The Effect of Solvents on Molecular Motion of Nitroxide Free Radicals Doped in Polystyrene and Poly(methyl methacrylate)

Zorica Veksli* and Wilmer G. Miller*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.
Received April 19, 1977

ABSTRACT: Linear poly(methyl methacrylate) and polystyrene were doped with nitroxide spin probes of various functionality and size. The temperature and solvent dependence were measured and compared with a covalently linked nitroxide (spin-labeled polymer) in the same polymer–solvent system. From the temperature dependence of the ESR spectrum two spin probes in PMMA were found to be hydrogen bonded to the polymer even at 170 °C. Within 40 °C of the glass transition the small, hydrogen-bonding spin probes were found to have a bimodal distribution of correlation times. The effect of the solvents chloroform and dimethylformamide on the motion of doped PMMA was determined. In all cases the behavior was qualitatively similar to the effect of the same solvents on spin-labeled PMMA. At low concentration of solvent the nitroxide motion was unaffected by the presence of solvent, at intermediate compositions two distinct populations of nitroxide motions were observed, and at high solvent composition the motion was describable by a single mean correlation time. With a nonhydrogen-bonding solvent and a hydrogen-bonding probe, the probe appears to stay hydrogen bonded to the polymer to high dilution.

In a previous paper[1] we have examined the effect of thermodynamically good solvents on molecular motion of a nitroxide free radical (Figure 1, I) covalently attached through an amide linkage (Figure 1, I′) to a methacrylate unit in poly(methyl methacrylate) (PMMA). The effects of solvent composition fell into three categories. At low solvent concentration, nearly to the point where the solvent had lowered the glass transition to ambient temperature, the motion of the nitroxide was uninfluenced by the presence of the solvent. Relaxation is thought to be dominated by χ_1 motion (Figure 1, I′). In the intermediate composition range, from near the composition needed to plasticize the polymer to as much as 75 wt % solvent in the case of chloroform, a bimodal distribution of nitroxide motions was observed which was not interconverting on the ESR time scale. A fraction of the nitroxides appeared to have a mean rotational correlation time nearly identical with the dry polymer. The remaining nitroxides had a much shorter mean correlation time. As the solvent composition increased the percentage of nitroxides undergoing the faster motion increased, and their correlation time decreased. Finally in the range of high solvent concentration a single fast motion component was observed. The fast motion was thought to be dominated by a local motion extending over a few bonds in the chain backbone, whose composition dependence was describable by the Fujita–Doolittle free-volume equation.[2]

In a parallel study[1] on the motion of an analogously attached nitroxide in styrene–methyl methacrylate copolymers (98:2), the nitroxide motion was similar to that in the PMMA study, indicating a primary response to the nitroxide methacrylate motion with a secondary response to the styrene matrix.

Inasmuch as it is generally simpler to prepare samples using a spin probe, i.e., a noncovalently bound nitroxide, then a covalently attached nitroxide we have looked at the effect of solvents on the motion of spin probes in nitroxide doped PMMA and polystyrene (PS). Analogous to the studies with covalently attached nitroxides it was found necessary to first investigate the temperature dependence of the motion in the dry polymers.

Experimental Section

Spin Probes. The structures of the spin probes are shown in Figure 1. Probe I was obtained from Aldrich Chemical Co., probes II and VI from Synvar, and probes III–V from Eastman Kodak Co.. All probes were used as received.

Doped Polymers. All PMMA samples were prepared from 100 000 nominal molecular weight linear polymer of unknown polydispersity (Monomer-Polymer Laboratories, Inc.). A 1–2 wt % solution of the polymer in a thermodynamically good solvent was prepared and the desired amount of the spin probe was dissolved in the polymer solution. The solvent was removed under reduced pressure and the sample was dried under vacuum. Spin probe concentration in the dry polymer was 0.2 wt % or less.

Doped polystyrene samples were prepared in a similar fashion using either 230 000 linear polystyrene, PS (230 000), obtained from Polysciences, Inc., or a linear styrene–methyl methacrylate (98.2) copolymer, PS (MMA), obtained by emulsion polymerization.

The preparation of the reference sample of covalently attached nitroxide, PMMA-I′ (Figure 1, I′), is described elsewhere.[1]

ESR. A Varian E-3 ESR spectrometer operating at a microwave frequency of about 9.15 GHz was used. The spectra were typically recorded in the vicinity of 3.2 kG with the modulation amplitude 1 G or less, and with attenuation power low enough to avoid saturation. Generally, polymer samples were prepared directly in the ESR measurement vessel (5-mm NMR tube or 2-mm Pyrex tube), both with and without sonication. When using highly volatile solvents, a Teflon plunger was inserted immediately after sample preparation in order to prevent solvent loss. This was found essential in order to have a known solvent composition.

Polymer–Solvent Systems. All solvents were reagent grade. In general, the polymer–solvent samples were prepared directly in the ESR sample cell. If the solvent composition was to be 30 wt % or less the solvent was added by vapor sorption. Higher solvent compositions were prepared by direct liquid solvent addition. In several instances samples of similar composition were prepared by both methods. Occasionally samples were prepared by removing solvent under reduced pressure from a dilute solution.

