideal case, the rate of extension, $\dot{\epsilon}$, is constant throughout the fluid and is independent of time. Material elements move along hyperbolic path lines such that

$$xy = A \qquad (2)$$

where A is a constant that is determined by the geometry of the die. The extensional strain of a material element that moves from x to x_0 is

$$\epsilon = \ln \frac{x}{x_0} \qquad (3)$$

and the residence time of the material element is:

$$\Delta t = \frac{1}{\dot{\epsilon}} \ln \left(\frac{x}{x_0} \right) \qquad (4)$$

Thus, the residence time at the stagnation point is unbounded and attains large but finite values near there; fluid elements can be exposed to the stretching flow for long times. This contrasts to many other
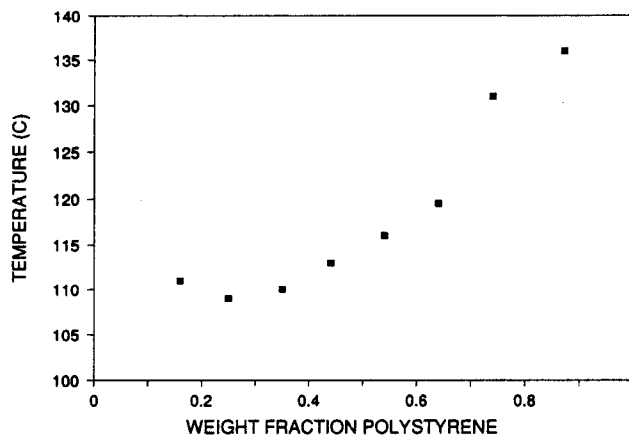

Fig. 1. The equilibrium cloud point curve measured in the stagnation flow die.
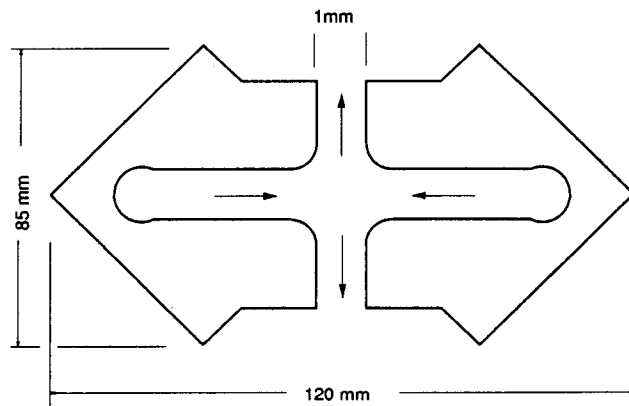

Fig. 2. A schematic of planar stagnation flow.

stretching flows, such as fiber spinning where an increase in the deformation rate leads to a substantial decrease in the residence time.

In the actual device, the flow is actually somewhat inhomogeneous; material elements that move near the stagnation point experience a higher strain than material elements that move along the outer stream surface, $xy = A$. Le Blanc and Malone (21) found by finite element simulation that the extension rates for a Maxwell fluid are roughly 15% larger than the ideal values near the stagnation point. However, in a neighborhood of the stagnation point the flow is still a planar extension, albeit at a slightly higher deformation rate. Unlike the ideal case, the flow near the die walls is mainly shear and, in fact, both extension and shear can be observed simultaneously, although the residence time of material passing through these regions will be different. Thus, *the region of primary interest is near the stagnation point, where the flow is well-defined.*

A planar stagnation flow die was made as small as possible in order to minimize the volume of material required for these experiments; this also maximizes the average extension rate for a given flow rate. For this die (c.f., *Fig. 2*), the depth in the z direction is $l = 12$ mm and the constant A in *Eq 2* is 10 mm^2. Circular glass windows (one inch quartz disks, Ace Glass Co.) were installed normal to the flow directions to permit optical studies of the entire flow field. A Goettfert Rheograph 2001 Capillary Rheometer was used to feed the blend through the die. The material was loaded into the rheometer cylinder, which is 20 cm long and 2.5 cm in diameter, and then extruded through the die at a rate that could be set at any value from 0.01 to 20 mm/s. The rate of extension can be estimated from the expression

$$\dot{\epsilon} = \frac{Q}{4Al} \qquad (5)$$

where Q is the volumetric flow rate. The corresponding range of extension rates is 0.01 to 20 s^{-1} but the range actually used in the experiments was 0.5 to 3.0 s^{-1}. The lower limit ensured a reasonable length of time for an experiment, while the upper limit was necessary to avoid flow instabilities.

The transparency of the blend in the die was determined by the intensity of a light directed through the die windows; it was sufficient to observe the transition visually because of the large and abrupt change in the intensity of transmitted light for this blend. To observe the region of the die where the change in transparency occurred and to determine the time of the development, all of the experiments were recorded either on video tape, or in a series of 35 mm photographs. The time after the start of flow when the flow-induced phase transition is first visible at the stagnation point is defined as the critical time.

