

ESR Studies of Molecular Motions at the Interphase Region of a Blendlike Polymeric Material

ÖNDER PEKCAN,^{1,*} YUSUF DEMIR,² and OLGUN GÜVEN²

¹Department of Physics, Istanbul Technical University, Maslak, 80626, Istanbul, Turkey; ²Department of Chemistry, Hacettepe University, Beytepe, Ankara, 06532, Turkey

SYNOPSIS

The molecular motions of spin probes at the interphase region of poly(methyl methacrylate) particles sterically stabilized by polyisobutylene (PIB) were studied by ESR spectroscopy. The correlation times (τ) were measured by using the methods of Freed and Kivelson. Activation energies for different modes of motion were calculated at wide temperature range between -140 and 140°C . Viscosities were estimated in methanol saturated PIB channels in the polymer particles. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It has been well known that the spin-probe technique is very useful to understand and characterize the molecular motions in synthetic and biopolymers.¹⁻³ Since the order of magnitude of anisotropy in a hyperfine coupling is about 10^8 Hz, the time scale of molecular motion required to average the anisotropy is shorter than 10^{-8} s. This makes the ESR technique important to study rapid molecular motion on the time scale of nanoseconds to picoseconds.

The basic problem arising from the use of this method is the relationship between the motions of a low molecular particle and those of the kinetic elements of macromolecules. It has been shown that the motions of spin probes in the high elastic state are determined by the short-range segmental motions.^{4,5} It was reported that spin-probe motions in the polymer films were influenced by differences in the side chains; this influence is strongly dependent on the side chain length.⁶

Rabold successfully applied the spin-probe method to several synthetic polymers, to study their molecular motions.^{7,8} Poly(methyl methacrylate) (PMMA) is one of the polymers on which molecular motions have been studied by the spin-probe technique.^{4,9} Kusumato et al. used the same method to

study segmental diffusion in the rubbers.¹⁰ All these authors analyzed the observed spectra based on the assumption that the rotational reorientation is isotropic. The correlation time, τ , of the rotational motion of the spin probe can be determined by the simplified expression of Freed et al.¹¹ for isotropic rotation in the slow motional region (10^{-9} s $<$ τ $<$ 10^{-7} s). However, for isotropic rotation in the fast-motional region (10^{-11} s $<$ τ $<$ 10^{-9} s), Kivelson's expression¹² has been widely used to estimate the rotational correlation times.

We used spin probes to study solvent penetration into polymer-blendlike particles.¹³ Recently, we reported the penetration of various solvents into PMMA particles sterically stabilized with polyisobutylene (PIB).¹⁴

In this work, ESR spectra of spin probes in PMMA-PIB particles were measured over a wide range of temperature and the correlation times (τ) were estimated by making use of Freed's and Kivelson's methods. These particles are spherical in shape and usually prepared by dispersion polymerization of methyl methacrylate (MMA) in cyclohexane in the presence of butyl rubber.¹⁵ The major component in this type of particle, PMMA homopolymer of broad molecular weight distribution, is present to about 95–97% by weight. During the reaction, grafting occurs between the butyl rubber and the growing PMMA chains. Most of the graft copolymer is buried in the particle interior where it forms an interconnected network¹⁶ from PIB. Some

* To whom correspondence should be addressed.

graft copolymer forms a monolayer on the particle surface, which serves as the steric stabilizer. Thus, these particles have an interpenetrating networklike global morphology. This global feature of the morphology has been of interest and studied carefully.¹⁷⁻¹⁹

In this article, our emphasis is focused on the interface between the PIB and PMMA phases where they mixed and formed an interphase domain.²⁰ Here, transport experiments were prepared with PMMA-PIB particle dispersion in an aliphatic hydrocarbon liquid with nitroxide radicals. Since this solvent will not swell PMMA itself, we inferred that PIB penetrated throughout the particle, exposing the interior of the particle to solvent and the spin probe. The composite nature of the nitroxide spectra of PMMA-PIB particles in methanol were interpreted in terms of the interphase structure in the particle. Spin-probed PMMA film was used as a model for the slow component of the ESR spectra of powder PMMA particles. The spectra of the free spin probes in methanol were used to check the behavior of the fast component of the ESR spectra of the methanol-saturated PMMA particle. The results are discussed in terms of the mode of the molecular motions in polymeric system over a wide range of temperature. Viscosities were estimated in methanol-swollen PIB phase of the particle at various temperatures.

