be interpreted as ionic domains for unstained films, although SAXS indicates the presence of clusters. This leads to several possibilities.

1. Most ionic domains are less than 2 or 3 nm in diameter and, therefore, might not be detectable in relatively thick sections. This would apparently rule out the presence of lamellae of ions with lateral dimensions or thickness of 3.5 nm, as proposed by Roche.[6]

2. The ion clusters are diffuse, resulting in very low amplitude contrast. This possibility does not limit the size or shape of the cluster.

The results of the amplitude contrast imaging with osmium tetraoxide stained sulfonated EPDM indicate that ionic domains probably do exist but average less than 2 or 3 nm in diameter. Hence, ultrathin specimens may make direct observation possible. We are preparing an ionomer based on styrene which will have a stainable double bond at each ionic group, will not have any phase separation other than ionic clusters, and can be microtomed at room temperature. We hope this polymer can be prepared in suitably thin films to allow determination of the structure of the domains.

Acknowledgment. We thank Dr. H. Nakamura for help in neutralizing several of the ionomers. Acknowledgment is made to the National Science Foundation for financial support (Grants DMR80-12724 (E.L.T.) and DMR78-09761 (W.J.M.), Polymers Program) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The use of the facilities of the Materials Research Laboratory at the University of Massachusetts is also gratefully acknowledged.

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Nitroxide Spin Probe Studies in a Block Copolymer

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ABSTRACT: Pulsed and CW EPR studies of a block copolymer of bisphenol A carbonate (BPAC) and dimethylsiloxane (DMS) containing a nitroxide spin probe are described. Below 220 K the line shapes consist of a single broad-line nitroxide spectrum which can be characterized by a motional correlation time $\tau_c > 10^{-7}$ s, whereas above 380 K the line shapes have the form of a typical three-line motionally narrowed nitroxide spectrum with the values $\tau_c < 10^{-9}$ s. At intermediate temperatures (220–380 K), the results of pulsed EPR experiments verify that the observed spectra are a superposition of a fast-phase spectrum ($\tau_c < 10^{-9}$ s) and a slow-phase spectrum ($\tau_c > 10^{-7}$ s). The fast phase is identified with the spin probes located in rubbery DMS block environments, and the slow phase corresponds to spin probes located in domains of associated BPAC blocks and/or in regions of DMS blocks whose segmental motions are restricted by the constraints imposed by the domains. The temperature dependence of the fast-phase fraction shows a good fit to a Gaussian distribution of the transition temperatures which describe the sudden onset of the motional narrowing. This distribution, which has a center at 374 K and a half-width of 88 K, is considered to be a measure of the distribution of polymeric main-chain segmental motional activity.

In this paper we describe the results of a study of the main-chain segmental motions associated with the glass transitions in the random alternating block copolymers of bisphenol A carbonate (BPAC) and dimethylsiloxane

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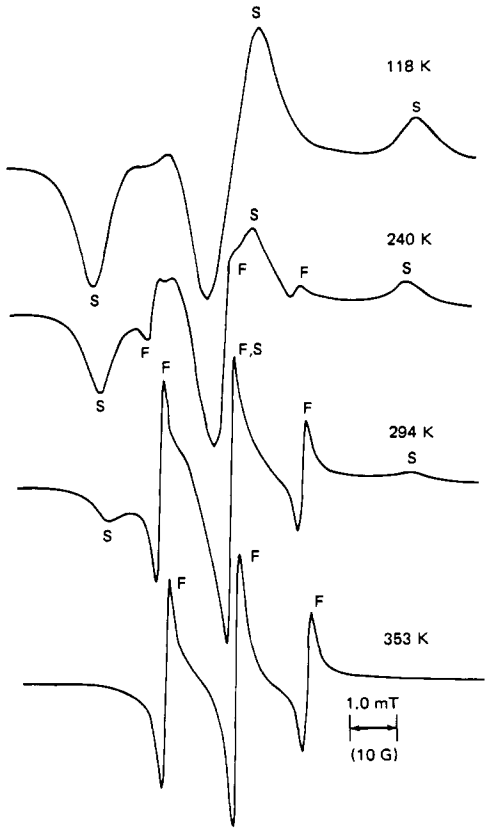

Figure 1. EPR derivative spectra observed at the different temperatures shown for a sample of the block copolymer with 50 wt % DMS/BPAC ($\overline{DP}_{BPAC}$ = 6, $\overline{DP}_{DMS}$ = 20) containing the spin probe TANOL. The derivative peaks associated with the slow phase and fast phase are denoted by S and F, respectively.

