Detection of Composition Heterogeneities in a Miscible Pair by ESR Spectroscopy: Poly(styrene-*co*-maleic anhydride)/ Poly(methyl vinyl ether) Blends and Semiinterpenetrating Polymer Networks

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ABSTRACT: The compatibility of the two components in semiinterpenetraing polymer networks (semi-IPNs) and corresponding linear blends was studied using the nitroxide spin-label and spin-probe methods. The semi-IPNs and blends were composed of poly(styrene-*co*-maleic anhydride) (P(S-*co*-MA)) and poly (methyl vinyl ether) (PVME). Stable nitroxide radicals as reporters were covalently attached to P(S-*co*-MA) via the maleic anhydride groups ("spin labels") or dispersed in the system ("spin probes"). Electron spin resonance (ESR) spectra were measured at the X band as a function of temperature and composition. The results obtained for the spin *probe* show that the molecular reporter is not sensitive to variations in the surrounding matrix; therefore no conclusions on the dynamics of the polymer system can be deduced from the ESR spectra. In contrast, the mobility of the spin *label* is sensitive to the segmental dynamics of P(S-*co*-MA): While only one spectral component is detected in the case of pure labeled (P(S-*co*-MA), two spectral components are observed for all blends and semi-IPNs, indicating dynamically different molecular environments for the P(S-*co*-MA) segments. The two spectral components are observed even in the miscible region, ≈50–60 K below the corresponding cloud-point temperatures. These results reflect fluctuations in the local composition of the mixtures, on a molecular scale <50 Å. The introduction of covalent cross-links in the semi-IPNs results in damping of these concentration fluctuations. The correlation times (τ_c) of the spin labels were related to the dynamics of the systems studied and to macroscopic properties such as T_g.

Introduction

Important polymer properties such as elastic moduli and thermal expansion coefficients, as well as translational diffusion coefficients of small molecules in polymeric hosts, change markedly in the glass transition region. These changes are closely related to the nature of molecular motions of the polymer chains in the vicinity of the glass transition temperature (T_g). Spin probes and spin labels have been widely used to obtain information about relaxation and transport processes in polymers. These reporters are paramagnetic species, commonly stable nitroxide radicals, which are dispersed ("spin probes") or covalently attached to the polymer matrix ("spin labels"). The electron spin resonance (ESR) spectrum of the nitroxide radical is a function of its rotational motion and is sensitive to the nitroxide mobility, with correlation times (τ_c) in the range 10^{-7}–10^{-11} s. Numerous studies have indicated that the mobility of the nitroxide radicals is related to the dynamics of the host polymer. While this correlation appears valid in the case of the spin labels, questions remain on how useful are the results obtained using spin probes.[1,2]

ESR spectra of spin labels reflect different environments in a given sample if the respective rates of motion are different.[3–5] If the nitroxide molecules are located in both phases of the heterogeneous two-component polymer system, the ESR spectra are composed of two components differing in their correlation times. This spectroscopic technique allows a close look into structural heterogeneities in multicomponent polymer systems, on a length scale too small (<50 Å) to be observed by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), or electron microscopy. The spin-label method has been applied to the study of phase separation in semi-IPNs based on a polyurethane network formed in the presence of linear poly(vinyl chloride) (PVC).[4]

We present the application of the spin-probe and spin-label methods to the study of dynamics and local phase behavior in the miscible polymer pair polystyrene (PS) and poly(vinyl methyl ether) (PVME). In order to attach a stable radical to the PS backbone, we used a copolymer of polystyrene with a small amount of maleic anhydride (MA) groups (4.8 wt %) and an amino-functionalized nitroxide radical. The labeling reaction is shown in Scheme 1. A small amount of MA groups appear to have a negligible effect on the phase behavior of this system: as in the case of PS/PVME mixtures, the MA-containing blends show a lower critical solution temperature (LCST).[6]

In previous publications, we have shown that poly(styrene-*co*-maleic anhydride) (P(S-*co*-MA)) can be cross-linked by the reaction of the MA groups with diamines.[7,8] In the present study, 4,4′-diaminodiphenyl methane (DADPM) was used as the cross-linking agent. The cross-linking density was controlled by the amount of added diamine. Semiinterpenetrating polymer networks (semi-IPNs) were obtained by cross-linking the copolymer in the presence of PVME. A schematic representation of the cross-linking reaction is shown in Scheme 2.

The present study was initiated with **four** main objectives. **First**, we were interested in comparing the sensitivity of spin probes and spin labels to the local dynamics and to the composition of the system. **Second**, we wanted to understand on the molecular level whether the broad glass transition regions obtained in P(S-*co*-MA)/PVME

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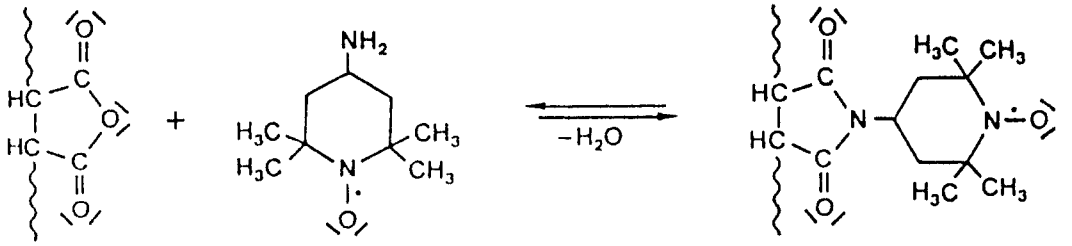
Scheme 1. Labeling of the P(S-*co*-MA) Copolymer with 4-Amino-TEMPO