EXPERIMENTAL

The structure of the nitroxide radicals used in this work as spin probes are shown in Figure 1. 3-Carbomoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (R_1) and 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolinyloxy (R_2) were purchased from Aldrich Chemical Co. and used as received. The polymer particles were prepared in a two-step process that has previously been described.¹⁵ PIB of nominal molecular weight 10,000 was added to a cyclohexane solution of MMA containing AIBN as a free-radical initiator. The solution was refluxed for several hours to induce polymerization of the MMA. The growing PMMA chains added across double bonds present in the PIB to give a graft copolymer soluble in cyclohexane. Polymerization was terminated before the copolymer became insoluble in the cyclohexane solvent. This material, the dispersant, was collected and purified by precipitation with methanol. The dispersant was then added to a second reaction vessel containing MMA and AIBN in cyclohexane. This

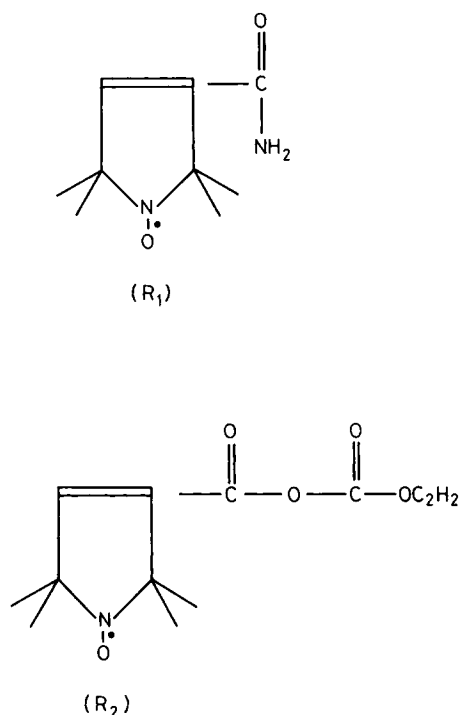


Figure 1 Chemical structure of the nitroxide spin-probes; R_1 (3-carbomoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy) and R_2 (3-carboxy-2,2,5,5-tetramethyl-1-pyrrolinyloxy).

solution was refluxed overnight. It became increasingly turbid as the reaction progressed.

The particles were separated from solvent and unreacted monomers by repeated cycles of centrifugation, decanting the supernatant liquid, and re-dispersing the particles in fresh solvent. Dispersions in cyclohexane could be freeze-dried and stored as a powder. The powders could be redispersed by subjecting their suspensions in alkane solvents to a few seconds exposure to an ultrasonic cleaning bath. These particles formed transparent solutions in ethyl acetate and in deuteriochloroform. NMR spectra of these latter solutions permitted the composition of the polymers to be determined.

PMMA particles used in this study had diameters of 1–3 μm . Spin probes were doped into these particles by the procedure described below. Nitroxide R_1 (or R_2) was first dissolved in methanol solution and then particles were added into the solution. Four days after solvent was removed and the sample was dried under vacuum (10^{-4} Torr) for 10 h in the ESR tubes, the tubes were sealed under vacuum. The weight ratio of the spin probe to powder particles was 10^{-4} . This sample was referred to as PCL. After waiting 4 days, the spin probe-particle suspension

was centrifuged and methanol was removed. After removing the solvent from the ESR tube, the sample was degassed by several freeze-pump-thaw cycles at 10^{-5} Torr on the vacuum line. At the end of degassing, no free solvent could be seen in the tube. The sample resembled an aggregate of gel-like material, which was called methanol-saturated particles (MSP).

The low molecular weight of the PMMA material was dissolved in an ethyl acetate solution and then 10^{-2} wt % nitroxide radical R_2 (or R_1) was added. A thin film of nitroxide-doped PMMA was cast from this solution. Films were dried under 10^{-4} Torr vacuum about 10 h in an ESR tube and sealed under vacuum. This sample (PMMAF) was used as a model for the motionally slowed ESR spectra of PMMA.

Samples of R_2 (or R_1) in methanol (10^{-4} m concentration) were prepared. They were sealed in an ESR tube after degassing via five freeze-pump-thaw cycles at 10^{-5} Torr on a vacuum line. The samples (NRM) were used as models for motionally narrowed isotropic ESR spectra. The solvent used in the preparation of samples was obtained from Merck. ESR spectra were recorded on a Varian E-L9 spectrometer operating at X-band frequency (9.1–9.5 GHz) and employing 100 kHz field modulation. The spectrometer was equipped with a variable temperature accessory along with a liquid nitrogen system.

RESULTS AND DISCUSSION

Figure 2(a) and (b) shows typical ESR spectra of the (R_2)-doped MSP and PCL samples, respectively, over a wide range of temperature. At the lowest temperature (-140°C), the spectra are broad with asymmetric triplets. The separation of the outer extremes ($2A_z$) are about 70 and 66 Gauss for MSP and PCL, respectively. These $2A_z$ values indicate that the mobility of the nitroxide was restricted due to rigid environment in the PMMA particle. As the temperature was raised above -90°C , which is the melting point of methanol, MSP represented a composite spectra with slow and fast components. However, PCL does not show any considerable change up to 80°C . $2A_z$ values of the slow component became narrower as temperature was raised in both samples. The fast component of MSP showed no change up to 80°C . A new narrowed component appeared, superimposed on the original broad component for the PCL sample above 100°C . $2A_z$ values of the fast component of MSP showed a sudden