Shear Flow

The steady flow between circular concentric parallel plates generates a shear flow with a range of deformation rates in a single experiment. Also, less material is needed for each experiment than for the stagnation flow and the sheared samples can be quenched rapidly to temperatures below the glass transition to provide solid samples for further study. An analysis of the hydrodynamics and the viscometric functions in this flow is given by Bird, *et al.* (22). The shear rate is independent of the axial position and is a linear function of radius

$$\dot{\gamma} = \frac{w}{H} r \qquad (6)$$

H is the sample thickness, r is the radius, and w is the rotational speed. The shear rate is a maximum at the outer edge of the disk ($r = R$) and decreases to zero at the center of the disk ($r = 0$).

The shear flow experiments were done using disks with a diameter of 25 mm on a Rheometrics Mechanical Spectrometer and solid samples were prepared by rapid quenching after the application of shear. The flow was generated at rotational speeds that ranged from 0.1 to 1.0 radians/s. For a 1 mm sample thickness, this corresponds to shear rates at the outer edge of the plate of 1.25 to 12.5 s^{-1}. The lower limit of this range was the minimum required to see an effect in the PS/PVME blend and the upper limit was fixed by the stability of the flow. After shearing, the disposable plates and the sample were quickly removed from the rheometer then quenched in liquid nitrogen. The time from the cessation of shear to the end of quenching was approximately 15 seconds.

RESULTS

Extensional Flow

The blend was extruded through the planar stagnation flow die and the optical transparency was observed. At temperatures above the LCST, the extensional flow was found to induce miscibility; preliminary experiments showing this effect have been reported by Katsaros, Malone, and Winter (9). We report more extensive results here, including the dependence on blend composition. More importantly, we have also found that *demixing* is induced at lower temperatures as described below; this appears to be the first observation of such an effect in blends.

Flow-Induced Miscibility

Figure 3 shows a typical development of flow-induced miscibility; the blend flows in from the right and left of the figure towards the stagnation point to outlets at the top and bottom. In this experiment, the temperature was 119.5°C which is 3 K above the cloud point temperature for this blend of 54/46 (w/w) PS/PVME. The blend was extruded at a speed of 2.5 mm/s, corresponding to an average extension rate of 2.55 s^{-1}. *Figure 3a* shows the blend at rest where it is phase separated and appears cloudy. *Figure 3b* shows the blend 18 seconds after the onset of flow where the light source behind the die is faintly visible in the region of highest extension near the stagnation point and extending along the centerline

Fig. 3. *Flow induced miscibility in the stagnation flow. (a) A 54/46 (w/w) PS/PVME blend 3 K above the cloud point temperature at rest. The phase-separated blend is cloudy. (b) The same blend 18 s after the onset of flow. (The blend flows in horizontally and exits vertically; the average extension rate is 2.55 s⁻¹. The region of highest extension is beginning to clear. (c) 22 s after the onset of flow. The clearing is more intense along the axis of highest extension although clearing also occurs near the die walls. (d) 28 s after the onset of flow. The entire flow region in the die has cleared.*

of the exiting streams. The pressure measured at the wall of the capillary rheometer ranged from 1.6 to 10 MPa; the stresses inside the flow were not measured. *Figure 3c* shows the blend 22 seconds after the onset of flow, when the miscible region has intensified and grown. There is also some clearing near the die walls, which is attributed to shearing. *Figure 3d* shows the blend 28 seconds after the onset of flow, where the entire flow region is clear; this did not occur in all cases, but only at extension rates greater than approximately 1 s⁻¹.

After the flow was stopped, the blend relaxed to the phase-separated condition in 20 to 120 seconds. In general, the relaxation to a phase separated condition was more rapid at higher temperatures and slower in cases where the flow had been applied for longer times but a systematic study of the relaxation was not made.

The development shown in *Fig. 3* is typical of the observations at other flow rates, temperatures, and blend compositions. To represent these results, we define a *critical strain* as the product of the average extension rate and the critical time; values of this

critical strain for a 35% polystyrene blend are shown in *Fig. 4a*. As the temperature increases, a higher critical strain is required at a given extension rate to induce miscibility. At low extension rates, the critical strain at a given temperature is a decreasing function of the extension rate, with a rate of decrease that is larger at higher temperatures. At very low extension rates, the critical strain and the critical time increase rapidly at all temperatures; the time and strain should be infinite at zero strain rate, corresponding to the equilibrium phase diagram. The dependence of the critical strain on the extension rate is much weaker at higher extension rates which would imply that above a certain extension rate (about 1.5 to 2.0 s^{-1}) the onset of flow-induced miscibility depends principally on the total deformation applied to the material. *Figures 4b* and *c* show similar behavior for blends of 44%, 56% polystyrene, respectively. (All of the samples were held for 20 minutes in the cell before starting the deformation in order to provide similar initial conditions for each run. For the induced miscibility, there may also be some effects of varying this time because of the kinetics of phase separation but we have not examined this aspect.)

The elevation of the cloud point due to the planar extensional flow is shown in *Fig. 5*. These curves were constructed by cross plotting the data at a given average extension rate and critical time. *Figure 5a* shows the elevation at an average extension rate of 1.0 s^{-1} and critical strains of 50 and 120. For the same extension rate and strain, the cloud point of the 44% PS blend increases more than at any other composition while the cloud point of the 64% blend increased the least. Thus, the extensional flow-induced miscibility is very composition dependent. *Figure 5b* shows a similar behavior at an average extension rate of 2.0 s^{-1}; as the average extension rate increases a lower critical strain is required for a given increase in the cloud point corresponding to a lower critical time.

