Mobility of Small Molecules in Viscous Media. I. Rotational Motion of Methylene Chloride Molecules in Polystyrene by Far-Infrared Spectroscopy

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ABSTRACT: This article describes the application of the Heisenberg description of spectroscopy ("distribution of amplitude with time") to a study of the mobility of CH_2Cl_2 in methylene chloride–polystyrene solutions. The experimental procedure involved the evaluation of the band shape of the ν_4 fundamental of CH_2Cl_2 (283 cm^{-1}) in the polymer solutions. The data are expressed in the form of correlation functions of the rotational motion of the halide molecules. It is established that the component of the rotational diffusion tensor along the twofold symmetry axis of the CH_2Cl_2 molecule decays to Brownian motion within a time interval of 0.4–0.5 ($\times 10^{-12}$) sec in these solutions. The corresponding rotational correlation times are 0.78–0.94 ($\times 10^{-12}$) sec. On the basis of a simple model, which describes the probability of nonrandom diffusion steps of the halide molecules in terms of the frequencies of opening and closing of "cages" in the polymer solutions, it is shown that there is no relevant connection between the macroscopic viscosity of the solutions and the rotational motion of the halide molecules

The characteristics of the mobility of a molecule within a condensed phase are of great theoretical and practical significance since they reflect the intermolecular forces between the different molecules. With particular reference to synthetic polymers, studies of the mobility of small molecules within a polymer matrix have been undertaken in order to understand the effects of plasticization on the polymer properties. Clearly, the subject is not restricted to synthetic polymers and its relevance to diffusion phenomena in biopolymers may be envisaged. The questions which one would hope to have answered by a study of the mobility of small molecules in polymeric media are manifold. (1) How does the macroscopic viscosity influence the mobility of a molecule on a given site in the viscous medium? Obviously the local intermolecular forces need not necessarily reflect the bulk viscosity. (2) Does the molecular weight of the polymer have a significant influence on the mobility of dissolved molecules? (3) Is the conformation of the polymer a determining factor? Furthermore, it would be very interesting to know more about the effects—on the molecular level—of substituents or reactive groups of the polymeric backbone on the mobility of small molecules.

In general, the more common techniques of studying the mobility of molecules fall into two categories of classical methods, namely, those which follow the approach to equilibrium by measuring, for instance, diffusion coefficients and those which determine an equilibrium property such as the vapor pressure. More recently, the phenomenon of proton nuclear magnetic spin–lattice relaxation has been employed to follow the diffusional behavior of dissolved molecules.[1,2] The advantage of this approach lies in the resulting "narrower averaging" of the molecular motion; that is to say, the experimental data describe the statistical average over a shorter path of diffusion (or a shorter time interval) than the classical techniques mentioned above.

Infrared frequency measurements, in which the solvent shift of a vibrational mode of the dissolved molecule is related to an intermolecular "molecule–environment" potential function, have also been used[3] ("distribution of amplitude with frequency"). The solvent shift method, however, is not entirely satisfactory since the number of adjustable potential parameters generally exceeds the number of experimental points which are obtainable by this technique.[3]

We would like to report here some data on the application of a completely different procedure, namely, the evaluation of the infrared band shape of a vibrational mode of a molecule in terms of a statistical picture of its molecular motion ("distribution of amplitude with time"). The system that was studied was a solution of polystyrene in methylene chloride. We evaluated the ν_4 fundamental of methylene chloride ($\sim$283 cm^{-1}) and therefore obtained a picture of the molecular motion of the halide molecules in the polymer solution. Methylene chloride was chosen because of its good solvent properties; polystyrene was chosen since it represents a prototype polymeric medium which may possibly interact with the solvent molecules by the more "nonspecific" intermolecular forces, presumably *via* the benzene ring.[4] Polystyrene is then somehow intermediate to polymers which possess merely aliphatic groups, such as polyethylene, and to polymers which bear strong polar groups, such as amino and ester groups. We have used atactic polystyrene of a very narrow molecular weight, not only because of the superior solubility of such material

(1) K. J. Liu, *J. Polymer Sci.*, **A2**, 697 (1967); see also K. J. Liu, International Symposium on Macromolecular Chemistry, Tokyo, Kyoto, 1966, paper VII-48.

