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

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ABSTRACT: Poly(methyl methacrylate) and polystyrene in linear and lightly cross-linked latex form were covalently labeled with a nitroxide amine free radical. In all cases the nitroxide was attached to a methacrylate unit through an amide linkage. The temperature dependence of the ESR spectrum of labeled, solid PMMA shows that at room temperature the nitroxide is relaxed by motion about the terminal C–N bond in the nitroxide moiety. The ESR spectra were measured as a function of solvent composition using the thermodynamically good solvents chloroform, benzene, and dimethylformamide. All six polymer–solvent systems showed qualitatively similar behavior. At low concentration of solvent the nitroxide motion was unaffected by the presence of solvent. In the intermediate concentration region two distinct populations of nitroxide motions were observed which were not interconverting on the ESR time scale. One population was being relaxed by terminal bond motion. The faster moving nitroxides were being relaxed predominately by local mode main chain motion which correlated with the effect of solvent on the monomeric friction coefficient. At high dilution all nitroxides were relaxed by the local mode mechanism.

Molecular motions in an amorphous polymer at temperatures considerably below its glass transition (T_g) are predominantly limited local motions such as side chain motion, terminal group rotation, and local mode relaxation or crankshaft motions.[1] Correlated backbone motion, having a much higher apparent activation energy than side chain motion, rapidly increases as the temperature is raised and above T_g approaches the relaxation frequency of side chain motions.[1-3] The addition of solvent or plasticizer to a glassy polymer lowers T_g. The lowering is dependent on the amount of diluent added and on the nature of the polymer–solvent pair.[4,5] A solvent thus lowers the temperature at which significant correlated main chain motion begins to occur. Above T_g low frequency relaxations, i.e., correlated backbone motions, are affected similarly by solvent and temperature. Although the monomeric frictional coefficient changes dramatically as diluent is added, a shift factor will bring low-frequency temperature and diluent relaxation data to a common curve.[1,6] Below T_g the motions are thought not to be describable by a monomeric frictional coefficient,[1] and the superposition of low-frequency temperature-diluent relaxation data does not seem to have been attempted.

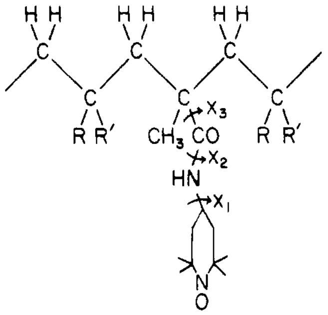
The ESR spectrum of a nitroxide free radical is sensitive to the rotational motion of the nitroxide over a wide range of rotational correlation times (10^{-6}–10^{-11} s). We have given preliminary accounts of the effect of solvents on nitroxide motion in labeled polystyrene (PS) and poly(methyl methacrylate) (PMMA)[7-9] and a more extensive study of the effect of nonsolvents.[9] In this manuscript the detailed results are presented for the effect of thermodynamically good solvents on motion of nitroxide spin labels covalently attached to PS and PMMA.

Experimental Section

Labeled Polymers. Linear poly(methyl methacrylate), PMMA (linear), had a nominal molecular weight of 100,000 and unknown polydispersity (Monomer-Polymer Laboratories, Inc.). Cross-linked PMMA spheres, PMMA (latex), and polystyrene spheres, PS (latex), were prepared by emulsion polymerization of the respective monomer

(Polysciences, Inc.) in the presence of 1 mol % ethylene glycol dimethacrylate, followed by surfactant stripping and isolation prior to labeling. The details are given elsewhere.[9]

The nitroxide amine 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl (Aldrich Chemical Co.) was covalently attached to the various polymeric preparations by way of the amide–ester interchange reaction of the nitroxide amine with the ester group of the polymer.[9,10] The nitroxide is thus attached to the polymer backbone by way of an amide linkage at the methacrylate carbon in both PMMA and PS. PMMA (linear) and PS (latex) were homogeneously labeled, and PMMA (latex) and PS (latex) were surface labeled by the amide–ester interchange reaction as described earlier.[8,9] The surface and the homogeneously labeled latexes typically had 100–200 spin labels per latex sphere of 450–1000 Å mean diameter. The morphology of the homogeneously labeled latex has been shown to be loosely connected spheres with a surface nearly the same as the original latex.[9] The morphology of the surface labeled latex is that of nonconnected spheres, as with the original latex. The homogeneously labeled PMMA (linear) had a spin label concentration comparable to the homogeneously labeled latex. Its morphology is that of a glassy polymer precipitated from solution with a surface area per unit mass more than an order of magnitude less than the latex preparations.[9]



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.

DSC. A Dupont 900 Scanning Calorimeter was used in determining T_g for PMMA (linear) in the presence of dimethylformamide. The T_g of all other polymer–diluent samples was determined with a Perkin-Elmer DSC-2 Scanning Calorimeter using hermatically sealed sample pans. Samples were weighted before and after calorimetric measurements, and the thermal data were discarded if a weight loss occurred.