Flow-Induced Phase Separation

The development of flow-induced phase separation below the LCST is shown in *Fig. 6* for a 64% PS blend at 111°C, which is 9 K below its cloud point temperature. The extrusion speed is 1.00 mm/s corresponding to an average extension rate of 1.02 s^{-1}. *Figure 6a* shows the blend initially at rest in the miscible region. After the onset of flow the blend phase separates rapidly as shown in *Fig. 6b*; note that demixing begins near the center axis of the die which is the region of the highest extension. The size of the phase separated region grows continuously as the experiment continues, as shown in *Fig. 6c*. In *Fig. 6d*, nearly the entire die region has phase separated approximately two minutes after the onset of flow.

The flow-induced phase separation does not appear to depend on extension rate and temperature in the same manner as the flow-induced miscibility; instead there seems to be a critical stress level. (This is different than the effect of an isotropic pressure, as
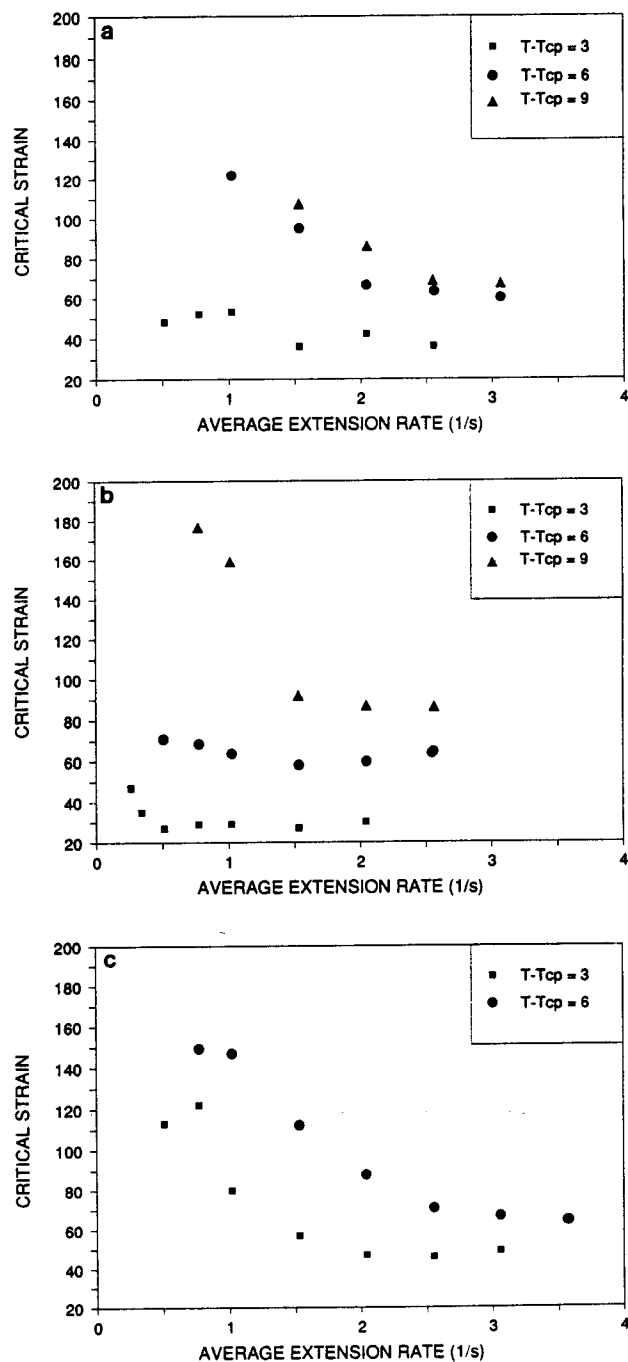

Fig. 4. *Cloud point elevation in the stagnation flow. (a) 35/65 PS/PVME with a cloud point temperature of 110°C. (b) 44/56 PS/PVME blend with a cloud point temperature of 113.5°C. (c) 54/46 PS/PVME blend with a cloud point temperature of 116.5°C.*

discussed below.) The flow-induced phase separation occurred for all compositions when the normal stress measured at the wall near the exit of the capillary rheometer exceeded approximately 30 MPa. *Table 1* summarizes the minimum wall normal stress required to induce phase separation for four compositions. The range of experimental parameters was limited since at pressures higher than 40 MPa and flow rates higher than 4.0 mm/s, the flow was unstable.

Figure 7 shows the temperatures at the onset of phase separation for four PS/PVME compositions. Flows at lower temperatures and at stress levels in excess of 30 MPa normal to the capillary wall will induce a phase separation, while those at higher temperatures or lower stresses will have no effect.