(2) W. G. Rothschild, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, paper I-70.

(3) W. G. Rothschild, *J. Chem. Phys.*, **42**, 694 (1965).

(4) See ref 2. The work reported there indicates that the rate of the relaxation mechanism which describes the relative translational–rotational diffusion of the halide molecules with respect to the polymer is (1) exponential in the molar ratio of the components and (2) changes abruptly at a ratio of one molecule of halide per one unit ($C_6H_5CHCH_2$) of polymer chain segment.

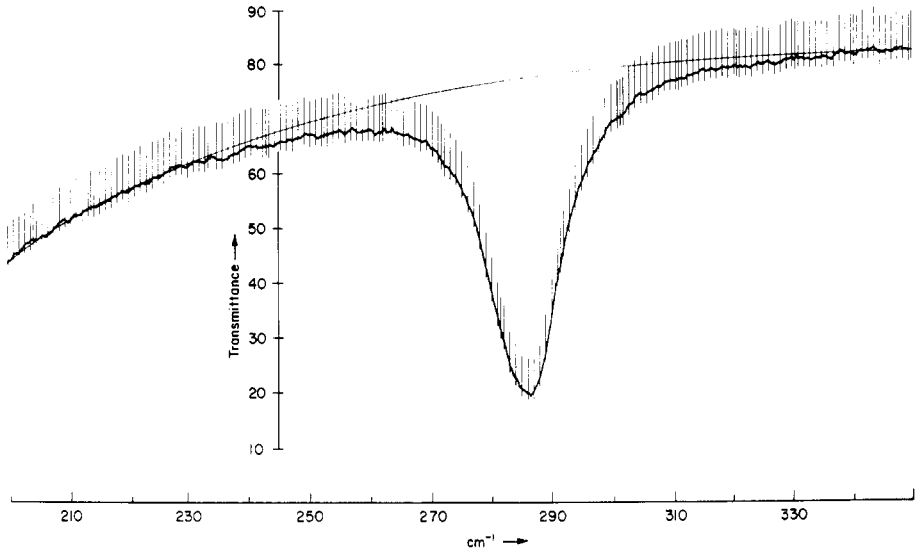

Figure 1. Absorption band of the ν_4 fundamental of methylene chloride in polystyrene; ratio of polystyrene to halide in terms of number of unit chain segments of polymer ($C_6H_5CHCH_2$) to number of molecules of halide $R = 0.5$. The absorption of the polymer was not compensated by a corresponding blank in this run; the polymer absorption is apparent in the wings of the band at 330 and at 235 cm^{-1}. For convenience's sake, the frequency scale was condensed by slowing the speed of the recorder.

but also in order to minimize, at first, any effects which may arise from the nonisotropy of the medium and from differences in the chain length, respectively.

The underlying principles and formulas of the procedure we wish to apply here have been reported by Gordon in a series of papers.[5] In short, the band shape of a particular vibrational mode of a molecule in its surrounding medium is described in terms of the Fourier transform of the time-dependent correlation function of the vibrational transition moment fixed in the molecule. The resulting dipole correlation function itself then gives a picture of the statistical rotational motion of the molecule as a function of time. To give a simple elaboration, this statistical average is, first, composed of the contributions of those molecules which are in their first, second, third, etc., rotational diffusion "step" during the successive arbitrary time intervals t_1, $t_2 - t_1$, $t_3 - t_2$, etc., commencing with the time of the vibrational (internal) transition as $t = 0$ and, second, the average is to be summed over all angular frequencies of the rotational motion of the molecule about its center of mass. We may imagine that during each rotational diffusion step the molecule rotates freely with a certain angular velocity ω through a certain angle; this diffusion step is terminated by a "collision" which causes the molecule to rotate (freely) for another time interval at a different angular velocity and through a different angle, again soon to be interrupted by the next collision until the angular motion has decayed to Brownian motion.[5]

We may indicate the "times of observation" of this method by considering the product of angular frequency and time, ωt: the most significant contributions to the intensity of the absorption band of the internal transition of the dissolved molecule arise from $\omega t \sim 2\pi$. Inserting representative values of angular frequencies (which are given by the moments of inertia of the molecule and the temperature) of the order of magnitude of 10^{12} cps, we can therefore expect to follow the molecular rotational diffusion during the first few 10^{-12} sec or so of its decay to Brownian motion.