Polymer–Solvent Systems. All solvents were reagent grade. In general, the polymer–solvent samples were prepared directly in the ESR or DSC 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

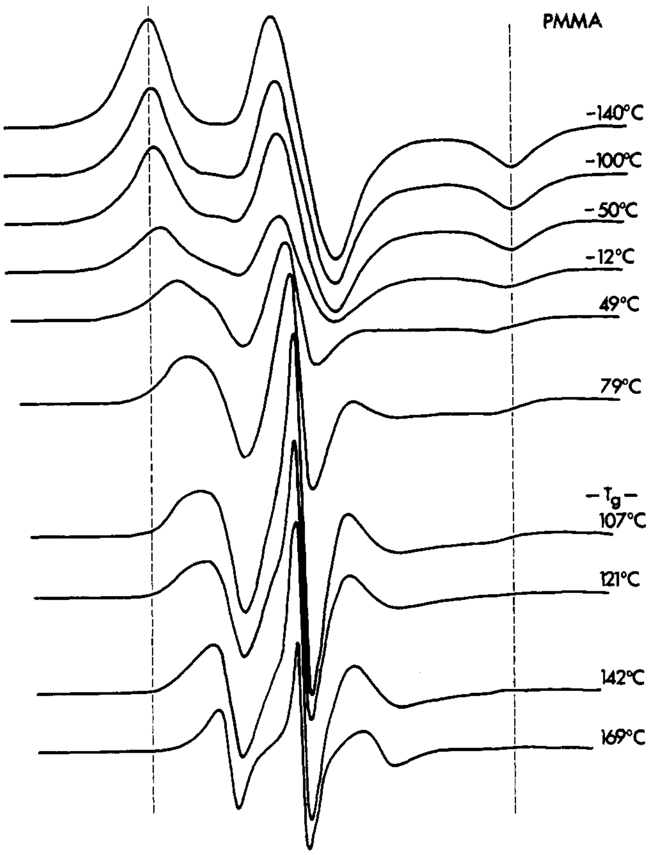


Figure 1. The temperature dependence of the ESR spectra of spin-labeled PMMA (linear). The dashed vertical lines are the positions of the outer hyperfine extrema at −140 °C. The T_g is 110 ± 5 °C by DSC.

Temperature Dependence of Nitroxide Motion in Solid PMMA (Linear). The temperature dependence of the ESR spectrum of spin labeled PMMA (linear) is shown in Figure 1. The outer hyperfine extrema are still moving further apart at −140 °C indicating the nitroxide motion is sufficient to affect the spectral line shape. As the temperature is raised the motionally slowed spectrum undergoes a continuous change eventually yielding a motionally narrowed, three-line spectrum above T_g. The motionally narrowed spectra may be analyzed, using the Kivelson theory[11] for isotropic motion, to obtain a rotational correlation time. At 169 °C the correlation time assuming isotropic rotation is 2.5×10^{-9} s. A more detailed line shape analysis indicates that the nitroxide motion is not isotropic even at 169 °C. However, we do not have sufficient data to fully analyze the rotational anisotropy as has been done for a small molecule nitroxide.[12]

We turn instead to the low-temperature, motionally slowed spectra. Correlation times may be determined from the Freed theory[13] without making a complete line shape analysis by employing various assumptions concerning the motion. Of interest are the ones using the outer extrema assuming isotropic motion,[14] or assuming highly anisotropic motion,[15] in particular, the χ_1 motion as indicated on the structural representation above. Assuming χ_1 motion only, the correlation times were calculated[15] and converted to correlation frequencies ($2\pi\nu = 1/\tau$). These are shown in Figure 2 together with correlation frequencies for PMMA as measured by dielectric relaxation, dynamic mechanical, and nuclear magnetic resonance spectroscopy.[16] ESR data above 80 °C are not shown as molecular motion about other bonds becomes important. Below −10 °C appropriate theoretical calculations have not been made.

At 25 °C the correlation frequency is $4 \pm 0.5 \times 10^7$ s^{-1} if one assumes only χ_1 motion. If instead we assume isotropic motion,[14] the correlation frequency is a factor of ~5 smaller. Although the correlation frequencies are similar using two extreme assumptions concerning the motion, a strong case can be made that the motion is principally χ_1 motion. The χ_2 motion is effectively zero as the CO–NH bond has much double bond character.[17] Therefore χ_3 and local main chain motion would have to be comparable to χ_1 motion in order to have isotropic motion of the nitroxide.

