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Fluorescence Evidence of Shear Flow-Induced Miscibility in a Blend of Polystyrene and Poly(vinyl methyl ether)

Introduction. Flow may cause molecular mixing of an otherwise phase-separated polymer blend, at least at temperatures near the coexistence temperature. It has been observed that polymer blends become transparent in shear[1] and in planar extension.[2] This was attributed to a transition from a phase separated to a molecularly mixed state. However, the optical transition can be equally well-explained by a size reduction of the composition fluctuations instead of mixing on a molecular scale. This question will be resolved in this study, using the fluorescence quenching technique[3,4] with PS/PVME as a model polymer blend.

The few early studies of the effect of flow on polymer blends (without solvent) conclude that shear and extension increase blend miscibility. Mazick and Carr[1] observed that the lower critical solution temperature (LCST) of a PS/PVME blend increases by 2–7 K at shear rates of 0.1–20 s^{-1}. Katsaros et al.[2] stretched a similar blend in a planar stagnation flow and found that an extensional field at extension rates of about 1 s^{-1} induces miscibility up to 10 K above the cloud point. Lyngaae-Jörgensen and Söndergaard[5] found a homogeneous structure in a sheared blend of SAN and PMMA above the LCST. However, their shear rates were extremely high ($>10^3$ s^{-1}). The effect of flow seems to differ for polymer solutions, for which most of the reports[6-10] indicate that flow narrows the miscibility gap.

In our experiments, using flow between parallel disks, we have prepared transparent blends by shearing samples above the LCST where they were initially phase separated. However, the question remained whether shear flow actually mixed the blend on a molecular level or if it simply reduced the composition fluctuations to a small scale, too small to scatter light. The decisive answer will be given by applying a fluorescence quenching technique[3,4] to our experiment.

Experiment. Materials. Polystyrene, M_w = 348.000, polydispersity = 1.9, supplied by Monsanto (Lustrex 101) was blended with poly(vinyl methyl ether), M_w = 48 000, polydispersity = 1.9, at weight ratios between 15 and 85 wt % PS. A labeled polystyrene, PS*[11] (chains of molecular weight 300 000 contain dimethylanthracene fluorescent groups in their middle), was added for this study. The PS* chain concentration was less than 7 ppm of anthracenic units to prevent any undesired intermolecular energy transfer.

Shear Flow. Samples were sheared on a Rheometrics mechanical spectrometer using parallel disks with a diameter of $2R$ = 25 mm. Disposable disks were used so that the sample could be removed quickly (15–30 s after the cessation of shear) from the shaft and the quenched below the glass transition temperature. A shear rate of $\dot{\gamma}_R$ = 0.16 s^{-1} was applied for 4 min (sample A) and 12 min (sample B), 3 K above the cloud point temperature ("*" in Figure 2). In this geometry, the shear rate is a linear function of the radius:

$$\dot{\gamma}(r) = \dot{\gamma}_R r/R$$

The shear rate is maximum at the outer edge ($r = R$) and decreases to zero at the center of the disk ($r = 0$).

Digitized Image. White light transmission pictures of the samples were obtained on Kodak SO 163 film. This film was digitized with an array of 256 × 256 pixels on an Optronix digitizer with an aperture of 100 μm and digitized step of 100 μm.

Fluorescence Emission and Transmission. Fluorescence emission measurements were performed under continuous illumination on a microscope developed at Laboratoire PCSM. PS* excitation and fluorescence emission were probed at wavelengths around 365 and 440 nm, respectively, by means of filters. The diameter of the illuminating beam was 1 mm. Fluorescence intensities were measured at nine radial positions r/R = 0, 0.2, 0.4, 0.6, and 0.8 of the disk-shaped samples.

Transmittance measurements as a function of r/R were carried out on the same equipment, by inserting identical filters (365 nm) on both excitation and emission beams. Fluorescence intensities were normalized by the maximum value at $r = 0$ and were corrected in order to take into account the thereby observed changes in turbidity. Data were also corrected for the changes in specimen thickness along the diameter, but this effect is actually very small.

