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Effects of Shear on Miscible Polymer Blends: In Situ Fluorescence Studies

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ABSTRACT: The effects of shear flow on the phase behavior of a miscible blend of polystyrene with poly(vinyl methyl ether) near the lower critical solution temperature have been investigated by fluorescence measurements. For this purpose approximately 1% of the polystyrene chains in the blend were labeled with anthracene and the fluorescence quenching was used as an indicator of miscibility. The modification of a Rheometrics RMS-800 rheometer for in situ fluorescence measurements along with simultaneous shear and normal stress studies under well-controlled temperature and deformation conditions is described. Following equilibration in the miscible state approximately 25 K below the coexistence temperature, slow heating to temperatures in the two-phase region shows that shearing at a constant rate increases the coexistence temperature. The elevation above the quiescent spinodal temperature is related to shear rate as $\Delta T/T_s = (0.015 \pm 0.002)\dot{\gamma}^{0.59\pm0.04}$ and this relation is independent of composition in the range of 20–60% (w/w) polystyrene, within the experimental error. Isothermal experiments in the two-phase region also show shear-induced mixing. The in situ fluorescence measurements provide a sensitive indicator of phase transitions that cannot be unambiguously identified by the measured shear stress and first normal stress difference alone.

Introduction

The large deformations and related stresses, which are unavoidable in processing, can strongly affect the phase behavior of partially miscible polymer blends. Nonequilibrium morphologies are generated and may eventually be frozen in. As a consequence, processing histories can have an important influence on the properties of many polymer blends.

In this paper, we focus on the effect of shear flow on the phase behavior of a miscible binary blend of polystyrene and poly(vinyl methyl ether). This blend has been well-studied in the absence of flow and convincing evidence of a true miscibility is available.[3,12,23]

The paper is organized as follows. Some important background concerning previous studies of deformation-induced miscibility changes in solutions and polymer blends is given in the next section, followed by a description of an apparatus with the necessary temperature control and the capability to perform in situ fluorescence measurements. A short description of the materials and blend preparation is followed by the Results section, which focuses on measurements of the coexistence temperature by in situ fluorescence measurements, the shear stresses, and the first normal stress difference. A separate Discussion offers some interpretations of the results.

Background

Deformation-induced phase transitions in polymeric liquids have been known since Silberberg and Kuhn[21] reported shear-induced mixing in ternary solutions of polystyrene and ethylcellulose in benzene. Like many polymer solutions, this mixture displays an upper critical solution temperature in a quiescent state; the apparent coexistence temperature at shear rates up to 270 s^{-1} decreased as much as 13 K. Koningsveld and Kleintjens[11] showed that the cloud point temperature for a solution of polystyrene in cyclohexane was lowered by approximately 1 K at shear rates of $\sim$4000 s^{-1}. Wolf and Kramer[26] and Wolf[27] found that shear rates up to 5000 s^{-1} reduced the UCST and also changed the shape of the coexistence curve in solutions of polystyrene in *trans*-decalin.

In contrast to observations of flow-induced mixing, solutions of polystyrene in bis(2-ethylhexyl) phthalate or in a mixture of *cis*- and *trans*-decalin were reported by Ver Strate and Phillipoff[25] to demix (became turbid) in the converging flow from a reservoir into a capillary tube. 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} were also reported by Rangel-Nafaile et al.;[20] they also gave a more comprehensive discussion of deformation-induced phase transitions in polymer solutions.

These interesting effects of flow led to quantitative studies with in situ measurements of mixing in more recent work. Small-angle light scattering studies of solutions of polystyrene and polybutadiene in dioctyl phthalate sheared at rates from 0.0067 to 670 s^{-1} in a cone and plate geometry were made by Hashimoto et al.[6] Scattering measurements made parallel and perpendicular to the flow direction showed that the UCST decreased by as much as 10 K in the "strong shear" regime (shear rate $\dot{\gamma} > 1\ s^{-1}$) according to $\Delta T_c/T_c = (2.6 \pm 0.6) \times 10^{-3}\dot{\gamma}^{0.50\pm0.02}$. It is interesting to compare this with the study on low molecular weight critical solutions of aniline and cyclohexane by Beysens et al.[1] By use of light scattering measurements in simple shear flow, the UCST was found to decrease by approximately 0.05 K in the strong shear regime and showed a similar shear rate dependence but with a much smaller proportionality factor, viz., $\Delta T_c/T_c = (5.90 \pm 0.66) \times 10^{-7}\dot{\gamma}^{0.56\pm0.03}$. The influence of shear on polymer blends may be even larger due to the higher viscosities and long relaxation times.

Blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) were first studied in steady shear flow by Mazich and Carr,[16] using a cone and plate geometry. The viscosity was measured with a Rheometrics mechanical spectrom-

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eter operated at a constant shear stress; optical measurements were not made, but an abrupt increase in the slope of viscosity versus temperature curve was associated with a phase transition. The temperatures where this change in slope was observed ranged from 2 to 7 K higher than the coexistence temperature measured under quiescent conditions.

Shear-induced mixing in a blend of a styrene–acrylonitrile copolymer with poly(methyl methacrylate) at high shear rates on the order of 1000 s^{-1} was also reported by Lyngaae-Jorgensen and Sondergard.[14] The samples changed from a "white and milky" to an "optically clear state" at a critical shear stress of approximately 80–100 kPa, and when the samples were quenched below the glass transition temperature after shearing, no microstructures on or above length scales of ~100 Å could be detected with transmission electron microscopy.