Shear Flow

Figure 8 shows photographs of sheared samples of a 44% PS blend that were quenched from 3 K above the cloud point temperature. Figure 8a shows a blend that was sheared at 0.16 rad/s for four minutes; at the outer edge of the disk the shear rate is a maximum and the blend appears transparent. Near the center the shear rate is lower and the blend is demixed and at intermediate radii the blend has partially cleared. Figure 8b shows the same blend
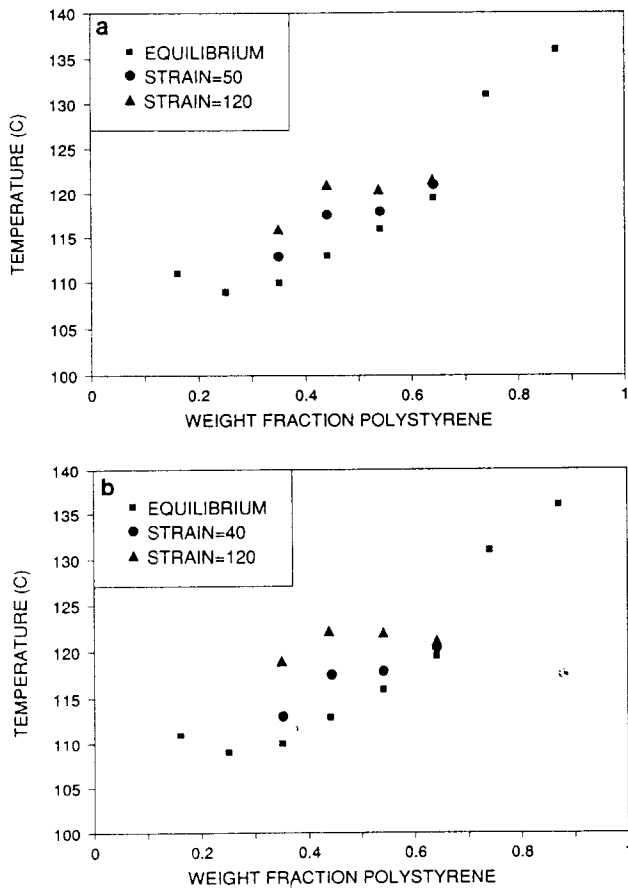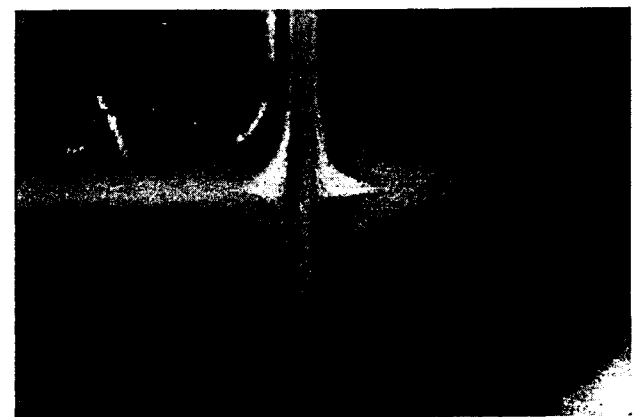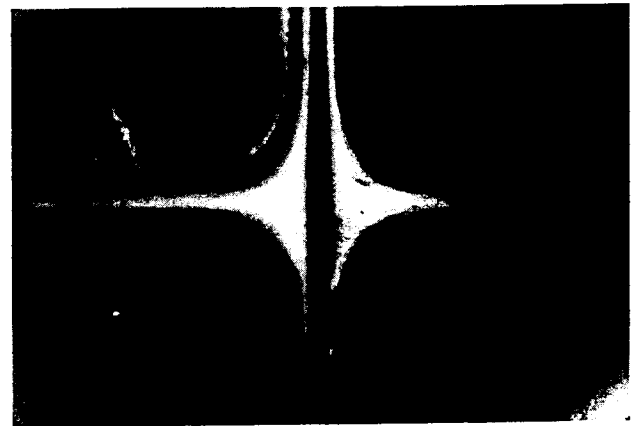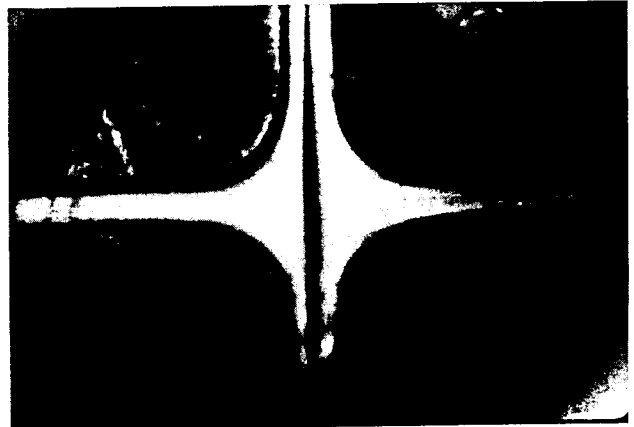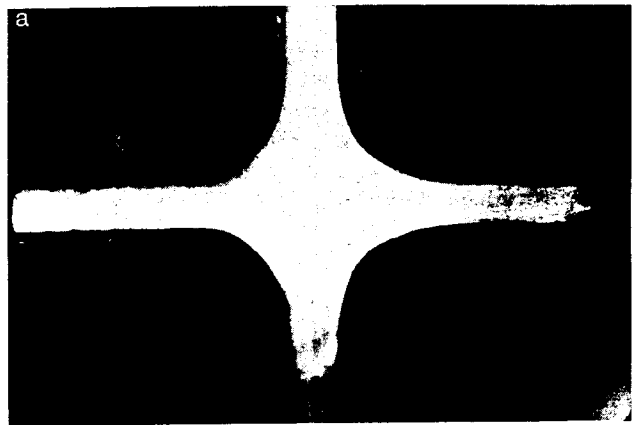