Results

Temperature Dependence of Nitroxide Motion in Solid PMMA and PS. The temperature dependence of the ESR spectra of spin probes I and II in PMMA (100 000) is shown in Figure 2. The temperature dependence of spin-labeled PMMA (100 000)-I′, shown also in Figure 2, has been discussed.[1] From about 80 °C down to about −160 °C, the spectrum of I′ is subtly but continuously changing and is thought to result from anisotropic nitroxide motion, predominantly to χ_1 motion (Figure 1, I′) about the terminal N–C bond. The spectra of spin probes I and II are superimposable on I′ at −93 and −43 with perhaps slight differences at 25 °C. At 67 °C they are considerly different. Inasmuch as probes I and II may be hydrogen bonded to the methacrylate carbonyl in the solid polymer, it became important to understand the spin probe motion in light of this possibility. A number of studies have been made with spin probes in solid polymers.[3–5] Motionally

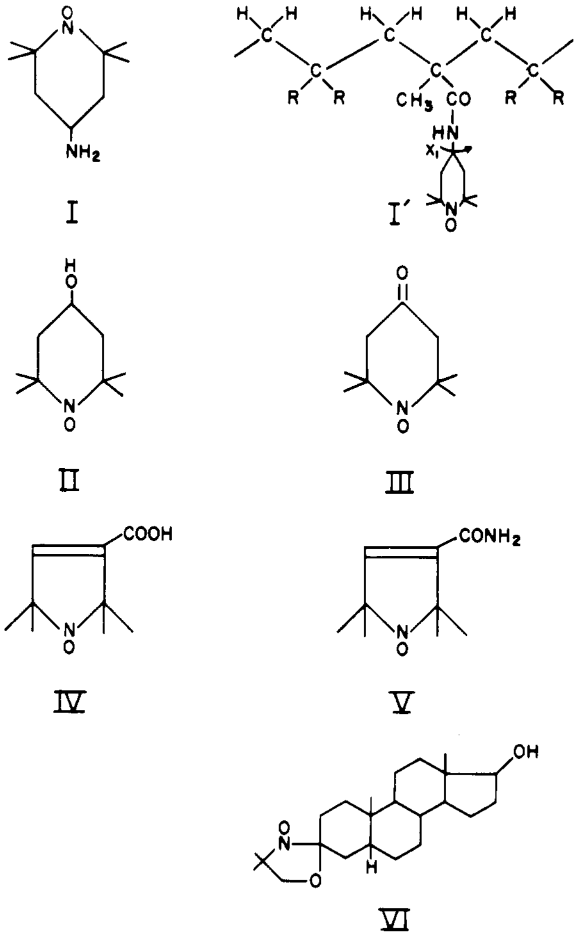

Figure 1. The structure of nitroxide spin probes (I–VI) and spin label (I′) used in this study.

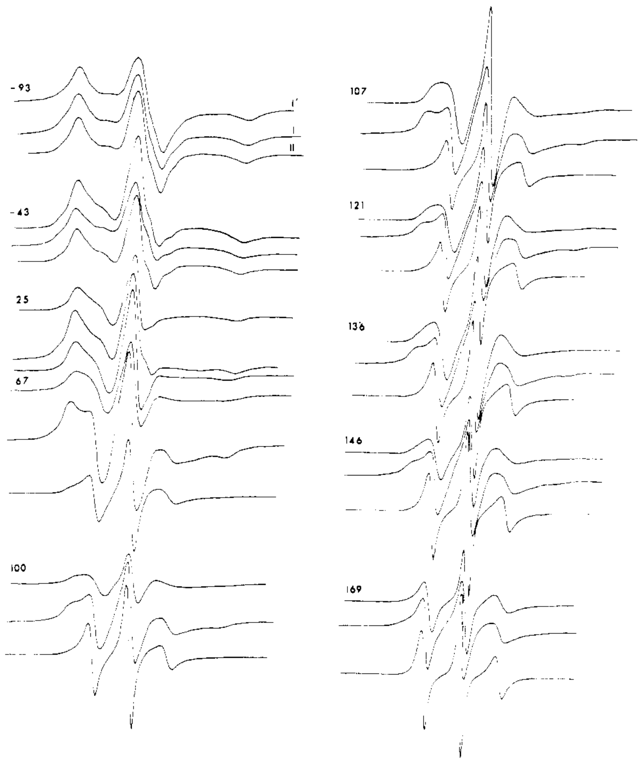

Figure 2. The temperature dependence of the ESR spectra of spin probes I and II in solid PMMA (linear) and in spin-labeled PMMA (linear)–I′.