(5) R. G. Gordon, *J. Chem. Phys.*, **39**, 2788 (1963); **43**, 1307 (1965); **44**, 1830 (1966).

Experimental Section

A. Spectroscopy and Sample Preparation. The absorption band of the ν_4 fundamental (symmetry species a_1) of CH_2Cl_2 in polystyrene at various concentrations was scanned with a Perkin-Elmer double-beam far-infrared spectrometer, (Model 301), paying particular attention to a careful measurement of the absorption in the wings of the band. The ν_4 fundamental, which is centered at about 286 cm^{-1}, lies in a frequency region where the absorption of even rather thick layers of polystyrene (and other polymers) can be compensated by an appropriate blank in the reference beam since the polymer absorption is rather weak and depends little on the frequency.[6] Furthermore, the ν_4 mode is not overlapped by other internal modes of CH_2Cl_2. There is, however, a broad continuum, which becomes more intense with increasing wavelength, underneath the ν_4 fundamental. This is shown in Figure 1. Such absorption continua become apparent in the solution spectra of almost all molecules; they are to be ascribed to an external motion, probably involving two or more molecules.[7,8] The main uncertainty in the conclusions to be drawn here is introduced by a certain arbitrariness with which the base line of the absorption spectrum of the ν_4 mode can be drawn, that is, the manner of subtracting the intensity of the continuous band. Fortunately, the continuous absorption levels off relatively rapidly at the higher frequency end of the ν_4 absorption band, which permits one to draw a fairly accurate base line. This is indicated in Figure 1 by the thin curve.

(6) If the blank in the reference beam absorbs appreciably, the resulting net absorption may contain a large error due to stray radiation in the spectrometer; see W. Luck, *Z. Elektrochem.*, **64**, 676 (1960).

(7) R. J. Jakobsen and J. W. Brasch, *J. Am. Chem. Soc.*, **86**, 3571 (1964).

(8) B. J. Bulkin and P. Bachmann, 22nd Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, Sept 1967, paper U-10.

The molecular weight of the atactic polystyrene was 3600, ratio $M_w/M_n < 1.10$. The material was obtained from Arro Laboratories, Inc.[9] The methylene chloride was Spectroquality reagent Matheson Coleman and Bell; its purity was confirmed by vapor phase chromatography. The concentration range of the samples varied between 0 and 2.0 in terms of the ratio R defined as the number of polymer chain repeating units ($C_6H_5CHCH_2$) per molecule of halide. The samples at the higher ratios were very viscous. They were prepared by distilling a known amount of the halide onto a known amount of the polymer contained in a tube on a vacuum system. The tube was then partially evacuated, sealed off, and stored in an oven at about 70° until a clear solution resulted. To fill the absorption cell (variable path, CsI windows, demountable cell from Research and Industrial Instruments) with this viscous solution, the still warm tube was cracked open and its content poured into one of the halves of the demounted cell. The cell was quickly assembled and its path length adjusted to a convenient value (0.19–0.70 mm). The absorption curves were scanned at various path lengths at a speed of approximately 1 cm^{-1}/min. No evaporation losses of the low-boiling halide occurred during the course of the scans. A thick plate of CsI and a disk of polystyrene of the same amount (g cm^{-2}) as the polystyrene in the sample cell were placed in the reference beam. The ratio of the spectral slit width to the half-width of the band amounted to 0.13 over the regions of stronger absorption and approximately to 0.2 in the outer wings of the absorption band. Therefore, slit function corrections were not applied.[10] All scans were performed at the ambient temperature in the sample compartment of the spectrometer (about 40°).