(DMS), using the methods of pulsed and CW electron paramagnetic resonance (EPR). We have used the spin probe technique wherein a stable nitroxide radical is dissolved in the block copolymers and acts as a probe of its dynamic environment.[1]

In the DMS/BPAC block copolymers there is evidence that the BPAC blocks associate into rigid domains which act as physical cross-links for the more mobile DMS blocks.[2] Since the cross-link density depends on the composition and block lengths, these copolymers range in type from rigid glassy solids to rubbery solids at room temperature.[3] These copolymers show a two-phase behavior in that the mechanical properties exhibit two major relaxations which have been attributed to two glass transition temperatures.[2] Thus in copolymer samples with a DMS/BPAC ratio of 50 wt % and number-average degrees of polymerization $\overline{DP}_{DMS}$ = 20 and $\overline{DP}_{BPAC}$ = 6 the relaxation occurring at 170 K has been associated with the onset of main-chain segmental motions in the DMS blocks, whereas the relaxation at 345 K has been associated with the onset of segmental motions in the BPAC blocks. The corresponding glass transition temperatures in the DMS and BPAC homopolymers are 150 and 423 K, respectively.

Experimental Section

Known weights of the stable nitroxide 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (TANOL) were dissolved in 10 mL of methylene chloride. Known volumes of these solutions were added to solutions of the block copolymer in methylene chloride, using micropipettes (500 and 100 μL). The block copolymer samples studied had a DMS/BPAC ratio of 50 wt % and number-average degrees of polymerization $\overline{DP}_{DMS}$ = 20 and $\overline{DP}_{BPAC}$ = 6. Thin transparent films were obtained when the solvent was allowed to evaporate slowly over a 48-h period. Trapped solvent was removed from the films by heating in a vacuum oven for 24 h at ~320 K. The films were cut into thin strips and compression molded at ≈400 K into 3.2-mm-diameter, 10-mm-long cylindrical samples.[4]

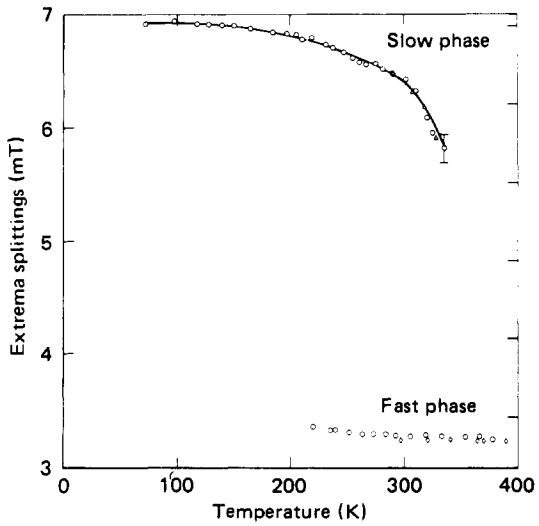

Figure 2. Temperature dependence of the extrema splitting values for the broad-line (slow phase) and the narrow-line (fast phase) spectra. The radical concentrations are 0.5, 0.09, and 0.04 wt % for the points indicated by ○, △ and ◇, respectively.