Fig. 5. Flow-induced shifts in the cloud point curve for the stagnation flow. (a) at an extension rate of 1.0 s^{-1} and critical strains of 50 and 120, (b) at an extension rate of 2.0 s^{-1} and critical strains of 40 and 90.

Fig. 6. Flow-induced demixing in the stagnation flow. (a) 64/36 PS/PVME blend 9 K below the cloud point temperature at rest; the blend is clear and miscible. (b) The same blend a few seconds after the onset of flow at an extension rate of 1.02 s^{-1}; phase separation occurs initially along the axis of highest extension. (c) After 1 minute; phase separation has grown in the center region of the die and also along the walls. (d) After 2 minutes; the phase-separated region has grown to include nearly the entire die.

sheared at 0.10 rad/s for four minutes where the induced miscibility region is much smaller.

The critical shear rate is defined as the value that corresponds to the radius where the blend first transmits light, and is calculated from the radial position, the plate separation and the rotational speed using *Eq 6*. In *Fig. 8a*, the critical radius is 4.7 mm from the center of the disk, the sample has a gap of 0.958 mm and the rotation speed is 0.16 rad/s, corresponding to a critical shear rate of 0.78 s^{-1}. The sample in *Fig. 8b* shows a critical shear rate of 0.87 s^{-1}.*Table 2* gives the average value of the critical shear rate for several rotational speeds, shearing times, and temperatures. For samples sheared 3 K above the cloud point temperature, the critical shear rate appears to be independent of the time of shearing. Samples sheared 6 K above the cloud point temperature required a much larger average critical shear rate. Thus, we find that the critical shear rate depends only on temperature. The values are somewhat larger than the extension rates where an induced miscibility was found.

Flow-induced phase separation was also observed by shearing samples well below the cloud point temperature and a typical quenched sample is shown in *Fig. 9*. (Note that this blend was never exposed to temperatures above its cloud point.) At the outer radius of the disk where the shear rate is high the blend is opaque and has phase separated. Near the center of the disk, the blend remains transparent and miscible; this was also observed for 54% and 64% PS blends. However, due to the high stress nec-
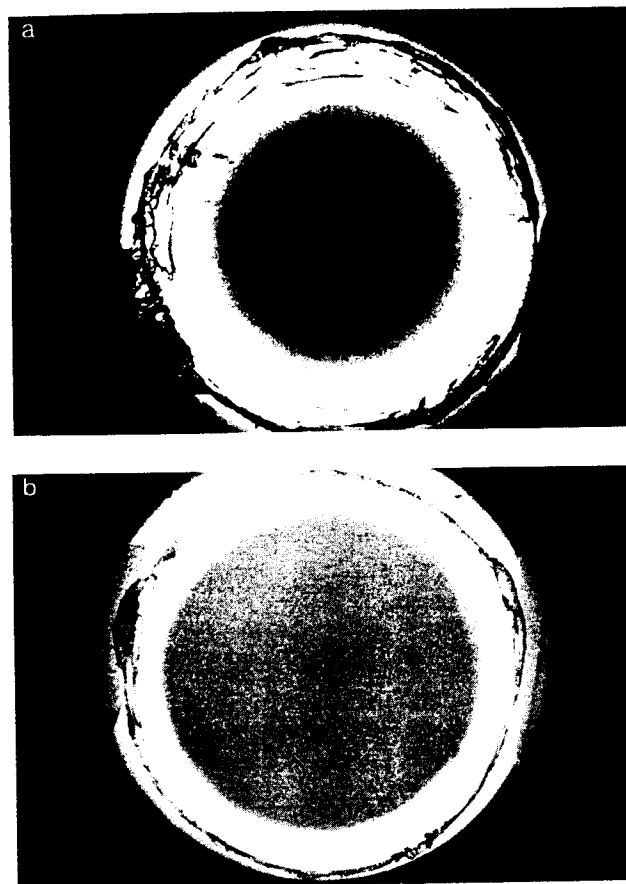

Fig. 8. *Shear flow-induced miscibility in the parallel plate geometry. (a) 44/56 PS/PVME blend 3 K above the cloud point temperature sheared at 0.16 rad/s for four minutes. (b) 44/56 PS/PVME blend 3 K above the cloud point temperature sheared at 0.10 rad/s for four minutes.*

Table 1. Conditions for Flow-Induced Phase Separation in the Planar Stagnation Flow.