Results and Discussion. Cloud Point Temperature with Constant Shear Stress. In order to have a macroscopic idea about the influence of the shear flow on the apparent phase diagram, we use a cone and plate apparatus, keeping the shear stress constant. From the one-phase region (20 K below the cloud point temperature at quiescent state), the temperature was slowly increased, and the changing viscosity, η, at constant shear stress was measured. Phase separation results in an upturn of the viscosity–temperature curve. Additional information is given by optical clarity of the sample.

The viscosity–temperature plot changes its slope at the transition from phase separated to mixed state. Typical results for a 44/56 PS/PVME mixture are shown in Figure 1. Other compositions from 15% to 75% (wt) PS show a similar behavior, and the apparent "cloud points" depend on the stress level, as shown in Figure 2. These data were obtained with a slow heating rate of 0.3 K/min and a reproducibility of about ±1 K. The upward shift of the phase diagram increases with the applied shear stress.

Digitized Image Analysis. The optical density variation of the sample is presented in Figure 3, in terms of

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Table I
Experimental Data. Shearing Times of 4 min (Sample A) and 12 min (Sample B)

UV beam position r/R	thickness, μm A	thickness, μm B	transmission, arbitrary units A	transmission, arbitrary units B	detected fluorescence, arbitrary units A	detected fluorescence, arbitrary units B	corrected fluorescence, arbitrary units A	corrected fluorescence, arbitrary units B
+0.8	850	990	581	1831	120	117	63	11
+0.6	870	1000	227	790	110	124	148	26
+0.4	870	1000	107	172	116	117	336	112
+0.2	880	1000	55	27	116	124	650	759
0	880	1000	39	21	126	130	1000	1000
−0.2	880	990	52	39	119	130	718	546
−0.4	880	980	96	141	116	135	377	160
−0.6	880	970	174	544	112	129	201	40
−0.8	870	950	273	962	114	80	128	14

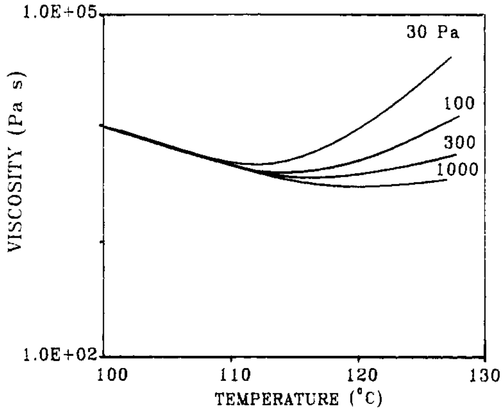

Figure 1. Plots of viscosity versus temperature for 44% wt PS sheared at different stress levels (cone–plate).

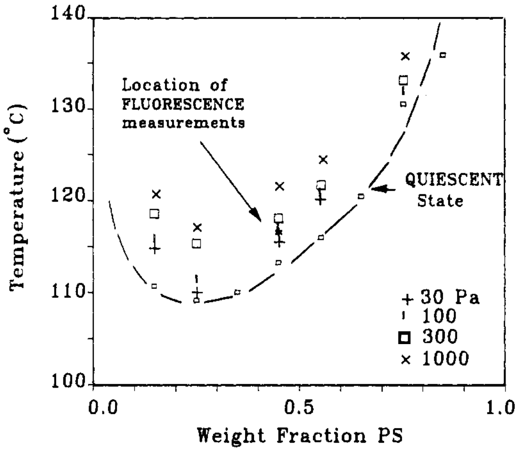

Figure 2. Cloud point temperature of PS/PVME blends and viscometrically determined coexistence temperatures at different stresses (from Figure 1).