Results

Temperature Dependence of the EPR Line Shapes. The EPR line shapes of samples containing different concentrations of TANOL spin probes were studied from 77 to 400 K at 9.5 GHz. Examples of the spectra obtained at different temperatures are shown in Figure 1. Between 77 and 220 K, the observed spectra (the spectrum taken at 118 K displayed in Figure 1 is a typical example) exhibit line shapes expected[5] from a nitroxide radical undergoing slow motions with a rate that increases with increasing temperature. Above 380 K the observed spectra consist of three motionally narrowed hyperfine lines. At intermediate temperatures (220–380 K), the observed spectra appear to be the superposition of two spectra: (1) a broad-line spectrum (the peaks belonging to this spectrum are denoted by S in Figure 1) and (2) three narrow lines centered close to the middle peak of the broad-line spectrum (the peaks belonging to this spectrum are denoted by F in Figure 1). The extrema splitting values (the difference in the magnetic field values between the outermost identifiable peaks in a particular spectrum) for the broad-line and narrow-line spectra are plotted as a function of temperature in Figure 2.

We attribute the broad-line spectrum to a slow phase[6] where the TANOL radicals are undergoing molecular motions and the narrow-line spectrum to a fast phase where the radicals are undergoing much faster motions. An alternative explanation for the line shapes observed above 220 K would be the following. The spectra are assigned to one radical phase, and the development of the spectrum with increasing temperature is attributed to an incomplete averaging of the hyperfine and g anisotropy brought about by anisotropic motion. We have employed several experimental approaches to establish that the former explanation, i.e., the presence of two superimposed spectra, is correct. The results obtained in the following experiments, which involve the paramagnetic relaxation times, are consistent with this conclusion.

Paramagnetic Relaxation Times. The broad-line and

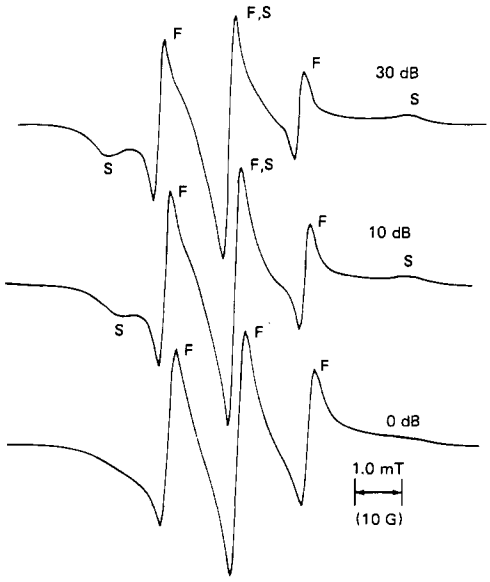

Figure 3. Dependence of the EPR line shapes on the applied microwave power. The spectra were obtained with 30, 10, and 0 dB settings of the microwave power attenuation incident on the cavity. The peaks associated with the slow phase and the fast phase are denoted by S and F, respectively. The measurements were made at 293 K.

narrow-line spectra show a different dependence on microwave power saturation, indicating different values of the electron spin–lattice relaxation time for the slow and fast phases. As shown in Figure 3, the amplitude of the broad-line spectrum can be reduced progressively by increasing the microwave power with little reduction in the amplitude of the narrow-line spectrum until at a power increase of 30 dB, the broad-line spectrum can be reduced to almost zero intensity.

Pulsed EPR experiments involving the generation of electron spin echoes show that the phase memory time T_M (the time characterizing the two-pulse electron spin echo envelope decay) is much longer for the slow phase than for the fast phase. This feature is clearly exhibited in the following way.

Microwave pulses are applied at $t = 0$ and $t = \tau$, and the electron spin echo appears at $t = 2\tau$ (see Figure 4d). A boxcar integrator is triggered at $t = 2\tau$ with a window width less than the echo width. The boxcar output is recorded as the magnetic field is swept, and the resulting echo-height spectrum at $t = 2\tau$ is obtained. The results for TANOL in the DMS/BPAC block copolymers are shown in Figure 4. The absorption line shape obtained from an integration of the derivative EPR spectrum is shown in Figure 4a. The echo-height spectrum obtained by using a two-pulse sequence (Figure 4d), with 20-ns pulse widths and an interpulse time τ = 800 ns, is shown in Figure 4b. There is no indication of the narrow lines in this spectrum, which indicates that T_M for these lines is less than 800 ns. Furthermore, by using a single $\pi/2$ pulse, it was possible to detect the free induction decay signals (Figure 4c) from each of the three narrow lines and record these signals with a boxcar integrator triggered at a time 150 ns after the $\pi/2$ pulse (Figure 4e). The free induction decay signals from the broad-line spectrum were not recorded in Figure 4c because the decay time is given by $\sim 1/(\gamma H') = 8$ ns, where H' is the amplitude of the microwave magnetic field ($H' = 0.7$ mT in these experiments) and γ is the electron gyromagnetic ratio. Thus, with a two-pulse sequence, the echo height responds only to the broad-line spectrum, whereas with a single pulse, the free induction decay signal responds only to the narrow-line