B. Numerical Evaluation. The expression[5] for the dipole correlation fraction $\langle \mathbf{u}(0)\mathbf{u}(t)\rangle$ in terms of the normalized spectral intensity $\hat{I}(\omega)$

$$\hat{I}(\omega) = I(\omega)/\int I(\omega)\, d\omega \tag{1}$$

is

$$\langle \mathbf{u}(0)\mathbf{u}(t)\rangle = \int \hat{I}(\omega) \cos [(\omega - \omega_0)t]\, d\omega \tag{2}$$

where $\mathbf{u}$ is the unit vector along the direction of the vibrational transition moment of the halide molecule. $I(\omega)$ is given by

$$I(\omega) = \frac{\sigma(\omega)}{\omega[1 - \exp(-\hbar\omega/kT)]} \tag{3}$$

where $\sigma(\omega)$ is the absorption coefficient as a function of the angular frequency ω and ω_0 is the frequency of the band center, that is to say, the frequency of the vibrational transition of the unperturbed (isolated) molecule. The Boltzmann factor in the denominator corrects for the induced emission. In this manner the expression $I(\omega)$ represents the "initial-state-averaged transition probability".[11] The integration is made over the whole band.

The approximate band center, ω_0, is obtained from the first moment of the band,[5] unless it is known from the vapor spectrum

$$\omega_0 \sim \int I(\omega)\omega\, d\omega / \int I(\omega)\, d\omega \tag{4}$$

This expression omits the effect of the solvent shift on the position of the band center; that is, the difference between the intermolecular potentials of the ground and the upper vibrational levels is neglected. The solvent shift of ν_4 is here of the order of only 3 cm^{-1}; its neglect, therefore, does not introduce a significant error.

The numerical evaluation of the data is most conveniently performed with the help of a computer. First, the band center, ω_0, is calculated from eq 4. The values of the frequency displacement, $\omega - \omega_0$, to be inserted into eq 2 are then obtained from the computed ω_0 and the observed frequencies ω. A typical run in steps of time intervals of 0.02 unit for a total interval of 2.0 units (in units of 10^{-12} sec) and in steps of frequency intervals of 0.97 cm^{-1} throughout the whole band width of about 100 cm^{-1} required approximately 100 sec on the General Electric −265 Time Sharing System (program written in Dartmouth ALGOL). It should be noted that $\sigma(\omega)$ in these examples is simply the value of the ordinate in terms of the complement (for instance 100 − transmission), taken with respect to the base line, in any convenient unit. In all numerical evaluations the intensities from the original bands, as shown in Figure 1, were read off without smoothing.

Results and Discussion

The fundamental ν_4 represents a C–Cl_2 deformation.[12] The change of the dipole moment during the transition is in the direction of the twofold symmetry axis (C_2) of the molecule. The rotational correlation functions computed here therefore describe that component of the rotational diffusion tensor which is parallel to the direction of the C_2 axis in the halide molecule. The results of the computations are shown in Figure 2 in a semilogarithmic plot for pure CH_2Cl_2 and polystyrene–methylene chloride solutions. A curve with $R = 2.0$, which lies very close (slightly below) the curve of $R = 1.5$, has been omitted. Inspection of Figure 2 shows that the decay of the correlation functions with time, *i.e.*, the decay of the rotational motion of the methylene chloride molecules to Brownian motion, is completed within approximately 0.4×10^{-12} sec since after this time interval the time decay of $\langle \mathbf{u}(0)\mathbf{u}(t)\rangle$ is exponential. For the point $t = 0$, we take the time at which the molecule is perturbed from its equilibrium thermal motion by the vibrational transition.

For comparison's sake we have added to Figure 2 the computed rotational correlation function of an unperturbed assembly of methylene chloride molecules, where "unperturbed" is understood to mean the limit $\tau \to \infty$ and τ is the average time between collisions of the molecules. As we have indicated above, the concept of "collision" is to be looked upon as the process which terminates a given rotational diffusion step of the molecule;[5] hence the curve represents the initial part of the correlation function of the freely rotating molecule.[13] If we compare this correlation function with the experimental correlation functions of the dissolved molecules, we see that the intermolecular forces begin to affect the rotational motion of the halide molecules within a time interval

(9) The polymer was not further purified and may have contained traces of benzene.