Both flow-induced mixing and demixing in a PS/PVME blend were reported by Katsaros et al.,[9,10] who studied both a planar extension and a continuous shear flow in a capillary. The extensional flow induced mixing up to 12 K above the coexistence temperature and also induced demixing at temperatures as much as 30 K below the coexistence temperature; both effects showed a significant composition dependence. Optical clarity was used as the criterion for mixing, and it was not clear whether shear flow actually mixed the blend on a molecular level or if it simply reduced the size of the phase-separated domains to a scale too small for significant scattering of visible light. This led to measurements of mixing at much smaller length scales by Larbi et al.,[13] who studied the effect of shear on the same PS/PVME blend containing trace amounts of a fluorescent, anthracene-labeled polystyrene (PS*). The fluorescence intensity of such blends after the addition of PS* provides a sensitive measurement of the phase segregation on very small scales.[2] The samples of Larbi et al.[13] were maintained 3 K above the spinodal temperature for 1 min, sheared between parallel plates, and then rapidly quenched below the glass transition temperature. Measurements of the fluorescence intensity as a function of radius showed a rapid decrease with increasing radius (and thus increasing shear strains), indicating the presence of intimate mixing on a size scale of a few angstroms. In order to obtain more quantitative information on flow-induced phase transitions and to capture transient effects while eliminating potential artifacts of quenching, in situ experiments are desirable.

In situ light scattering measurements in a sheared blend of poly(ethylene–vinyl acetate) and solution chlorinated polyethylene were reported by Hindawi et al.[8] A constant stress (23 kPa) was applied to samples held between parallel plates and decreases in the scattering intensity perpendicular to the flow were found at small angles and for quench depths up to 27 K. After cessation of shearing, the intensity returned to its original level in times on the order of 100 s.

Nakatani et al.[17] studied the shear dependence of the concentration fluctuations in the single-phase region of blends of deuterated polystyrene (PSD) with poly(vinyl methyl ether), and also deuterated polystyrene with polybutadiene. Small-angle neutron scattering measurements in a Couette flow indicated that at small scattering angles (large fluctuations) the scattered intensity parallel to the flow was reduced by shear near the LCST; the effect was considerably smaller perpendicular to the flow.

There have been attempts to model flow-induced demixing in polymer solutions by combining the Flory–Huggins expression for the equilibrium free energy of mixing with a term proportional to the trace of the stress tensor. Flow-induced mixing has also been modeled by a more mechanical approach accounting for finite droplet size and the effects of interfacial tension. Tirrell et al.[22] gave a useful and more detailed review of these efforts and much of the (relatively scarce) data, pointing out the need for more comprehensive studies. Critical phenomena for classical fluids in a uniform shear flow have also been analyzed by Onuki and Kawasaki,[18] a renormalization group method; they predicted that shear flow would decrease the UCST and that the spatial correlation function would be anisotropic. Onuki[19] predicted that shear may enhance aggregation of droplets in critical fluids in the nucleation and growth regime, leading to increased rates of phase separation, but that if the shear exceeds a relatively small critical value, even critical droplets may be broken, leading to a complete suppression of the droplet formation. The dynamics of concentration fluctuations for polymer solutions in simple shear flow were studied by Helfand and Frederickson,[7] who showed that scattering may be greatly enhanced by shear flow even at conditions in the one-phase region, significantly above the UCST.

Flow can have a strong influence on the phase behavior of polymeric mixtures and both flow-induced mixing and demixing have been reported in solutions and blends. These effects in polymer blends need to be quantified by carefully planned experiments in well-controlled flows with in situ mixing measurements. The literature suggests that the applied shear rate can characterize the effects of flow, although there are also suggestions that a critical stress exists for shear-induced phase transitions; consequently we prefer the measurement of both shear and normal stresses with shear rate as a parameter. The work by Larbi et al.[13] and Nakatani et al.[17] underscores the importance of detecting the mixing on small-length scales.

Experimental Section

Materials and Sample Preparation. Polystyrene was obtained from Monsanto and had $M_w = 258\,850$ and a polydispersity of 1.55; PVME was obtained from Scientific Polymer Products and had $M_w = 85\,000$ and a polydispersity of 1.39. The molecular weights were measured by Dr. J. Swadesh at Polymer Labs Inc., Amherst MA, using GPC with a light scattering detector. The anthracene-labeled polystyrene with $M_w = 200\,000$ was prepared according the description given by Valeur at al.[24]

Blends were prepared in toluene with different compositions of PS/PVME and trace amounts of PS* (corresponding to 6 ppm of anthracene in the blend). The solvent was evaporated from cast films by exposure to air at room temperature for 48 h. They were then dried in the oven at 70 °C under vacuum for 10 days to remove traces of moisture and toluene. The samples were then allowed to reach thermal equilibration at 90 °C under a dry nitrogen atmosphere for 2 h before experiments were performed. These conditions were found to minimize moisture effects.

The labeled polystyrene is fluorescent in the visible region when excited by photons in the ultraviolet region, as shown in Figure 1, but this fluorescence is quenched when anthracene is in close proximity (on the order of a few angstroms) to the ether group in PVME. If a PS/PVME/PS* sample is continuously excited, the emitted fluorescence intensity of the sample in its well-mixed state is low and when the sample demixes the fluorescence intensity increases rapidly. The dashed lines in Figure 1 show the transmittance of the filters used in the current study, which were chosen to provide sufficient sensitivity without significant interference between the signals.