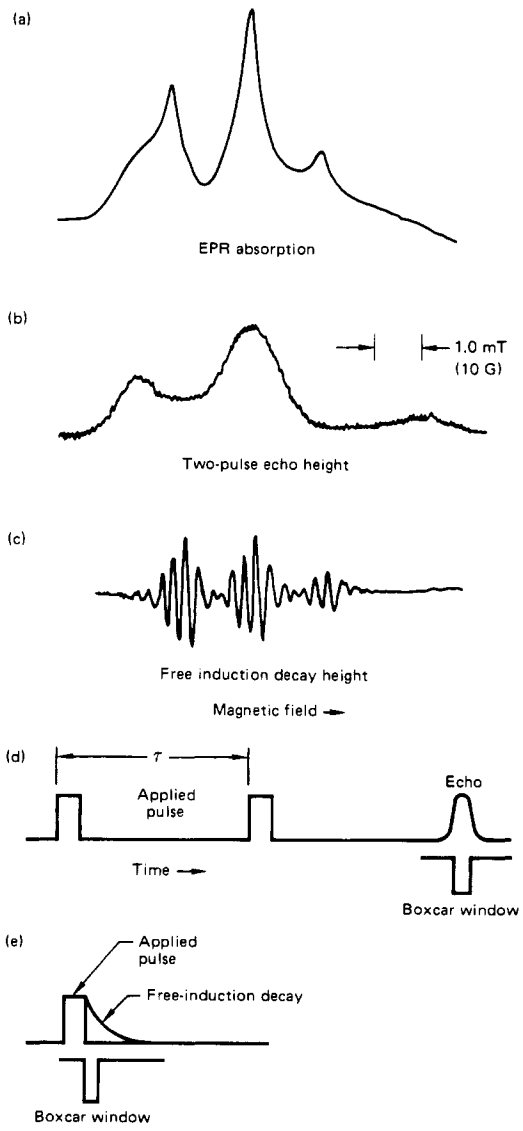

Figure 4. EPR absorption, echo-height spectrum, and free induction decay response together with the pulse sequences used with a sample of the DMS/BPAC block copolymer containing TANOL.

spectrum. These experiments indicate that the broad-line spectrum is inhomogeneously broadened, whereas the narrow lines are homogeneously broadened (almost).[7] Thus the broad-line and narrow-line spectra have different characters, which conclusively proves that two radical phases[6] are present.

Temperature Dependence of Radical Phases. The temperature dependence of the spectra observed between 220 and 400 K indicates that the number of radicals in the fast phase[6] increases at the expense of the number of radicals in the slow phase, but at any given temperature the relative number in each phase is reproducible on cycling the temperature. We define α as the number of radicals in the fast phase divided by the number of radicals in the slow phase.

We have measured α as a function of temperature between 220 and 369 K from a double integration of the first-derivative spectra. This measurement was accomplished by digitizing and integrating the first-derivative spectra, using a multichannel signal averager (Nicolet 1070). Figure 5 is a typical example of the results. The second integral was obtained by evaluating the areas under each spectrum in Figure 5b with a calculator (Hewlett-Packard 9810A) and a digitizer (Hewlett-Packard 9864)

