Concentration Fluctuation of Poly(ethylene oxide) in a Blend with Poly(methyl methacrylate) and Phase Separation Behavior Studied by the Spin-Label Method

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ABSTRACT: The electron spin resonance (ESR) line shape of nitroxide radical labels attached to poly-(ethylene oxide) (PEO) chains in a blend with isotactic poly(methyl methacrylate) (PMMA) was studied as a function of temperature. Two spectral components with different rates of motion—a "fast" component and a "slow" component arising from the radicals—are observed in the temperature range 48–85 °C. It can be concluded that the fast and slow components should be attributed to nitroxide radicals trapped in the PEO-rich and PMMA-rich regions in the blend, respectively. From the temperature dependence of the fast spectral component, there are at least three relaxational regions: (I) the relaxation of PEO chains in the PEO-rich phase of a phase-separated system, (II) the disappearance of concentration fluctuation of PEO chains, and (III) the relaxation of PEO chains in a molecularly compatible system. Drastic broadening of the line width of the fast component was observed at 68 °C between regions I and II with rising temperature, whereas the width narrowed markedly at the same temperature with cooling. This reversible transition can be attributed to molecular mixing and phase separation. Thus an upper critical solution temperature (UCST) exists at 68 °C. In region II, the broadening of the line width also occurred more gradually with rising temperature than that in the phase transition. The concentration of PEO chains in region II appears to fluctuate with a frequency of ca. 10^9 s^{-1}.

Introduction

Many authors have studied polymer blends extensively by a variety of methods. However, there are few studies by electron spin resonance (ESR).[1-3] It is well-known that the ESR method is a simple and effective way of determining molcular mobility on a time scale of $\sim 10^{-9}$ s. We have developed spin-label technique to investigate the structure and dynamic behavior of polymer chains at a particular site in a complicated system.[4] In some cases, ESR spectra of the spin label can also reflect different environments in a given sample with different rates of motion. Two spectral components arising from chemically identical radicals having different mobilities are detected. The heterogeneity in the local environments observed by the ESR method is due to different intermolecular interactions between the polymer chains.

In this study, we report an ESR method that exploits the temperature dependence of the spectrum obtained from nitroxide spin labels attached to poly(ethylene oxide) (PEO) chains in a blend with poly(methyl methacrylate) (PMMA). Some authors have studied blends of PEO and PMMA.[5] One of the conclusions is that one homogeneous amorphous phase is present for PEO/atactic PMMA and PEO/syndiotactic PMMA blends, whereas the PEO/isotactic PMMA amorphous system is phase separated.

We first present the results of a spin-label study in relation to the molecular compatibility of PEO and isotactic PMMA chains. We next characterize the heterogeneity in the polymer blend by studying (i) the concentration fluctuation of the PEO chains in a compatible system and (ii) the two component phases in a phase-separated system and assess molecular mixing, phase separation, and molecular motion of the PEO chains in the blend.

Experimental Section

Materials. Spin-labeled PEO was prepared by the method of Törmälä et al.[6] For instance, 3-carbonyl-2,2,5,5-tetrameth-

ylpyrroline-1-oxyl radical (Aldrich Chemical Co. Ltd.) was esterified with poly(ethylene oxide) (Katayama Science Co. Ltd.) Isotactic PMMA was prepared by anionic polymerization of MMA monomer (Tokyo Kasei Co., Ltd.) using *tert*-butylmagnesium bromide catalyst at −78 °C.[7] The number-average molecular weight ($\bar{M}_n$) is 6000 for PEO and 5000 for PMMA. Polydispersity ($\bar{M}_w/\bar{M}_n$) is <1.20 for both materials.

Preparation of Blends. Blends were made by mixing spin-labeled PEO and PMMA in ratios of 1:1, 1:4, and 1:10 by weight. Films were prepared by casting from $\sim$3 wt % of benzene solution at 60 °C. The notation used for these samples is EM1, EM4, and EM10.

ESR Measurements. Samples were stacked in ESR sample tubes evacuated to 10^{-5} mmHg. ESR measurements were carried out with a JEOL FE3XG spectrometer with a connected MEL-COM 70/25 computer. The signal of diphenylpicrylhydrazyl (DPPH) was used as a g value standard. The magnetic field sweep was calibrated with the known splitting constant of Mn^{2+}.

