ever, some indication on the accuracy of our results by the spread of independent, individual values of τ_c for a given ratio R. The greatest spread was found for $R = 0.5$, where τ_c varied between 0.76 and 0.89 ($\times 10^{-12}$) sec. The trend of slightly increasing average values of τ_c with increasing polymer concentration is corroborated by a corresponding trend in the slopes of the exponential parts of the correlation functions.[20]

We conclude with an estimate of the effect of the chlorine isotopes Cl-35 and Cl-37 on the band shape. For this purpose we compute the isotope shifts of the ν_4 mode of CH_2Cl_2 for the species $CH_2{}^{35}Cl^{37}Cl$ and $CH_2{}^{37}Cl_2$, which are present in natural CH_2Cl_2 with the relative abundances of ~0.67 and ~0.11, respectively ($CH_2{}^{35}Cl_2 = 1$).[21] We find a shift of ~ -2 cm^{-1} for $CH_2{}^{35}Cl^{37}Cl$ and a shift of ~ -4 cm^{-1} for the much less abundant species $CH_2{}^{37}Cl_2$. The isotope shift for $CH_2{}^{35}Cl^{37}Cl$ is of about the same order of magnitude as the solvent shift (see part B of the Experimental Section). Using a band center shifted by -2 cm^{-1}, we have computed $\langle \mathbf{u}(0)\mathbf{u}(t)\rangle$ and found that its values differ insignificantly within the scope of our work. The values of τ_c in Table I would decrease by about 8%.

Summary

The usefulness of a picture of a "distribution of amplitude with time" for a description of the mobility of small molecules in a highly viscous medium is clearly demonstrated by the fact that it has enabled us to obtain quantitative information about the rotational diffusion of CH_2Cl_2 in polystyrene-methylene chloride solutions without recourse to any model. It was established that the rotational motion of the CH_2Cl_2 molecules decays to Brownian motion within a time interval of 0.4–0.5 ($\times 10^{-12}$) sec in these solutions and that the corresponding rotational correlation times are 0.78–0.94 ($\times 10^{-12}$) sec, independent of the macroscopic viscosity.

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(20) The slopes decrease with increasing polymer concentration; *i.e.*, the diffusion constant decreases with increasing amounts of polymer; see W. H. Furry, *Phys. Rev.*, **107**, 7 (1957), eq 19.

(21) We neglected the motion of the hydrogen atoms and considered a triatomic model XCl_2, that is, two Cl atoms bound to the center of a mass of X = 14 mass units. The angle Cl–X–Cl, the bond distance X–Cl, and the force constants of the X–Cl stretch and Cl–X–Cl deformation (which correspond to ν_4 of CH_2Cl_2) were taken from R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952), and J. C. Decius, *ibid.*, **16**, 214 (1948). The shift of the Cl–X–Cl deformation mode, upon replacing ^{35}Cl by ^{37}Cl, was computed using eq II.190 and II.191 of ref 12. See also Figure 2 of ref 3 for measurements of the comparable isotope shifts of a bending mode of $CHCl_3$.

Nuclear Magnetic Resonance Studies of Polyisobutylene Solutions

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ABSTRACT: The nuclear magnetic relaxation of solutions of polyisobutylene (PIB) has been examined over a range of concentrations and temperatures in a "good" solvent, carbon tetrachloride, and a "poor" solvent, perdeuteriobenzene. The spin-lattice relaxation time, T_1, is essentially independent of concentration at sufficient dilution, for a particular solvent, but depends somewhat on the nature of the solvent. The spin-spin relaxation time, T_2, depends strongly on the concentration, but approaches a limit with sufficient dilution. The temperature dependence of T_2 in the PIB-C_6D_6 system changes abruptly in the vicinity of the θ temperature. The relaxation processes are discussed in comparison with viscoelastic data in the literature.

Nuclear magnetic resonance (nmr) has played only a limited role in the study of polymer solutions.[1-8] The theoretical problem in the study of nmr relaxation presents difficulties in addition to those encountered in the interpretation of viscoelastic behavior.[3,6] In qualitative terms, however, we can reasonably expect the nuclear magnetic relaxation of polymer molecules in solution to involve a variety of factors, such as the nature of the polymer-solvent system, the molecular weight of the polymer, the concentration of the solution, and the temperature.