change around 100°C . At higher temperatures ($> 130^\circ\text{C}$), the broad component disappeared and the narrow one turned into a sharp triplet as in the spectrum of the viscous liquid state for both samples. R_1 with MSP and PCL showed similar results as the above samples. ESR spectra of the spin-probed PMMAF sample behaved similarly to the PCL spectra in the same temperature range.¹³ The temperature dependence of peak-to-peak separation of the two outer extremes ($2A_z$) for MSP and PCL samples are shown in Figure 3. PMMAF exactly mimicked the PCL's temperature behavior.¹³ However, the $2A_z$ values of the slow component of the MSP sample showed a slightly different temperature dependence than that of the PMMAF and PCL samples. Peak-to-peak separation of the fast component of MSP imitated the behavior of NRM at low temperatures.¹³ The peculiar feature at 90 – 120°C , where $2A_z$ increases with temperature, may be an artifact due to loss of some of the methanol in the sample to the vapor phase above the powder.

Correlation Times

The rotational correlation times (τ) for the spin probes in the polymeric systems and NRM samples were estimated mainly in slow and fast motional regimes. These regimes were separated from each other by T_{50} , the temperature at which the separation of the outermost peaks ($2A_z$) of the ESR spectra of nitroxides are 50 Gauss. The temperature range below T_{50} was accepted as the slow motional region (5×10^{-9} s $< \tau < 10^{-7}$ s) for the spin probes, where the spectra are broad and have asymmetric triplets. In this region, τ was calculated by using the method developed by Freed et al.¹¹ given by

$$\begin{aligned}\tau &= a(1 - S)^b \\ S &= A'_z/A_z\end{aligned}\quad (1)$$

where A'_z is the measured separation of the outer extrema, and A_z , the rigid limit value for frozen spin probes. Selection for the a and b parameter values are dependent upon the diffusion models.²¹ In this work, the Brownian diffusion model was chosen¹¹ and a and b values were estimated as 5.4×10^{-10} and -1.36 , respectively.

In the fast motional region (10^{-11} s $< \tau < 5 \times 10^{-9}$ s) above T_{50} , where spectra have relatively sharp triplets, τ was calculated using an equation based on the theory of Kivelson¹²:

$$\tau = C \left[\left(\frac{h(0)}{h(-1)} \right)^{1/2} - \left(\frac{h(0)}{h(+1)} \right)^{1/2} \right] \Delta H_{pp} \quad (2)$$

where $h(0)$ and $h(\pm 1)$ are the measured peak-to-peak amplitudes of three lines of the ESR spectrum of the nitroxide radical. ΔH_{pp} is the width of the central peak in Gauss and C is a characteristic parameter for the nitroxide and the particular experimental conditions employed. C was calculated from the anisotropy of hyperfine constants of R_1 and R_2 and found to be 6.6×10^{-10} s/Gauss for both nitroxides.

Correlation times obtained by the two different methods were plotted in semilogarithmic scale

against the inverse of the temperature for PCL, PMMAF, and for the slow component of MSP in Figure 4. Correlation times for the slow component of MSP behaved quite differently from the other solid samples, indicating the existence of trace methanol in the PMMA phase or the PMMA-PIB interphase of the methanol-saturated particle. τ values of the slow component of the MSP samples were much smaller than the τ values of PCL and PMMAF, which may suggest that the solid phase of MSP is not as rigid as the solid phase of PCL (or