(10) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952); see Table II.

(11) H. B. Levine and G. Birnbaum, *Phys. Rev.*, **154**, 86 (1967), eq 4.7.

(12) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1962, p 317.

(13) See R. G. Gordon, *J. Chem. Phys.*, **44**, 1830 (1966), eq III.2. For CH_2Cl_2, an asymmetric rotor, we have performed the integration over the three rotational constants [see R. J. Myers and W. D. Gwinn, *ibid.*, **20**, 1420 (1952)] and the three components of the angular frequency ω.

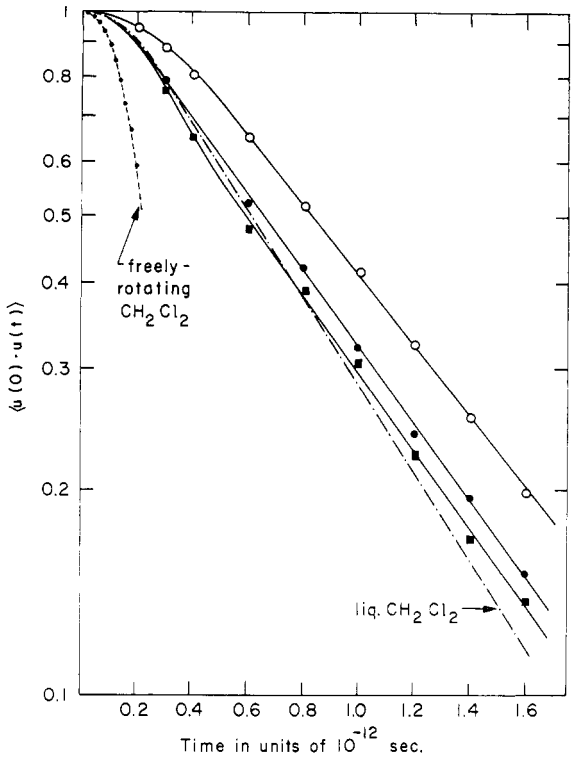

Figure 2. Rotational correlation functions of methylene chloride in polystyrene–methylene chloride solutions obtained from the band contours of the ν_4 mode of CH_2Cl_2. The experimental points are the averages of two to four independent determinations: R = 0.5 (■), 1.0 (●), and 1.5 (○). The correlation functions of pure liquid CH_2Cl_2 and for the freely rotating molecule (computed, see text) are also shown. The experimental points for the pure liquid CH_2Cl_2, all of which fall very close to the drawn curve, have been omitted; temperature ~40°.

of the order of magnitude of 10^{-14} sec after the onset of the motion.

The data are now evaluated in terms of a correlation time, τ_c, of the rotational motion. This correlation time indicates how fast the correlation function decays to small values. We note that all experimental correlation functions lie above that of the freely rotating molecules; the hindering effect of the medium therefore causes the rotational motion of the CH_2Cl_2 molecules to slow down throughout the whole range. The correlation times are computed from the correlation functions displayed in Figure 2 according to [14]

$$\tau_c = \int_0^\infty \langle \mathbf{u}(0)\mathbf{u}(t)\rangle \, dt \qquad (5)$$

For the upper limit of the integral it suffices to use 2×10^{-12} sec, since for $t \gg 2 \times 10^{-12}$ sec the correlation function becomes very small. We have collected the results of the calculation of τ_c in Table I.

The data of Table I indicate that the macroscopic viscosity of the solution, which varies over many orders of magnitude in the range of polymer concentration studied here, is essentially irrelevant with respect to the characteristics of the rotational diffusion

(14) H. B. Levine and G. Birnbaum, *Phys. Rev.*, **154**, 86 (1967), eq 7.7. For a definition of the correlation (or relaxation) time, see A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, 1960, p 271.