Scheme 2. Cross-Linking of P(S-*co*-MA) in the Presence of Diamines

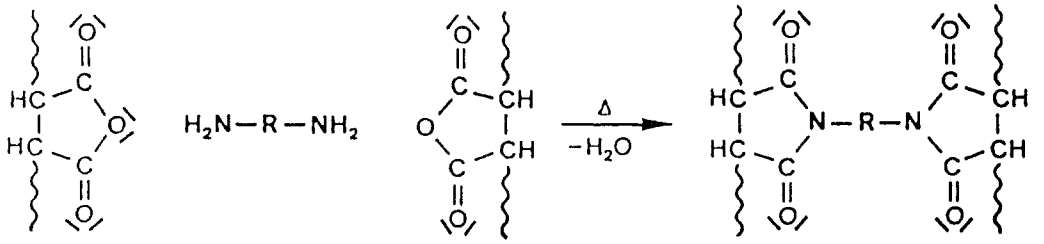


Table 1. Characterization of the Polymers

polymer	M_n/g mol^{-1}	M_w/M_n	T_g/K
P(S-*co*-MSA)	90 000[a]	2.3[a]	381[b]
PVME	35 000[a]	1.6[a]	248[b]

[a] GPC. [b] DSC.

blends and semi-IPNs via DSC and DMA reflect a local dynamic heterogeneity, although the glass transition temperatures are well below the onset of phase separation.[8] **Third**, we wanted to compare the ESR results deduced from spin-labeled PS in PVME/PS blends with evidence of local heterogeneities derived from fluorescence measurements,[9] NMR,[10,11] and dielectric relaxation experiments[12] as well as by the observation of a thermorheological complex behavior in the DMA analysis.[7,8] **Fourth**, we wanted to evaluate the influence of cross-linking of the PS chains on the local structure in PVME-*cross*-PS semi-IPNs and to compare it with the corresponding blends.

Selected initial results have been reported.[8]

Experimental Section

Materials. Laboratory-grade PVME from BASF (M_n = 16 000, M_w/M_n = 3) was fractionated to obtain a polymer of narrow molecular weight distribution. Technical-grade P(S-*co*-MA) with a maleic anhydride content of 4.8 wt % was purified by dissolution in toluene, precipitation in isopropyl alcohol, and vacuum drying. Some analytical data of the starting polymers are given in Table 1. All solvents (analytical grade) and DADPM were used as received.

Spin-Labeled P(S-*co*-MA). The labeling was done by mixing 100 mL of a 5 wt % solution of P(S-*co*-MA) in toluene with 10 mL of a toluene solution containing 7 mg of 4-amino-2,2′,6,6′-tetramethylpiperidinyl-1-oxyl (4-amino-TEMPO, from Aldrich). The mixture was stirred for 2 days and precipitated in isopropyl alcohol. To remove unreacted radicals from the polymer matrix, the procedure of dissolving and reprecipitation of the labeled copolymer was repeated at least 4 times. Isopropyl alcohol was used for precipitation during the cleaning process, because it is a good solvent for the amino-functionalized nitroxide radicals. The line width of the ESR signal was measured to check the correct label concentration and to prevent line broadening due to magnetic dipolar interactions.

Preparation of Labeled Blends and Semi-IPNs. A typical experimental procedure is given for the preparation of a semi-IPN containing 50 wt % P(S-*co*-MA): 1 g of labeled P(S-*co*-MA) (=4.8 × 10^{-3} mol of repeating units) and 1 g of PVME were dissolved in 8 mL of toluene. To get a degree of cross-linking of 1 mol % with respect to P(S-*co*-MA), 9.8 mg of DADPM was dissolved in toluene. The two solutions were mixed and the homogeneous reaction mixture was poured into a flat-bottomed petri dish. Gelation occurs after ≈40 min. The solvent was slowly evaporated, and the resulting films were further dried under vacuum for 2 weeks. The blends were prepared in the same way but without the cross-linking agent.

Preparation of Spin-Probe Samples. For the preparation of these samples, 5 g of polymer was mixed with 7 mg of 2,2′,6,6′-tetramethylpiperidinyl-1-oxyl (TEMPO, from Aldrich) in toluene. The solvent was slowly evaporated, and the resulting films were further dried under vacuum for 2 weeks. TEMPO was chosen because it contains no functional groups and cannot be covalently attached to the two polymeric components.

ESR Measurements. Spectra were measured at the X band with a Bruker 200 D SRC spectrometer operating at 9.7-GHz and 100-kHz modulation. Data acquisition was controlled by an IBM PC/XT and the software EPRDAS. Spectra as a function of temperature were measured with the Bruker variable-temperature unit ER 4111 VT. The absolute value of the magnetic field was controlled using the Bruker ER 035 M NMR gaussmeter. Calibration of g values was based on Cr^{3+} in a single crystal of MgO (g = 1.9796). All samples were allowed to equilibrate for at least 10 min after approaching the corresponding temperature. Typical parameters for spectra acquisition were as following: modulation amplitude 0.5–1 G, microwave power 2 mW, sweep width 200 G, scan time 50 s, time constant 10 ms, 4096 points, and 10 scans.