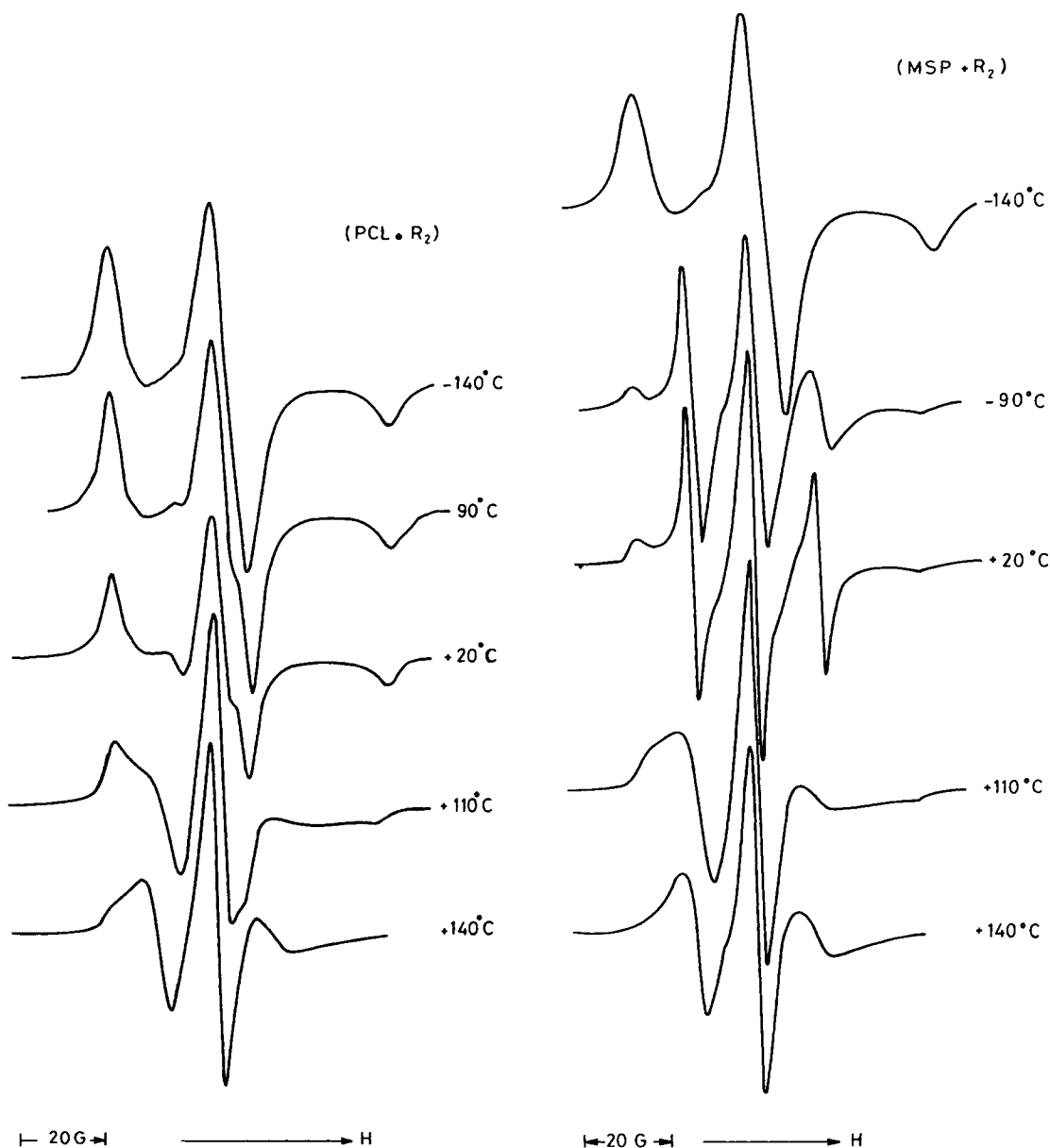


Figure 2 ESR spectra of R_2 -doped (a) powder (PCL) and (b) methanol-saturated (MSP) PMMA particles at various temperatures.

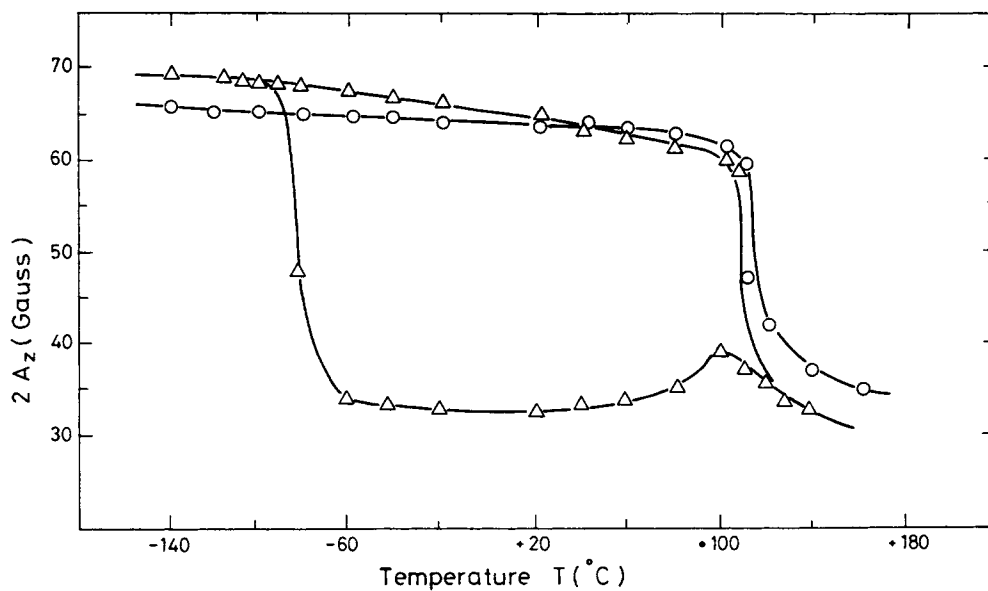


Figure 3 The temperature variation of the outermost peak to peak separation ($2A_z$) for the R_2 probe: (—○—○) PCL and (—△—△) MSP samples. Smaller $2A_z$ values (< 50 G) indicate that the fast and larger $2A_z$ values (> 50 G) correspond to slow components of the composite ESR spectra of the MSP sample.