Apparatus and Measurements. Special fixtures and accessories were designed for the Rheometrics mechanical spectrometer (RMS-800, Rheometrics, Inc., Piscataway, NJ) to allow in situ fluorescence measurements and to improve the temperature control system; see Figure 2. An inert atmosphere was maintained by enclosing the sample in an environmental chamber

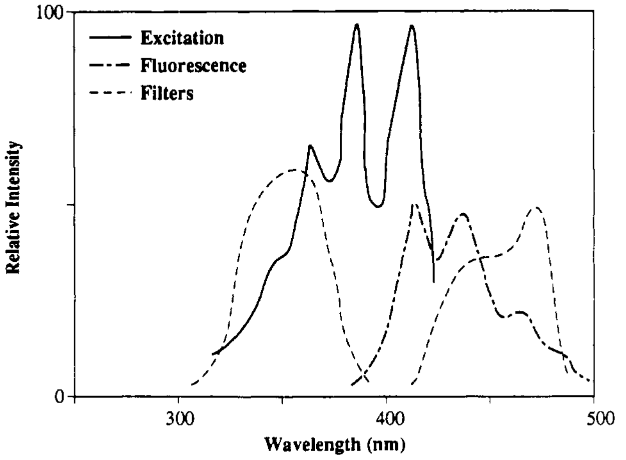

Figure 1. Excitation and emission spectra of the labeled polystyrene along with the transmittance of the filters used in the current study.

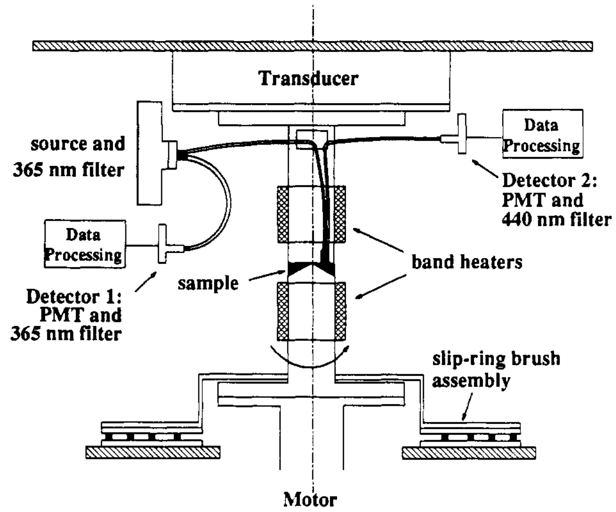

Figure 2. Schematic of the modified rheometry equipment. The specially built fixtures for the Rheometrics, RMS-800, have band heaters mounted on them for improved temperature control. A bifurcated fiber optic probe is flush-mounted on the stationary upper plate to allow in situ fluorescence measurements.

fed with a stream of dry nitrogen. The amount of nitrogen used with the new heating system is significantly lower than with the heater gun of the RMS-800 and the heating is not as noisy.

The two rheometer fixtures (built at U.S. Army Labs, Natick, MA) are heated by electrical band heaters (75 W, custom-made by Heatron Inc., Leavenworth, KS). The heater leads have good flexibility, abrasion resistance, and a closely woven fiber glass sleeve that allows operation up to 600 °C. Two separate time-proportional temperature controllers (CN-8611 TCA, Omega Engineering Inc., Stamford, CT) with a cycle time of 10 s and a proportional bandwidth of 20 K operate the heaters. The thermocouples for temperature control were placed on the heating band close to the sample to provide short response times. This configuration gives no measurable overshoot or thermal gradients along the radius of the sample and the temperature can be maintained at a set point, or ramped in the operating range (0.1–10 K/min) with a resolution of 0.2 K, as measured with several thermocouples embedded in the sample along the radius.

The lower fixture is mounted on a motor, which rotates to drive the flow. The lower heater and thermocouple connect to the temperature controller by means of a slip-ring brush assembly (Model SR 2300-4-2.75, Maurey Instrument Inc., Chicago, IL) consisting of four concentric coin-silver rings mounted on an epoxy-fiberglass composite disc. The contact holder with three precious metal contacts per ring is mounted on another epoxy fiber glass disk. Since the composite disks cannot withstand temperatures above 80 °C, they are removed from the heating elements and mounted at the bottom of the lower fixture on an aluminum base, which has several holes to minimize the heat transfer between the fixture and the disk. For safety reasons, the outer two rings are connected to the thermocouple while the inner rings provide connections between the controller and the heater. The rotating contact does not measurably influence the temperature control in the operating range 25–350 °C.

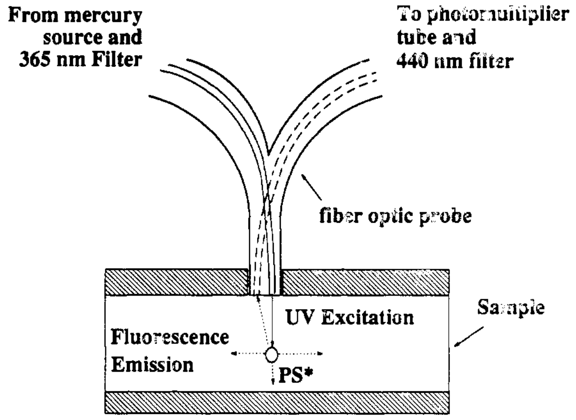

Figure 3. Schematic showing detail for sample end of the bifurcated fiber optic. Approximately half of the fibers in the probe carry UV photons with a wavelength near 365 nm from the mercury lamp to the sample and the other half carry the fluorescence emitted by the sample to detector 2.

A fused-silica (quartz) fiber optic probe, which has a higher transmittance to UV than glass fibers, was custom-made by Fiber Optics Technology Inc., Pomfret, CT. The probe is bifurcated at both the light source end and the sample ends and is flush-mounted to the stationary upper plate. The probe has a 1-mm diameter, which allows observation of a sample area large compared to molecular dimensions but small compared to the sample size; rheological measurements are not altered by the flexible fiber optic lead as checked by steady-state measurements on standard samples of poly(dimethylsiloxane). At the light source end of the probe, half of the fibers carry photons from a mercury arc lamp (Model 68740, Oriel Corp., Stratford, CT) through a 365-nm filter to the first photomultiplier tube (Model 7068, Oriel Corp.); the other half carry photons to the sample. At the sample end of the probe half of the fibers carry photons from the supply to the sample as it undergoes flow while the other half carry the signal emitted by the sample through the 440-nm filter to a second, identical photomultiplier tube.