Dielectric relaxation data, primarily a measure of the ester group motion, are very instructive in understanding χ_3 motion. At 25 °C the ester group relaxation frequency in PMMA is about seven orders of magnitude slower than the nitroxide relaxation. Changing the ester from methyl to ethyl to *n*-butyl

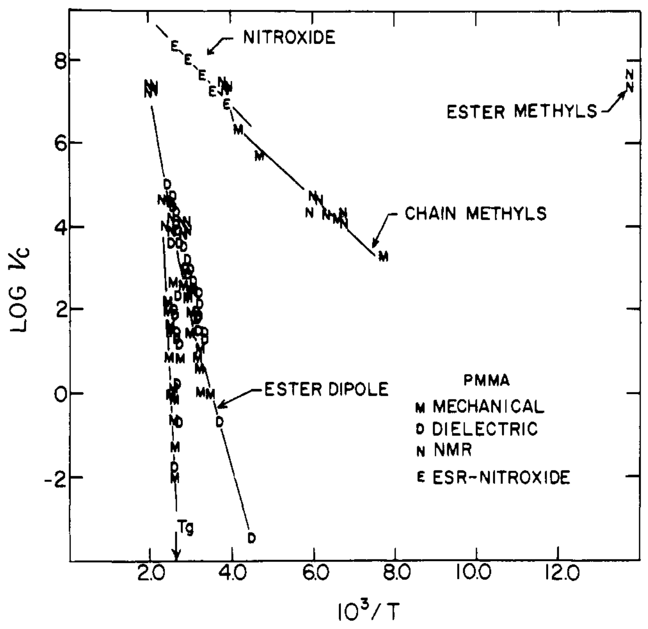


Figure 2. Temperature dependence of the correlation frequency for nitroxide motion about χ_1 (terminal bond) and the corresponding dielectric, dynamic mechanical, and NMR data for relaxation in PMMA.[16]

leaves the ester relaxation virtually unaffected at 25 °C.[16] Replacing the α-methyl with a chlorine has little effect on the ester relaxation.[16] However, replacing the α-methyl with a hydrogen, as in poly(methyl acrylate), or reversing the ester group, as in poly(vinyl acetate), increases the ester relaxation frequency by 6–7 orders of magnitude.[16] It is clear that the α-methyl severely restricts the ester group motion in the methacrylates. Inasmuch as we do not expect the carbonyl motion to be significantly faster in the nitroxide substituted moiety than in other methacrylates, the interpretation of the nitroxide relaxation as corresponding to χ_1 motion in the bulk polymer at room temperature is highly plausible.

The Arrhenius parameters of spin probe relaxation in polymers above T_g are frequently anomalous, suggesting that the nitroxide relaxation has "no explicit physical meaning".[18] The relaxation, which can be correlated with the WLF equation,[1] is found to be independent of the size and structure of the radical and is determined "solely by the properties of the polymer".[18] If a similar situation exists with our covalent label, then interpreting the motion as χ_1 motion, though plausible, is equally meaningless. The Arrhenius parameters determined from Figure 2 are 5 ± 0.5 kcal mol^{-1} for the energy of activation and $3 \pm 2 \times 10^{11}$ s^{-1} for the preexpotential factor. The preexponential factor is normal and not anomalously high as in the case of the spin probes where values as high as 10^{21} have been reported.[19] The activation energy is greater than the barrier height for rotation about the N–C single bond in methylamine[20] but less than the activation energy for rotation about N–C single bonds with steric hindrance.[21] Conformational calculations on PMMA[22] as well as space filling molecular models suggest that χ_1 rotation may encounter intramolecular steric hindrance. Thus in our system the magnitude of the preexponential factor as well as the apparent activation energy is consistent with nitroxide relaxation being dominated by χ_1 rotation in the bulk polymer at room temperature. These arguments become particularly significant when considering the results on solvent effects.

Solvent Dependence of Nitroxide Motion in Spin-Labeled PMMA and PS. Addition of *N,N*-dimethylformamide (DMF) to PMMA (linear) results in a series of spectra shown partially in Figure 3. As solvent is added, the outer hyperfine extrema remain constant and a motionally narrowed, three-line spectrum grows in on top of the motionally slowed spectrum, quite in contrast to the temperature dependence. Such a superposition is indicative of two noninterchanging populations of nitroxide radicals. Inasmuch as the outer extrema of the "slow" component appeared to be solvent independently a computer simulation was attempted assuming the spectrum of the "slow" component was the same as that for the dry polymer, plus a fast component spectrum based on the Kivelson treatment assuming isotropic rotation.[11] The input parameters were the percentage, the rotational correlation time, and the intrinsic line width of the fast component. The percent fast motion was obtained by a double integration of the fast and the slow component spectra before combining. Such a simulation proved quite successful and the calculated spectra are shown in Figure 3 together with the percentage fast motion. An intrinsic fast motion line width of 1 G was used. Slight variation in this value gives an even better fit to the experimental spectra. The rotational correlation times corresponding to these simulated spectra are shown in Figure 4. Extraction of the fast component spectrum at low percentages is difficult and the motion is also likely to still be anisotropic. Calculation of a correlation time under these circumstances was not attempted.