Results

ESR spectra of the spin labels and spin probes in blends with different compositions were measured in the temperature range 100–430 K at intervals of 10 K or less. Selected spectra are shown in Figure 1 for the spin-labeled pure copolymer P(S-*co*-MA) and a blend with a PVME content of 60 wt % and in Figure 2 for the corresponding spin-probed systems. The temperature dependence of the spectra is due to changes in the rotational rate of the nitroxide radical, characterized by the correlation time (τ_c). The two motional regimes usually detected in ESR experiments correspond to the slow motional spectra, with correlation times in the range of 10^{-7}–10^{-9} s, and the "averaged" or motionally narrowed spectra, with τ_c in the range 10^{-9}–10^{-11} s.

The spectra of pure spin-labeled P(S-*co*-MA) in Figure 1a are characteristic of a label in one type of environment. At low temperatures (slow-motion regime), the ESR spectrum approaches the rigid limit spectrum, with a characteristic separation between the two outer peaks (extreme separation, or $2A_{zz}$) of about 70 G. With increasing temperature, the spectral lines narrow and the outer peaks shift inwards. The mobility of the nitroxide radicals in pure P(S-*co*-MA) does not reach the motionally

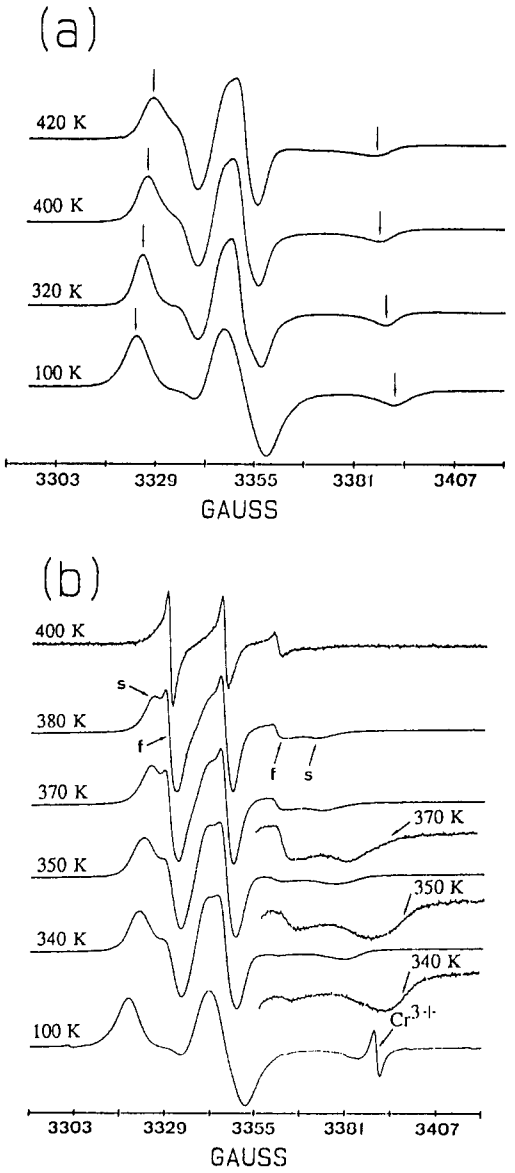


Figure 1. X-band ESR spectra as a function of temperature for (a) pure spin-labeled P(S-*co*-MA) and (b) spin-labeled P(S-*co*-MA) in a blend containing 60 wt % PVME. The extreme separation $2A'_{zz}$ is the interval in G between the vertical bars. Two spectral components are observed in the blend at some temperatures and are marked with "s" (slow) and "f" (fast), respectively. Vertically expanded portions of some spectra are also shown and are shifted with respect to the corresponding full spectra.