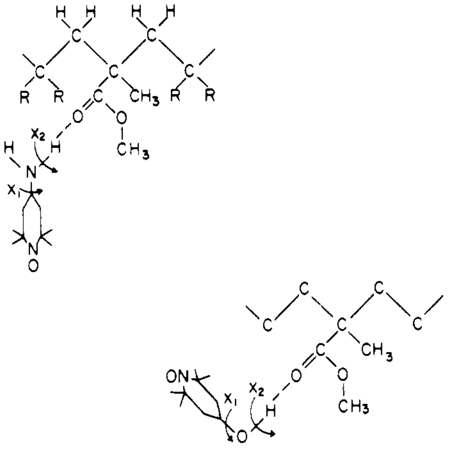

Figure 3. Possible mode of hydrogen bonding of spin probes I and II to PMMA.

slowed spectra have been interpreted assuming isotropic motion. It seems clear that if the probes are hydogen bonded as indicated in Figure 3, the motion is not likely to be isotropic in the glassy polymer. If the motion is anisotropic at low temperature, due to hydrogen bonding, one must decide if the change in spectral line shape, as the sample is warmed, is a result of faster anisotropic motion or is a composite spectrum. Confusion may occur if a motionally narrowed spectrum is superimposed on a motionally slowed spectrum, as the superposition looks, in many instances, qualitatively similar to faster anisotropic motion. A careful semiquantitative assessment must be made. Let us first compare spectra B, C, E, and G in Figure 4. Spectra C, E, and G are similar in that each shows a low-field double maximum and a high-field double minimum. We have shown previously that B is due primarily to motion about χ_1 (Figure 1, I′) whereas C is a superposition of two nonintroconverting populations with considerably different rotational correlation times.[1] Spectra G and H, typical of ESR spectra for solutions of end labeled, helical poly(γ-benzyl α-L-glutamate),[6,7] have been shown definitely to be χ_1 type motion[8] though having a shorter correlation time than B. Comparing I, H, and G, as well as the theoretical calculations,[8] it is clear that when the rate of anisotropic motion is increased such that the low- and high-field doublets appear, then $A_{\parallel}'$, two times the separation of the outer extreme (see Figure 4), will be reduced considerably from its low-temperature limit. This, however, was not the case when solvents were added to PMMA–I′ (ref 1 and Figure 4, C), and it is not the case with solid PMMA–I and PMMA–II when the temperature is increased (Figure 2 and Figure 4, E, F). It is thus our conclusion that the spectra in Figure 2 represent, in certain temperature ranges, a superposition of two populations of nitroxides with different rotational correlation times.

In Figure 5 we see that the temperature dependences of $A_{\parallel}'$ for the slow-motion component of PMMA–I′, PMMA–I, and PMMA–II are all similar though PMMA–I and PMMA–II probably have slightly lower values. This more quantitatively confirms the doublets as due to superposition rather than as increased rate of anisotropic motion. Furthermore the slow motion component in PMMA–I and –II seems most likely to be χ_1 motion, as χ_2 motion (Figure 3) would lead to a reduction in $A_{\parallel}'$.

As the temperature increases the free volume of the sample increases. The faster relaxing component which grows into the PMMA–I and –II spectra above room temperature must be due either to a fraction of the nitroxides gaining additional motion or to a fraction no longer remaining hydrogen bonded. The fast motion component in PMMA–II has a rotational

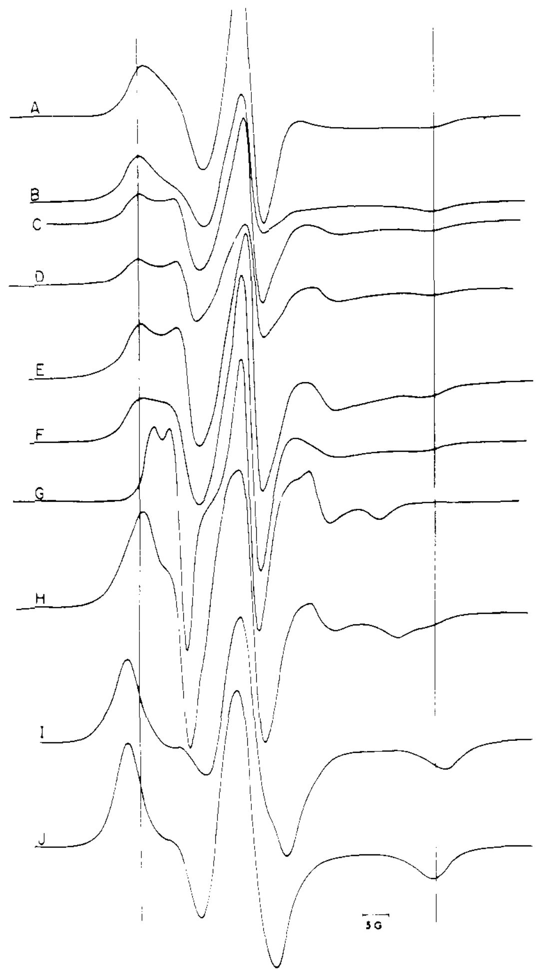

Figure 4. ESR spectra of A, PS(230 000)-III (25 °C); B, PMMA-I′ (25 °C); C, PMMA-I′, 16 wt % DMF (25 °C); D, PMMA-I, 4.6 wt % DMF (25 °C); E, PMMA-I (79°C); F, PMMA-II (40 °C); G, poly-γ-benzyl L-glutamate (180 000)-I′ (end labeled) 75 wt % DMF (25 °C); H, poly-γ-benzyl L-glutamate (120 000)-I′ (end labeled) 50 wt % DMF (25 °C); I, poly-γ-benzyl L-glutamate (180 000)-I′ (end labeled) (25 °C); J, poly-γ-benzyl L-glutamate (180 000)-I′ (end labeled) (80 °C). The vertical lines correspond to $2A_{\|}'$ for solid PMMA-I′ at 25 °C. The poly-γ-benzyl L-glutamate data are taken from ref 6 and 7.

correlation time, assuming isotropic rotation, of 2.2×10^{-9} at 100 °C and 1.2×10^{-9} at 169 °C. By contrast spin probe III (Figure 1, III) doped in PMMA, a case in which the spin probe cannot be hydrogen bonded to PMMA, has a rotational correlation time of 3×10^{-11} s at 100 °C and 1.5×10^{-11} at 150 °C.[3,9] Inasmuch as the molecular size and geometry of probes II and III are virtually identical except that II can hydrogen bind to the PMMA side chain it seems clear from the large difference in correlation time between the two probes that II is still hydrogen bonded to the PMMA at elevated temperatures. Both populations of spins in PMMA-I and -II are thus due to hydrogen-bonded probes.