Results and Discussion

Temperature Dependence of ESR Spectra of Spin-Labeled PEO. Figure 1 shows the change in the spectra from the spin-labeled PEO in the EM10 blend with increasing temperature. The outermost splitting widths of the main triplet spectra due to hyperfine coupling caused by the nitrogen nucleus were measured at various temperatures. The width between the outermost peaks of the spectrum narrowed with increasing temperature because of averaging of the anisotropic hyperfine coupling due to rotational motion of the PEO chains. Complete averaging gave rise to the isotropic spectrum as shown in Figure 1d.

Törmälä et al.[6] studied solid- and liquid-state relaxations in spin-labeled PEO in detail. We can compare the ESR spectra in pure PEO matrices with those in the blends of PEO and PMMA. Two significant differences are found as follows.

(1) For the blend, two spectral components with different rates of motion—the "fast" and the "slow" components
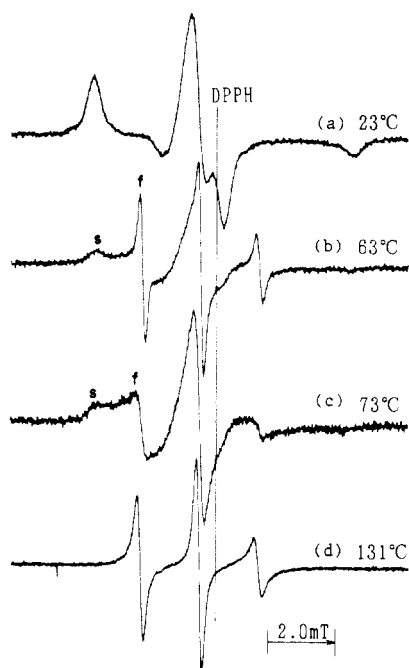
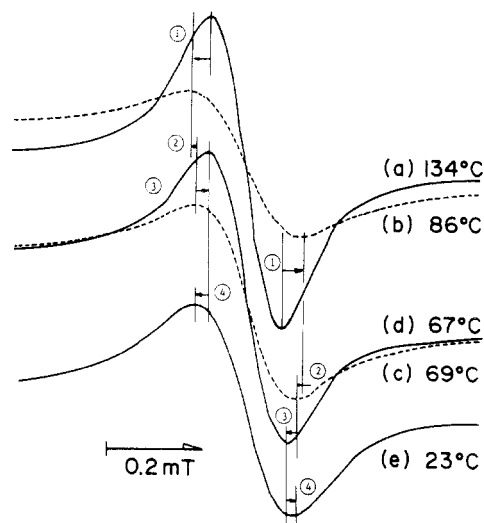**Figure 1.** ESR spectra of spin-labeled PEO in PEO/PMMA (EM10) blend at various temperatures. The spectra of DPPH, $g = 2.0036$, is the vertical line. At 63 and 73 °C the low-field slow and fast components are indicated by "s" and "f", respectively.

Figure 2. Change in fast component's spectrum with decreasing temperature. Enlarged spectra at low-field are shown. The numbers 1–4 and the arrows indicate the directions of the changes in the peaks.

Figure 3. Maximum slope line width (ΔH_{msl}) of fast spectral component vs observation temperature. The line widths at low-field were observed with decreasing (O) and increasing (●) temperature.

arising from the radicals—are observed in the temperature range 48–85 °C, whereas only one component is detected over the entire temperature range for the pure matrices. The fast and slow components observed in the blend can be attributed to radicals in the mobile and rigid regions, respectively. The same experiments were carried out for the EM1 and EM4 samples. The ESR spectra change substantially as a function of PEO content in the blend. The amount of the fast component (the mobile radicals) increased with PEO content. As discussed in the next section, molecular mobility in the PEO matrices is higher than that in the PMMA matrices.

These results mean that the nitroxide radicals are affected by the environments of the radical sites, for example, the states of aggregation, and the fast and slow spectra (the isotropic and anisotropic spectra) are attributed to the spin-labeled PEO trapped in the PEO-rich and PMMA-rich regions, respectively. The structural heterogeneity in local environments of the blend could be clearly observed by the ESR method.