Multiple photomultiplier tubes are used to provide a dynamic reference that allows a sensitive and accurate measurement of the ratio of emitted to incident light. All of the measured fluorescence intensities at different temperatures and shear rates are reported with the following convention. Before any experiment, the sample is removed from the vacuum oven and then undergoes thermal equilibration under quiescent conditions and in a dry nitrogen atmosphere at 90 °C for 2–3 h until the *relative fluorescence intensity*, I_1/I_2, reaches steady state, I_1 is the intensity of UV light measured by the photomultiplier tube in detector 1, which is proportional to the intensity of light incident on the sample, and I_2 is the intensity measured at detector 2, which is proportional to the fluorescence intensity emitted by the sample. All relative fluorescence measurements at other temperatures are normalized with the relative fluorescence intensity at 90 °C in the quiescent state to minimize noise due to fluctuations in the mercury lamp intensity and sample inhomogeneities.

The flush-mounted fiber optic probe delivers UV light to the sample and also receives the fluorescence signal emitted by the sample, as shown schematically in Figure 3. The blend is optically clear in the one-phase state and the fluorescence signal corresponds to the integrated intensity from the entire thickness of the sample; after phase separation the fluorescence increases rapidly but the penetration depth of the incident light decreases due to the increasing opacity of the sample. This penetration depth is typically on the order of 100 μm, as estimated from fluorescence intensity measurements in transmission described by Larbi et al.[13] on a PS/PVME sample with a thickness of ~1000

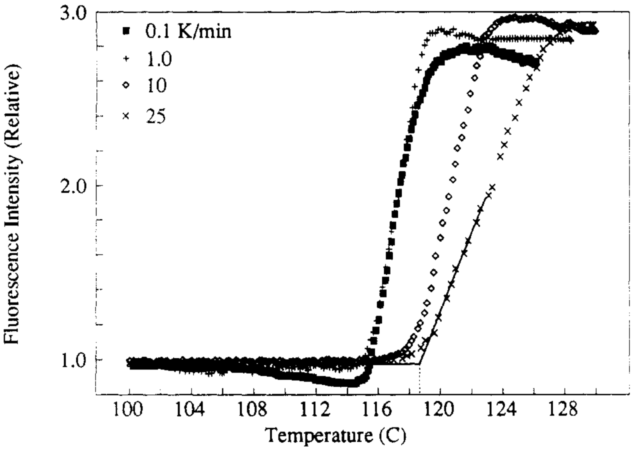

Figure 4. Spinodal temperature of a 60/40 PS/PVME blend determined by obtaining the phase transition temperature at increasing heating rates until the transition temperature is independent of the rate (under quiescent conditions). The phase transition temperature is identified from the intersection of the two straight lines such as those shown at heating rate of 25 K/min.

μm. In those measurements, there was a measurable increase in the fluorescence intensity of a phase-separated sample as compared to the clear sample, while measurements in reflection from the same phase-separated samples show a substantial increase in the fluorescence signal compared to the transmission measurements; this indicates that the penetration depth is a significant fraction of the sample thickness though much less than 1000 μm.

Results

Equilibrium-Phase Diagram. Fluorescence measurements can be used for the determination of both the spinodal and the binodal curves if the heating rate is appropriate, as demonstrated by Halary et al.[3] For these measurements a PS/PVME/PS* sample was placed between glass slides and protected from the atmosphere at 90 °C (20–30 K below the quiescent phase transition temperature) for 2 h for thermal equilibration. The sample was then heated at rates ranging from 0.1 to 25 K/min and the fluorescence intensity measured as a function of temperature. The sample thickness and was 0.5 mm as for the in situ measurements, and the same optical equipment used for the in situ measurements was used. The temperature measurements were made with a small thermocouple embedded in the sample.

The typical evolution of the fluorescence intensity with temperature for a 60/40 PS/PVME blend at various rates of heating is shown in Figure 4; similar results for the 40/60 and 20/80 samples are shown in Figures 5 and 6. The phase transition was identified as the point where the fluorescence intensity increases rapidly, using a construction as shown in Figure 6. The phase transition temperature identified on different samples of the same composition could be reproduced within ±0.5 K. Heating rates of 1 K/min and less gave the same phase transition temperature and show a similar evolution of the fluorescence intensity; the transition at these low rates is identified with the binodal temperature. For fast heating, when the phase transition temperature becomes independent of the rate, we find the best approximation of the spinodal temperature. The transition temperatures for fast and slow heating are shown in Figure 7.

Shear Flow with in Situ Fluorescence Measurements. Two protocols were used to study the effects of shear flow near the LCST. The first was designed to measure the coexistence temperature of the sample during slow heating under steady shear flow. The second protocol prescribed isothermal experiments in the same range, allowing comparison with the results of first protocol.

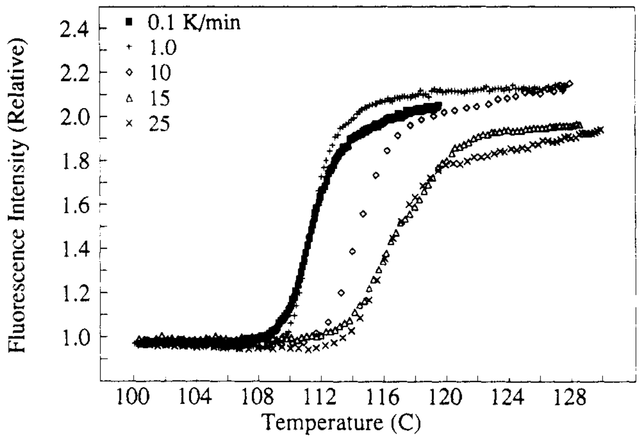

Figure 5. Transition temperatures for a 40/60 PS/PVME blend determined by fluorescence intensity measurements in a quiescent state at different heating rates.