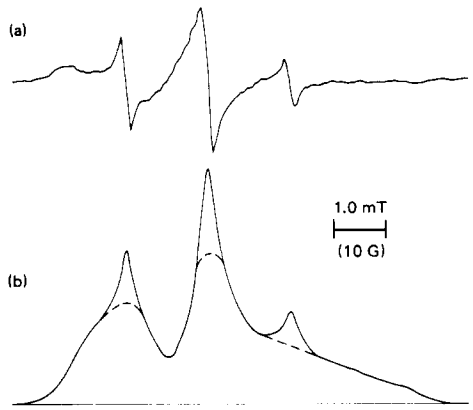

Figure 5. (a) Typical derivative EPR spectrum of TANOL in the block copolymer with 50 wt % DMS/BPAC ($\overline{DP}_{BPAC}$ = 6, $\overline{DP}_{DMS}$ = 20). (b) EPR absorption spectrum resulting from an integration of a. The dashed lines are estimates of the broad-line spectrum.

after disentangling the line shapes in the overlap region. The errors in determining α are set by the accuracy of the spectral overlap estimation, i.e., the locations of the dashed lines in Figure 5b. The low- and high-field lines of the broad-line spectrum are fairly well determined; it is the estimates of the overlap of the central lines that primarily establish the errors. However, by allowing for equal areas beneath each line of the fast phase, this error can be minimized. The temperature dependence of α shown in Figure 6 indicates that log α is approximately linearly proportional to $1/T$ from 220 to 400 K, with a slope given by $\Delta H/R$, where R is the gas constant and ΔH = 20.5 ± 3.5 kJ/mol.

Discussion

The temperature dependences of the observed line shapes are consistent with the idea that above 220 K there are two radical phases[6] present. As indicated by the line shapes and the results in Figure 2, the motional correlation times for the spin probes in both phases decrease with increasing temperature but at any given temperature the motions are much faster in one phase than in the other.

The onset of the motional narrowing of the EPR spectrum of a spin probe in a solid polymer can be crudely characterized by a critical temperature T_c, above which the probe is in the fast motional region. Thus for temperatures above T_c, the values of the motional correlation time, τ_c, are less than a set value; i.e., $\tau_c < 10^{-9}$ s. As previous work[8] indicates, T_c depends on the size of the probe, but for a given probe T_c is often related to the value of the glass transition temperature of the polymer since the T_c values can be determined by the main-chain segmental motions of the polymer. The fast phase is therefore assigned to spin probes located in rubbery DMS block environments, i.e., DMS blocks undergoing main-chain segmental motions. The slow phase is identified with spin probes located in domains of associated BPAC blocks and/or in regions of DMS blocks whose segmental motions are restricted by the constraints imposed by the rigid BPAC domains. Thus this model incorporates the idea of distributions (in frequency and/or amplitude) of segmental motional activity along the DMS chains—a concept which has been demonstrated in pulsed NMR studies[9] and which can be realistically expected from the known morphology[2] of the DMS/BPAC block copolymers.

Yet the idea of distributions of segmental motions resulting from restrictions imposed by the rigid associated BPAC blocks raises the question of why only two spectra are observed. At any temperature above the lower limit

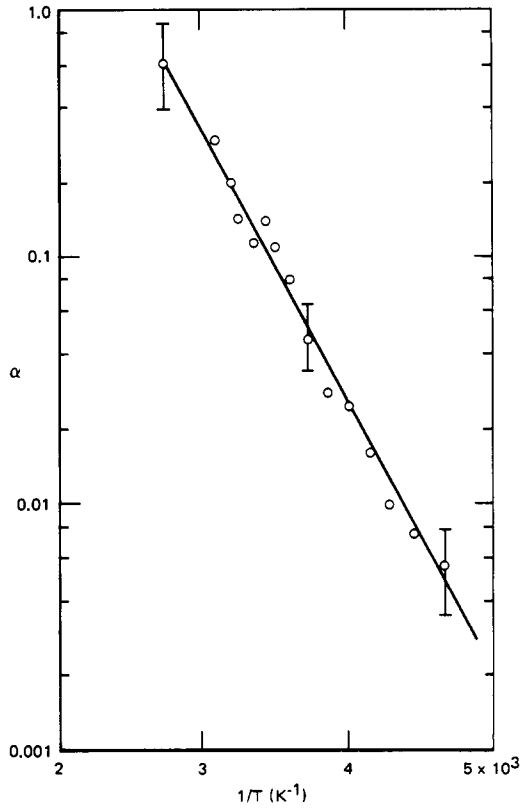

Figure 6. Temperature dependence of α [=(number of radicals in the fast phase)/(number of radicals in the slow phase)] for the block copolymer with 50 wt % DMS/BPAC ($\overline{DP}_{BPAC}$ = 6, $\overline{DP}_{DMS}$ = 20).