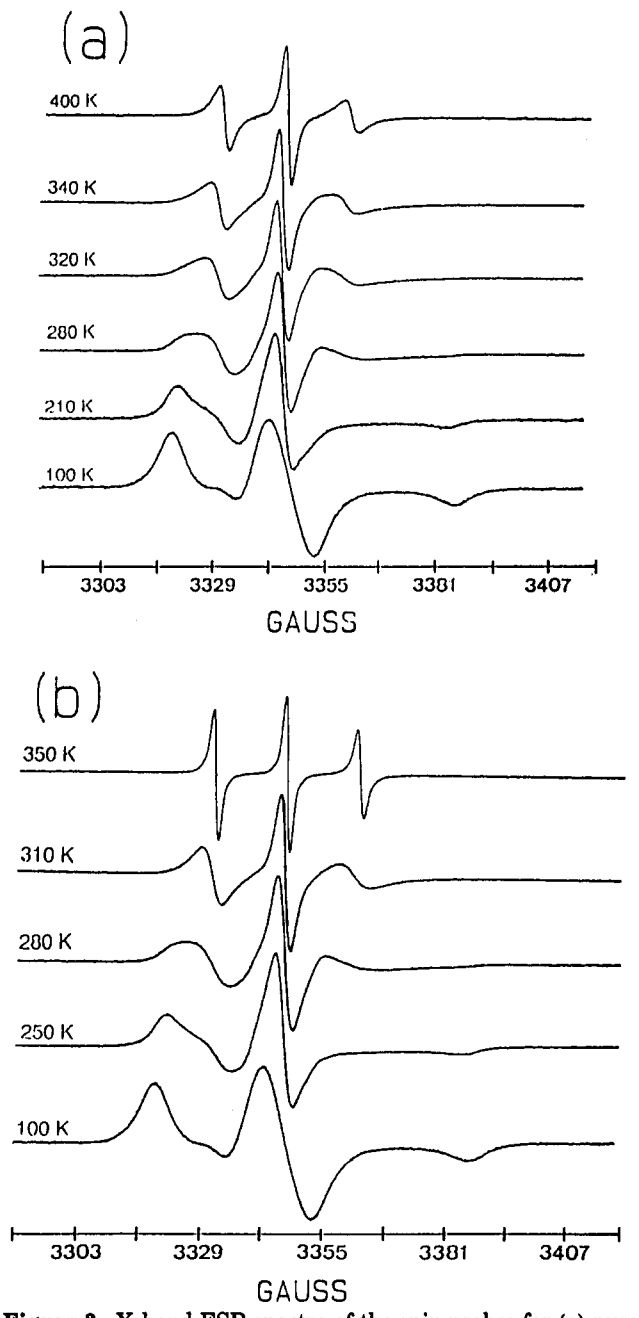


Figure 2. X-band ESR spectra of the spin probes for (a) pure P(S-*co*-MA) and (b) spin-labeled P(S-*co*-MA) in a blend containing 60 wt % PVME.

narrowed regime in the experimentally accessible temperature regime, which is limited by degradation of the radical at high temperatures.

The ESR spectra of spin-labeled P(S-*co*-MA) in a blend with 60 wt % PVME (Figure 1b) in the low-temperature region are similar to the spectra of pure spin-labeled P(S-*co*-MA), Figure 1a. In the range 340–390 K, however, the spectra are composed of two components differing in their outer peak splitting and line shapes. These two spectral components are attributed to nitroxide radicals with different mobilities. At even higher temperatures ($T >$ 390 K), the two components are not clearly separated. We will give a molecular explanation for the observed spectral splitting below.

The spectra of the spin probes in pure P(S-*co*-MA) (Figure 2a) and in the blend (Figure 2b) differ mainly at higher temperatures, compared to the spectra of the spin-labeled analogues. The outer peaks splitting $2A'_{zz}$ is significantly reduced with increasing temperature compared to the labeled systems, indicating a higher mobility of the spin probe in the polymer matrix. In contrast to the spin-labeled P(S-*co*-MA), the spectra of the spin probes show, especially for pure P(S-*co*-MA) at higher temperatures, a central line of higher amplitude, suggesting a dynamic anisotropic state of rotation.[13] Only one spectral component in the P(S-*co*-MA)/PVME blend is observed for the spin probes in all systems.

The variation of $2A'_{zz}$ as a function of temperature for all measured systems is shown in Figure 3. The variation of the outer peaks splitting for pure labeled P(S-*co*-MA) in the experimental temperature range is rather small, indicating that the dynamics of the polymer does not change markedly in this temperature range. Above 400 K, $2A'_{zz}$ decreases, indicating the onset of motional narrowing.

The extreme separation for spin-labeled P(S-*co*-MA) in the blends at low temperatures is similar to that in pure P(S-*co*-MA). However, at a characteristic temperature T_h, the outer peaks splitting decreases strongly with

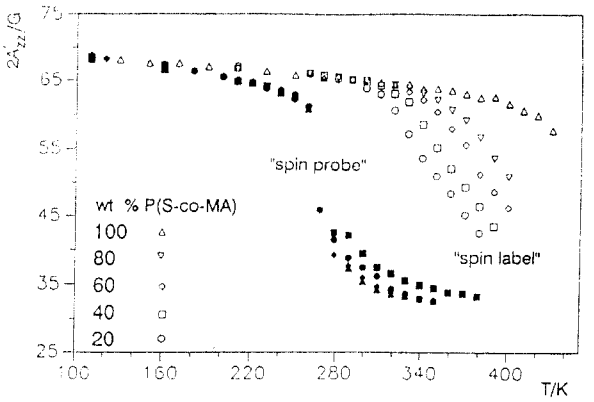


Figure 3. Outer peaks splitting $2A'_{zz}$ as a function of temperature for spin-labeled P(S-*co*-MA) and spin probes in different blends.

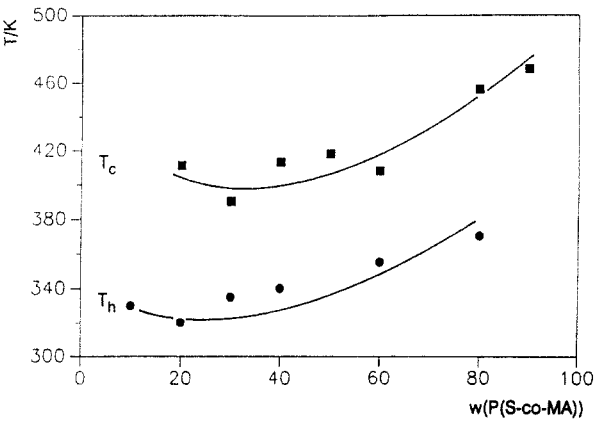


Figure 4. T_h and T_c as a function of composition for P(S-*co*-MA)/PVME blends.

increasing temperature. The transition is shifted to lower temperatures with increasing PVME content in the system. This effect reflects the increased mobility when PVME is added and is analogous to the decrease of the glass transition temperature with increasing PVME content in the blends.