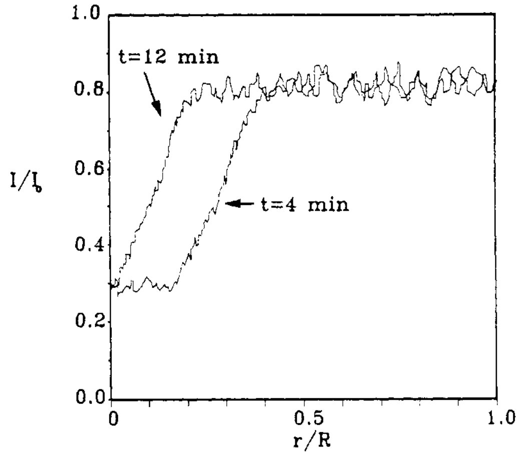

Figure 3. Optical density variation along the radii of samples A and B.

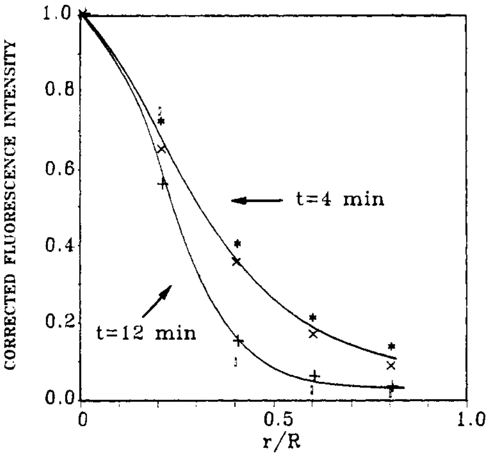

Figure 4. Radial distribution of fluorescence intensity (corrected).

the relative intensity I/I_0 as a function of r/R. We find two plateaus on each curve and a gradual transition at radial positions which correspond to shear rates between 0.03 and 0.067 s^{-1} after 4 min (or between 0.003 and 0.35 s^{-1} after 12 min). The transparent region widens with shear rate, i.e., the transition shifts to a lower shear rate which corresponds to the reduction of radius. The high transparency in the outer region suggests a homogeneous structure with a characteristic scale of 1 μm or less, including the possibility of molecular mixing. Under the applied shear stress, the two-phase domains may break up into droplets of the discontinuous suspended phase.[7,8] This effect should be most pronounced at the outer edge where the shear stress is maximum.

In the transition region from opaque to clear, the sample becomes orange. The transmitted light is selectively scattered by the two-phase structure.

Fluorescence Emission Analysis. The fluorescence decays steeply from the center to the outer edge of the sample, as shown in Figure 4. These data were averaged from four measurements (Table I). In such experiments, a decrease of fluorescence intensity means that the PS* labels are within about 5 Å of an ether group of the PVME.[3] The higher the shear rate (increasing values of r/R) and the longer the shearing time, the more advanced is the mixing.

Actually, complete quenching of fluorescence emission would require that all PS* are in close contact with PVME molecules, which is not achieved even in a perfectly mixed sample. The lowest possible fluorescence value was measured on samples after annealing for 48 h at 3 K below the cloud point temperature in the one-phase region. The corrected fluorescence intensity was 14 ± 5 (same relative units as in Table I). This shows that sample B at $r/R > 0.8$ is molecularly mixed while sample A is just barely mixed at the outer edge.

Conclusions. The present fluorescence data, which overcome the size problem of the previous optical studies, confirm that shear flow may induce mixing on a molecular scale. The flow increases the mutual miscibility of the pair PS/PVME.

The size of composition fluctuations does not collapse abruptly at a critical shear rate, but it is gradually reduced over a range of shear rates. The transition sharpens with increased shearing time, and it moves to lower shear rates. The width of the transition may be attributed to the broad distribution in molecular weight of both polymers and, possibly, to variations in the tacticity of the PVME.

Optical clarity is found to be an indication for mixing on a molecular scale, but it is not a conclusive test. As can be expected, the transition from an opaque to an optically clear blend occurs at a smaller radius (lower shear rate) than the fluorescence quenching transition. Regions of the sample were found to be transparent for white light and, at the same time, strongly fluorescent. In this case, the size of the composition fluctuations simply was below the wavelength of visible light and above the molecular scale.

Our studies are limited to PS/PVME for which the fluorescence quenching phenomenon occurs so conveniently. The method may be extended to other blends by using donor/acceptor tracers[12,13] on the molecules.