At room temperature and lower a bimodal distribution of correlation times is not observable, i.e., the spectra are interpretable as resulting from a single mean correlation time which we feel corresponds to χ_1 motion. Inasmuch as the correlation time for this anisotropic motion can be estimated[8] from $A_{\|}'$ we have compared the change in $A_{\|}'$ in going from −160 to 25 °C using a variety of spin probes with PMMA and PS. We find $\Delta A_{\|}'$ to be 2.0 ± 0.5 G for PMMA-I′, PMMA-I, PS(MMA)-I′, PS(MMA)-I, and PS(230 000)-I. Using the smaller ring probes IV and V, each of which may hydrogen bond with PMMA and exhibit anisotropic χ_1 type motion, $\Delta A_{\|}'$ is 1.0–1.2 G. Using nonhydrogen-bonding probe III in PS(MMA), $\Delta A_{\|}'$ is 5–6 G over the same temperature change. By contrast probe VI in PMMA, PS(MMA), and PS(230 000) shows a change of only 0.4 G in going from 25 to −160 °C. These results further support our interpretation except, perhaps, for the probe IV and V results. However, motion in IV and V about the C–C bond attaching the carboxyl to the ring may very well be restricted due to partial double-bond character resulting from adjacent double bonds. If so, motion closest to the nitroxide moiety would be a χ_2 type motion about the hydrogen bond analogous to that in Figure 3. Such motion would be sterically restricted as the molecular geometry of the nitroxide moiety is not cylindrically symmetric when viewed along the hydrogen bond axis.

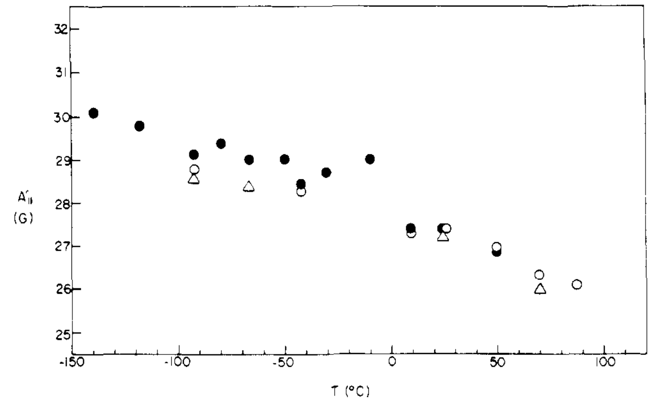

Figure 5. The temperature dependence of the outer hyperfine extrema ($A_{\|}'$) for the slow-motion component of PMMA–I′ (●), PMMA–1 (○) and PMMA–II(△).

A final point to be made with respect to the solid-state results concerns the line width of the low-field and the high-field lines. The outer line half-width at half-height[10,1] at −160 °C is typically 4–5 G, which is much larger than is typically found.[10,11] When the temperature is raised the half-width decreases and reaches 2–3.5 G at 25 °C while $A_{\|}'$ decreases only a few percent. Theoretically, raising the temperature should result in an increase in half-width due to lifetime broadening.[10,11] The unusually large half-wdiths at low temperature are undoubtedly due to a very heterogeneous environment and a wide range in intermolecular inhomogeneous broadening. Raising the temperature with concomitant increase in molecular motion results in averaging out the environmental heterogeneties which decreases the half-width more than lifetime broadening due to increased nitroxide motion increases the half-width. Similar observations have been made in other solid polymers.[7,11]

Solvent Dependence of Nitroxide Motion in Doped PMMA and PS. Three PMMA spin probe solvent systems were extensively studied for comparison with covalently attached spin label PMMA-solvent systems.[1] They were PMMA-I in DMF and PMMA-I and PMMA-III in $CHCl_3$. These systems were chosen so that one probe and one solvent were hydrogen bonding, whereas the other probe and the other solvent offered little hydrogen bonding capability. Qualitatively the results were similar to the results with the covalently attached nitroxide PMMA-I′ in that at low solvent composition the motion of the spin probes was not influenced by the presence of solvent: at intermediate compositions two noninterconverting populations of probes were observed, and at high solvent composition a motionally narrowed spectrum only was observed. The results are summarized in Figures 6–8 together with the corresponding PMMA-I′ data.[1] Correlation times for the motionally narrowed components were calculated assuming isotropic rotation[13] and for the motionally slowed component assuming anisotropic (χ_1) rotation.[8]