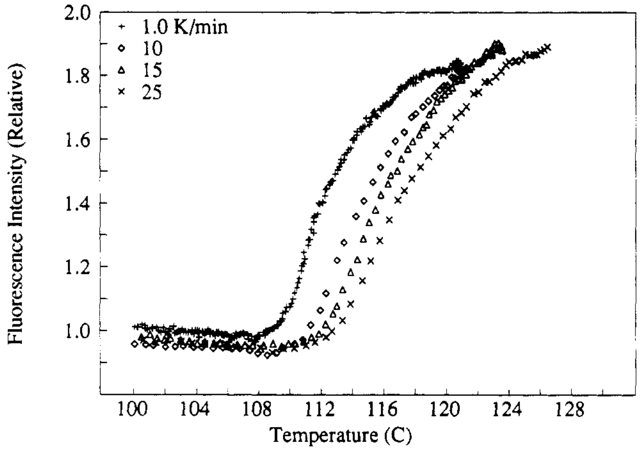

Figure 6. Transition temperatures of a 20/80 PS/PVME blend determined by fluorescence intensity measurements in a quiescent state at different heating rates.

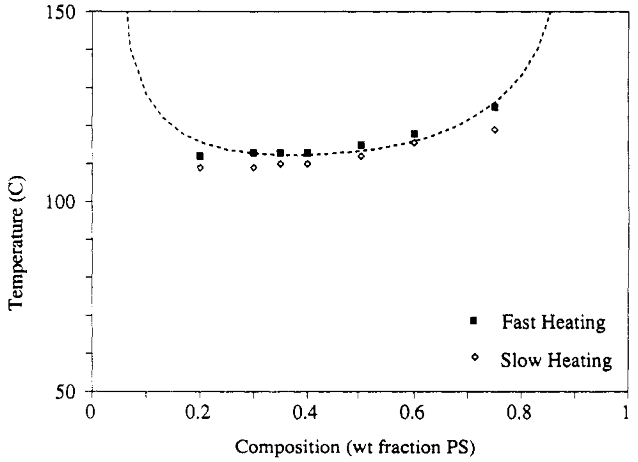

Figure 7. Phase transition temperatures at high and low heating rates as a function of composition.

Protocol A. The sample was equilibrated at 90 °C for approximately 2 h until the fluorescence reached a steady state and then heated at a rate of 1 K/min while being sheared at constant rates (1, 2, 4, 6, and 8 s^{-1}). The flow was arranged so that the net strain on the sample at the equilibrium coexistence temperature was 50 shear units; this was found to give a steady flow in experiments over the entire range of interest. The fluorescence intensity,

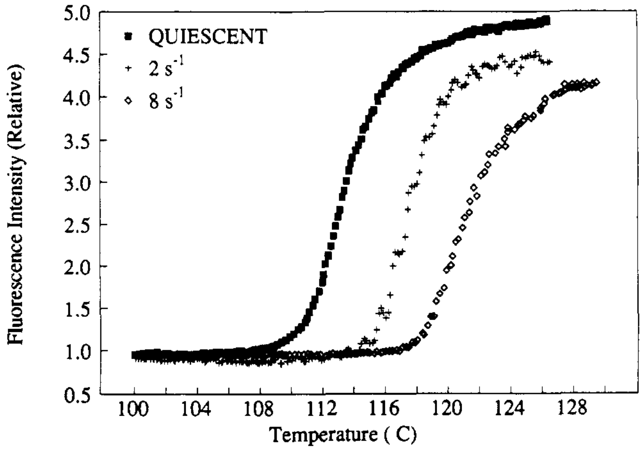

Figure 8. Relative fluorescence intensity for a 20/80 PS/PVME blend as a function of temperature and shear rate, using protocol A.

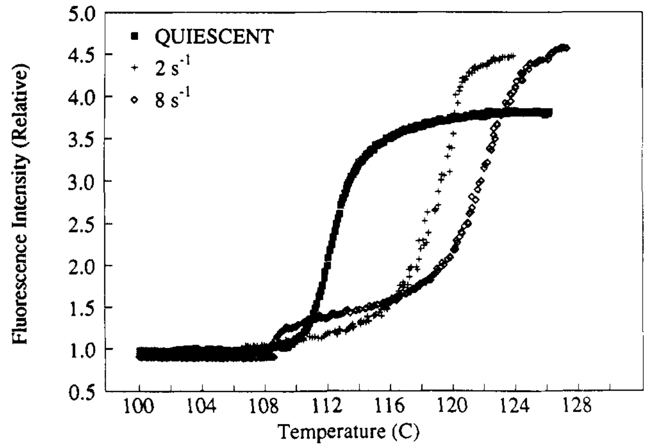

Figure 9. Relative fluorescence intensity for a 40/60 PS/PVME blend as a function of temperature and shear rate measured by use of protocol A. There is some indication of phase separation near 109 °C at a shear rate of 8 s^{-1}, and the steady-state intensities are larger than under quiescent conditions in contrast to the results shown in Figure 8.