Shown also in Figure 4 are the correlation times with benzene and chloroform as solvents. To first approximation the three polymer–solvent systems behave similarly. As solvent is added a fast motion nitroxide component begins to grow in as the glass transition is lowered by the solvent and approaches the temperature of measurement. A motionally slowed component whose motion is affected little by solvent becomes increasingly less prominent, and after sufficient solvent has been added only the fast component remains. A detailed comparison, however, shows significant differences among the three systems. With DMF and benzene the slow motion component is no longer present shortly after T_g has been reached; whereas with $CHCl_3$ a slow motion component is still present at 70 wt % solvent. With DMF and $CHCl_3$, after the slow motion component is gone, the fast component gives a classical motionally narrowed spectrum. For instance, the low field component is Lorzentian. Under similar conditions the benzene spectra are neither Lorzentian nor Gaussian. Furthermore, the peak-to-peak derivative line height of the low-field component is larger than that of the center line, which is theoretically impossible for isotropic motion but possible if the motion is still anisotropic.[23] We thus feel that the fast motion component in the benzene–PMMA system is still moving anisotropically out to very high dilution, and the values calculated on the assumption of isotropic fast motion are somewhat in error.

Consideration of the chain geometry, and the relaxation data (Figure 2), and its interpretation in the previous section suggests to us that isotropic nitroxide motion cannot be achieved in our systems unless local mode main chain motion becomes at least comparable to χ_1 and χ_3 rotations. Inasmuch as translational diffusion in plasticized polymers can be nicely correlated to free volume theory and the monomeric friction coefficient,[1,24–26] implying dependence of main chain motion, it seemed plausible to consider the solvent dependence of the fast motion rotational diffusion in a similar manner. For translational diffusion the Fujita–Doolittle equations in linear form are[1]

$$1/\ln a_c = f_2 + (f_2^2/\beta')/v_1 \qquad (1)$$

or

$$1/\ln a_c = f_2^0 + (f_2^{02}/\beta')/(v_1 - v_1^0) \qquad (2)$$

depending on whether the reference state is taken as pure polymer or a solution of solvent volume fraction v_1^0, respec-

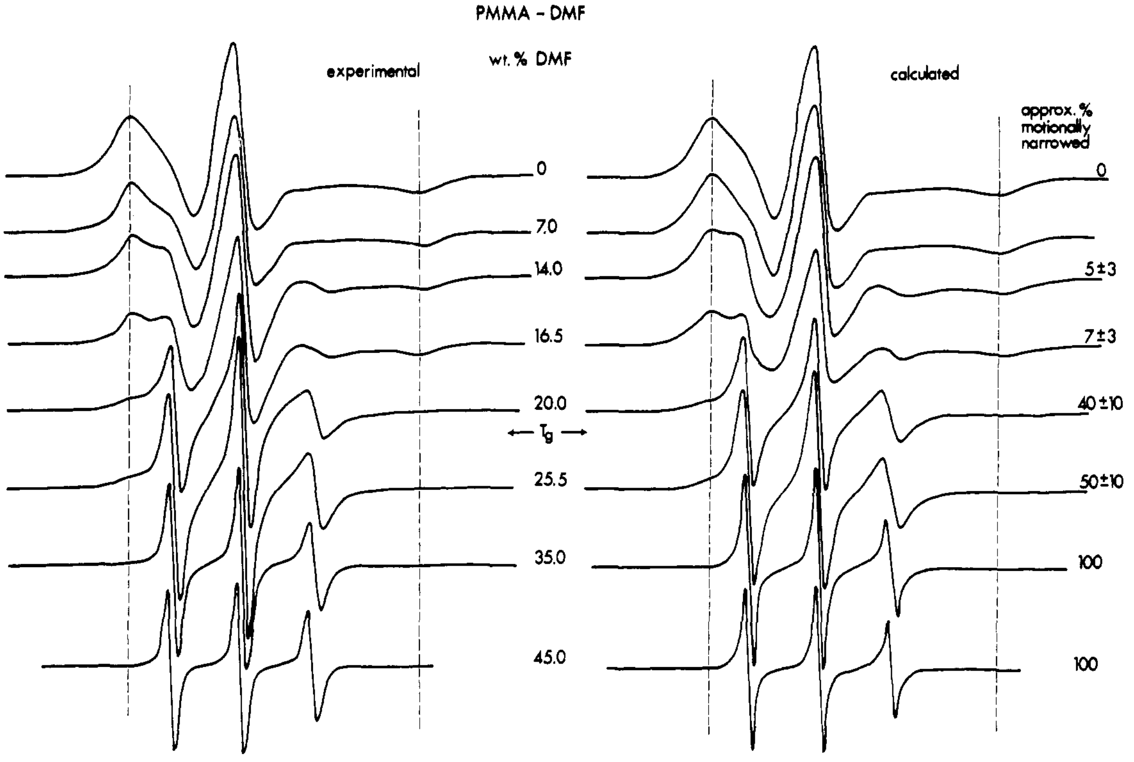


Figure 3. The ESR spectra of spin-labeled PMMA (linear) as a function of DMF composition at a nominal temperature of 25 °C. The dashed vertical lines indicate the position of the outer hyperfine extrema in the dry polymer. Also shown are spectra simulated as superposition of two independent spectra, one being that of the dry spin-labeled polymer and the other a motionally narrowed, three-line spectrum. The percent of the nitroxide labels undergoing fast motion as used in the simulation is given on the right, and the corresponding rotational correlation times are given in Figure 4. The solvent composition at which the glass transition is lowered to the temperature of measurement is indicated also (22 wt % by DSC).