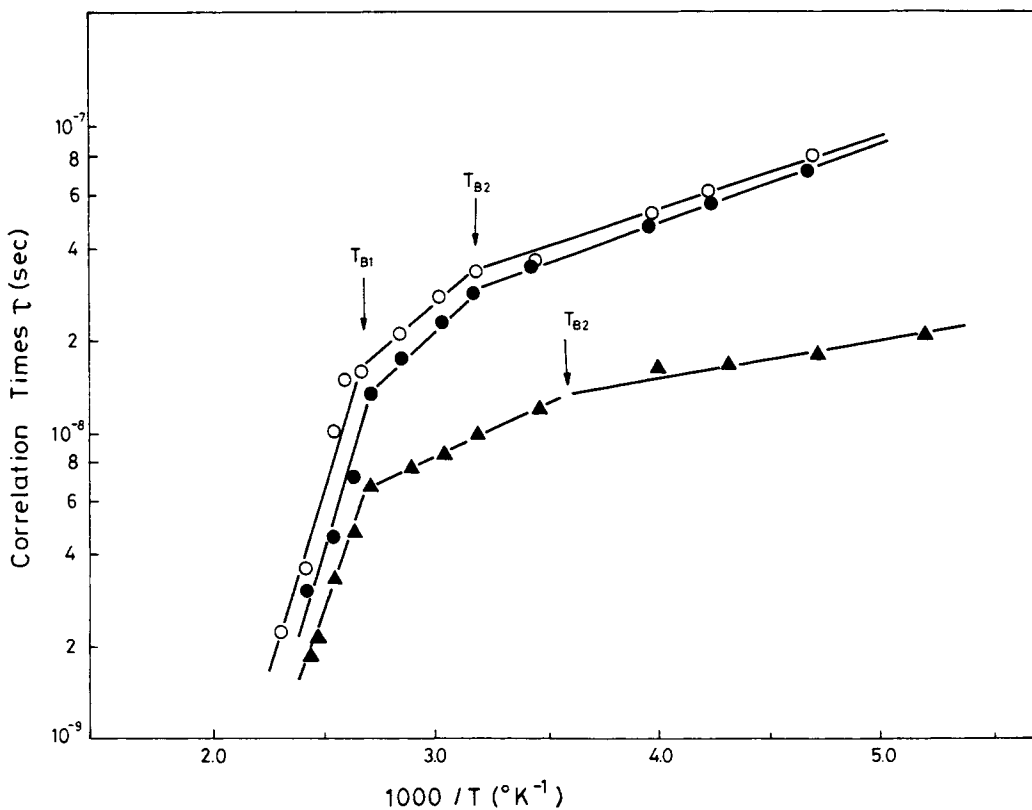


Figure 4 Arrhenius plots of the correlation times (τ) obtained from Eqs. (1) and (2) for the R_2 probe: (—○—○) PCL, (—●—●) PMMAF, and (—▲—▲) MSP (slow component) systems.

PMMAF). Presumably, some methanol penetrated into the PMMA-PIB interphase domain through the PIB network^{20,22} where spin probes are trapped in the swollen PIB microchannels in the MSP sample. Here, the environment for the spin probe is less rigid than the environment in PCL and PMMAF samples.

τ values for the fast component of MSP are compared with the τ values for NRM against the inverse of temperature in Figure 5. Correlation times of the fast component of the MSP sample were slightly larger than the τ values of the NRM sample in the given temperature range, which might indicate that the rotational mobility of the spin probe was restricted by the polymer chains in the PIB network. In other words, nitroxides see a more viscous environment in methanol-swollen PIB than in pure methanol. The results presented in Figures 4 and 5 can be explained by the interphase structure in the PMMA-PIB blendlike particles.²⁰ A cartoon representation of the interphase structure is depicted

in Figure 6 for illustration. Fast and slow ESR components of MSP are due to the spin probes located in the PIB-rich region and PIB channels in the PMMA-rich region at the interphase domain, respectively.

At these temperature ranges, correlation times for R_1 and R_2 probes in these polymeric systems were found to be similar, which may indicate that τ values of these radicals are not affected by their sizes in the PIB channels even in PCL samples.

Activation Energies and Breaking Temperatures

Arrhenius plots of correlation times for slow ESR components of all polymeric samples are partitioned into three regions with respect to temperature (see Fig. 4). Activation energies (ΔE) measured at low-, medium-, and high-temperature regions and the breaking temperatures (T_B) between these regions are listed in Table I for the corresponding samples. In all regions, Arrhenius plots presented