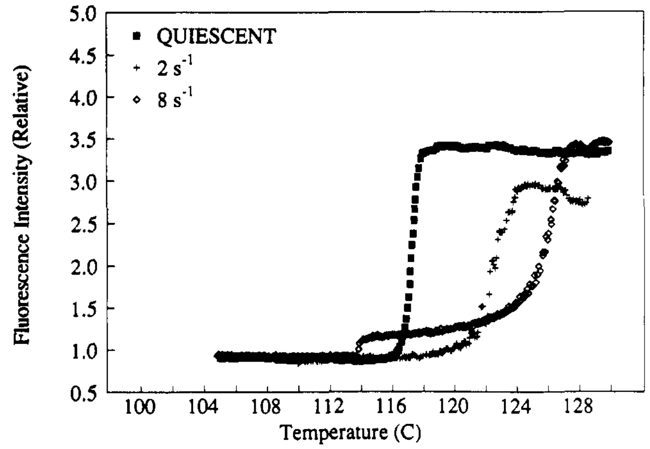

Figure 10. Relative fluorescence intensity for a 60/40 PS/PVME blend as a function of temperature and shear rate measured by use of protocol A. This sample shows behavior similar to the 40/60 blend, but with reduced levels of fluorescence.

shear stress (τ), and first normal stress difference (N_1) were measured throughout the experiment.

The relative fluorescence intensity measured for 20/80, 40/60, and 60/40 PS/PVME samples is shown in Figures 8–10. In each case, the apparent coexistence temperature increases with increasing shear rate. On further heating, all of the samples completely phase separate with much larger increases in fluorescence in the later stage.

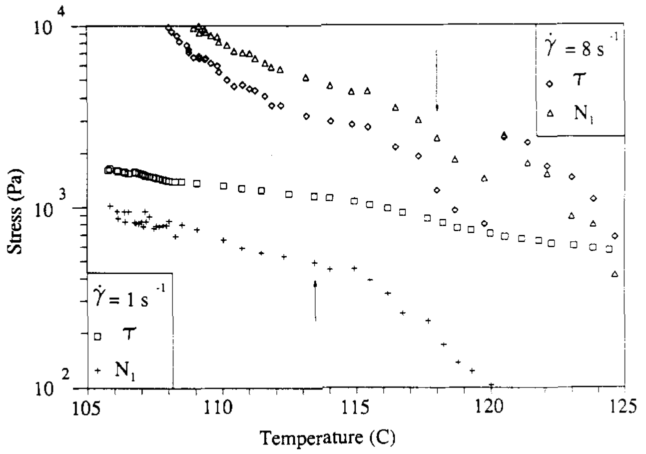

Figure 11. Shear stresses, τ, and first normal stress difference, N_1, measured for a 20/80 PS/PVME sample, using protocol A. At a low shear rate, $\dot{\gamma} = 1$ s^{-1}, the shear stress is insensitive to the phase separation in comparison to the fluorescence (↑); the normal stress difference is somewhat more sensitive. At a higher shear rate, $\dot{\gamma} = 8$ s^{-1}, the shear stress and normal stress difference both show a large oscillation somewhat above the phase-separation temperature detected with fluoresence (↓).

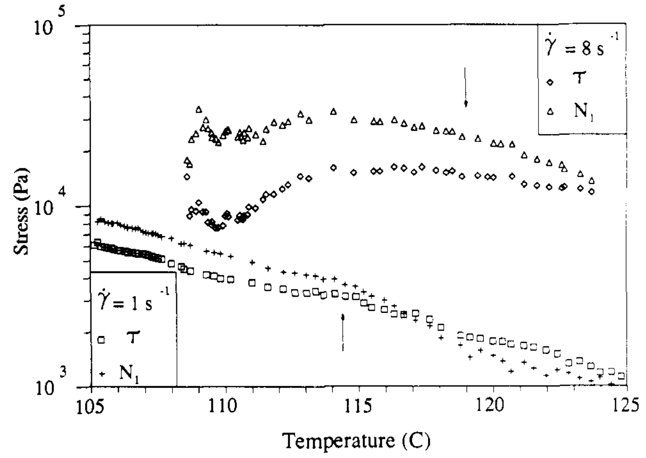

Figure 12. Shear stress and first normal stress difference for a 40/60 PS/PVME sample heated at 1 K/min, using protocol A. The shear stress and normal stress difference at low shear rates are very insensitive to the phase transition (↑); at high shear rates, the only nonmonotonic behavior evident in the stresses occurs at temperatures well below the transition detected by fluorescence (↓).

Figure 11 shows the shear and normal stress results for a 20/80 PS/PVME sample. At low deformation rates, the shear stress shows very little change near the coexistence temperature and cannot be used to identify the phase transition. The first normal stress difference is somewhat more sensitive with a larger negative slope occurring several degrees above the coexistence temperature. The results at shear rates of 2 and 4 s^{-1} were similar; at temperatures much higher than the coexistence temperature, the shear stress also dropped considerably but the onset of phase separation could not be reliably detected by rheometry. At a shear rate of 8 s^{-1}, the shear and normal stress difference decreased with temperature before subsequent significant increases over a small range of temperatures above the coexistence value.

Figure 12 shows the corresponding results for 40/60 PS/PVME blend (the results for a 60/40 composition were similar); the stress measurements were even more insensitive to the precise position of the phase transition and

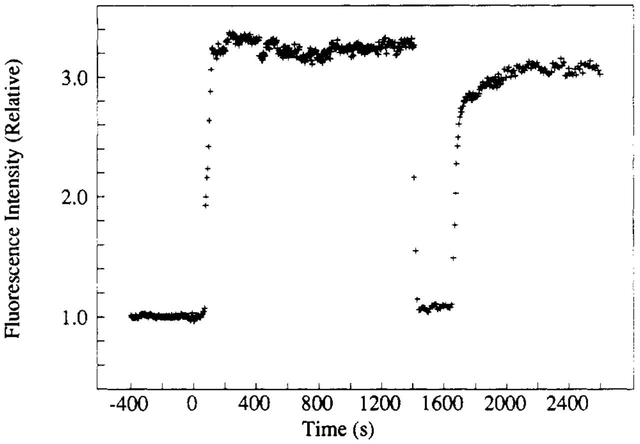

Figure 13. Evolution of the relative fluorescence intensity in isothermal experiments (protocol B) for a 60/40 PS/PVME blend at 120.5 °C and a shear rate of 2 s^{-1}. The heating was started from an initial temperature of 90 °C at $t = 0$ and shear flow at a rate of 2 s^{-1} was imposed from 1400 to 1700 s. The steady-state intensities should be compared to those in Figure 10.

at higher temperatures decreased more rapidly than at the lower PS compositions.