We report here some observations of nmr relaxation in some polyisobutylenes (PIB) in two solvents, carbon tetrachloride (CCl_4) and perdeuteriobenzene (C_6D_6), over a range of temperatures and concentrations. Since the proton magnetic resonance of the polymer was examined, it was a simplification to use these proton-free solvents. From viscometric studies,[9] CCl_4 is regarded as a "good" solvent for PIB, whereas benzene is classed as a "poor" solvent. The aim of the present work is to examine differences, not previously explored, in the nmr relaxation of such contrasting systems and to relate the information from nmr studies to the findings from other methods.

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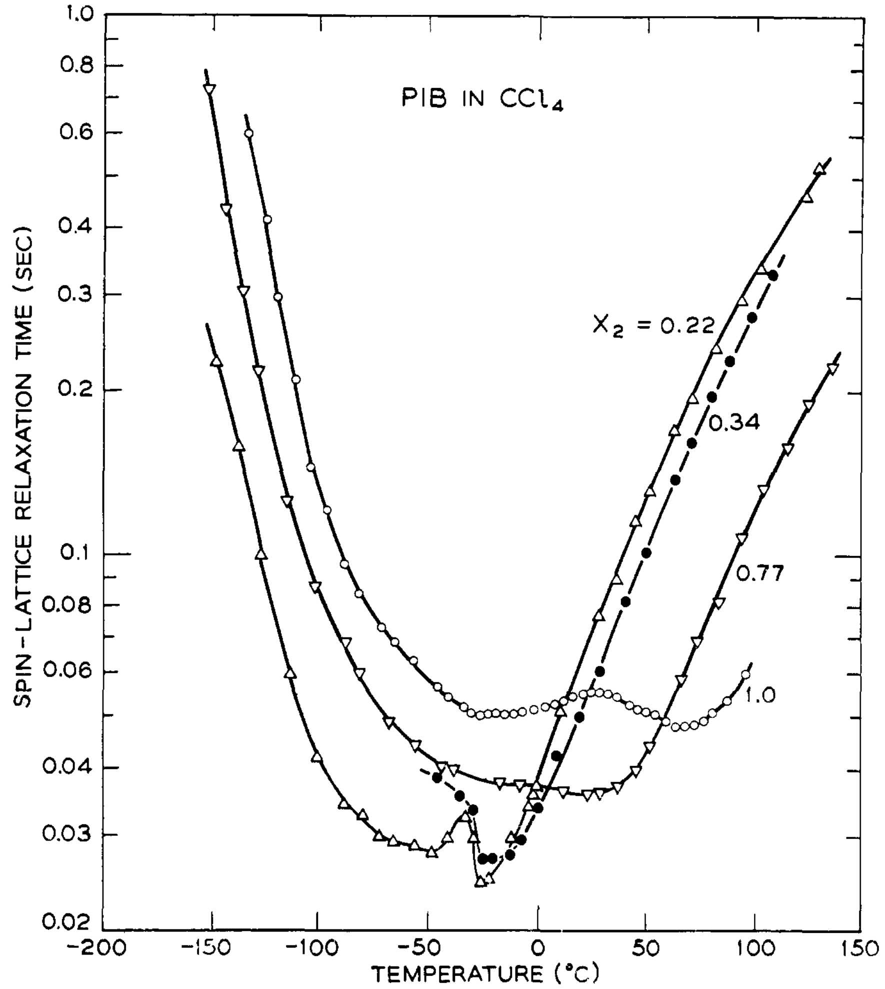

Figure 1. Temperature dependence of the spin–lattice relaxation time, T_1, in solutions of PIB in CCl_4 at various mole fractions of monomer units (X_2 = 1 for pure PIB).

Experimental Section

The pulsed nmr apparatus has been described elsewhere.[10] Measurements were made at a radiofrequency of 50 MHz. The pulses were 1–3 μsec in length and the recovery time of the receiving circuit following a pulse was about 12 μsec. The nmr spin–lattice relaxation time, T_1, was found by observing the null in the free-induction decay following 180–90° sequences.[11] The spin–spin relaxation time, T_2, was found by the "spin-echo" method.[12] The field homogeneity of the electromagnet was fairly good, about 0.05 G/cm in the vicinity of the sample. It was difficult to detect spin echoes in the more dilute solutions. Somewhat greater sensitivity was available through measurement of the steady-state resonance width, with a Varian A-60 spectrometer (only at room temperature). T_2 was obtained from the line width, δH, through the usual relation $T_2 \cong 2/\gamma\delta H$, where γ is the proton gyromagnetic ratio.