The slow-motion component has an $A_{\|'}$ which remains in-

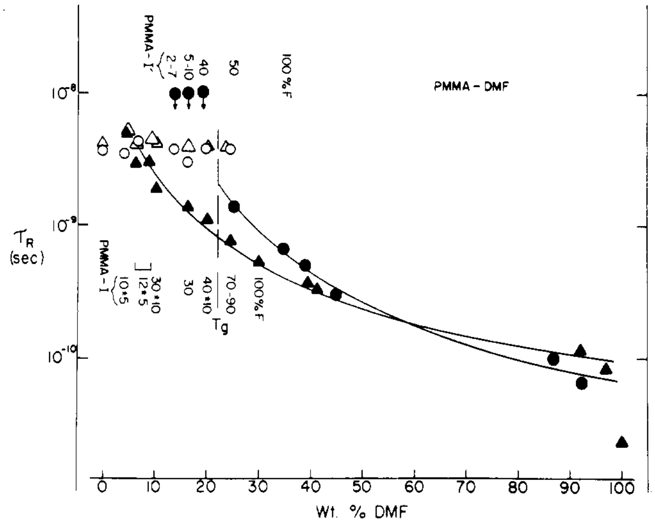

Figure 6. The concentration dependence of the rotational correlation times of PMMA–I (△ and ▲) and PMMA–I′ (○ and ●) in DMF at a nominal temperature of 25 °C. The slow-motion correlation time (open figures) was calculated assuming anisotropic (χ_1 in Figures 1 and 3) rotation[8] while the fast component was either calculated assuming isotropic rotation[13] (●, ▲) or observed to be present but a correlation time was not calculable (↕). The estimated percentage of the spins undergoing the faster motion is indicated. The vertical dashed lines indicate the solvent composition at which T_g reaches the temperature of measurement.

dependent of composition so long as it is observable in all three probe-solvent systems. This leads then to a solvent-independent motion similar to that observed with the covalently attached label (ref 1 and Figure 6–8). With PMMA-I in DMF the faster motion component appears at lower solvent composition, and at any composition a greater fraction of the spin probes is observed in the fast component, when compared with its covalent analogue. Inasmuch as we deduced in the previous section that probe I is H bonded to the methacrylate side chain in the dry polymer it is tempting to suggest that the probe H bonds with the solvent and hence undergoes rapid motion long before the polymer is plasticized. The data are inconclusive concerning this point. The nearly identical correlation times for the covalently and noncovalently attached nitroxides from 20 to 97 wt % solvent would suggest that the probe is attached. The substantial increase in motion in going from 97% solvent to pure solvent is not a viscosity effect and supports the idea of an H-bonded probe. However, PS(230 000)–I dissolved in DMF (39 wt %) has a correlation time only a factor of 2 smaller than corresponding PMMA–I solution. Since probe I cannot H bond to polystyrene it could be argued that this supports probe I not being H bonded to PMMA over a wide range in solvent composition. Even with additional studies of spin probes and labels relevant to this work[7] it is not possible to make a definitive argument concerning the location of the nitroxide undergoing fast motion.

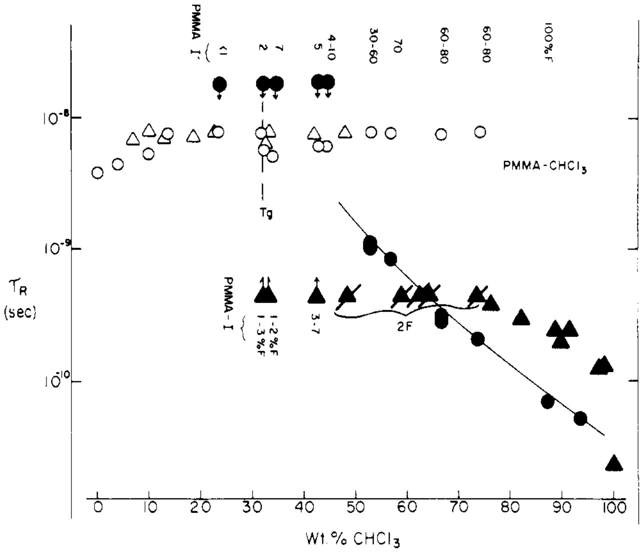

Figure 7. The concentration dependence of the rotational correlation times of PMMA–I (△ and ▲) and PMMA–I′ (○ and ●) in CHCl$_3$. The compositions where a superposition of two motionally narrowed spectra are observed with PMMA–I are indicated by ▲ (the correlation times were not meaningfully determinable). All other designations are as in Figure 6.

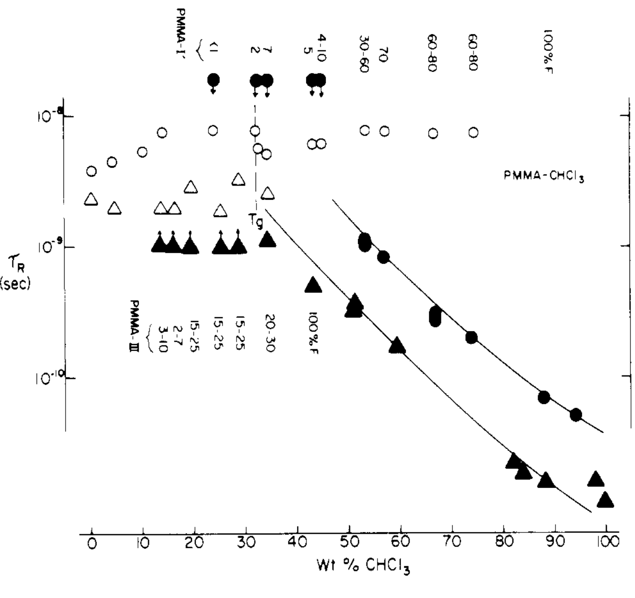

Figure 8. The concentration dependence of the rotational correlation times of PMMA–III (△ and ▲) and PMMA–I′ (○ and ●) in CHCl$_3$. All designations are in Figure 6.