tively. Here f_2 is the fractional free volume polymer in a solution of solvent volume fraction v_1, β' is a parameter which in concentrated solutions is approximately the fractional free volume of the solvent, and a_c is the ratio of the diffusion coefficient at concentration v_1 to that in the reference state. As the diffusion coefficient is inversely related to the frictional coefficient and the relaxation and correlation times, a_c is also a ratio of either of these variables in the reference state to its value in the solution of interest. Assuming that the rotational diffusion behaves similarly to translational diffusion in concentrated polymer solutions, the DMF and $CHCl_3$ fast component data were plotted according to eq 2 and are shown in Figure 5 where the reference stated was taken to be the most dilute solution. Although the most concentrated solution showing a fast relaxation is the more logical reference state, difficulties in obtaining a correlation time from the ESR data preclude its use. The plots are reasonably linear with β' being 0.1 to 0.2. Alternatively eq 1 may be utilized by assuming a relaxation time for the pure polymer. A wide range of assumed values, each greater than 10^{-8} s, yield linear plots. The solid curves in Figure 4 were calculated using the parameters obtained from the linear plots.

Spin-labeled polystyrene showed qualitatively similar behavior to PMMA as solvents were added. At low volume fraction solvent the ESR spectra were insensitive to solvent. Eventually a fast motion component would grow in and at sufficiently high solvent concentrations only an isotropic, motionally narrowed spectrum was observed. The correlation times are shown in Figure 6. In contrast with labeled PMMA, the fast component in labeled PS did not always appear as T_g approached room temperature. With benzene and $CHCl_3$, it appeared at considerably higher dilution. A plot of the fast component data according to eq 2 is shown in Figure 5. The β' for the benzene data is reasonable (0.15) but is much too high for DMP. Although the high dilution data for $CHCl_3$ indicate isotropic motion, the variation with concentration is too small to apply eq 2.

Discussion

Anisotropic Rotation in the Solid State. From a motionally slowed nitroxide ESR spectrum a unique set of relaxation times cannot be determined, as more spectroscopic parameters need to be known more accurately than are generally available. Our interpretation that the nitroxide relaxation is predominately χ_1 motion is compatible with known relaxation in PMMA as shown in Figure 2. Conformational restrictions in the disubstituted PMMA chain are severe[22] and it is not surprising that χ_3 motion is considerably more hindered than χ_1 motion in the solid state. A theoretical interpretation[15] of the ESR spectra of nitroxide-labeled, helical poly(benzyl glutamate)[27] is a clear precedent for such anisotropic motion. We were led to believe earlier[7,8] that the motion was not highly anisotropic due to the absence of the low-field doublet.[15,27] Its absence, in fact, is a result of the slowness of the relaxation plus effects of inhomogeneous broadening and a heterogeneous environment.

The relaxation of a fraction of the spin labels was uneffected by the solvent even when the polymer had been plasticized with a thermodynamically good solvent. This strengthens our conclusion that the dominant relaxation mechanism in the bulk polymer at room temperature is intramolecularly hindered χ_1 rotation, and not relaxation modulated by surrounding polymer matrix.

Influence of Sample Preparation. Three types of labeled samples were used in these studies, homogeneously labeled linear polymer, and both surface and homogeneously labeled, lightly (1 mol %) cross-linked latex spheres. The differences in sample type strongly affected the results in studies with