(2) The spectrum of only one component observed at temperatures above 85 °C in the blend is broader than that in the pure PEO matrices. The line shapes can be quantified by the amplitude ratios, $R_{\pm} = (h_0/h_{\pm})^{1/2}$, where h_{+1}, h_0, and h_{-1} are the amplitudes of the low-field, center-field, and high-field signals, respectively. The values of R_+ and R_- are close to 1 at temperatures above 100 °C.[6] However, $h_{+1} < h_{-1} < h_0$; $R_{\pm} < 1$ was observed even at 131 °C in the blend as shown in Figure 1d. The rotational correlation time calculated by Kivelson's theory[8] changes substantially as a decreasing function of PEO content in the blend. These facts indicate that the mobility of the spin-labeled PEO in the blend should be lower than that in the pure PEO matrices. The spin-labeled PEO is molecularly and uniformly mixed with PMMA in the higher temperature region, and the molecular motion of the PEO chains is disturbed by the PMMA chains in the molecularly mixed system.

Molecular Mixing and Phase Separations. In general, the line width of the ESR spectrum narrows with
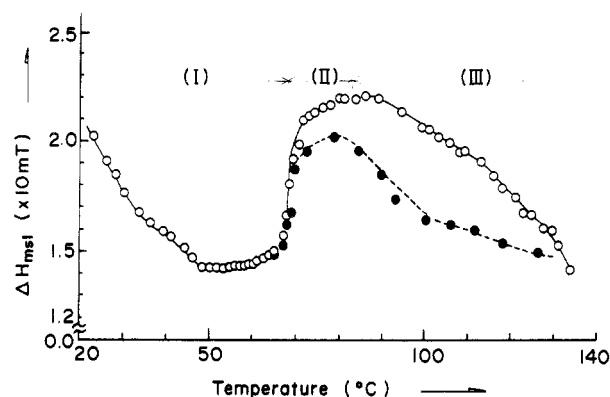
increasing temperature because of motional averaging of the anisotropic interactions between electron and nuclear spins. Surprisingly, the fast component's spectrum broadens considerably between 63 and 73 °C as shown in Figure 1b,c. Figure 2 shows the ESR line shapes of the fast component at low field at various temperatures. Figure 3 shows the temperature dependence of the maximum slope line width (ΔH_{msl}) of the spectrum with cooling and heating. An abrupt jump of the line width is found at 68 °C. These results are almost reversible in a heating and cooling cycle.

A more quantitative treatment of the results was done by estimating the rotational correlation time (τ) of the radicals from the ESR spectra. In the region of rapid rotation the time could be calculated by the following equation, which is based on Kivelson's theory:[8]

$$\tau = 8.7 \Delta H_{msl0}[R_- - R_+] \times 10^{-10}$$

where ΔH_{msl0} is the line width of the center peak. Shiotani et al.[9] have shown how to analyze ESR spectra from polymers in terms of anisotropic motions. They also showed no marked difference between the calculated correlation times derived from the isotropic rotation and the anisotropic reorientation with a small degree of anisotropy. For simplicity, we applied the isotropic rotation. Figure 4 shows the temperature dependence of the
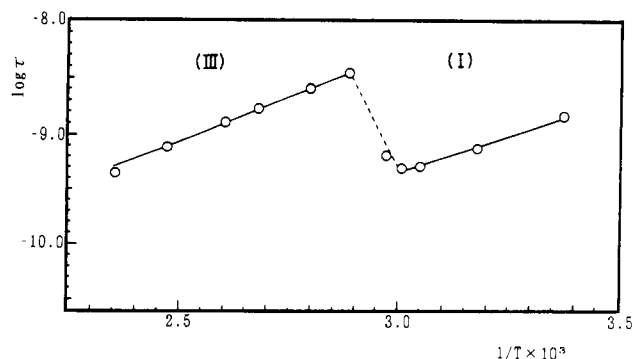
Figure 4. Temperature dependence of rotational correlation time (τ) for mobile labels.
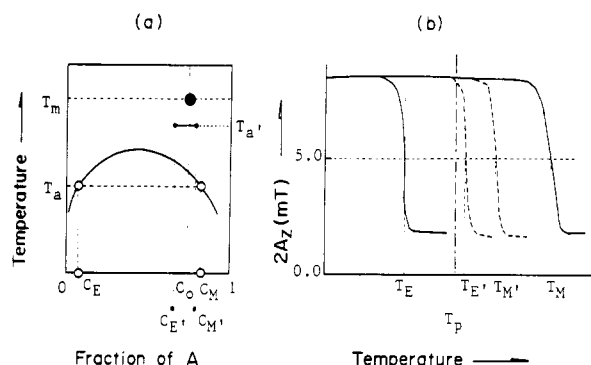
Figure 5. Schematic illustrations of phase diagram of UCST type (a) and expected curves for outermost splitting width ($2A_z$) vs temperature (b). Other symbols are described in the text. T_m, $T_{a'}$, and T_a are temperatures in the molten, concentration-fluctuated, and phase-separated states, respectively.