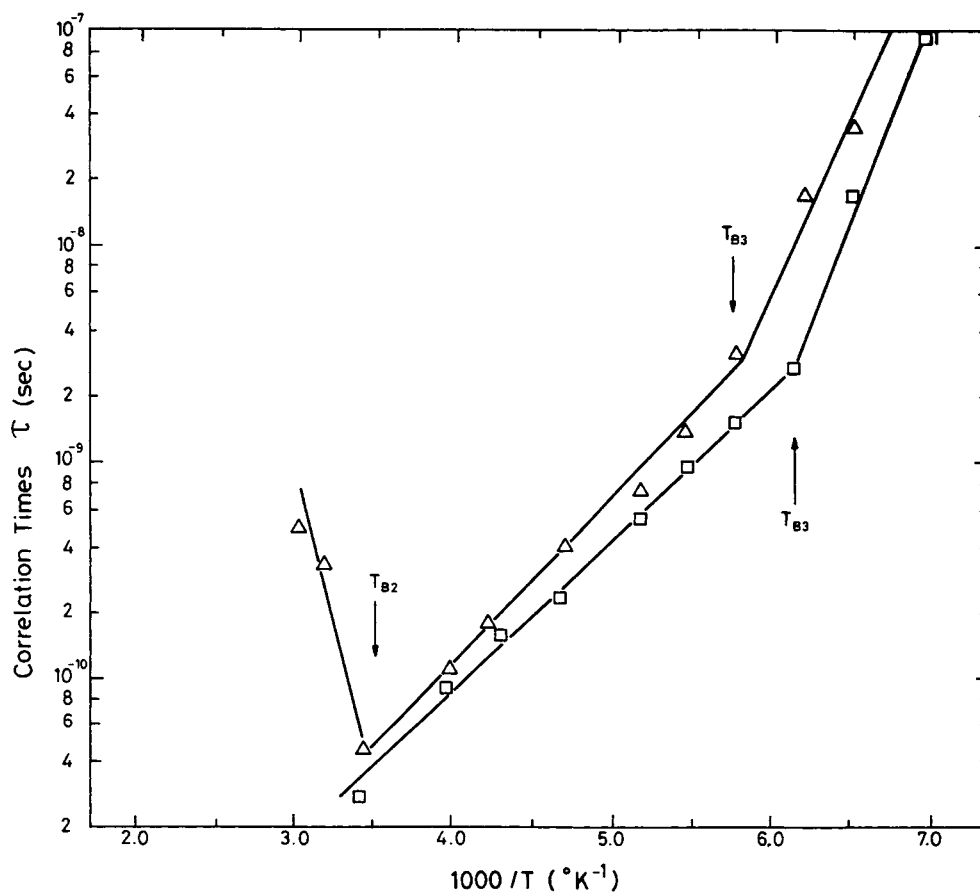


Figure 5 Arrhenius plots of the correlation times (τ) obtained from Eqs. (1) and (2) for the R_2 probe: (— Δ — Δ) MSP (fast component) and (— \square — \square) NRM systems.

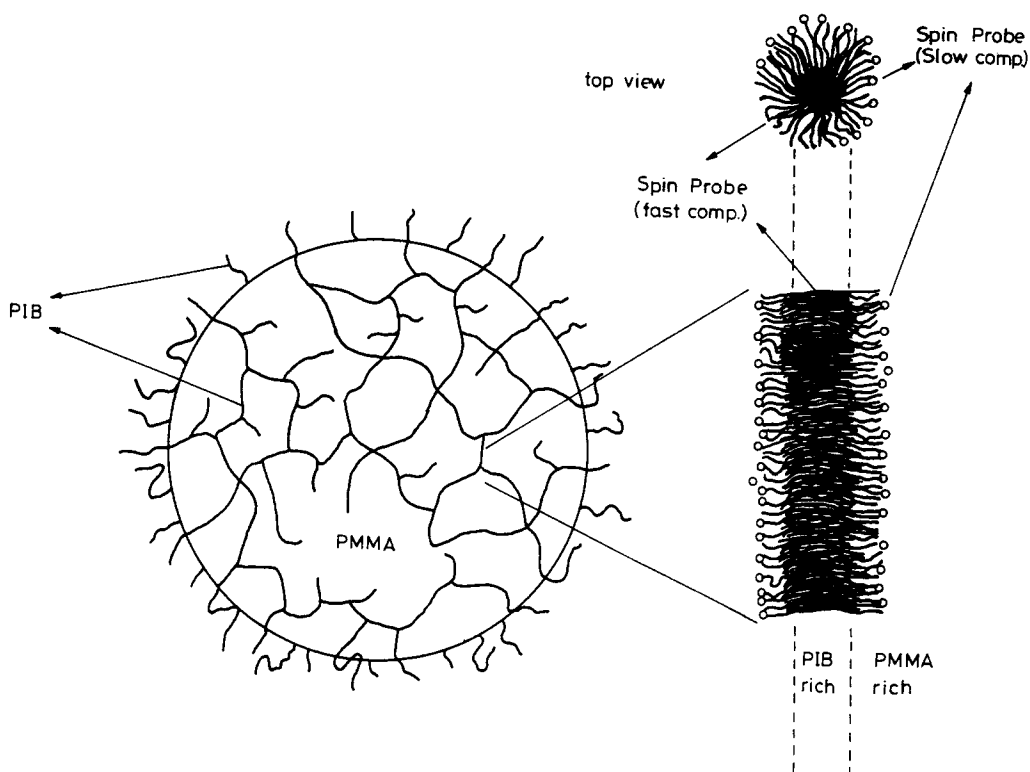


Figure 6 Cartoon representation of the interphase domain of the PMMA-PIB particle.

good linear behavior. At the low-temperature region, below $T_{B2} = 40^\circ\text{C}$, a very slow variation was observed in correlation times for all samples and activation energies (ΔE_3) were found to be between 0.5 and 0.9 kcal. However, at the intermediate region, between T_{B1} and T_{B2} , activation energies (ΔE_2) for the PCL and PMMAF samples were measured larger than for the MSP samples.