of the onset of segmental motions, one expects to observe the superposition of a series of spectra, each characterized by a correlation time that can range in value from the slow to the fast motional extremes. However, the observed spectra appear to indicate only two situations of fast and slow motions with no intermediate cases. This puzzling feature has led us to formulate the following explanation.

Assume that the temperature dependence of the extrema values for all spin probes in identical environments have the form shown by the solid lines in Figure 7a. This situation would occur if the activation energy for the motion of the spin probe was large at temperatures close to T_c and would imply that the motional narrowing for the probe spectrum occurs over a narrow temperature range. All observed spectra obtained at different temperatures would then consist of only two types: a slow-phase spectrum and a fast-phase spectrum.

A distribution in polymeric segmental motion (in either amplitude or frequency) implies that spin probes at other sites with different rigidities exhibit different values of T_c, e.g., T_{c1}, T_{c2}, ..., T_{cN} in Figure 7b. Thus a distribution in segmental motional activity produces a distribution in T_c values. At any temperature T, the observed spectrum then consists of two superimposed spectra, a slow phase corresponding to spin probes with $T < T_c$ and a fast phase with $T > T_c$.

A meaningful interpretation of the temperature dependence of α in Figure 6 and what ΔH represents depends on how the spin probes can get from the slow phase to the fast phase. This, in turn, depends on the exact type of molecular motions the radical undergoes. There are two extreme situations. The radicals can undergo fast translational diffusion so that they can freely diffuse across the region between the fast- and the slow-phase locations to establish a temperature-dependent equilibrium of numbers

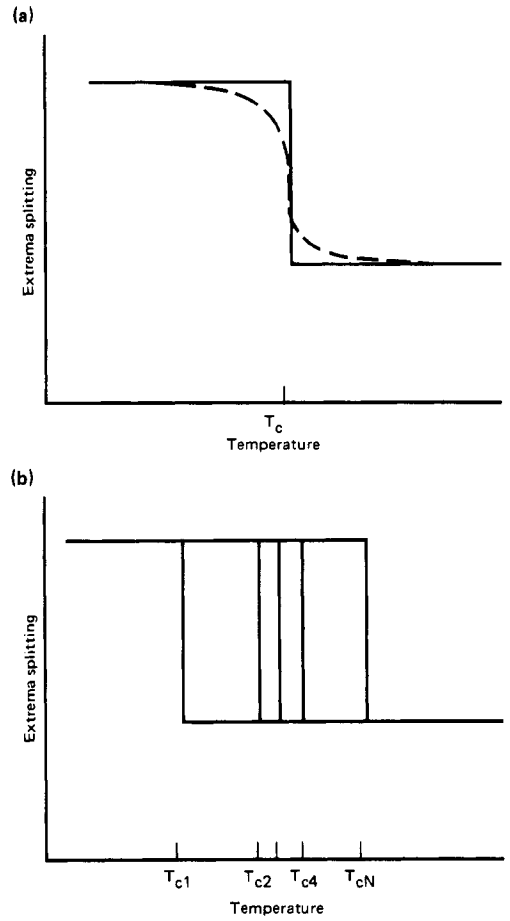

Figure 7. (a) Idealized temperature dependence of the extrema splitting for a typical spin probe (solid line). The dashed line is the more realistic behavior. (b) Assumed temperature dependence of the extrema splitting values for the spin probes undergoing different rotational motions because of their different environments. The distribution of probe motions is characterized by a distribution of T_c values, T_{c1}, T_{c2}, ..., T_{cN}.

of probes in the rubbery and rigid regions. The slope of the temperature dependence of ln α, and hence ΔH in Figure 6, is then determined by the difference in the heats of solution of the radical in the rubbery region and in the rigid regions.