rotational correlation time for the mobile labels. In the relaxation regions, regions I and III, the correlation times decrease with increasing temperature because of the motional narrowing. On the other hand, an abrupt jump of the times is found at ca. 68 °C as expected from Figures 1–3. How can we interpret this experimental fact? In general, molecular motions of polymeric chains are characterized by both intrachain and interchain interactions. In the miscible polymer blend system, polymer chains are mixed with each other at the molecular level. As mentioned above, the molecular motion of the PEO chains in the PEO/PMMA blend is slower than that in the pure PEO matrices. This is compatible with the lower glass–rubber transition temperature (T_g) of PEO (–65 °C) than that of isotactic PMMA (60 °C).[5b] This fact suggests that the closer location of the PMMA chain to the PEO chain causes a hindrance to the mobility of the PEO chain and that the mobility is a decreasing function of concentration of PMMA chains, C_E. (The rotational correlation time (τ) is an increasing function of C_E.)

Figure 5 shows a schematic phase diagram of upper critical solution temperature (UCST) type and the expected temperature dependencies of the outermost splitting width of the main triplet spectra ($2A_z$) for various samples. The temperature at which the width is 50 G (5 mT), T_{50G}, is a good measure of the mobility of spin-labeled PEO. In a phase-separated system, the concentrations of the PMMA chains in the PEO-rich and PMMA-rich phases can be represented as C_E and C_M, respectively. C_0 in Figure 5 stands for the PMMA concentration in the preparation of the blend. It is well-known that the correlation time is ca. 7×10^{-9} s at T_{50G}.[10] As a result, anisotropic (slow) and isotropic (fast) spectra should be observed when the correlation times are longer and shorter than 7×10^{-9} s, respectively. Consequently, two spectral components in

the phase-separated system from the spin-labeled PEO should be observed in a temperature range of T_E and T_M, where T_X means T_{50G} for the spin label trapped in a region of concentration C_X.

Since the correlation time for the slow component is calculated to be ca. 5×10^{-8} s by Freed's theory,[11,12] the superposition of the fast and slow spectra can be characterized by a bimodal distribution of motional correlation times whose principal values differ by more than 1 order of magnitude.[13] The bimodal distribution at the temperature below the transition point, 68 °C, reflects different environments in the blend, corresponding to the PEO-rich and PMMA-rich phases in the phase-separated system. In the present study, the slow and fast spectra from the spin labels of two principal correlation times, τ_M and τ_E were observed in the PEO/PMMA blend at the lower temperatures. In other words, $\tau_E < \tau_0 < \tau_M$ was found when $C_E < C_0 < C_M$. Here, τ_X means the rotational correlation time of the PEO chain in the region of PMMA concentration C_X.

On the other hand, molecular mixing proceeds with increasing temperature, and the PMMA concentrations in the PEO-rich (C_E) and PMMA-rich (C_M) phases tend to approach the value of C_0 for UCST type behavior. The abrupt jump of the correlation time for the mobile labels at the transition point, 68 °C, shown in Figure 4 indicates that molecular mixing occurs. Thus the correlation time τ_E tends to increase to τ_0 as C_E increases to C_0. The decreasing of τ_M from the anisotropic spectrum (the slow component) could not be observed clearly in our study because the value of C_M is close to C_0 in the EM10 blend.

These facts provide a compelling argument that molecular mixing proceeds by heating and phase separation occurs by cooling at an upper critical solution temperature, 68 °C, in the EM10 blend. These transition phenomena may be related with crystallization and melting of PEO and/or PMMA. However, it is well-known that the growth rate of PEO spherulites decreases with increasing PMMA content.[14] The crystallization temperature even for the EM1 blend sample with a PEO/PMMA ratio of 1:1 is found to be lower than 46 °C by DSC measurement. Lemieux et al.[15] reported the melting temperature of iso-tactic PMMA is 155 ± 1 °C. The crystallization and melting temperatures of PEO and PMMA are different from the transition temperatures, 68 °C, found in the present study. Consequently, we can conclude that the phenomena observed by the ESR method should not reflect a liquid–solid phase transition but a liquid–liquid phase transition.