The variation of the extreme splitting of the spin probes with temperature (Figure 3) differs significantly from the behavior of the labeled systems. The break in the $2A'_{zz}$ vs T curves occurs, however, at the same temperature for all examined blends, suggesting that the probe is insensitive to composition variations. This insensitivity to composition explains the presence of only one spectral component in systems containing the spin probes. For these reasons, the probe results will not be considered further, and all the conclusions presented in this paper are based on the spin label results.

Discussion

In this section, we will consider the local dynamical and composition heterogeneities in the blends, the comparison between the blends and the semi-IPNs, the correlation between T_g and T_{50G}, and the dynamics in the blends in the slow-motional regime, based on the correlation times (τ_c) calculated from the ESR spectra.

1. Local Heterogeneity in P(S-*co*-MA)/PVME Blends. The ESR spectra of pure spin-labeled P(S-*co*-MA) consist of only one spectral component over the entire temperature range. The observation of *two* spectral components in the blends indicates that the P(S-*co*-MA) segments exist in dynamically different molecular environments due to local composition fluctuations in the blend.[8] The labeled P(S-*co*-MA) copolymer segments exist in a PVME-rich, more flexible, environment, resulting in a high mobility of the label *and* in a P(S-*co*-MA)-rich, more rigid matrix.

The occurrence of two spectral components differing in their mobility above the characteristic temperature (T_h) is observed for all blends. The temperatures T_h, together with the cloud-point temperatures (T_c) obtained from light scattering for the same system,[6] are plotted as a function of blend composition in Figure 4. Both T_h and T_c show a similar dependence on the composition, but the T_h values are shifted to lower temperatures. The approximate temperature difference between T_h and T_c is ≈70 K, well above the experimental uncertainty in the determination of T_h.

In order to detect inhomogeneities in a sample by light scattering, the size of the separated domains must be of the order of the wavelength λ, or ≈200 nm. The ESR method is more sensitive and is able to uncover heterogeneities on a molecular scale <50 Å.[4] The present results suggest that composition heterogeneities exist in P(S-*co*-MA)/PVME blends on a molecular scale even at temperatures far below the binodal curve. The ESR results are in agreement with spin-diffusion NMR experiments, where the suggested range of homogeneities is ≈30 ± 15 Å.[11]

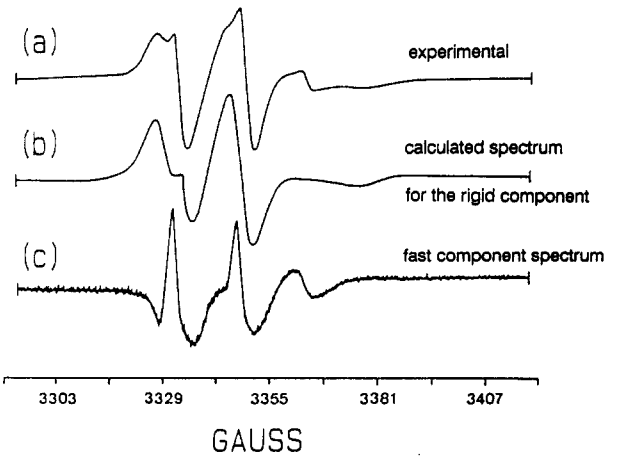


Figure 5. (a) Experimental spectrum of labeled P(S-*co*-MA) in a blend containing 60 wt % PVME, (b) simulated spectra of the rigid component, and (c) resulting spectrum after subtraction of b from a.

A study of PS/PVME blends using fluorescent probes suggested that the two blend components (PS and PVME) possess different chain dynamics in the homogeneous region of the PS/PVME phase diagram.[9] The ESR results presented here uncover the existence of varying segment mobilities within one polymeric component, the P(S-*co*-MA) copolymer. A similar dynamic inhomogeneity is expected to exist for the second blend component (PVME) but has not been detected in our experiments because only the copolymer was spin labeled.

Spectral simulations were used to obtain quantitative information about the relative content of the "fast" and "slow" component in the superposed spectra in the blends and semi-IPN's. For this purpose, we simulated the spectra of the "rigid" component using a simulation program of Freed et al.[3] and subtracted this component from the complex spectra in which two components were detected. The isotropic Brownian diffusion model was used in the simulations. The principal values of the ^{14}N hyperfine and g tensors of the amino-functionalized nitroxide radical in the P(S-*co*-MA) matrix were obtained from the simulation of the spectra in the rigid limit, measured at 100 K.