The perdeuteriobenzene, from Merck Sharp and Dohme of Canada, Ltd., was over 99% pure in deuterium content. The carbon tetrachloride was reagent grade. The fractionated polyisobutylenes were provided through the courtesy of Dr. Donald Beeson, Esso Research and Engineering Co. The molecular weights were derived either from single-point viscosity measurements or from intrinsic viscosities. Most of the nmr data were obtained with the sample of highest molecular weight, M_v = 1,129,000, but some measurements were made with lower molecular weights: 40,000, 105,000, and 543,000. The solutions were prepared by weighing out the polymer in a tared glass sample tube, adding about the right amount of solvent, sealing the tube with the contents chilled by liquid nitrogen, and weighing the combined polymer and solvent. To make the sample homogeneous, the sealed tube was heated for several hours at 60° and the sample was then allowed to equilibrate at room temperature for 1 week or longer. Since the two solvents differ greatly in molecular weight, the concentrations are given in terms of the mole fraction, X_2, of isobutene units in the solutions, rather than in terms of weight fraction. It should be noted that even the most dilute solutions studied here were rather concentrated in terms of familiar measurements of light scattering and intrinsic viscosity.

Spin–Lattice Relaxation Time

Figure 1 shows the temperature dependence of the spin–lattice relaxation time, T_1, of PIB in CCl_4 and Figure 2 shows the behavior of the perdeuteriobenzene solutions. These graphs report studies of the highest molecular weight PIB, but essentially the same results were found with limited measurements of the other three polymer samples. The lower temperature minimum in T_1, occurring at −25° in the undiluted PIB, is known[13] to be governed by rotation of the CH_3

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[10] W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **35**, 10 (1964).

[11] H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

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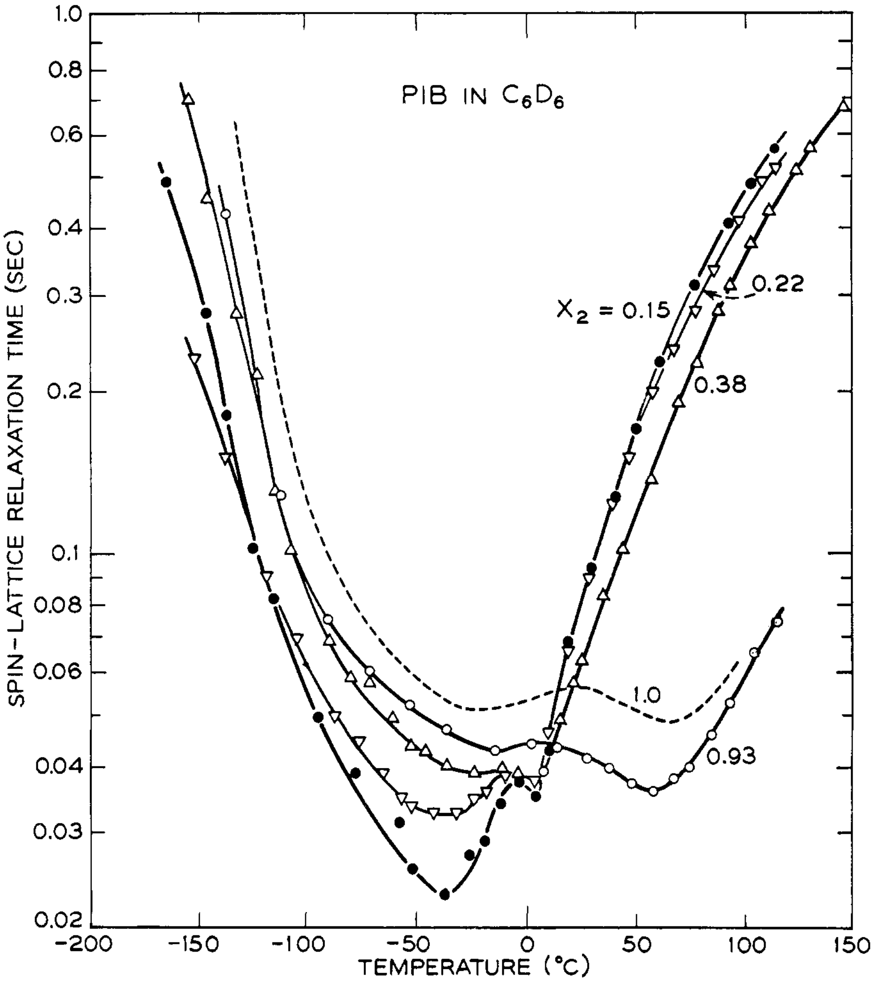