It has been reported that the molecular motions of the spin probe are functions of various factors such as oscillation, rotation, and translation.²³ Activation energies of small-scale motion consisting of oscillation and rotation are much less than 10 kcal

and that of large-scale motion such as translational diffusion is measured much greater than 10 kcal.²⁴ In our particles, since the spin probe is trapped in the interphase domain, activation energies at the lowest temperature region, below T_{B2} , might correspond to γ relaxation of PMMA. However, at the intermediate region, ΔE_2 energies of the motional process of all samples may be associated with slower rotational motion (rotational vibration). Consequently, below T_{B1} , the degree of motional freedom in the side-chain region is apparently not sufficient enough to bring about translation of the spin probe in the polymer matrix. An increase in

Table I Activation Energies and Breaking Temperatures in Different Polymeric Systems

Polymeric Systems	Radical	ΔE_1 (kcal)	T_{B1} ($^\circ\text{C}$)	ΔE_2 (kcal)	T_{B2} ($^\circ\text{C}$)	ΔE_3 (kcal)
PCL	R ₁	13.8	100	2.1	40	0.55
	R ₂	11.5	110	3.1	40	0.85
MSP (slow component)	R ₁	9.1	105	1.6	13	0.50
	R ₂	10.1	100	1.5	12	0.65
PMMAF	R ₁	10.3	95	1.9	40	0.77
	R ₂	11.6	100	2.9	40	0.81

Table II Activation Energies and Breaking Temperatures of NRM and the Fast Component of MSP Samples

	Radical	T_{B2} (°C)	ΔE_3 (kcal)	T_{B3} (°C)	ΔE_4 (kcal)
MSP (fast component)	R ₁	7	3.9	-90	7.1
	R ₂	13	3.7	-95	6.1
NRM	R ₁		3.4	-100	7.0
	R ₂		3.0	-110	8.4

temperature above T_{B1} might result in a phase transition of the side-chain motion, which may induce an increase in the activation energies. Above T_{B1} , the activation energies of the spin probe in all polymeric systems were over 10 kcal, indicating that nitroxide translated and jumped throughout the polymer matrix above T_{B1} . The observed activation energies above T_{B1} were much smaller than those of the main-chain motion (40–150 kcal)²⁵ but closer to those of the side-chain motion (19 kcal) of PMMA.²⁶ From this we conclude that it is not unreasonable to assume that the molecular motion at this temperature range is a random rotation of the ester side chain of PMMA for all polymeric systems that we have used.²⁷

The first breaking point, T_{B1} , between the ΔE_1 and ΔE_2 regions can be assigned to the glass transition temperature of PMMA, which was measured around 105°C for all solid samples. The second breaking point, T_{B2} , which was found to be 40°C for PCL and PMMAF and 10°C for MSP samples, is a characteristic temperature for PMMA,²¹ which can be attributed to the onset of the slow rotational motions. Here, it is interesting to note that T_{B2} was found to be very sensitive to the environment, due to swelling of the PIB phase by methanol; however, T_{B1} did not change from the PCL to MSP samples. Presumably, no methanol is left in the MSP sample at this temperature.

Activation energies and breaking temperatures of the fast components of MSP samples were com-

pared with those of the NRM samples in Table II. T_{B2} temperatures of fast components were found to be similar to those of slow components for the MSP samples. T_{B3} values of the fast component of MSP samples measured slightly higher than the melting point of methanol. For both samples, ΔE_3 activation energies for the probe in MSP samples were observed to be similar to the probe in the melting NRM samples, which can be accepted in the slow translational regime. Here, to account for the peculiarities of the rotational and translational mobilities of the low molecular particles (spin probes), we have to take into account the blendlike structure of the polymer particle. One can easily assign the fast component of MSP samples to the spin probe in the highly swollen PIB-rich region.

Using Stokes law,²⁸ quantitative analysis can be made to estimate viscosities in the PIB-rich region in the interphase domains of methanol-swollen polymer particles. If the rotational motion of the nitroxide is assumed to be that of rigid sphere with radius " r " rotating in a liquid with viscosity η at temperature T , then the motional correlation time τ is given by Stokes law as follows:

$$\tau = \left(\frac{4\pi r^3}{3k} \right) \frac{\eta}{T} \quad (3)$$

where k is the Boltzman constant. Equation (3) was used to find the viscosities when the nitroxide is in the fast regime ($\tau < 5 \times 10^{-9}$ s), which is above T_{50} .