Turning to PMMA-I in CHCl$_3$, a solvent not expected to H bond with the probe, the spectra are nearly identical with their covalently attached counterparts up to 45 wt % solvent, both in the solvent composition needed to make a double population of spins appear as well as in the approximate ratio of spin intensities. This is summarized in Figure 7. Between 45 and 75% solvent a new situation appears. A 48% solvent sample shows a superposition of three noninterconverting populations, whereas samples containing 60–75% solvent show a clear superposition of two motionally narrowed spin populations. These are shown in Figure 9. The apparent correlation time for the noncovalent probe, where determinable, is larger than the correlation time for the covalently attached label at the same solvent composition. Before analyzing these data we will present the data for PMMA-III in CHCl$_3$.

A summary of the spectra for PMMA-III in CHCl$_3$ is shown in Figure 8, together with the corresponding data for PMMA-I′.[1] At no concentration are two fast components observable as with PMMA-I in CHCl$_3$. A fast component is observable at lower solvent compositions than with the covalently attached nitroxide, and in the double population region a much larger fraction of the spins is motionally narrowed. Below 10 wt % solvent a motionally narrowed component, if present, was obscured by the motionally slowed component. In the composition range 50–100 wt % solvent the short correlation times are about a factor of 5 smaller for PMMA-III compared to PMMA-I′ and about a factor of 10 smaller than PMMA-I. Inasmuch as probe III is not thought to hydrogen bond to either polymer or solvent the composition

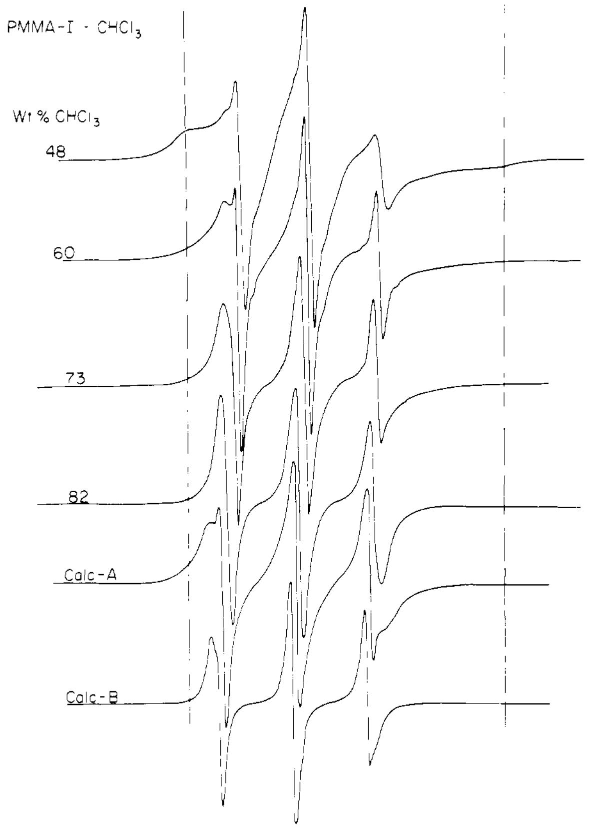

Figure 9. Spectra of PMMA-I in CHCl$_3$ at the indicated composition. The dashed vertical lines indicate $A_{\parallel}'$ for the dry polymer. A and B are simulated spectra (see text for details).

dependence of the correlation time is primarily a measure of the effect of the presence of the polymer on solvent properties. Up to 20 wt % polymer has very little effect on the motion of the probe. Nuclear magnetic resonance[14-17] and infrared[18] spectroscopy studies on polymer–solvent interaction typically show that the presence of polymer has little if any effect on the solvent up to 20–30% polymer. At higher polymer compositions the polymer begins to have signficant effects. The spin probe behaves similarly.