Blend Composition (wt% PS)	T-T_{cp} (K)	Extension Rate (l/s)	Wall Normal Stress (MPa)
35	−35.0	3.1	31.0
44	−25.0	3.1	29.5
54	−13.0	2.0	32.0
64	−4.0	2.6	27.0

Table 2. Shear Rates Corresponding to Flow-Induced Miscibility in Shear Flow for a Blend With a Weight Ratio of PS/PVME of (44/56) Which Has a Cloud Point of 113.5°C.

T-T_{cp} (K)	Time (min)	γ_{cr} (l/s)
3.0	2.0	0.63
3.0	4.0	0.76
3.0	6.0	0.63
6.0	4.0	2.90

essary to induce a phase separation, a stable flow was very difficult to obtain and a reliable estimate of the critical stress or deformation rate for flow-induced phase separation in shear flow was not possible. However, the turbidity is clearly an indication of phase separation. We also note that the shear flow is essentially constant pressure, although the stress field may be quite anisotropic; this is further evidence that the induced miscibility cannot be attributed simply to changes in the pressure level.
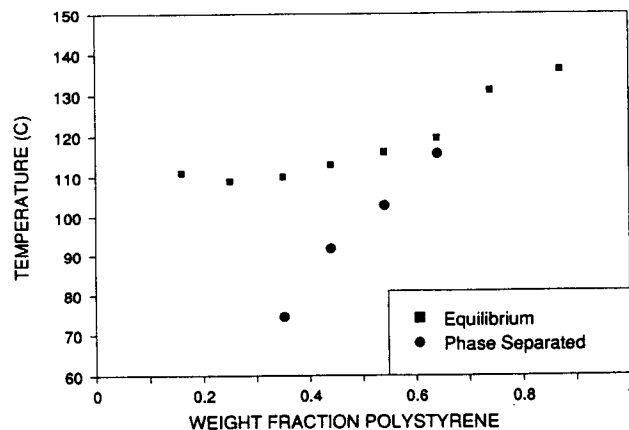

Fig. 7. *The onset of flow-induced phase separation at various compositions. The pressure measured at the wall of the capillary rheometer of is approximately 30 MPa for each composition.*

DISCUSSION

Miscibility in a mixture of two chemically dissimilar homopolymers usually requires an energetically favorable (specific) interaction. This can best be ex-

Fig. 9. Shear-induced demixing. The sample is 44% PS sheared at 0.1 rad/s for two minutes at a temperature 25°C below the equilibrium cloud point.

plained by consideration of the Gibbs free energy of mixing

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

The entropy of mixing can be estimated from the combinatorial entropy of mixing on an incompressible lattice. For a binary blend this is

$$\Delta S = -R(N_1 \ln \phi_1 + N_2 \ln \phi_2) \qquad (8)$$

where N_1 and N_2 are the number of moles of each species and ϕ_1 and ϕ_2 are the volume fractions. The enthalpy of mixing is often estimated from a van Laar type expression

$$\Delta H = RT\phi_1\phi_2 x_{12} \qquad (9)$$

The interaction parameter, x_{12}, describing the energy of interaction of unlike molecules can be written

$$x_{12} = z\frac{\Delta w}{RT} \qquad (10)$$

where z is the coordination number on the lattice and Δw is the average interaction energy

$$\Delta w = w_{11} + w_{22} - \tfrac{1}{2} w_{12} \qquad (11)$$

The entropy change is negative and relatively small in polymer blends because the number of molecules per unit volume is small. In order for a blend to be miscible the enthalpy change and thus Δw must be negative but not necessarily large in magnitude. In other words, an unlike 1-2 contact must be more energetically favorable than like contacts, $w_{12} > \tfrac{1}{2}(w_{11} + w_{22})$. An energetically favorable contact between segments of unlike molecules is called a specific interaction, e.g., hydrogen bonding, charge transfer complexes, acid-base interactions, and dipole moments. In some cases, the effect of the specific interactions also depends on the local alignment of the polymers and the energetically unfavorable dispersive forces occurring at contacts that do not exhibit a favorable specific interaction. Actually, the interaction of unlike chain segments is repulsive for some local orientations and attractive for other ori-

entations in which the two functional groups that constitute a specific interaction are in contact (23). The overall contribution of the interaction term to the free energy of mixing thus depends not only on the strength of the specific interaction, but on the ability of these interactions to come in contact.

The volume change on mixing also contributes to the free energy as shown in Eq 7. Sanchez (24) showed that the stability criteria for a binary mixture can be expressed as

$$\left(\frac{\partial^2 G}{\partial \phi^2}\right)_v - v\beta \left(\frac{\partial^2 G}{\partial \phi \partial v}\right)^2 > 0 \qquad (12)$$

where β is the isothermal compressibility of the mixture and v is the specific volume. Since β is positive, compressibility has a destabilizing effect and because β increases with temperature, this is more pronounced at higher temperatures. The compressibility effect is a common explanation for lower critical solution temperature behavior in polymer blends (23).