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Registry No. PVME, 9003-09-2.

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Observation of Penultimate Effect by ESR of the Model-Propagating Acrylate Radical

The penultimate effect[1] in radical copolymerization has been the subject of considerable debate for a long time in connection with the propagation models such as complex[2] and terminal[3] ones. It is well-known that the copolymerization systems which are reasonably explained by the penultimate model have often contained nitrile monomers as a comonomer.[4] Tirrell and co-workers[5] demonstrated a remarkable reduction of reactivity of the radical bearing a cyano group in a penultimate unit for the attack of acrylonitrile by simple model copolymerization reaction of acrylonitrile and styrene. They explained such reduction by the development in the transition state of dipolar repulsion between cyano groups on the monomer and radical. Recently it has been pointed out by kinetic study that the penultimate model may be a general one applicable to copolymerization systems not involving acrylonitriles such as styrene/methyl methacrylate (MMA)[6] and *p*-chlorostyrene/methyl acrylate[7] systems.

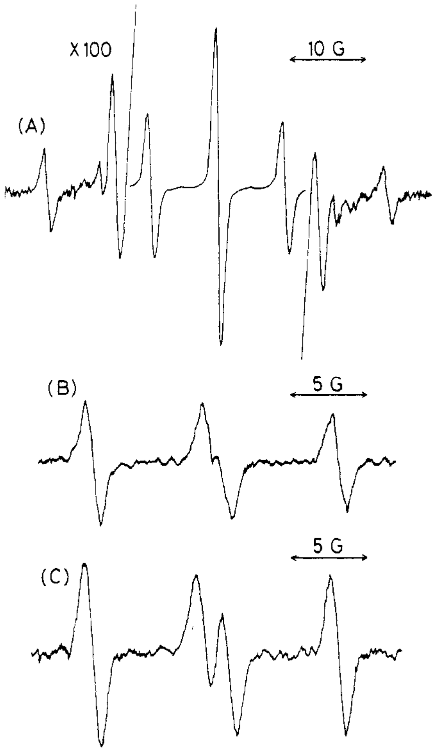
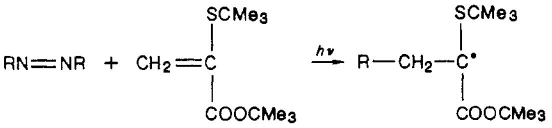


Figure 1. ESR spectra of the radical I in chlorobenzene at 24 °C. (A) R = CMe_3, (B) R = $Me_2CHCH_2C(CN)Me$, (C) R = $Me_2C(OMe)CH_2C(CN)Me$.

Thus far, the debate has been about direct spectroscopic observation of a penultimate effect and the elucidation of its origin. We will demonstrate here that the electronic and conformational structures of a radical itself are indeed sensitive to the nature of the substituent at a penultimate unit and even at a penpenultimate unit by ESR of the model-propagating acrylate radical I.



$$RN{=}NR + CH_2{=}\overset{\overset{\displaystyle SCMe_3}{|}}{\underset{\underset{\displaystyle COOCMe_3}{|}}{C}} \xrightarrow{h\nu} R{-}CH_2{-}\overset{\overset{\displaystyle SCMe_3}{|}}{\underset{\underset{\displaystyle COOCMe_3}{|}}{C^\bullet}}$$

I

Radical I was generated by the photoreaction of *tert*-butyl α-*tert*-butylsulfenylacrylate[8] and corresponding azo compounds in chlorobenzene in an ESR cell under an atmosphere of nitrogen at 24 °C.[9] Figure 1 shows the typical ESR spectra of relatively stable radical I, which gives rise to intense ESR spectra permitting resolution of ^{13}C hyperfine splitting (hfs) in natural abundance presumably because of the captodative substituent effect.[10] In spectrum A (R = CMe_3 in radical I), α-^{13}C satellite lines are also observed in the wings of the spectrum as well as the central 1:2:1 triplet due to the splittings by two

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