Protocol B. The sample was heated into the two-phase region and maintained at a constant chosen temperature until the fluorescence intensity reached a steady state. Steady shear flow was then imposed on the sample and the evolution of the shear stress and first normal stress difference was measured.

The results for a typical experiment are shown in Figure 13. After the fluorescence intensity reached a steady-state value at 90 °C, the blend was heated (starting at $t = 0$) at 5 K/min to 120.5 °C where the fluorescence intensity eventually reached a level of 3.2. After the imposition of a shear rate of 2 s^{-1}, the intensity decreased in approximately 15 s to a value near that of the completely mixed initial state. Upon cessation of the flow, the intensity increased once again and reached a value corresponding to the phase-separated state in approximately 600 s. Shear rates of 4 and 8 s^{-1} had similar effects on the fluorescence intensity, but a shear rate of 0.5 s^{-1} gave a significantly higher steady-state intensity, suggesting the possibility of "weak" and "strong" shear regimes as proposed by Onuki.[19]

In all of these experiments, the measured shear stress and normal stress difference exhibited an overshoot and then reached steady-state values that are in good agreement with those measured under protocol A.

The results of a similar experiment at 124 °C are shown in Figure 14. The fluorescence intensity reached a steady state value of 3.2 in the phase-separated state, and after introduction of the flow at a shear rate of 8 s^{-1}, the fluorescence dropped rapidly to a new steady state at an intensity of 1.7; this is quite close to the value shown in Figure 10 at the same temperature and shear rate. The time scale for demixing after cessation of flow is on the order of 100 s when the original intensity is regained. The dynamic evolution of the stresses was similar to that discussed above.

Discussion

The phenomenon of static quenching of the fluorescence emission of anthracene-labeled polystyrene by poly(vinyl methyl ether) has been used extensively to study the equilibrium-phase behavior of PS/PVME blends. In this study, this technique is used as an important part of in situ measurements in shear flow for the first time. We concentrate on the rheology in the single-phase region where it is well-defined and use the fluorescence measurements to provide an early and sensitive detection of phase separation. The fluorescence intensity in the two-phase region has not yet been related to an interfacial length scale and hence cannot be interpreted quantitatively.

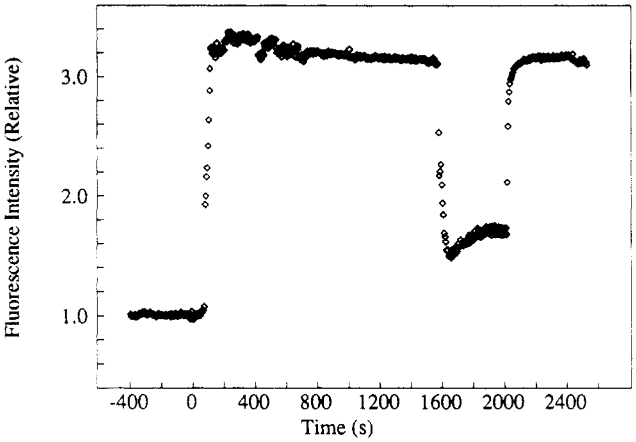

Figure 14. Evolution of the relative fluorescence intensity in isothermal experiments (protocol B) for a 60/40 PS/PVME blend at 124 °C and a shear rate of 8 s^{-1}. The heating was started from an initial temperature of 90 °C at $t = 0$ and shear flow at a rate of 2 s^{-1} was imposed from 1500 to 2000 s. The steady-state intensities should be compared to those in Figure 10.

The fluorescence intensity was stable and the transition was quite sharp and easily identified; reproducibility was also satisfactory. At high heating rates the fluorescence intensity during phase separation was lower, possibly on account of the relatively slower kinetics of phase separation. The difference in the spinodal and the binodal temperatures for the three compositions studied was 2–3 K, in quantitative agreement with the results reported by Halary and Monnerie[4] on a similar PS/PVME blend.

The in situ fluorescence measurements in shear flow were stable and comparable in signal-to-noise ratio to the quiescent measurements. Even at shear rates as high as 8 s^{-1}, the stability of the intensity was satisfactory. Protocol A was designed to measure the coexistence temperature under steady shear flow. Shear flow at a constant rate was imposed during a slow heating of the sample from below its LCST so that the flow would attain a steady state by the time the sample reached the quiescent spinodal temperature. The results from protocol A indicate that shear flow increases the apparent coexistence temperature and extends the single-phase region. It is interesting that shear rates as small as 1 s^{-1} shift the apparent phase transition temperatures beyond the quiescent spinodal temperature and seem to suppress the nucleation and/or growth rates, as suggested by Onuki.[19]

The introduction of shear flow at higher shear rates resulted in an increase in the fluorescence intensity as well as a higher steady value of the intensity, indicating a *flow-induced demixing* in blends with higher polystyrene content. For the shear flow experiments using protocol A, there is a slight increase in the fluorescence at relatively low temperatures and higher shear rates in the early stages of the flow for the 40/60 and the 60/40 samples, e.g. Figures 9 and 10. The origin of this early increase in fluorescence is unclear. There are previous reports of shear-induced demixing in a PS/PVME blend below the LCST.[9,10] On the other hand, it is also known that this blend undergoes some concentration fluctutations of large amplitude at zero shear and near the spinodal[5] and the effect of shear