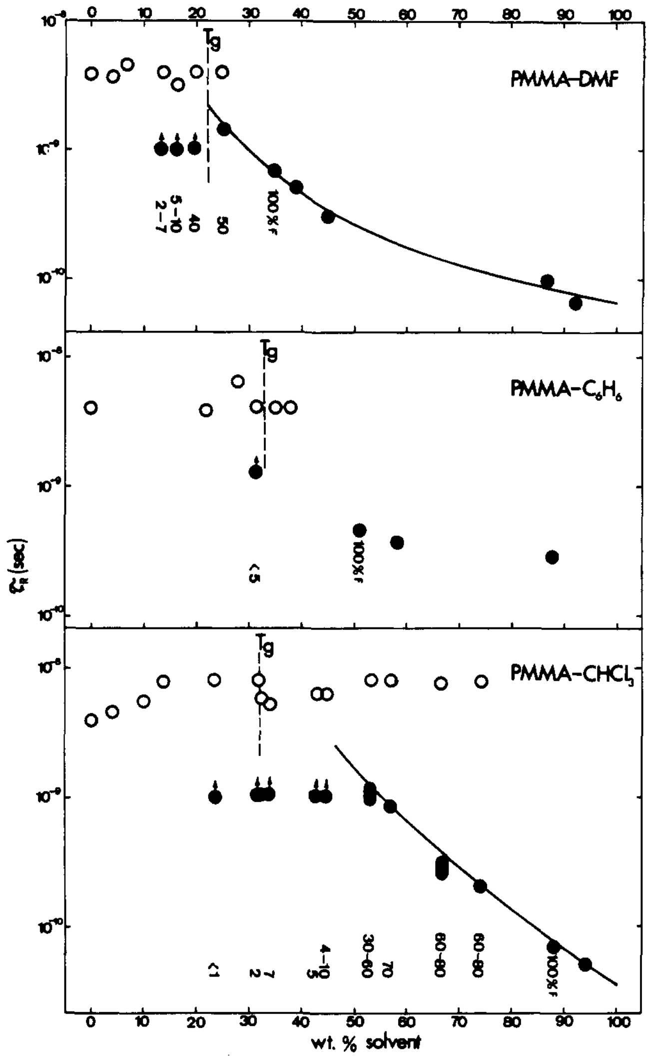


Figure 4. The concentration dependence of the rotational correlation times of nitroxide labeled PMMA at room temperature. The slow motion component (○) was calculated assuming anisotropic (χ_1) motion[15] while the fast component was either calculated assuming isotropic rotation[11] (●) or observed to be present but a correlation time was not calculable (↑). The vertical dashed lines indicate the solvent composition at which T_g reaches the temperature of measurement. The percent of the spin labels undergoing fast motion as determined by computer simulation is indicated. The solid curves through the fast motion component were calculated from a Fujita-Doolittle free volume diffusion equation[1,19] (eq 1 and 2). The DMF and $CHCl_3$ data were obtained using homogeneously labeled PMMA (linear) and the benzene data with surface labeled PMMA (latex).

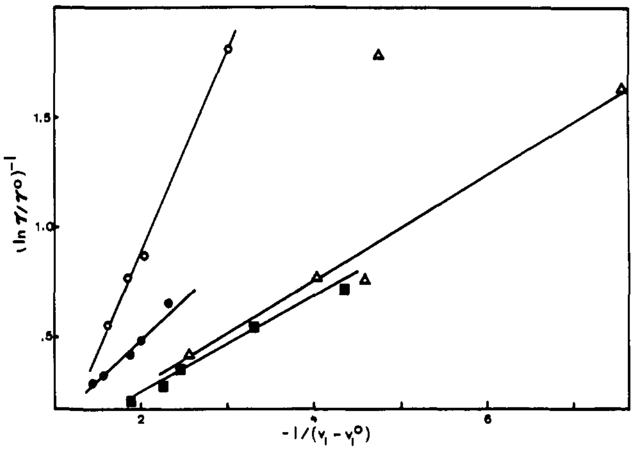


Figure 5. Fast component data (Figures 4 and 6) plotted according to eq 2 assuming Fujita-Doolittle free volume dependence on concentration for DMF on PMMA (linear) (●) or PS (latex) (○), for $CHCl_3$ on PMMA (linear) (■), and for benzene on PS (latex) (△).

nonsolvents[9] and might influence the results with good solvents. In terms of bulk properties 1% cross-linking had an insignificant effect on T_g, as was anticipated.[28] The solvent composition at which the glass transition was lowered to the temperature of ESR measurements did not depend on the sample. Our values do differ somewhat from others[4] which we believe is due to differences in the method of measuring T_g and in molecular weight. Although the bulk properties of the various preparations were similar, we have ample evidence that the nitroxide motion was dependent on both the type of sample and the sample history. If any of the labeled polymers were annealed a few degrees below T_g so that the volume and enthalpy relaxed, the ESR line shape was subtly but definitely changed. The separation of the outer extrema remained constant but the line shape in the center region of the sectrum was altered. The low, flat intensity region between the central region and the upfield extrema was reduced on annealing, and in some cases the line width at half-height of the extrema narrowed. These observations suggest that the nitroxide environment is becoming more homogeneous and that there is probably a distribution of nitroxide motions which is being altered slightly by the volume relaxation. When solvent was added to an annealed sample, the results were qualitatively similar to the unannealed sample but quantitatively different. The difference was primarily in the percent of fast motion component and was most pronounced at intermediate solvent compositions where significant amounts of both fast and slow components are observed. In general there was less fast motion with the annealed samples at the same solvent composition. Also in this composition range the percent of fast motion depended on whether the sample was prepared by adding solvent to the dry polymer or by concentrating a dilute polymer solution. Although all data shown in Figures 3, 4, and 6 were obtained using unannealed polymers, the quantitative differences in the percent fast motion may be due at least partially to sample preparation.

The polymer latexes were cross-linked in the undiluted state, i.e., during emulsion polymerization. When they are highly swollen the chains will become extended and the chain backbone dynamics will be altered. The correlation time of the fast motion component shows less concentration dependence with the cross-linked polymers than with the linear polymers and at high dilution tend to be larger than with the linear polymers. These results may be related to the cross-linking.