Figure 2. Temperature dependence of the spin–lattice relaxation time, T_1, in solutions of PIB in C_6D_6 at various mole fractions of monomer units.

groups and the higher temperature minimum is due to extensive rotational and translational motion of the chain segments.[13] The presence of a small quantity of solvent has the expected plasticizing effect: with increased freedom of chain motion the associated T_1 minimum is shifted to lower temperatures and the relaxation time is shortened. It is seen that T_1 at the higher temperatures is insensitive to further dilution when the polymer is sufficiently plasticized. The abrupt change in T_1 observed in the more dilute solutions at about 5° for the PIB–C_6D_6 system and near −28° for the PIB–CCl_4 system corresponds in each case to the freezing of the solvent. The T_1 minima that occur just before these abrupt changes are only apparent minima: were it not for the freezing of the solvents, the T_1 minima would undoubtedly have occurred at still lower temperatures.

On the other hand, the low-temperature minimum in T_1 is seen to decrease further with greater dilution. Although both polymer–diluent solutions are solid at these temperatures, the solvent has an obvious effect in facilitating the rotation of the methyl groups, which in the pure polymer are known to be severely constrained in their rotation owing to mutual hindrances.[13] Nevertheless, the T_1 minima in even the most dilute solutions that could be measured occur at temperatures some 60° higher than in *n*-alkanes, rubber, and polypropylene.[10,14] Thus, the steric hindrance among the methyl groups of PIB is still important in spite of the effect of the solvent. The detailed nature of the hindrances to CH_3 rotation in PIB is not clear, but plainly they do not arise chiefly from interactions between CH_3's attached to the same chain carbon atom.

Figure 3 compares T_1 in the two solvents, at the same molar concentration of solute, $X_2 = 0.22$. This is a concentration at which T_1 depends little on dilution at the higher temperatures, although it is seen that the relaxation is somewhat faster in the good solvent at a given temperature than in the poor solvent. This difference very likely reflects a greater amplitude of segmental motion in the better solvent and presumably underlies the greater swelling action observed in light scattering and viscometric studies of polymers in good solvents compared with poor solvents. At temperatures below the freezing points of the respective solvents, the T_1 minimum corresponding to CH_3 rotation is seen to depend greatly on the nature of the solvent: the minimum for the better solvent occurs some 25° lower than for the poorer solvent and the relaxation time is shorter, which suggests that the

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(14) J. E. Anderson and W. P. Slichter, *J. Phys. Chem.*, **69**, 3099 (1965).

