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EPR Investigations of Irradiation Effects on Polymers Containing Nitroxide Spin Probes Exhibiting a Bimodal Distribution of Motional Correlation Times

The electron paramagnetic resonance (EPR) method employing stable nitroxide radicals as spin probes is becoming increasingly important in the study of molecular motions and morphology in polymeric substances.[1] This communication is concerned with a new experimental approach involving γ irradiation and thermal heat treatment techniques for polymers containing nitroxide spin probes that exhibit a bimodal distribution[1,2] of motional correlation times. The implications of these results on the molecular motions of the spin probes and the associated polymer main-chain segmental motions will be discussed.

The polymer system studied was the alternating block copolymer consisting of equal amounts (wt%) of bisphenol A-polycarbonate (BPAC) and poly(dimethylsiloxane) (DMS), containing nominally 0.08 wt % of the spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL).[3] Before irradiation, the copolymer samples show essentially three different types of EPR spectra, depending on the temperature at which the measurement is made.[4] These spectra are displayed in Figure 1.

At low temperatures between about 77 and 220 K, the EPR spectra consist of broad hyperfine lines whose overall line shape is that expected from a single type of TANOL spin probe undergoing slow tumbling motions[5] (see Figure 1a). Above approximately 360 K, the observed spectra exhibit three motionally narrowed hyperfine lines (Figure 1c). At intermediate temperatures, approximately from 220 to 360 K, the observed spectra appear to be the superposition of the broad line (Figure 1a) and narrow line (Figure 1c) spectra (see Figure 1b).[6] (In Figure 1, the peaks that belong to the broad line spectrum are denoted by S and those of the narrow line spectrum by F.) We have also found that the ratio of the integrated EPR intensity of the narrow line spectrum to the broad line spectrum, denoted by α, increases with increasing temperature.

The broad line spectrum represents a slow motional phase (S) of TANOL radicals with long correlation times, while the narrow line spectrum represents a fast motional phase (F) with short correlation times. In terms of the proposed model for the microstructure of the BPAC/DMS block copolymers,[7] the fast phase consists of TANOL radicals located in rubbery DMS regions which are undergoing fast main-chain segmental motions, whereas the slow phase is composed of TANOL radicals undergoing slow tumbling in rigid BPAC domains and/or in rigid DMS regions whose segmental motions are restricted by their proximity to the BPAC domains. Thus, the assumption that the spectrum of Figure 1b consists of both the broad line and narrow line spectra indicates that both rigid and rubbery regions are present in the copolymer system.

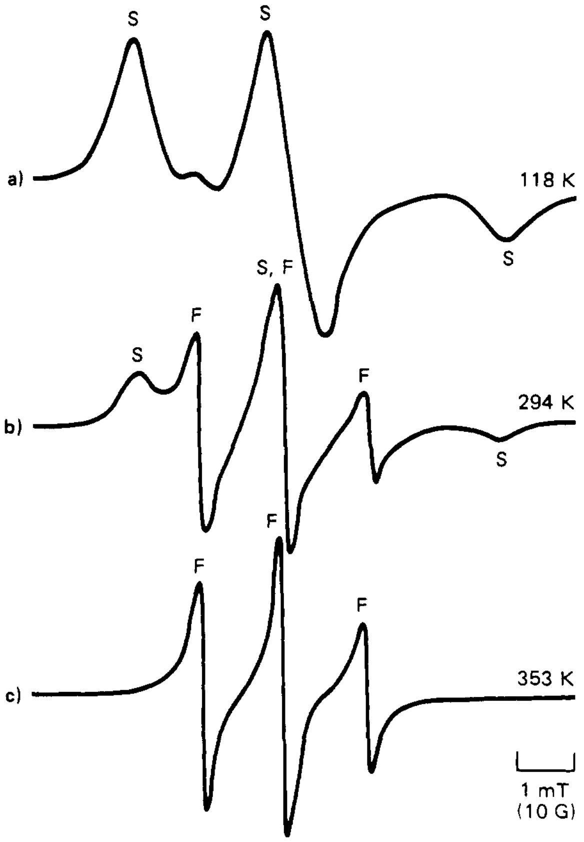

Figure 1. First-derivative EPR spectra observed at different temperatures from TANOL spin probes in 50–50 wt % BPAC-/DMS block copolymer.

One should also consider the possibility that the EPR spectrum of Figure 1b arises from a single radical phase that undergoes anisotropic motion[5] resulting in an incomplete averaging of the hyperfine and g-anisotropy. Another important consideration is concerned with the interphase regions between the mobile and rigid regions where the segmental motions and the radical motions should be intermediate between the fast and slow rates. If the TANOL radical translational diffusion rates across the interphase regions are fast but still slow enough that the spectra are not dynamically averaged, the rapid radical penetration between the fast and slow phases will determine a temperature-dependent equilibrium of interconverting fast and slow spin probe species characterized by α. Alternatively, if the translational diffusion rates are slow compared to the time of the experiment, the fast and slow phases are noninterconverting species, and the temperature dependence of α is a measure of how the relative amount of mobile regions changes with temperature. As described below, the irradiation and thermal treatment experiments provide some definitive information about these questions.