In Figure 5, we present the ESR spectra at 373 K of labeled P(S-*co*-MA) in a blend containing 60 wt % PVME

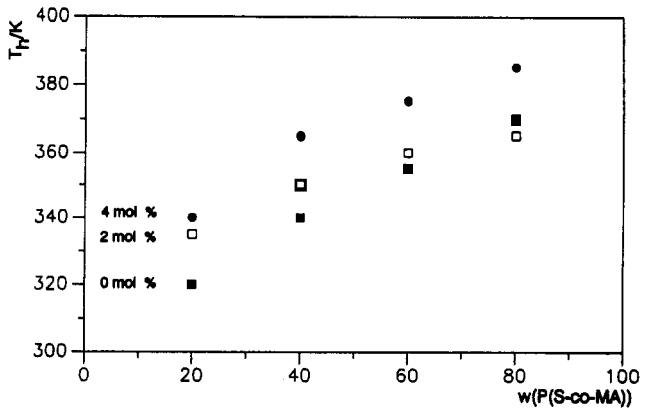


Figure 6. Transition temperature between the two motional regions, T_h, as a function of composition for blends and semi-IPNs with different cross-linking densities.

(5a), the simulated spectrum of the rigid component (5b), and the spectrum obtained after substraction of the two spectra (5c). This procedure was repeated for several compositions and temperatures. The deconvolution method is very sensitive to a large number of parameters of the spectra, especially to the line widths. Within certain limits, however, an estimate of the relative intensities of both spectral components can be extracted. The results indicate that the intensity of the fast component is only 5–15% of the intensity of the rigid component. It seems that only a small amount of the labeled P(S-*co*-MA) exists in a highly dynamic state, and the major part of the labeled chains has a lower mobility. The advantage of the ESR method is the ability to detect the minor component, because the corresponding line widths are significantly narrower that those of the major component. A similar situation exists in blends of poly(styrene-*co*-acrylic acid) with poly(ethylene oxide), where the more rigid component, the copolymer, was spin labeled.[14]

The observation of two spectral components differing in their mobility should not be taken as evidence for only two discrete dynamic states of the P(S-*co*-MA) chains. More likely, the system has a *range* of P(S-*co*-MA) chain dynamics, centered on the two types of sites detected in the ESR experiments. Support for this picture is obtained by inspection of the spectrum obtained as a result of the subtraction, Figure 5c: The unusual line shape, with decreasing amplitude from low to high field, can be simulated by a distribution of ESR parameters.[4] Such a distribution is a result of a distribution of regions with different polarities. In the system presented here, we expect a higher polarity in regions that are rich in PVME, compared to regions that are rich in P(S-*co*-MA).

2. Microheterogeneity in PVME-*cross*-P(S-*co*-MA) Semi-IPNs. Cloud-point measurements of P(S-*co*-MA)/PVME blends and semi-IPNs indicate that cross-linking results in a decrease of the homogeneous region in the phase diagram: T_c is lower for the cross-linked samples.[7,8] To examine the influence of covalent junctions on the microheterogeneity in the P(S-*co*-MA)/PVME system, we cross-linked spin-labeled P(S-*co*-MA) with DADPM and characterized the samples via ESR spectroscopy, as was done for the blends.

The ESR spectra of the semi-IPNs are comparable to the spectra of the uncross-linked mixtures. At low temperatures, we obtain the rigid limit spectra with an extreme separation of ≈70 G. With increasing temperature, $2A'_{zz}$ decreases, and at T_h, we observe the appearance of a second spectral component with a higher mobility. The T_h values for the blends and semi-IPNs with different cross-linking densities (0, 2, and 4 mol %) are shown in Figure 6 as a function of composition. The temperature where a second component in the ESR spectra is detected increases with increasing cross-linking density. Cross-linking of the spin-labeled P(S-*co*-MA) is expected to restrict the chain mobility. The higher T_h values for the IPNs, compared to the blends, suggest that the reduced dynamics of the polymer matrix hinders the formation of concentration fluctuations and a higher temperature is needed in order to obtain the concentration inhomogeneity necessary to observe the splitting of the nitroxide mobility in the ESR spectra. These results are in accord with the theoretical predictions that phase separation in IPNs will essentially stop at a length scale similar to the mesh size of the network[15] and with neutron scattering experiments that indicated damping of concentration fluctuations by cross-links in the system.[16,17] Cross-links effectively constrain the concentration fluctuations to be smaller than those present in a linear blend.

Table 2. T_{50G}, T_g, and ΔT for P(S-*co*-MA)/PVME Blends

P(S-*co*-MA), wt %	T_g/K	T_{50G}/K	ΔT/K
10	249	359	110
20	253	353	100
30	257	368	111
40	266	367	101
60	296	380	84
80	328	395	67
100	383	460	77

3. Correlation between T_{50G} and T_g. T_{50G} is defined as the temperature where the separation of the outermost peaks ($2A'_{zz}$) in the ESR spectrum of the nitroxide radical in the polymer matrix is 50 G.[3] The correlation between T_g and T_{50G} in many polymers has been discussed at length;[4,18–21] several authors have suggested that T_{50G} is a high-frequency glass transition temperature.[22,23] Because the rotational frequency at T_{50G} is ≈5 × 10^8 Hz for nitroxides, T_{50G} is generally higher than the T_g normally measured at a frequency of ≈1 Hz.

Table 2 shows the variation of T_{50G} with T_g for the different P(S-*co*-MA)/PVME blends. For pure P(S-*co*-MA), the T_{50G} value is not reached in the experimentally accessible temperature region. For this case, the T_{50G} value was estimated by extrapolating a plot of $2A'_{zz}$ as a function of temperature (Figure 3). For all blends, the T_{50G} values are ≈90 K above T_g.