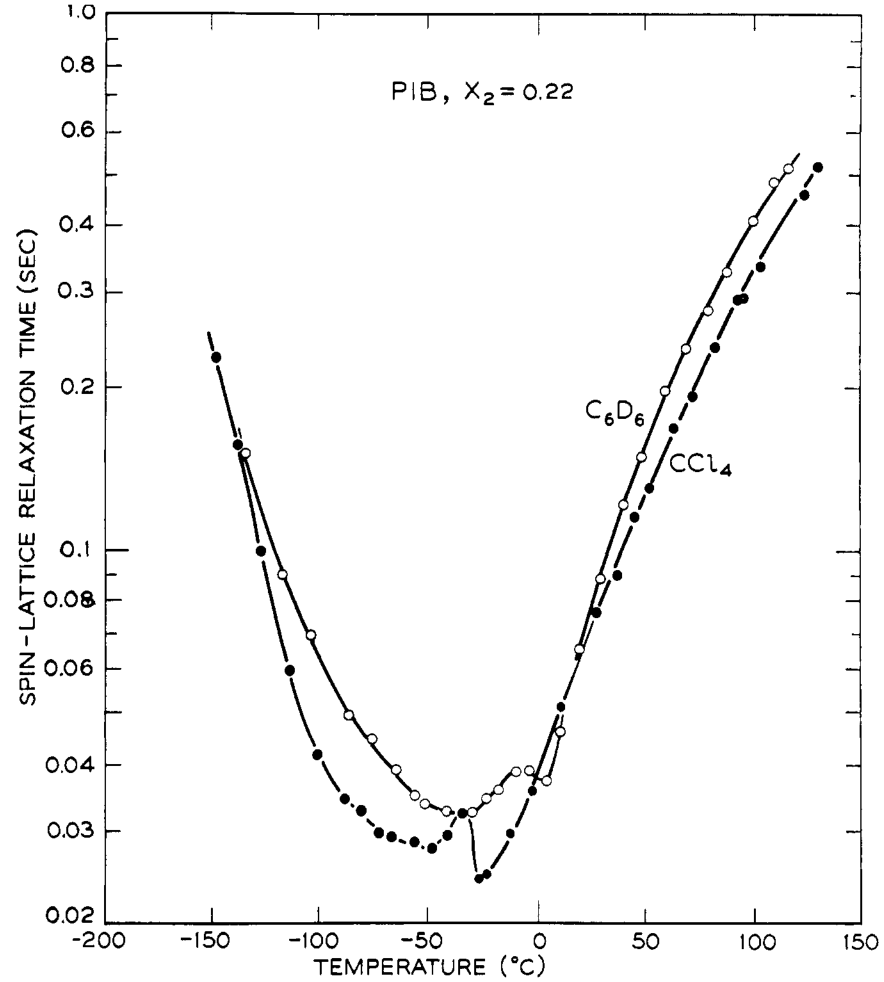

Figure 3. Comparison of the spin-lattice relaxation time of PIB in CCl_4 and in C_6D_6 at the same molar concentration, X_2 = 0.22.

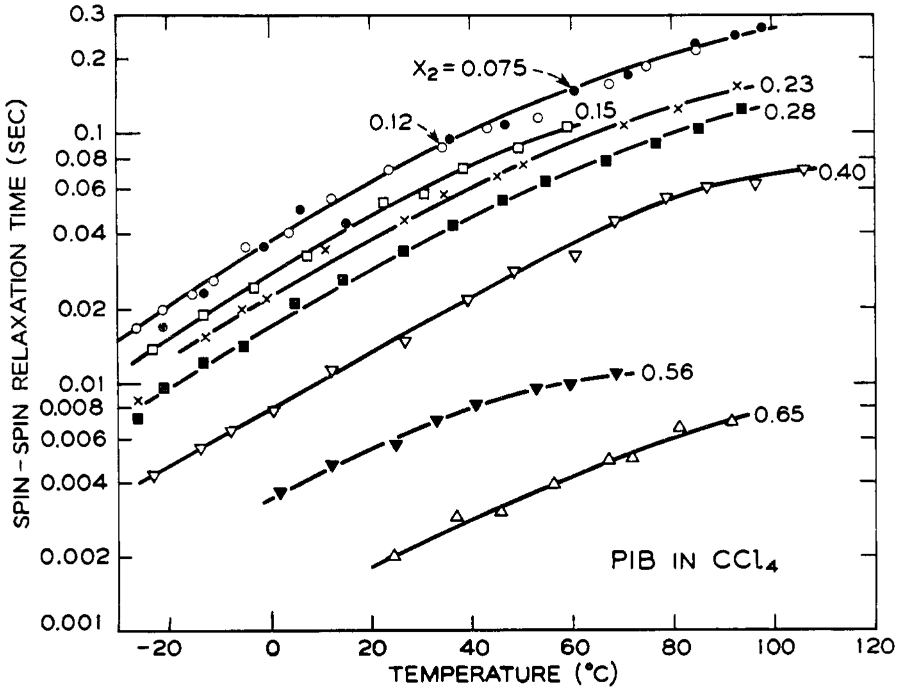

Figure 4. Temperature dependence of the spin-spin relaxation time, T_2, in solutions of PIB in CCl_4 at various mole fractions of monomer units.