TABLE I
CORRELATION TIME OF THE ROTATIONAL MOTION OF THE C_2-SYMMETRY AXIS OF METHYLENE CHLORIDE IN POLYSTYRENE

Environment	τ_c, 10^{-12} sec
Pure liquid	0.78
R^a = 0.5	0.81
R = 1.0	0.84
R = 1.5–2.0	0.94

[a] Ratio of numbers of unit chain segments of polystyrene to numbers of molecules of halide.

of the halide molecules. We shall show this in a more quantitative way as follows. We assume a simple model of the rotational diffusion of the halide molecule by putting it into a "cage" within the polymer solution and propose that the halide molecule is able to rotate through a certain angle whenever the polymer cage opens due to the vibrational *intra*molecular motion of the polymer chains. The halide molecule would suffer a "collision" with a polymer chain segment when the cage closes—a collision which will degrade its rotational motion to Brownian motion. We make no suggestions on the size of the rotational diffusion steps of the molecule during the time interval the polymer cage is open, but we note that these diffusion steps may occur through relatively large angles.[15] As a representative value of the vibrational frequency of a skeletal motion of a polymer chain, we take 150 cm^{-1} = 450 × 10^{10} cps.[16] The time during which the polymer cage is open is then ~0.2 × 10^{-12} sec, or about equal to the time interval of the initial *non-exponential* part of the correlation functions (see Figure 2). In other words, it is equal to the time during which the rotational diffusion is *other* than random.

We have neglected here the effect of the translational motion of the polymer chains on the lifetime of a "cage," but this effect will be small since it is precisely the polymer–polymer interactions which are reflected in the macroscopic viscosity of the solution.[17] This interaction presumably would tend to keep the polymer chains locked in a fixed relative position for times much longer than τ_c of Table I.[18]

Error Estimate

The most significant test of the accuracy of the data would be to measure another CH_2Cl_2 vibrational mode of symmetry species a_1. Unfortunately, the remaining fundamentals and combination bands of species a_1 are either very weak or are in frequency regions where polystyrene absorbs appreciably.[19] We have, how-

(15) See the Introduction of ref 13.

(16) An infrared mode of polystyrene, describing essentially the bending of the CC bond connecting the phenyl group to the chain, has been assigned by C. Y. Liang and S. Krimm to a frequency of 196 cm^{-1}; see *J. Polymer Sci.*, **27**, 241 (1958). An out-of-plane skeletal mode, involving rotation about the CC bonds, has been estimated to be at 140 cm^{-1} for polyethylene; see S. Krimm, *Fortschr. Hochpolymer. Forsch.*, **2**, 51 (1960).

(17) N. E. Hill, *Proc. Phys. Soc.* (London), **67B**, 149 (1954); **68B**, 209 (1955).

(18) The over-all molecular motion of the halide molecules is, of course, a translation–rotation (see ref 5); the correlation functions shown here describe only the randomization of the angular motion of the molecules.

(19) J. Morcillo, L. J. Zamorano, and J. M. V. Heredia, *Spectrochim. Acta*, **22**, 1969 (1966), see Table I.

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%.

(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.

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.

(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.

(1) A. W. Nolle, *Phys. Rev.*, **98**, 1560 (1955); *Bull. Am. Phys. Soc.*, [II] **1**, 109 (1956).
(2) J. G. Powles, *Arch. Sci.* (Geneva), **10**, 253 (1957).
(3) A. Odajima, *J. Phys. Soc. Japan*, **14**, 777 (1959).
(4) D. W. McCall, D. C. Douglass, and E. W. Anderson, *J. Polymer Sci.*, **59**, 301 (1962).
(5) D. W. McCall, D. C. Douglass, and E. W. Anderson, *ibid.*, **1A**, 1709 (1963).
(6) R. Ullman, *J. Chem. Phys.*, **43**, 3161 (1965).
(7) W. P. Slichter and D. D. Davis, *Bull. Am. Phys. Soc.*, [II] **11**, 166 (1966).
(8) K.-J. Liu, *J. Polymer Sci.*, **5A-2**, 697 (1967).
(9) T. G Fox and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 194 (1949).