The temperature dependence of relaxation processes for an amorphous polymer above its glass transition can be described using the Williams–Landel–Ferry (WLF) equation[24]

$$\log a_T = \log\left(\frac{\tau_c(T)}{\tau_c(T_g)}\right) = -(C_1(T - T_g))/(C_2 + T - T_g) \quad (1)$$

where $\tau_c(T)$ is the correlation time at temperature T, $\tau_c(T_g)$ is the correlation time at the reference temperature chosen as the glass transition temperature determined by DSC, and C_1 and C_2 are constants that depend on the polymer system. The temperature shift between the high-frequency and the low-frequency glass transition was calculated according to eq 1, using the literature data for PS: C_1 = 12.7 and C_2 = 49.8 K.[25] The calculated temperature shift of 80 K is in good agreement with the extrapolated value obtained for pure PS (T_{50G} ≈ 460 K, T_g = 383 K). The deviations between the calculated and measured temperature shift (Table 2) for the mixtures are harder to interpret, because the glass transitions of the blends are very broad and thus are difficult to define in the intermediate composition range and also because

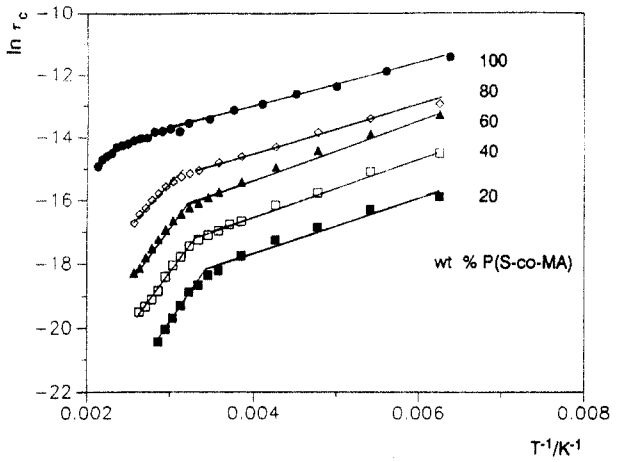


Figure 7. Variation of the correlation time (τ_c) with the reciprocal temperature for pure P(S-*co*-MA) and for the slow component in the P(S-*co*-MA)/PVME blends. The straight lines are best fits to the experimental points in the low- and high-temperature motional regions.

the values for C_1 and C_2 of the blends are not expected to be identical to the C_1 and C_2 constants of pure PS.

A quantitative relationship between T_{50G} and T_g, based on the free volume theory of Bueche, has been proposed[26] and is given in eq 2, where f is the ratio of the molecular

$$T_{50G} - T_g = 52[2.9\, f(1 - \ln f) - 1] \qquad (2)$$

volumes of the probe to the polymer segment undergoing local motions at T_g. Using eq 2 and ΔT values from Table 2, we have obtained a constant value of f ($f \approx 1$) for the spin-labeled P(S-*co*-MA)/PVME blends. This result is in good agreement with the observation for other labeled polymer systems[17] and indicates that the effective volume of the labeled polymer segment is similar to that of an unlabeled segment. This conclusion is an additional confirmation of the covalent binding of the nitroxide radical to the polymer backbone and an indication that the dynamical properties of the polymer are not affected by the presence of the label. For spin probes, the value of f is much smaller than unity and strongly depends on the size of the nitroxide probe.[17]

4. Dynamics of P(S-*co*-MA)/PVME Blends from Correlation Times (Slow Tumbling Region). Several approaches have been proposed for the determination of the correlation times in the slow-motional region from ESR spectra. The best method to obtain τ_c is, of course, by spectral simulation. An alternative method that allows a reasonable estimate of the correlation time can be obtained from the temperature dependence of $2A'_{zz}$:[27,28]

$$\tau_c = a(1 - S)^b \qquad (3)$$

The ratio $S = 2A'_{zz}(T)/2A_{zz}(100\ \text{K})$ is calculated based on the rigid limit value $2A_{zz}$ measured at 100 K. Coefficients a and b are sensitive to the motional model and the intrinsic line width. In the present study, the Brownian diffusion model was used and an intrinsic line width of 5.0 G was determined from a simulation of the rigid limit spectra for P(S-*co*-MA) and the blends at 100 K. For these conditions, the values of a and b are 8.52×10^{-10} s and −1.16, respectively.[3]

Arrhenius plots of τ_c vs $1/T$ over the entire temperature range measured for labeled P(S-*co*-MA) in blends containing various amounts of PVME are shown in Figure 7. Two clearly separated, motional regimes are evident. With

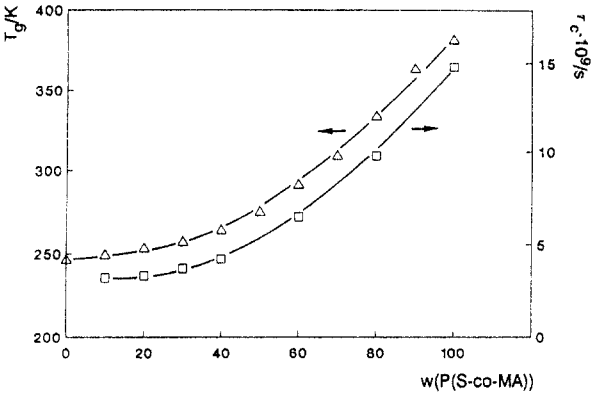


Figure 8. Correlation times (τ_c) for the slow component at 370 K of spin-labeled P(S-*co*-MA) chains in blends and glass transition temperatures (T_g) as a function of blend composition.