For polymer mixtures with specific interactions, the random mixing assumption for the entropy of mixing (Eq 8) is no longer valid. In this case, the overall entropy of mixing is usually written as

$$\Delta S = \Delta S_C + \Delta S_{NC} \qquad (13)$$

where ΔS_C is the combinatorial entropy of mixing for a random orientation; for a lattice this is given by the Flory-Huggins expression in Eq 8. The non-combinatorial entropy of mixing ΔS_{NC} is a correction for cases where some local orientation is important, as is the case of polymer blends with specific interactions. This orientation decreases the overall entropy of mixing which is unfavorable to miscibility since it increases the free energy. Unfortunately, there is no currently accepted expression for the non-combinatorial entropy of mixing although empirical parameters are often used to describe this effect.

Thus, the lower critical solution temperature behavior in polymer blends can be explained by three major contributions to the free energy of mixing. First, the compressible nature of the system and the decrease in entropy due to the orientation caused by favorable specific interactions tend to destabilize the mixture. Second, an increase in the difference of the solubility parameters at elevated temperatures will also lead to a destabilization. Third, the directionally dependent specific interactions that are a necessity for miscibility in a homopolymer blend must be in sufficient contact. The majority of the available contact sights do not contain a favorable interaction, but rather unfavorable London dispersive forces. The functional groups that are responsible for the favorable interactions limit the rotational degrees of freedom both energetically and sterically. At lower temperatures, many rotational degrees of freedom are lost and a higher than expected proportion of specific interactions may occur. At elevated temperatures, the orientations are more random and the dispersive

forces become dominant, which can lead to LCST behavior (23).

The unique features of the lower critical solution temperature phase behavior in polymer blends is a result of a delicate balance of favorable and unfavorable temperature and composition dependent contributions to the free energy of mixing. In order for there to be at least partial miscibility between two different homopolymers, these contributions must be a result of energetically favorable, directionally dependent specific interactions. It is possible that a small perturbation in the contribution of these intermolecular interactions, such as a change in the probability that the specific interactions come in contact, can significantly alter the phase behavior of the polymer mixture.[2]

The two contributions to the heat of mixing are the energy per contact of unlike molecules x_{12} and the number of contacts of unlike molecules $\phi_1\phi_2$. (We assume that the contact of unlike molecules is an energetically favorable specific interaction.) The overall enthalpic contribution to the free energy of mixing depends on how many specific interactions are in contact as well as the energy of the interaction.

For example, Coleman, Serman, and Painter (27) found that in a partially miscible polymer blend at equilibrium only 60 to 80% of available specific interactions effectively come in contact. This effective fraction of specific interactions decreases with increasing temperature and leads to LCST phase behavior. Thus, there appears to be a "critical" fraction of specific interactions which must be in contact for a blend to be miscible. A polymer blend that is phase separated at a temperature above its LCST has fewer than the critical fraction of specific interactions in contact. When the blend is stretched in a flow field, the fraction of specific interactions in contact can increase and surpass the critical fraction, which would lead to flow-induced miscibility

The entropy of mixing (*Eq 8*) is determined from the total number of configurational degrees of freedom for both macromolecules. If one of the blend components is preferentially stretched and oriented in a flow field, the total number of configurational degrees of freedom and thus the entropy of mixing (relative to the unstretched state) is reduced. The effect of reducing the entropy of mixing is unfavorable to miscibility and deformation can lead to phase separation of a miscible blend.

Thus, flow-induced changes in miscibility can be interpreted as the result of competing effects of deformation on the enthalpic and entropic contributions to the free energy of mixing. Deformation tends to enhance specific interaction contact and can increase miscibility by increasing favorable enthalpic contributions. Deformation also reduces the configurational degrees of freedom and can decrease mis-

cibility by reducing the entropy of mixing. It is difficult to predict which of these effects will dominate but this work suggests that the favorable enthalpic contributions dominate for small deformations and higher temperatures while entropic contributions dominate at larger deformations and lower temperatures. The entropic contributions also tend to be more important for blends with a higher viscosity.

We expect that the deformation necessary to induce miscibility is related to the amount that each of the polymers is stretched. This stretching can be quantified by the change in the ratio of the root mean square end to end distance of the stretched polymer to the value at equilibrium. Expressions for the ratio of the root mean square end to end distance as a function of the stress tensor using various polymer chain models are given by Bird, *et al.* (30)

The simplest of these is the infinitely extendible Hookean dumbbell which is only qualitative, but is simple to use. The ratio of the root mean square end to end distance of the stretched polymer $\langle R_2 \rangle$ to its value at equilibrium for a Hookean dumbbell is (30)

$$\frac{\langle R^2 \rangle}{\langle R^2 \rangle_{eq}} = 1 - \frac{tr\tau}{3nkT} \qquad (14)$$

where τ is the polymer contribution to the stress tensor and n is the number density of polymer segments. From this expression, the stretching ratio can be estimated for a variety of flows. For example, upon the sudden inception of a planar elongational flow this ratio is given by

$$\frac{\langle R^2 \rangle}{\langle R^2 \rangle_{eq}}$$

$$= 1 + \frac{2}{3}\dot{\epsilon}\lambda \left\{ \frac{1 - e^{-(1-2\lambda\dot{\epsilon})t/\lambda}}{1 - 2\lambda\dot{\epsilon}} - \frac{1 - e^{-(1+2\lambda\dot{\epsilon})t/\lambda}}{1 + 2\lambda\dot{\epsilon}} \right\} \qquad (15)$$

where $\dot{\epsilon}$ is the extension rate, λ is the time constant for the Hookean dumbbells, and t is time. This expression gives the dependence of the stretching ratio on extension rate and strain (which appears as the product of extension rate and time).