Concentration Fluctuation of Poly(ethylene oxide) in a Blend with Poly(methyl methacrylate). To confirm the phase separation behavior as mentioned in the previous section, we observed a structural development during isothermal annealing near the transition temperature, 68 °C. After the EM10 blend is stored at 130 °C for 10 min and mixed homogeneously, the sample is quenched to 66 °C, and the ESR spectra are then observed as a function of storage time at the same temperature. As shown in Figure 6, two spectral components—the fast and slow components—appear, and the intensity of the fast spectrum from the mobile radicals is enhanced with storage time. Thus the amounts of the spin-labeled PEO trapped in the PEO-rich region increase by transitional molecular diffusion of PEO chains from the PMMA-rich region to the PEO-rich region. This experimental fact also reflects the phase separation process at temperatures below the transition point, 68 °C.
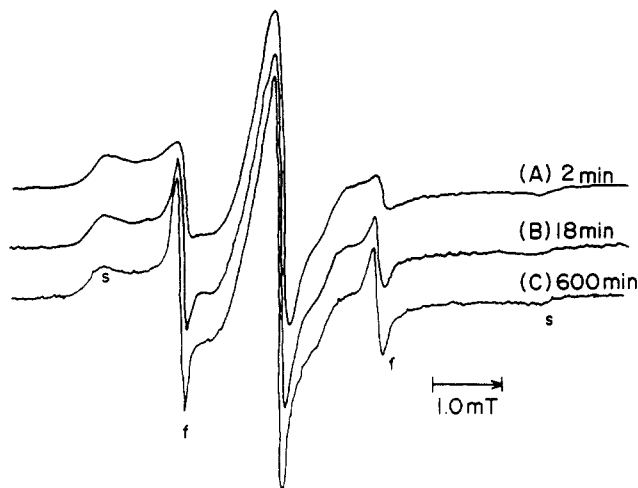
Figure 6. Variation of the ESR spectra from spin-labeled PEO in PEO/PMMA (EM10) blend with storage time. The ESR spectra are for samples annealed and observed at 66 °C. The slow and fast components are indicated by "s" and "f", respectively, in spectrum C.

The same experiment was carried out at 80 °C. Two ESR spectral components also can be observed, but the spectra remain unchanged with storage time in contrast to the result from the annealing at 66 °C, indicating that the spin-labeled PEO is trapped in a one-phase region and that phase separation does not occur. We raise one question. Why can two spectral components with different rates of molecular motion be observed in a one-phase region at a temperature above the transition point, 68 °C? In Figure 5 are drawn hypothetically the narrowing curves of $2A_z$ vs temperature for the spin labels trapped in the regions of concentration $C_{E'}$ and $C_{M'}$.

If the rate of concentration fluctuation between $C_{E'}$ and $C_{M'}$ in the one-phase region is lower than the frequency for the observation, two spectral components should be observed in a temperature range of $T_{E'} \sim T_{M'}$. To elucidate the concentration fluctuation, we obtained the exact temperature dependence of the line width of the fast component as shown in Figure 3. The maximum slope line widths are plotted as a function of observation temperature. There are at least three relaxation regions. As mentioned in the previous section, the relaxations, regions I and III, can be found in Figure 4. It can be concluded that the motional narrowings of the line width in regions I and III should be attributed to the relaxations of the PEO chains

trapped in the PEO-rich region of a phase-separated system and those in a molecularly mixed phase, respectively. In the intermediate region II (68–85 °C), the broadening (narrowing) of the line width occurs more gradually with increasing (decreasing) temperature than that in the transition of molecular mixing (phase separation). It can be considered that the relaxation in region II reflects the disappearance (appearance) of concentration fluctuation of PEO chains in the blend. When the rate of the concentration fluctuation prevails over the frequency of observation with rising temperature, we cannot distinguish the PMMA concentration in the PEO-rich region from that in the PMMA-rich region.

The line width broadens (narrows) gradually with the gradual disappearance (appearance) of the concentration fluctuation. The rotational correlation time is ca. 10^{-9} s at 85 °C as shown in Figure 4. Now we apply the value of $1/\tau_0$ as an approximate frequency for the observation of the concentration fluctuation. Consequently, it can be considered that the rate of the concentration fluctuation of PEO chains in the molecularly mixed phase is of the order of magnitude of 10^9 s^{-1}.

References and Notes

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