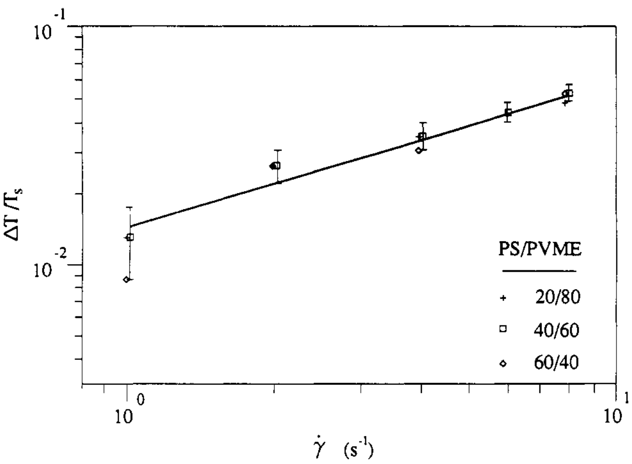

Figure 15. Increase in the apparent coexistence temperature above the quiescent spinodal temperature normalized by the quiescent spinodal temperature as a function of shear rate for three blend compositions.

may be to amplify these fluctuations except for off-critical blends such as the 20/80 sample, where nucleation and growth may dominate. A more detailed study of the microstructure under these conditions is desirable.

Several studies suggest that shearing near the LCST induces an anisotropic-phase structure where the concentration fluctuations along the shear direction are strongly suppressed.[17] We emphasize that in the work described here, we use the fluorescence measurements exclusively as an early detection of demixing and we cannot offer a quantitative interpretation of the data for the later stages of phase separation, where scattering could be used to yield information on the domain sizes and distribution.

The results from the isothermal measurements (protocol B) were complementary to those from protocol A, indicating the samples in the latter case had negligible thermal gradients at the slow heating rates applied here. For relatively small temperature jumps into the two-phase region, the results indicate that there is a critical shear rate that induces mixing. The increase in the apparent coexistence temperature above the quiescent spinodal temperature is plotted as a function of shear rate and composition in Figure 15. Within the experimental error (~1 K), the apparent phase transition temperature can be correlated with the shear rate, is independent of the composition, and can be represented by $\Delta T/T_s = (0.015 \pm 0.002)\dot{\gamma}^{0.59\pm0.-4}$. To our knowledge, this is the first quantitative report of the composition dependence for the reationship between the shift in coexistence temperature and the shear rate for miscible polymer blends. This result was independent of the time for which the sample was held in the two-phase region before commencing the flow, and shear rates higher than the critical value were equally effective in mixing. The shear-induced mixing is very rapid but the time scale for demixing is relatively long on account of the absence of flow in the latter case. A square-root dependence of the shift in apparent phase transition temperature on the shear rate was first observed in critical fluids with low molecular weights by Beysens et al.[1] Hashimoto et al.[6] found a shear-induced homogenization for polystyrene and polybutadiene in dioctyl phthalate; the dependence on shear rate was similar but the composition dependence was not investigated.

In critical binary fluids, in the weak shear case, Onuki[19] predicted a viscosity increase due to phase separation and a strong normal stress effect. In contrast, we find a significant increase in the viscosity only at low polystyrene content and at relatively high shear rates, although the normal stress does seem to be more sensitive to the phase separation in qualitative agreement with the predictions.

Motivated by an analysis of dilute solutions of elastic dumbbells by Marrucci,[15] Rangel-Nafaile et al.[20] modeled the nonequilibrium-phase behavior of a polymer solution by adding the first normal stress difference to the Flory–Huggins free energy of macromolecules in stagnant solution. This approach was successful in predicting the experimentally observed changes in temperature of 3–28 K, with no adjustable parameters to account for the flow. In this study on PS/PVME blends, we have not yet found a simple correlation between the shift in the coexistence temperature and the shear stress or the first normal stress difference measured at the coexistence temperature.

A comparison of the in situ fluorescence measurements with the shear stress and first normal stress difference shows that the apparent coexistence temperature could not be accurately determined by use of stresses alone and the sensitivity of the fluorescence measurements is highly desirable in detecting the phase separation. At low shear rates, N_1 exhibited a significant change in the slope above the coexistence temperature but the shear stress was insensitive to the phase transition. At higher shear rates and especially at high polystyrene content, the shear stress and first normal stress difference were both insensitive to the transition. A noteworthy feature was that at temperatures of about 5–10 K higher than the coexistence temperature the stresses all decreased rapidly.

Conclusions

In situ fluorescence measurements have been successfully performed during shear flow of a binary miscible blend of polystyrene and poly(vinyl methyl ether) in a cone and plate rheometer. The high sensitivity and versatility of the technique allows a simple design, stable fluorescence signals, and easily identified phase transitions. The apparatus provides good temperature control, has no strain limitations, and is rugged and versatile for several rheospectroscopic measurements. This approach is substantially simpler and less expensive than the small-angle neutron scattering technique, which has sensitivity at comparable length scales. However, the fluorescence measurements described here cannot provide quantitative information on the microstructure as can be deduced from scattering results; the rotational rheometer is also limited to moderate shear rates in order to maintain stability of the flow.

For the PS/PVME system under study, the shear rate is the most convenient parameter to correlate the effect of flow near the LCST. The apparent phase transition temperature increases with slightly more than a square-root dependence on the shear rate and is independent of the composition. The results in Figure 15 can be summarized by $\Delta T/T_s = (0.015 \pm 0.002)\dot{\gamma}^{0.59\pm0.04}$.

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