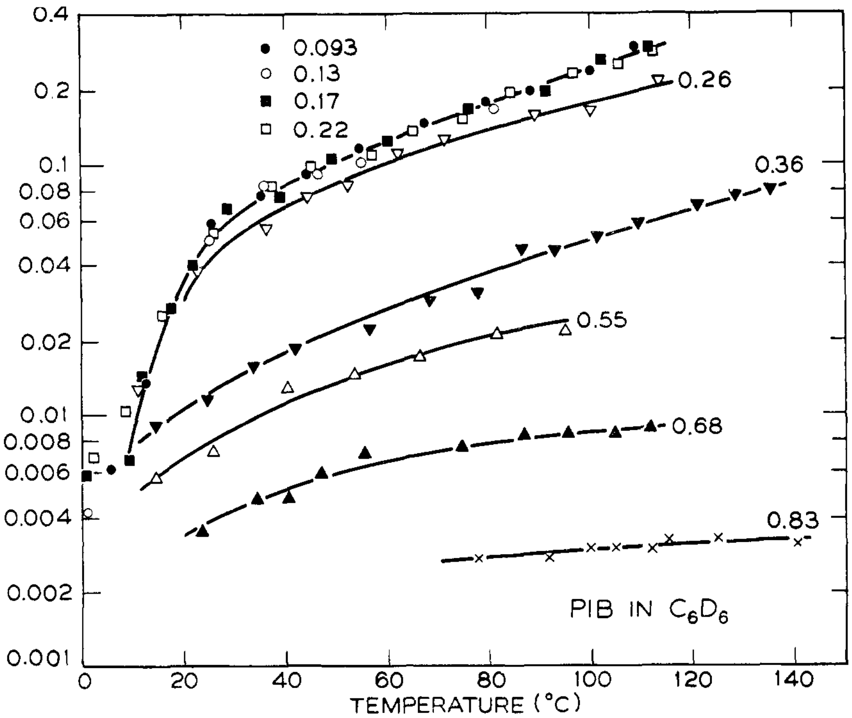

Figure 5. Temperature dependence of the spin–spin relaxation time, T_2, in solutions of PIB in C_6D_6 at various mole fractions of monomer units.

frozen-in molecular conformation in the presence of the better solvent is relatively free of constraint to rotation of the methyl groups.

Spin–Spin Relaxation Time

Figure 4 shows the temperature dependence of the spin–spin relaxation time, T_2, of PIB in CCl_4 and Figure 5 shows the behavior of the C_6D_6 solutions. T_2 generally increases with increasing dilution of the polymer, at a given temperature. This trend reflects the development of greater segmental mobility as the system is changed from a plasticized polymer to a concentrated solution. Two features are noteworthy. First, T_2 appears to approach a limit with increasing dilution at a given temperature, for each solvent. Second, the curves in the PIB–C_6D_6 system show two distinctly different slopes when the polymer concentration is low enough. An additional detail is that the curves become concave downward at the higher temperatures. Although such curvature might be caused by the development of diffusion of the polymer molecules, which has been measured[5] in solutions of PIB of low molecular weight in the presence of a large gradient of magnetic field, such an effect seems unlikely in this case. Instead, it seems probable that the curvature here is due to the distilling off of some of the solvent to the top of the sample tube, so that the polymer solutions become more concentrated.

We have noted that all of these solutions are quite concentrated in usual terms of the theory of dilute polymer solutions. Because of polydispersity and because the space pervaded by polymer molecules in solution is not an exact quantity, there is some vagueness concerning the overlap between neighboring molecules. It is clear, however, that the concentrations used here correspond in most cases to substantial overlap between neighboring molecules. A simple estimate, based on calculating the distance between centers of molecules hexagonally close-packed with occupied volumes given by the radius of gyration,[15] indicates that in the solutions studied here the polymer molecules of mol wt $\sim 10^6$ become separated only at the lowest dilutions used ($X_2 \lesssim 0.05$). For the polymers of lower molecular weight, the critical concentrations for overlap are of course correspondingly higher.

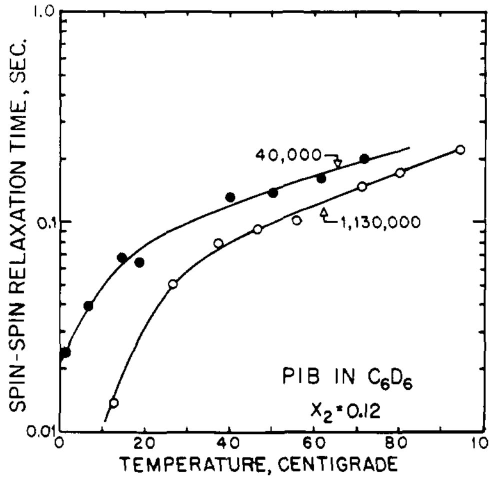

Figure 6. Temperature dependence of T_2 for PIB of mol wt 40,000 and 1,130,000 in C_6D_6 at the same mole fraction of monomer units.

Thus, at a given temperature, T_2 appears to approach a limit on increasing dilution at concentrations that are above those corresponding to separation of the solute molecules. Nolle has reported[1] that T_2 for PIB–CCl_4 solutions approaches a limit of about 0.07

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(15) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 612 ff; G. C. Berry, *J. Phys. Chem.*, **70**, 1194 (1966).