We turn again to PMMA-I in CHCl$_3$, in particular the 48 through 74 wt % CHCl$_3$ spectra (Figures 7 and 9). The spectrum in 48 wt % CHCl$_3$, composed of one motionally slowed component and two motionally narrowed components, would most likely be a result of a double population of polymer bound nitroxides and a third nitroxide component not hydrogen bonded to the polymer. From 50 to 75 wt % solvent the spectra would then be interpreted logically as one polymer bound and one nonpolymer bound component. We attempted to simulate these spectra using as variables the correlation times, inhomogeneous line widths, population distribution, and effective hyperfine splitting. Two such attempts are shown in Figure 9. Spectrum A was calculated using 15% spins of 2.5×10^{-11} s correlation time (the dilute solution, nonbounded value), 85% spins of 8×10^{-10} s correlation time, and a 1 G difference in the isotropic hyperfine splitting. Spectrum B differed only in that 50% of the spins had a correlation time of 2.5×10^{-11} s and 50% a correlation time of 4×10^{-10} s. These spectra resemble the 67 and 74 wt % CHCl$_3$ spectra, respectively. However, they are by no means unique. Although the calculated spectra are quite sensitive to the input parameters, the distribution of populations can easily be traded off against the correlation times over wide ranges. In additiom the possibility exists of line broadening as a result of interconversion between the bounded and nonbounded states. At best, we can state that the motionally narrowed spectra suggesting a double population could be accounted for assuming bound and nonbound components. At higher solvent compositions, where the apparent isotropic correlation time is larger than its covalent counterpart, we were not able to simulate the spectra by a superposition of noninterconverting spins.

Discussion

The Solid State. The hydrogen bonding of spin probes I and II to PMMA is reasonable to expect and seems plausibly established. The findings of Rabold[19] using probe II doped in PS further confirm this view. The value of $A_{\parallel}'$ is 29 G at 20 °C and drops to 20 G at 60 °C, quite in contrast to the results shown in Figure 5.

We turn next to the bimodal distribution of correlation times, which we observe with spin probes hydrogen bonded to the side chains as we approach the glass transition, but not in the spin label attached so close to the polymer chain that we get χ_1 motion only in the absence of backbone motion. The literature is not entirely instructive as to the uniqueness of these observations. Many times representative spectra are not given, and it is easy to confuse a composite spectrum with a motionally slowed anisotropic spectrum. For example, Rabold[19] and Kusumoto, Yonezawa and Motozato[20] clearly felt that they were observing composite spectra, whereas Bullock, Cameron, and Smith criticize this interpretation.[21] In the discussion surrounding Figure 4 simple criteria were given which can generally be used to distinguish these two situations. Utilizing these criteria it is clear that the spectra in question are composite and not motionally slowed anisotropic spectra. Thus, Rabald,[19] using spin probe I, finds a bimodal distribution in the amorphous polymers PS and poly(vinyl chloride) at temperatures considerably below the glass transition. In semicrystalline polyethylene composite spectra are observed with probe I above the glass transition from about −100 to −50 °C. However, with a spin label attached directly to the backbone composite spectra are not observed until about 50 °C (our interpretation of Figure 2 of ref 21), over 100 °C above the glassy transition. With noncrystalline polymers the bimodal distribution of correlation times below the glass transition may be a result of a microheterogeneous environment. This is consistent with our finding that annealing can change the distribution[1] and is not inconsistent with our suggestion[1] that the double population may be a reflection of differences in rates of conformational interconversion among various stereochemical sequences.

Motional Effects on Spin Probes in the Presence of Solvents. Our studies show that spin probes, whether hydrogen bonded to the polymer or merely doped nonspecifically, behave similarly to covalently attached spin labels in that a bimodal distribution of correlation times always exists in the vicinity of the solvent composition necessary to bring the glass transition down to the temperature of measurement. The quantitative details depend upon the polymer–probe–solvent system. The system PMMA-III-CHCl$_3$ seems the most straightforward inasmuch as probe I should not hydrogen bond to either polymer or solvent. If in this system one considers the spin probe motion to monitor the effect of the polymer on the motion of the solvent, the parallel composition dependence in the range 50–100% solvent for PMMA-III and PMMA-I suggests a common mechanism. This mechanism is presumably the segmental jump frequency of the polymer and its mediation by the solvent. Inasmuch as the jump frequency will depend on the local stereosequences the bimodal distribution of correlations in the high polymer concentration region is consistent with differences in rotamer conversion.

The differences between PMMA-I-CHCl$_3$ and PMMA-

III–$CHCl_3$ show clearly the presence and effect of hydrogen bonding of I to the polymer. To a good approximation probe I behaves as if it were covalently bonded to PMMA. In DMF probe I was expected to hydrogen bond to the solvent with increasing solvent concentration. The extreme similarity between these data and PMMA–I′ makes any detailed interpretation impossible.