Table III Viscosities (η) in the Methanol-swollen PIB Phase of MSP and NRM Samples at Various Temperatures— η Values Were Calculated from Eq. (3) in Centipoise

Temperature (°C)	Radical	-100	-80	-20	+13
MSP (fast component)	R ₁	0.432	0.136	0.025	0.028
	R ₂	0.366	0.119	0.018	0.012
NRM	R ₁	0.177	0.085	0.017	0.003
	R ₂	0.187	0.074	0.017	0.005

Using the fast-component values of τ from Figure 5 and taking $r = 3.6 \text{ \AA}$, η values were estimated in the MSP samples at several temperatures. These viscosities are compared with the viscosities of the NRM samples in Table III at corresponding temperatures. η values in the MSP samples were larger than those of the NRM samples, indicating that the environment for the spin probe in methanol-swollen PIB is always much more viscous than in free methanol. The lowest viscosity in the MSP sample was obtained at T_{B2} , at which the motion of the spin probe in swollen PIB was least restricted by the side-chain motion. Even at this temperature, η values for the MSP samples were observed about an order of magnitude larger than in free methanol.

We thank Professor M. A. Winnik for supplying the latex material and documents to read.

REFERENCES

1. P. Törmälä and J. J. Lindberg, in *Structural Studies of Macromolecules by Spectroscopic Methods*, K. J. Ivin, Ed., Wiley, New York, 1976, p. 255.
2. R. F. Bayer and S. E. Keinath, Eds., *Molecular Motion in Polymers by ESR*, Harwood, New York, 1978.
3. L. J. Berliner, *Spin Labeling. I. Theory and Application*, Academic Press, New York, 1976.
4. A. L. Kovarskii, J. Plavcek, and F. Szöcs, *Polymer*, **19**, 1137 (1978).
5. A. T. Bullock, G. G. Cameron, and P. M. Smith, *J. Polym. Sci.*, **11**, 1263 (1973).
6. K. Takashi, Y. Ei, K. Tadayoshi, and H. Shinji, *Polym. J.*, **16**, 317 (1984).
7. G. P. Rabold, *J. Polym. Sci.*, **7**, 1187 (1969).
8. G. P. Rabold, *J. Polym. Sci.*, **7**, 1203 (1969).
9. Z. Veksli and W. G. Miller, *Macromolecules*, **10**, 1245 (1977).
10. N. Kusumoto, S. Sano, N. Zaitso, and Y. Motozato, *Polymer*, **7**, 448 (1976).
11. S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Phys. Chem.*, **76**, 1858 (1972).
12. D. J. Kivelson, *J. Phys. Chem.*, **33**, 1904 (1960).
13. Ö. Pekcan, Y. Kaptan, Y. Demir, and M. A. Winnik, *J. Coll. Interface Sci.*, **111**, 269 (1986).
14. Ö. Pekcan and Y. Demir, *J. Appl. Polym. Sci.*, **43**, 2169 (1991).
15. Ö. Pekcan, M. A. Winnik, L. Egan, and M. D. Croucher, *Macromolecules*, **16**, 699 (1983).
16. Ö. Pekcan, M. A. Winnik, and M. D. Croucher, *J. Polym. Sci. Polym. Lett.*, **21**, 1011 (1983).
17. Ö. Pekcan, M. A. Winnik, and M. D. Croucher, *Phys. Rev. Lett.*, **16**, 641 (1988).
18. Ö. Pekcan, L. S. Egan, M. A. Winnik, and M. D. Croucher, *Macromolecules*, **23**, 2210 (1990).
19. Ö. Pekcan, *Chem. Phys. Lett.*, **20**, 198 (1992).
20. Ö. Pekcan, *J. Appl. Polym. Sci.*, to appear.
21. M. Shiotani and J. Sohma, *Polym. J.*, **9**, 283 (1977).
22. M. A. Winnik, Ö. Pekcan, B. Disanayaka, and M. D. Croucher, *Isr. J. Chem.*, **2**, 31 (1991).
23. N. Kusumoto, in *Molecular Motion in Polymers by ESR*, R. F. Boyer and S. E. Keinath, Eds., Harwood, New York, 1980, p. 233.
24. N. Kusumoto, S. Sano, and T. Kijima, *Rep. Prog. Polym. Phys. Jpn.*, **20**, 519 (1977).
25. F. Johnson and J. C. Randon, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 1995 (1973).
26. T. Tetsutani, M. Kakizaki, and T. Hudeshima, *Polym. J.*, **14**, 305 (1982).
27. M. Shiotani, J. Sohma, and J. H. Freed, *Macromolecules*, **16**, 1495 (1983).
28. G. E. Pake, *Paramagnetic Resonance*, Benjamin, New York, 1962, Chap. 5.

Received June 21, 1993

Accepted October 5, 1993