On the other hand, if the radical undergoes only rotational diffusion at a fixed location and the translational diffusion between the rubbery and rigid regions is slow, then the probe can go from the slow phase to the fast phase only when the boundary defining the region of segmental motional activity recedes past it. The temperature dependence of α is then a measure of how the relative amounts of rubbery and rigid regions change with temperature.

Experiments with γ-irradiated DMS/BPAC samples containing TANOL spin probes have shown that below ≈330 K, the rate for translational diffusion between the rubbery regions and the rigid regions is very slow.[10]

For temperatures just above 220 K, only the less restricted parts of the DMS chains located at the center of the blocks will undergo segmental motions to allow the spin probes located there to be in the fast phase. As the temperature is increased and this segmental motion grows out from the center of the DMS chains, more spin probes will be in the fast phase. This model can therefore account for the temperature dependence of α. Moreover, it also explains why even at temperatures as low as 220 K, the lines in the fast-phase spectrum are narrow.

The above model can be described quantitatively in the following way. Consider all n_i probes in the same ith environment and assume that the temperature dependence of the extrema values for each of the n_i probes is of the form shown in Figure 7a. For $T < T_c$, $s = n_i$ and $f = 0$, where s and f are the numbers in the slow and fast phases, respectively, and for $T > T_c$, $s = 0$ and $f = n_i$.

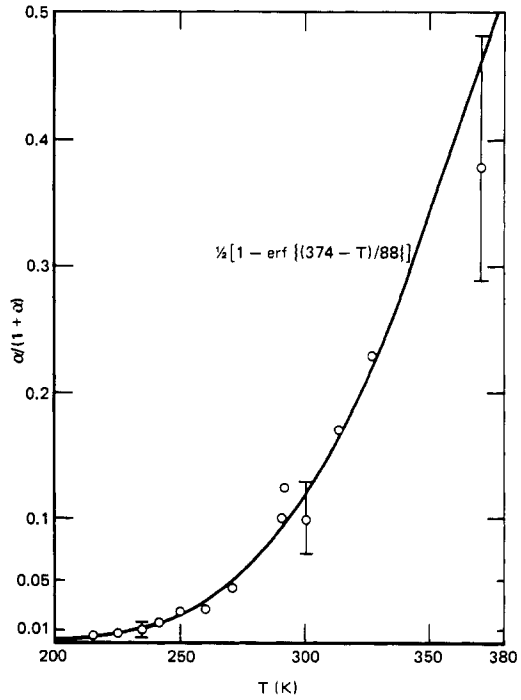

Figure 8. Observed temperature dependence of $\alpha/(1 + \alpha)$. The solid line assumes a Gaussian distribution of T_c values and is given by $^1/_2\{1 - \text{erf}[(T_0 - T_c)/\Delta]\}$, with $T_0 = 374$ K and $\Delta = 88$ K.

As a result of the constraints on the segmental motions, assume a distribution of T_c values. For reasons of mathematical tractability, assume a Gaussian probability function for the distribution; i.e., the probability that the transition temperature has the value T_c is given by $P(T_c)$ with

$$P(T_c) = \Lambda \exp[-(T_0 - T_c)^2/\Delta^2] \quad (1)$$

where T_0 is the center of the distribution, Δ is the half-width of the distribution, and Λ is the normalization factor.

The fast-phase fraction observed at a temperature T is given by[11]

$$\frac{f}{N} = \frac{\alpha}{(1+\alpha)} = \frac{2}{\Delta\pi^{1/2}}\int_{-\infty}^{T}\exp\left[-\frac{(T_0 - T_c)^2}{\Delta^2}\right]dT_c \quad (2)$$

$$\frac{f}{N} = \frac{1}{2}\left(1 - \frac{2}{\Delta\pi^{1/2}}\int_{T}^{T_0}\exp\left[-\frac{(T_0 - T_c)^2}{\Delta^2}\right]dT_c\right) \quad \text{for } T < T_0 \quad (3a)$$