Acknowledgments. This work was supported in part by the U.S. Public Health Service (GM-16922), by the Education Committee of the Rubber Division, American Chemical Society, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) On leave of absence from Institute Ruđer Bošković, Zagreb, Yugoslavia.
(2) (a) Z. Veksli and W. G. Miller, *Macromolecules,* **10,** 686 (1977); (b) J. Fujita and A. Kishimoto, *J. Chem. Phys.,* **34,** 393 (1961).
(3) A. L. Buchachenko, A. L. Kovarskii, and A. M. Wasserman, *Adv. Polym. Sci.,* 26 (1976).
(4) P. Tormala and J. J. Lindberg, "Structural Studies of Macromolecules by Spectroscopic Methods", K. J. Ivin, Ed., Wiley, New York, N.Y., 1976, pp 255–272.
(5) P. L. Kumler and R. F. Boyer, *Macromolecules,* **9,** 903 (1976).
(6) E. L. Wee and W. G. Miller, *J. Phys. Chem.,* **77,** 182 (1973).
(7) C. C. Wu and W. G. Miller, *Macromolecules,* in press.
(8) R. P. Mason, C. F. Polnaszek, and J. H. Freed, *J. Phys. Chem.,* **78,** 1324 (1974).
(9) A. L. Kovarskii, Thesis, IKhF AN SSR, Moscow, 1972.
(10) R. P. Mason and J. H. Freed, *J. Phys. Chem.,* **78,** 132 (1974).
(11) R. P. Mason, E. B. Giavedoni, and A. P. Delmasso, *Biochemistry,* in press.
(12) A. T. Bullock, G. G. Cameron, and P. M. Smith, *Eur. Polym. J.,* **11,** 617 (1975).
(13) D. Kivelson, *J. Chem. Phys.,* **33,** 1094 (1960).
(14) K. J. Liu and R. J. Ullman, *J. Chem. Phys.,* **48,** 1158 (1968).
(15) J. F. Anderson and K. J. Liu, *J. Chem. Phys.,* **49,** 2850 (1968).
(16) W. G. Rothschild, *Macromolecules,* **5,** 37 (1972).
(17) F. Heatley and J. H. Scrivens, *Polymer,* **16,** 489 (1975).
(18) W. G. Rothschild, *Macromolecules,* **1,** 43 (1968).
(19) G. P. Rabold, *J. Polym. Sci., Part A-1,* **7,** 1203 (1969).
(20) N. Kusumoto, M. Yonezawa, and Y. Motozato, *Polymer,* **15,** 793 (1974).
(21) A. T. Bullock, G. G. Cameron, and P. M. Smith, *Eur. Polym. J.,* **11,** 617 (1975).

Diffusion of *n*-Alkanes in Poly(dimethylsiloxanes)

William Millen and Stephen Hawkes*

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331.

Received February 4, 1977

ABSTRACT: Plots of *n*-alkane carbon number against diffusional friction coefficient in two dimethylsiloxanes of different molecular weight (4×10^5 and 3.5×10^4) intersect. It is proposed that diffusion of shorter *n*-alkanes is governed by free volume which is greater in the higher molecular weight polymer, while diffusion of the longer *n*-alkanes is governed by segmental relaxation speed which is greater in the lower polymer. The specific volume of the higher polymer at 100 °C is 1.102 and the coefficient of expansion is 9.98×10^{-4} $cm^3/cm^3/°C$ over the range 30 to 250 °C. The nonlinearity of the friction coefficient with *n*-alkane carbon number is confirmed.

Unusually high diffusion coefficients for *n*-alkanes in the highly viscous poly(dimethylsiloxane) gum (General Electric "SE-30") (9.5×10^6 cSt at 25 °C, mol wt = 4×10^5) relative to less viscous poly(dimethylsiloxanes) have been noted by Butler and Hawkes[1] and Kong and Hawkes.[2,3] Their work with SE-30 and General Electric "SF-96-2000" (2000 cSt at 25 °C, mol wt = 3.5×10^4) has been repeated using a more rigorous equation[4] for determining diffusion coefficients from chromatographic data. In addition, their work has been extended to include diffusivities of some higher molecular weight *n*-alkanes which they had been unable to determine.

Calculation of Friction Coefficients

The friction coefficient for a molecule at vanishingly small concentrations in the bulk of a polymer can be calculated using the equation

$$\zeta_1 = kT/D \qquad (1)$$

where k is the Boltzmann constant and D is the diffusivity of the penetrant. The diffusivities of a series of *n*-alkanes in SE-30 and SF-96-2000 at various temperatures have been determined,[4] and the friction coefficients calculated from eq 1 are listed in Table I.

Auerbach et al.[5] have suggested that the friction coefficient for *n*-alkanes in polymers is approximately linear with the chain length of the *n*-alkane. This was not found to be the case for *n*-alkanes in a variety of polysiloxanes[3] and is also inconsistent with the data in Table I which are plotted in Figures 1 and 2 and are clearly nonlinear.

The friction coefficient for a monomer unit of a polymer, ζ_0, has been shown by Ferry[6] to be approximately equal to ζ_1 for a penetrating molecule of the same size. This proposal can be shown to be consistent with data calculated here by extrapolating the log ζ_1 values at 100 °C for the lowest two *n*-alkanes in Table I linearly down to *n*-pentane. The results of this extrapolation are shown in Table II along with the ζ_0 value listed by Ferry[6] for a monomer unit for a poly(dimethylsiloxane).

Density and Expansion Coefficient of SE-30

The unusually high diffusivity of a few *n*-alkanes in SE-30 has been noted previously[1–3] and it has been suggested[3] that these high diffusivities (low ζ_1) are due to the higher free volume present in SE-30 which is evidenced by its lower density relative to the lower molecular weight poly(dimethylsiloxanes).

While a literature value was available,[1] the unusual diffusion characteristics of *n*-alkanes in SE-30 seemed to warrant an independent determination of its density and thermal expansion coefficient. Accordingly, the density of SE-30 was measured between 30 and 250 °C using a stainless steel density bottle and the results are listed in Table III.

The thermal expansion coefficient was determined by a linear regression analysis of the specific volume listed in Table III, against temperature, and resulted in the following equation for specific volume ν in cm^3/g where T is in °C, 1.002 is the specific volume at 0 °C, and 9.98×10^{-4} is therefore the thermal expansion coefficient.