increasing PVME content and decreasing glass transition temperature in the blends, the boundaries between the two regions are shifted to lower temperatures. Similar results have been obtained for the semi-IPNs. For all systems, the activation energies E_a were determined in the two regimes from the slope of the straight lines. In the low-temperature region, $E_a(\text{low } T) = 8.0 \pm 4.0$ kJ/mol, and in the high-temperature regime, $E_a(\text{high } T) = 34 \pm 4$ kJ/mol. Within this experimental error, the activation energies are identical for all examined blends and semi-IPNs. The activation energy determined in the low-temperature regime is smaller compared to that in the high-temperature region, in agreement with other spin-labeled experiments.[4] The mobility of the nitroxide label at temperatures below the glass transition is activated by local relaxation modes in the polymer matrix, which do not need a large free volume for the relaxation process. In general, such *sub*-T_g relaxations have very small activation energies.

The activation energies determined in the high-temperature range are found to be the same, within the experimental uncertainty, for all the samples we examined. This observation indicates that regardless of the model used in the calculation of the correlation times, the molecular motions of the label attached to the P(S-*co*-MA) backbone in different blends are activated by the same molecular process. Though the activation energies are much smaller compared to the values usually observed in the glass transition region (200–400 kJ/mol), we suggest that the observed dynamics is correlated to the α relaxation: As shown below, the τ_c values and the corresponding glass transition temperatures have a similar dependence on composition.

The correlation times of spin-labeled P(S-*co*-MA) in the different blends will now be compared. This comparison was done in two ways. First, τ_c values were compared at a fixed reference temperature (T_R) so that with changing blend composition (and changing T_g) the interval between T_R and T_g increases with increasing PVME content in the system. Second, the comparison was made at a constant temperature *difference* between the experimental temperature (T_{exp}) and the glass transition temperature (T_g). In this case, T_{exp} increases with increasing P(S-*co*-MA) content.

In Figure 8, we present the correlation times at a fixed reference temperature, $T_R = 370$ K, of the rigid spectral component of labeled P(S-*co*-MA) in the blends, as a function of blend composition. Also shown in Figure 8 are the glass transition temperatures of the blends. With increasing PVME content in the mixtures, the mobility of the spin label attached to P(S-*co*-MA) increases. The

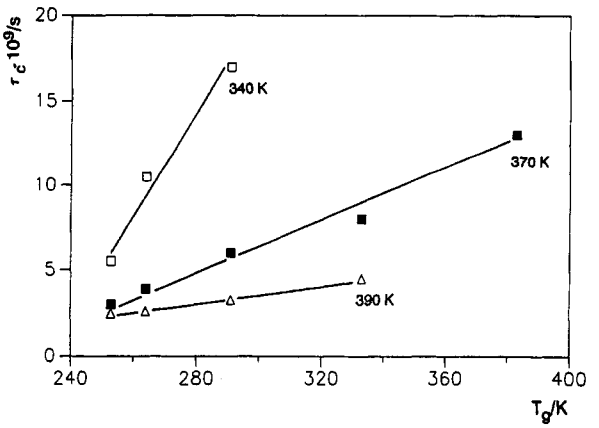


Figure 9. Correlation times (τ_c) for the slow component at 340, 370, and 390 K of spin-labeled P(S-*co*-MA) chains in blends as a function of the corresponding T_g.

calculated correlation times and the T_g values show a similar dependence on the composition.

The correlation times of the rigid spectral component in P(S-*co*-MA) chains as a function of T_g at different reference temperatures (340, 370, and 390 K) are plotted in Figure 9; the plots suggest a linear correlation between τ_c and T_g. With increasing T_R, the slope of τ_c vs T_g decreases. This observation reflects the temperature interval between T_{50G} and T_g: at $T_R \approx 340$ K, we observe the behavior of the chains close to T_{50G}, where τ_c is very sensitive to temperature and the slope of τ_c vs T_g is higher (Figure 9).

Conclusions

In this study, we have shown that information about the local environment in miscible blends and semi-IPNs based on P(S-*co*-MA) copolymers and PVME can be obtained from ESR spectra of a covalently bonded spin label. While the ESR spectra of the spin probes dispersed in the polymer are insensitive to the dynamics of the polymer matrix, the spectra from spin labels are closely related to the dynamics of the P(S-*co*-MA) chains. The major point of this work is the observation of molecular heterogeneities and composition fluctuations in this system at temperatures well below the macroscopic phase separation. The structural heterogeneities appear as a dynamic heterogeneity of the labeled P(S-*co*-MA) chains. The composition fluctuations are significantly dampened by covalent cross-linking in the semi-IPNs. The difference between T_g and T_{50G} can be understood by an analysis of the results based on the WLF equation. Finally, the correlation times deduced from the ESR spectra and the molecular view of the system can be directly compared with the macroscopic property T_g.

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