$$\frac{f}{N} = \frac{1}{2}\left(1 + \frac{2}{\Delta\pi^{1/2}}\int_{T_0}^{T}\exp\left[-\frac{(T_0 - T_c)^2}{\Delta^2}\right]dT_c\right) \quad \text{for } T > T_0 \quad (3b)$$

$$\frac{f}{N} = \frac{1}{2}(1 \mp \text{erf}\,[(T_0 - T_c)/\Delta]) \quad (4)$$

Figure 8 is a replot of the data shown in Figure 6 in the form $f/N = \alpha/(1 + \alpha)$ vs. temperature. The data exhibit good agreement with eq 3a for the values $T_0 = 374$ K and $\Delta = 88$ K.

Conclusions

The values of T_0 and Δ obtained from a fit of the tem-

perature dependence of α, assuming a Gaussian probability distribution for T_c, are an indirect measure of the distribution of main-chain segmental motional activity in the block copolymer. Several factors can contribute to this distribution of motional activity. First, a gradient of motion in amplitude and/or frequency along the DMS blocks exists which is a direct result of the motional constraints imposed by the rigid BPAC blocks in domains.[9] Second, there are distributions of block lengths in these block copolymer samples.[12,13] These differences in block length will lead to chain-to-chain variations in the gradient of motional activity along the DMS chains. Third, regions exist where the BPAC blocks are not all in domains but rather some are interspersed to some degree into the DMS regions. The tendency for the BPAC domains to break up increases as the temperature approaches the glass transition associated with the BPAC domains. Hence the effect of a distribution of segmental motions in the BPAC blocks will be greatest above 300 K. All three of these factors probably contribute to the distribution of segmental motions in the DMS/BPAC block copolymer studied. However, without well-characterized block copolymer samples, where each of these factors can be varied independently, it is not clear how the separate contributions to T_0 and Δ can be estimated.

The value $T_0 = 374$ K implies that there is some slow phase present above the glass transition temperature associated with the BPAC domains (345 K). This suggests that spin probes are located in the domains as well as in the regions with DMS block environments.

Our assumption that the onset of radical rotational motions takes place over a narrow temperature range implies that there is a bimodal-like distribution of motional correlation times. The slow-phase component consists of spin probes with $\tau_c \gtrsim 10^{-7}$ s, whereas the fast-phase component is composed of spin probes with $\tau_c \lesssim 10^{-9}$ s. The spin probes with the values 10^{-9} s $< \tau_c < 10^{-7}$ s constitute such a small number that their contribution to the observed line shape is small.

The real situation for the temperature dependence of the extrema values for a spin probe in a particular environment probably corresponds more closely to the dotted lines in Figure 7a. As a consequence, the spectra of both the slow and the fast phases will be broadened by the inclusion of contributions to the spectral line shape from probes with intermediate correlation times (10^{-9} s $< \tau_c <$ 10^{-7} s). The larger the contributions from these intermediate correlation times, the less bimodal-like the distribution of correlation times becomes. However, we do not rule out the possibility that there may be polymeric materials where the spin probes exhibit spectra which appear to be the superposition of only a slow phase and a fast phase but which result from a wide distribution of correlation times, which is not necessarily a bimodal distribution. A comparable situation has already been analyzed[14] and applied to proton NMR results to explain the temperature dependence of the line shapes and relaxation times.

In a previous EPR study[15] of nitroxide spin probes in other types of block copolymers, a superposition of broad-line and narrow-line spectra was also reported. The broad-line spectrum was attributed to spin probes in the interfacial material between the rigid and the rubbery phases. In the DMS/BPAC block copolymers, the chain lengths between the domains are much shorter ($\sim$5 nm), the interfacial material is not clearly defined, and hence an identification of the broad-line spectrum with spin probes located in the interfacial region is not appropriate in our studies.

Samples of TANOL in the DMS and BPAC homopolymers exhibited EPR line shapes that were distinctly different from those described above for the block copolymers. Thus, at each temperature between 220 and 400 K, the spectra could be characterized by only one value of the motional correlation time. This result is confirmation that the two-phase nature of the spin probe EPR spectra is a characteristic feature of the block copolymer.

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