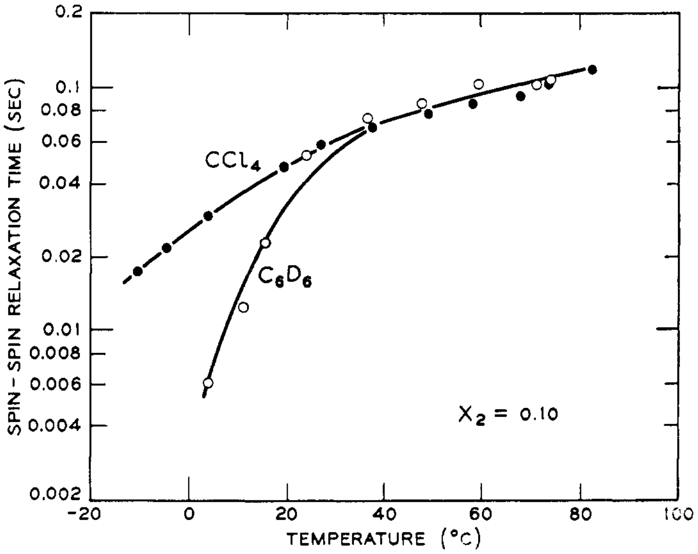

Figure 7. Comparison of the spin-spin relaxation time, as a function of temperature, for PIB in CCl_4 and C_6D_6 at the same molar concentration of solute.

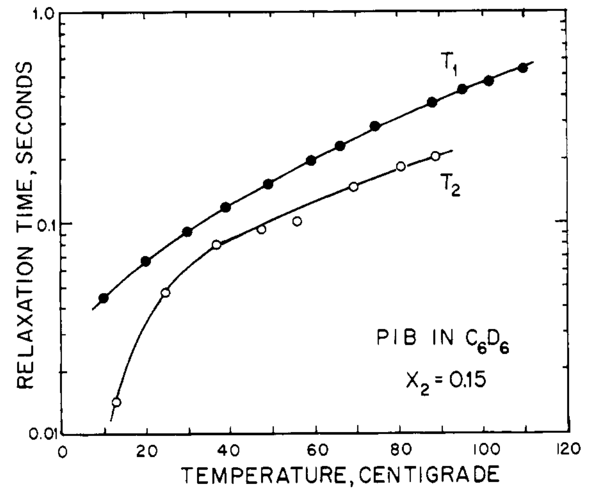

Figure 8. Comparison of the temperature dependence of T_1 and T_2 in the PIB–C_6D_6 system.

sec upon dilution at room temperature and that this limit is independent of molecular weight between 1700 and 2 × 10^6. McCall, Douglass, and Anderson[5] have reported that T_2 is much larger than this, ~0.15 sec, for low molecular weight PIB (M_v = 1700) in CCl_4. The present studies are in essential agreement with this latter work. Evidently the influence of molecular weight is greater than was determined by Nolle: in Figure 6 we see T_2 as a function of temperature for two PIB's in C_6D_6, at the same mole fraction of isobutene units (X_2 = 0.12). The dependence on molecular weight is quite clear. In the case of the polymer of lower molecular weight (M_v = 40,000), the dilution is sufficient for separation of the solute molecules, so that there is the possibility of extensive molecular reorientation to contribute to the lengthening of T_2. Such motion should be inhibited in molecules that overlap.

The existence of two distinct slopes in the T_2-temperature curves of the PIB–C_6D_6 solutions at sufficient dilution appears to be a manifestation, at the molecular level, of the θ transition seen in macroscopic experiments at 24° in this polymer-solvent system.[9] The θ temperature is defined[16] in the limit of infinite molecular weight. Thus the change in slope of the T_2-temperature curve occurs at lower temperatures with lower molecular weight of the polymer. The θ point for the PIB–CCl_4 system is quite low, deduced from theory to be about −88°,[9] and therefore the critical miscibility that characterizes the θ transition is not a factor in these studies in that system.

In Figure 5, it is also seen that at temperatures below the bend, the values of T_2 at several concentrations coincide, even though they may diverge above the change in slope. This behavior is again in keeping with the picture of molecular behavior below the θ point:[15] the polymer segments prefer their own environment to that of the solvent and thus T_2 is little affected by further dilution.