Effect of Solvent on Nitroxide Motion. Our results show that the nitroxide motion depends on the polymer-solvent pair as well as on composition and is not related simply to the amount of solvent uptake as has been proposed.[29] The six polymer-solvent systems do, however, show similar behavior in that low solvent concentrations have no effect on the nitroxide motion, at intermediate concentrations two populations of nitroxides of very different motional properties are observed, and in dilute polymer solutions no slow moving component is observable. Observation of two distinct populations indicates that on the ESR time scale the populations are not interconverting. Several factors indicate that the fast motion is related to local mode polymer backbone motion. In PMMA the appearance of the fast component was closely correlated to the solvent composition necessary to bring T_g down to the temperature of measurement. The finding that with DMF and $CHCl_3$ the solvent dependence of the fast component relaxation follows sensibly the Fujita-Doolittle equation suggests that the motion depends on the change in monomeric friction coefficient with solvent composition. If the fast motion component were dependent on side chain (χ_1 and χ_3) motion only, it is difficult to understand why the appearance of such motion would be related to T_g. Alternatively, one can ask why the fast component should follow the Fujita-Doolittle equation. At least two relaxation mechanisms would be operative, the local mode backbone motion and the χ_1 motion. The χ_1 motion, an internal bond rotation dominating the relaxation in the solid polymer, would have a small concentration dependence if it is controlled by intramolecular steric hindrance. The nitroxide motion thus may be characterized as a weakly solvent dependent χ_1 motion and a strongly solvent dependent motion which would be local mode backbone and concurrent χ_3 motion. The reciprocal of the mean relaxation is, of course, the sum of the reciprocal of the independent relaxations. As solvent is added the monomeric frictional coefficient is dramatically reduced and the local mode backbone motion dominates the nitroxide relaxation. One might then expect the Fujita-Doolittle equation to be followed.

Motion in PMMA in *o*-dichlorobenzene and in PS in pentachloroethane has been studied by ^{13}C NMR up to about 25 wt % polymer.[30] In *o*-dichlorobenzene the backbone CH_2 motion in PMMA has a mean correlation frequency of ~10^{-9} s at 7 wt % polymer and ~10^{-8} s at 24 wt % polymer at 30 °C. In all cases a distribution of many chain motions is evident. Similar NMR studies have not been made with our solvent systems. Proton NMR studies[31] indicate that benzene interacts more weakly than $CHCl_3$ with PMMA. This is consistent with our finding that benzene imparts anisotropic relaxation to the nitroxide to high dilution, whereas $CHCl_3$ imparts isotropic relaxation. Both solvents are thought to interact with the side chain,[31] but little is known about the relative effect of solvents on local mode backbone motion. Our spin label is in all cases attached to a methacrylate unit. If the nitroxide were relaxed by motion of the methacrylate unit only, the results for PMMA and PS should be the same in a given solvent. To a first approximation this is true. The onset of the fast component in labeled polystyrene is related not so much to the polystyrene T_g as to the onset of motion with the same solvent in labeled PMMA. However, benzene imparted isotropic motion in polystyrene but anisotropic motion in PMMA. The motions responsible for the nitroxide motion cannot then extend more than a few bonds along the main chain. These local mode backbone motions have been considered theoretically[32-36] but have little experimental verification.

The nitroxide motion responds to solvent in qualitatively the same way in the six polymer–solvent systems studied. If local backbone motion is responsible for the appearance of the fast component, it is not surprising that the onset of motion corresponds to the lowering of T_g in PMMA, as viscoelastic measurements indicate that solvent effects all backbone modes similarly, to a good approximation. What was more surprising was the existence of a double population of nitroxide motion over the intermediate concentration range. It seems unlikely that a thermodynamically good solvent would be inhomogeneously distributed in this concentration range, although at lower polymer concentrations inhomogeneities appear to be observed by NMR.[37] We can at present only speculate as to the origin of the bimodal distribution of correlation times. In this concentration region chain entanglements are significant and effect the polymer relaxation modes.[1,38] Dielectric relaxation studies on polar solvents in nonpolar polystyrene show a bimodal distribution of solvent relaxations in a concentration region comparable to ours.[39] This, of course, does not infer a bimodal distribution of polymer relaxations. A more plausible explanation may lie in the variation in this rate of conformational interconversion among the various stereosequences along the chain. Inasmuch as neutron scattering results[40-42] show clearly that the population of the various chain conformations is the same in the bulk polymer as in dilute solution theta solvents, one would assume that the same would be true over the entire composition range. Our results suggest that the nitroxide relaxation is dependent on only a few local bonds, and therefore may depend on the rate of conformational interconversion of only one or two dyads surrounding the nitroxide. The conformational energy calculations[22,43] suggest that the rate of conformational interconversion might well depend on the stereochemical sequence in that the barrier to pass from one rotational state to another depends on the stereochemistry. The nitroxide is assumed to be attached randomly, independent of local stereochemistry. At low solvent composition all backbone motion is too slow to affect the nitroxide, while at high solvent composition the motion is too fast to distinguish rates of interconversion by observing the nitroxide motion. At some intermediate composition the differences in interconversion would have its most observable effect on the nitroxide motion. The correctness of this argument awaits further study.