Figure 10 shows the predictions of *Eq 15*. The strain is plotted as a function of the product of the extension rate and the characteristic time at stretching ratios ranging from 1 to 10. The lines of constant temperature in *Figs. 6–9* are qualitatively consistent with the lines of constant stretching ratio which would indicate the existence of a critical stretching ratio corresponding to conditions necessary to induce miscibility. The critical stretching ratio increases with the temperature difference above the cloud point and seems to be the most important parameter to quantify the effect of flow on polymer blend miscibility.

The strains in *Fig. 10* are much lower than the critical values measured in the experiments. However, the Hookean dumbbell model is expected to give only qualitative agreement because of the assumptions that polymer molecules are infinitely extensible, that they have no frictional resistance to the

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[2] Actually, it has been discovered that favorable specific interactions are not required in certain homopolymer-copolymer or copolymer-copolymer blends. A "miscibility window" can exist in a blend that is devoid of favorable interactions provided that a certain distribution of unfavorable interactions is present. This effect is described in *Refs.* 25, 23 and 26.

deformation, and that they follow a linear force law for all extensions. The finitely extensible nonlinear elastic (FENE) dumbbell model developed in Bird, *et al.* (30), is an improvement over the Hookean dumbbell model at higher deformations and would be expected to display the same qualitative behavior but is far more complex. For quantitative agreement with these experiments, a good transient model is presently not available and outside the scope of this work.

The observation of flow-induced demixing at lower temperatures is contrary to what might be expected from an increased stress, based on measurements made on quiescent samples subjected to an isotropic pressure. As discussed above, quiescent samples subjected to pressures up to 80 MPa in the study by Walsh and Rostami (12) and up to 200 MPa in the work of Maeda, Karasz, and MacKnight (11) were found to induce miscibility (increase the LCST) in several polymer blends. We also note that the phenomenon is not uniform throughout the die as would be required if the effect were due strictly to the increased pressure. The phase separation starts in the region of highest stretching near the stagnation point. Therefore, the flow-induced phase separation is due to the applied deformation and the related stresses, which are not described adequately by an isotropic pressure.

It is possible that enhancing specific interaction contact by flow increases the LCST curve and that the entropy reduction by flow raises the UCST (which is consistent with previous studies of polymer solutions). However, since the UCST in blends is usually below the glass transition temperature, direct measurements are difficult. Some extrapolations of the phase behavior of the blend components in solution indicate the presence of a UCST, but these are difficult to interpret.

CONCLUSIONS

Shear and extensional flows can have a significant effect on the miscibility for a blend of polystyrene with poly(vinyl methyl ether). The extensional deformation found in the planar stagnation flow induces miscibility near the LCST by elevating the cloud point temperature of this blend by as much as 12 K; the effect is dependent on the extension rate, the strain and the composition. Shear flow-induced miscibility was also observed in parallel plate geometry, although the effect of shear on polymer blend miscibility is not as dramatic as the planar stagnation flow.[3]

The stretching ratio (the ratio of root mean square end to end distance of the stretched polymer to the polymer at equilibrium) appears to be an important parameter in the induced miscibility. Our data are qualitatively consistent with a critical stretching ra-

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[3] Recent studies of fluorescence quenching in samples quenched after shearing reveal that this effect is a genuine miscibility at the molecular level and not simply the result of deforming the domains in a phase-separated sample to create a phase-separated microstructure with domains too small to scatter light (31).
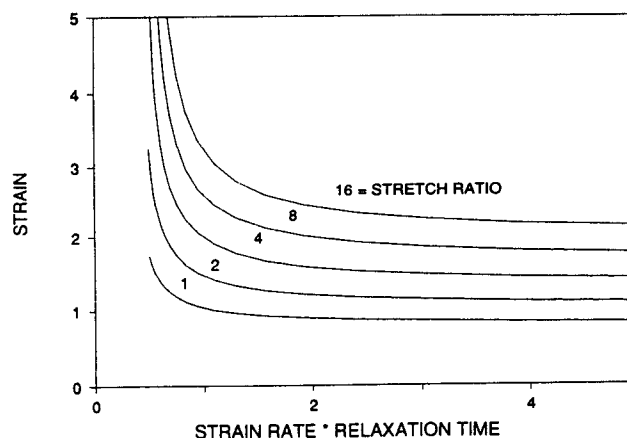

Fig. 10. Contours of the stretching ratio for Hookean dumbbells in a transient biaxial extension, which is the idealized flow in the stagnation die. The stretch ratio is the fraction of the equilibrium end-to-end distance by which the polymer molecule has been extended.

tio for flow-induced miscibility of a blend at a given temperature above its cloud point.

At lower temperatures, 20 to 30 K below the equilibrium coexistence temperature, flow-induced phase separation was observed in both shear flow and extensional flow. The stress, rather than deformation rate appears to be the most important parameter in flow-induced phase separation.

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