Figure 7 compares the T_2-temperature variation of PIB in the two solvents at the same dilution. It is seen that the curves for the two systems are essentially superposed above the θ point of the PIB–C_6D_6 system. A comparable finding is given by the work of McCall, Douglass, and Anderson[5] in comparisons of the PIB–CCl_4 and PIB–CS_2 systems at the *same mole fraction* of solute (the data in their paper were expressed in terms of weight concentration): T_2 was found to be essentially independent of the nature of the solvent, although it was longer than in the present studies at a corresponding concentration of monomer units, since the molecular weight of the polymer was quite low in those experiments.

Thus, although the nature of the solvent is important in determining the spatial distribution of the polymer chain and in particular the factor α which expresses the linear deformation,[17] there is no significant effect on the spin-spin relaxation. As Nolle has suggested,[1] the spin-spin relaxation of polymers in solution is evidently governed by the reorientation of chain segments. An earlier conclusion[7] stated that T_2 in

(16) See ref 15, Chapter XIII.
(17) See ref 15, Chapter XIV.

fairly dilute solutions depends on the identity of the solvent, but the comparisons involved not only different solvents but also PIB's from different sources, even though nominally of similar molecular weight. The present study, involving comparisons between two PIB–solvent systems with the same PIB, indicates that the spin–spin relaxation is insensitive to the nature of the solvent above the θ temperature.

Discussion

In the theory of the nuclear magnetic relaxation of very simple systems,[18] it is predicted (and found experimentally) that $T_1 = T_2$ when the frequency of molecular reorientation is sufficiently great, that is, when the temperature is high enough. There is no trend toward coalescence of T_1 and T_2 in the present studies, however, as is demonstrated in Figure 8. This separation of T_1 and T_2 has been observed before in molten PIB[13] and in PIB solutions.[1,5] Evidently the spin–lattice and spin–spin relaxations are controlled by different processes, but the details are obscure. Viewing the relaxation as a mechanism controlled by thermal activation of the familiar Arrhenius form, it follows that the activation energy for the T_2 process in Figure 8 is about 3.5 kcal/mol (and is similar for the T_1 and T_2 processes in all the dilute solutions studied here). In contrast, the activation energy for viscous flow is several times as large.[19] This disparity points again to the character of the motion involved in the T_2 process, presumed to depend on segmental reorientation. The barriers to intramolecular rotation in PIB appear to be rather small.[20] Thus, the temperature coefficient of the nuclear magnetic relaxation reflects this segmental reorientation, not the grosser motion involved in viscous flow.

Acknowledgment. We are grateful to our colleagues, Dr. D. C. Douglass, Dr. S. Matsuoka, and Dr. D. W. McCall, for sharing with us their discussions of relaxation in polymers. In addition, we thank Dr. McCall for his helpful comments on this paper.

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On the Chromophore of Polyacrylonitrile. II. The Presence of Ketonic Groups in Polyacrylonitrile

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ABSTRACT: Polyacrylonitrile prepared by free-radical catalysts contains an absorption of varying intensity in the 265–275-mμ region. The intensity of this absorption increases upon addition of base. This spectral behavior is explained in terms of a keto–enol equilibrium of a β-ketonitrile, where the enol anion is strongly colored.

Previously, we have shown that the chromophore of discolored polacrylonitrile consists of a random copolymer of conjugated imine and nitrone bonds.[2a] This is an extension of the structure suggested by McCartney,[2b] Burlant and Parsons,[3] and Grassie and McNeill.[4] The latter demonstrated that polymethacrylonitrile could be prepared in a stable form which would not discolor when heated, if the monomer was rigorously purified and the proper free-radical catalyst was used to initiate the polymerization.[5] They concluded that the polymerization of nitrile groups needs an initiator and showed that nucleophilic agents are capable of functioning as such. On the other hand, polyacrylonitrile cannot be obtained in a heat stable form. When heated to approximately 180°, it turns various shades of yellow to brown. Grassie and Hay concluded that the discoloration of polyacrylonitrile is an inherent property of the polymer molecule and suggested that the tertiary hydrogens in polyacrylonitrile (PAN) were sufficiently acid to start the polymerization of the nitrile groups.[6] Friedlander, Brandrup, Peebles, and Kirby[7] have shown that model compounds of PAN, which contain a 1,3 arrangement of nitrile groups, are heat stable under nitrogen, while PAN is not. Therefore, the $(\text{–CH}_2\text{CHCN–})_x$ must be relatively heat stable and some other group as a defect must be present in the polymer which can act as an initiator of the discoloration reaction.

Evidence for various defects in PAN has been reported. Beevers,[8] Schurz, Zah, and Ullrich,[9] and

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