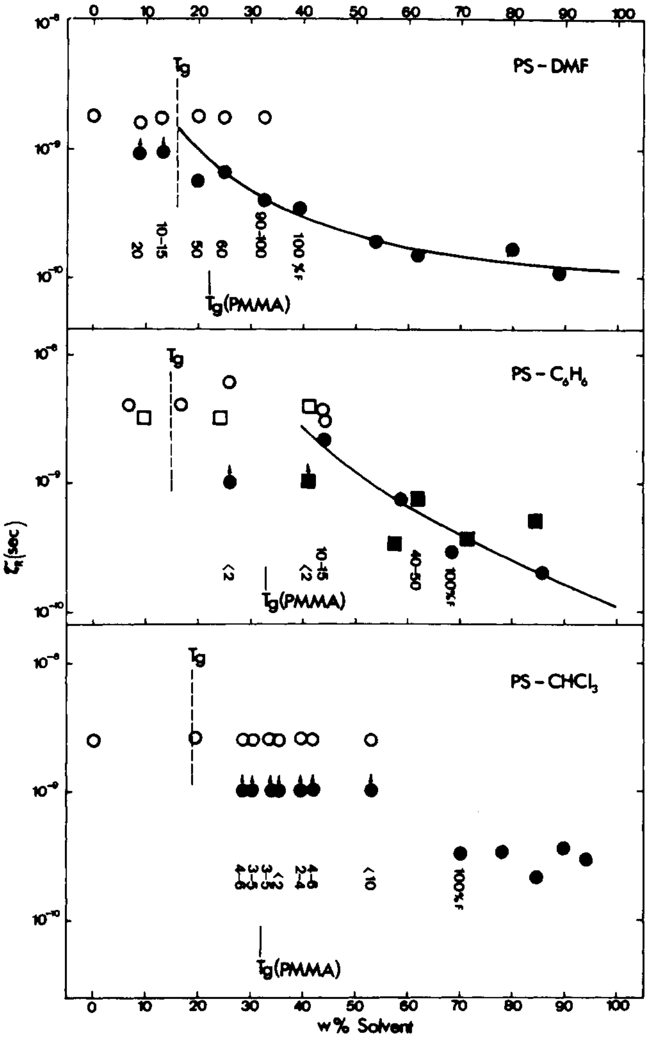


Figure 6. The concentration dependence of the rotational correlation time of nitroxide labeled polystyrene at room temperature. Analogous to Figure 4 except that the benzene data were obtained using surface (○, ●) and homogeneously labeled (□, ■) PS (latex) and the DMF and $CHCl_3$ data with surface labeled PS (latex).

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A Hypothesis on Polymer Chain Configurations. Helical Wormlike Chains

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ABSTRACT: The following hypothesis on polymer chain configurations is presented: "On the bond length or somewhat longer scales, any real chain may be represented by the continuous helical wormlike chain, i.e., a hybrid of the three extreme forms of rod, coil, and helix." Various salient aspects of the new model itself are deduced from this hypothesis. The basic model parameters are the curvature λ^{-1} of the elastic potential curve multiplied by $2/kT$ at its minimum, the radius ρ and pitch h of the characteristic helix corresponding to minimum energy, and the shift factor M_L, defined as the molecular weight per unit contour length. In particular, it is concluded that M_L is closely related to the length scales to be adopted for a given chain and that the parameter λ^{-1} may be used as an absolute measure of chain stiffness for all types of real chains.

Since the beginning of the theoretical or statistical-mechanical investigations of the properties of polymeric systems, Kuhn random flight or Gaussian chains[1-3] have long retained an important place as standard molecular models for randomly coiled, flexible macromolecules. The details of the chemical structure of real chains are smeared out in such models, but this suffices to permit understanding of the majority of basic physical processes such as excluded volume effects and steady-state transport and dynamical phenomena.[2,3] As is well known, the random-flight model may be characterized by the so-called Markov nature such that the mean-square end-to-end distance is proportional to the number of bonds in the chain in its unperturbed state without excluded volume. However, the Markov nature breaks down for real short chains and is valid only asymptotically for long enough chains, particularly for semiflexible or stiff chains. This non-Markov nature arises from a sort of stiffness or static rigidity, as introduced by the constraints on the internal degrees of freedom such as fixed bond lengths, fixed bond angles, and hindered internal rotations. Necessarily, the study of such effects and also various configuration-dependent properties requires molecular models on the atomic level. There is little doubt that among these, rotational isomeric state models[4-7] are best established and most widely accepted at the present time.

However, the rotational isomeric state model is not always convenient in use, especially in the study of the properties usually covered by the random-flight model. The difficulty may often be overcome by adopting continuous models such as the Kratky-Porod (KP) wormlike chain[3,8,9] and its modifications.[10] Such models, smearing the detailed chemical structure, are therefore similar to the random-flight model in spirit but can interpolate from the two extremes of random coil and rod to preserve the non-Markov nature. In recent