The copolymer samples were irradiated with a γ-ray flux of 1.2×10^6 rad/h at room temperature for periods ranging from 3 days to 1 week, by using an existing ^{60}Co source. As a result of the γ irradiation, the EPR intensities of both

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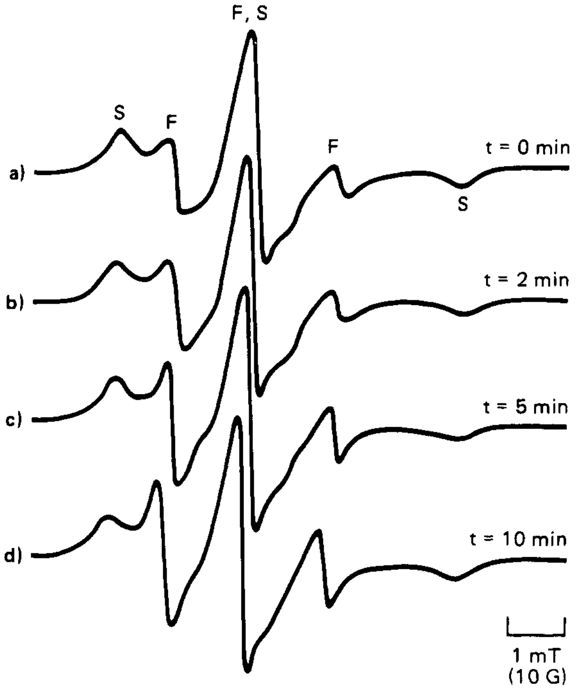

Figure 2. EPR spectra observed at room temperature for the BPAC/DMS copolymer containing TANOL which was γ irradiated for 1 week and subsequently received thermal heat treatment at 333 K for various times (t).

the narrow line and broad line spectra decreased as a function of the irradiation time. Moreover, the intensity of the narrow line spectrum decreased measurably faster than the broad line spectrum (see Figure 2a), so that α decreased with increasing irradiation time. When the irradiated samples remained at room temperature, α remained nearly constant at the new value for at least several days. When the irradiated samples were heated above approximately 333 K for a typical time of 10 min, α returned to the original value representative of the unirradiated samples. Figure 2 illustrates this process for the irradiated sample which received heat treatment at 333 K for the times indicated.

The foregoing experimental results eliminate the possibility that the EPR line shape of Figure 1b may be due to a single radical phase that undergoes an anisotropic motion. If there were only one phase, the effect of γ irradiation would be a uniform reduction of all component lines in the EPR spectra. The distinctly different responses of the broad lines and narrow lines to γ irradiation conclusively indicate two different spectra and hence two phases in the form of two environments for the TANOL spin probes.

The observed decrease in the EPR intensities by γ irradiation is believed to arise from the destruction of the TANOL radicals by their reaction with the primary defect radicals generated by γ irradiation. The reason for the preferential decrease in intensity of the narrow lines over the broad lines may be the result of rapid translational motion of the radicals within the rubbery regions of the copolymer, resulting in a faster collision rate with the defect radicals. Thus it appears that the principal effect of the defect radicals is to destroy the TANOL radicals, rather than to significantly change the polymer bulk properties through possible cross-linkings. The observed return of α to the original value exhibited by the unirradiated samples following heat treatment at elevated temperature does not represent any regeneration of the TANOL radicals destroyed by γ irradiation; instead, it arises from a redistribution of the TANOL radicals (remained after irradiation) between the rigid and rubbery phases.

The observation that α can be perturbed and attain different steady values as a result of γ irradiation and thermal heat treatment indicates that the TANOL radical translational diffusion rates across the interphase regions between the rubbery and rigid phases are extremely slow below 333 K. Otherwise, at a given temperature, regardless of irradiation and heat treatment α would approach a specific value unique to this temperature within a short period of time. Therefore, it is concluded that α values observed for the unirradiated copolymer samples at different temperatures below 333 K are representative of the relative amounts of the rubbery to the rigid regions of the copolymer system.

We believe that the behavior of the TANOL spin probes as displayed in the BPAC/DMS copolymer system under γ irradiation and thermal treatment is a general phenomenon occurring with other types of nitroxide spin probes associated with a bimodal distribution of motional correlation times; that is, the translational diffusion between the rigid and rubbery regions of a copolymer system is generally slow. Moreover, this new experimental approach should be useful for studying the effects of temperature and low molecular weight plasticizing solvents on the microstructure of block copolymers.

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