Mobility of Small Molecules in Viscous Media. II. Translational Motion in the System Methylene Chloride–Polystyrene by Nuclear Magnetic Relaxation and Viscosity

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ABSTRACT: Spin–lattice relaxation and spin-echo measurements were performed on CH_2Cl_2 in CH_2Cl_2–polystyrene (atactic) solutions of 1–0.24 volume fraction CH_2Cl_2 and of narrow-distribution molecular weight 3600 and 97,200. The translational correlation times determining solvent–solvent and solvent–polymer relaxation, respectively, increase in this concentration domain by a factor of 50–100; this effect is significantly greater for the higher molecular weight series. The data imply that only one solution environment, as defined by an inherent trapping time for a diffusing CH_2Cl_2 molecule, exists in this system at each composition. Critical volumes and the numbers of polymer segments required for the molecular transport processes were estimated from the activation energies of solvent spin–lattice relaxation and of solution viscosity. It turns out that the number of polymer segments whose motion permits chain slippage is not exceedingly larger than that inducing solvent diffusion for the 3600 molecular weight solutions. The data obtained with the polymeric solutions are compared with the corresponding results in the system CH_2Cl_2–ethylbenzene.

Since the pioneering work of McCall,[1] Douglass,[2] Bovey,[3] and Stejskal and Tanner,[4] a series of papers on the microdynamic characteristics of solvent molecules in polymeric media by spin–lattice relaxation and spin-echo measurements has been published.[5-10] We wish to report here some data on the mobilities of CH_2Cl_2 in CH_2Cl_2–polystyrene (atactic) solutions obtained by a combination of these techniques and viscosity measurements. We had previously published a report on the orientational motion of CH_2Cl_2 in this system[11] and have now extended this work to a description of the translational mobility. We have carried the experiments over a wide concentration range and have attempted to answer the following questions. (1) Are there any distinctly observable environments for "solvent binding?" (2) What is the range of the molecular trapping times of the solvent molecules? (3) Does their translational motion reflect some type of "second-order" transition of the polymer? (4) How many polymer segments are involved in the motion of the solution cage? (5) Is there a simple correlation between translational solvent mobility and solution viscosity?

The CH_2Cl_2–polystyrene system was chosen since it is our aim to discuss the effect of *chain* molecules on solvent diffusion: perturbing effects—which may arise from specific interactions, tacticity, crystallinity, molecular weight dispersity, poor solvation properties, and disparity between molecular size of diffusate and monomeric chain segment—are thus minimized.

Method

We give here a short summary of the manner of extracting the results from the measurements as well as a brief discussion of the various underlying assumptions and approximations we have applied.

The measured spin–lattice relaxation time T_1 of the protons of CH_2Cl_2 in the CH_2Cl_2–polystyrene solutions can be expressed by

$$T_1^{-1} = (T_1^{-1})_{intra} + (T_1^{-1})_{ss} + (T_1^{-1})_{sp} \quad (1)$$

where the three terms describe, in the usual manner,[12] the intramolecular rate due to orientational motion of an individual CH_2Cl_2 molecule and the intermolecular rates due to translatory–rotatory motion between solvent molecules and between solvent and polymer. The fractional contributions of the three processes to the observed T_1^{-1} are shown in Table I as a function of solution composition.

To arrive at the values in Table I, we have first estimated $(T_1^{-1})_{intra}$. As shown in previous work,[11] the (Debye) correlation time describing the orientational motion of a CH_2Cl_2 molecule in polystyrene increases by a mere 30% when going from the pure liquid to concentrated CH_2Cl_2–polystyrene solutions. Furthermore, since column 4 in Table I shows that $(T_1^{-1})_{intra}$ contributes relatively little for the higher polymer concentrations, we make a negligible error by using $(T_1^{-1})_{intra} = 0.018$ sec^{-1} (pure CH_2Cl_2)[13] throughout the whole concentration range. $(T_1^{-1})_{ss}$ is now computed with the help of the measured self-diffusion coefficient D_s of CH_2Cl_2 in the medium, at a function of concentration, and the well-known relation[12]

$$(T_1^{-1})_{ss} \approx (2/5)\pi\hbar^2\gamma^4 N_s/dD_s \quad (2)$$

where we take for d the Lennard-Jones diameter. For clarity sake, it is useful to state the approximations which underlie the use of this simple equation. (On the other hand, Table I shows that the contribution of $(T_1^{-1})_{ss}$ is not great, particularly

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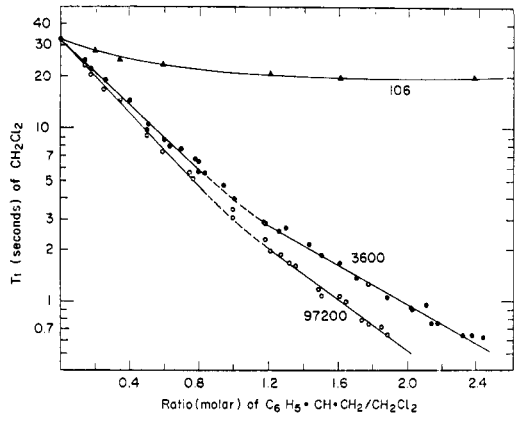

Figure 1. Experimental spin–lattice relaxation time T_1 of CH_2Cl_2 in CH_2Cl_2–polystyrene solutions; temperature about 35°. R = the number ratio of monomeric chain segments to CH_2Cl_2 molecules. Molecular weight of polystyrene: ●, 3600 (35 monomer segments per chain); ○, 97,200 (935 segments); ▲, corresponding values in ethylbenzene solution.

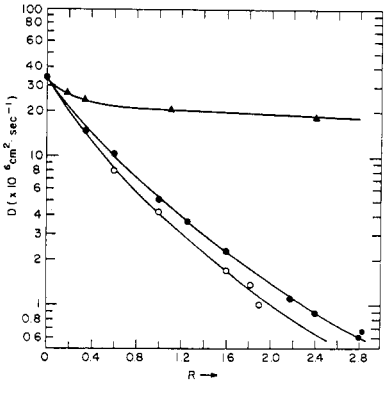

Figure 2. Self-diffusion coefficients of CH_2Cl_2 in CH_2Cl_2–polystyrene (●, 35 monomer segments per chain; ○, 935 monomer segments per chain) and CH_2Cl_2–ethylbenzene (▲); temperature about 35°. R = the number ratio of monomeric chain segments to CH_2Cl_2 molecules.

TABLE I
THE MAJOR FRACTIONAL CONTRIBUTIONS TO THE OBSERVED INVERSE SPIN–LATTICE RELAXATION TIME OF CH_2Cl_2 IN CH_2Cl_2–POLYSTYRENE SOLUTIONS

R[a]	Wt % polymer	Vol fraction of CH_2Cl_2	Fractional (normalized to unity) contributions from $(T^{-1})_{intra}$[b]	$(T_1^{-1})_{ss}$[c]	$(T_1^{-1})_{sp}$[d]
0.2	17	0.80	0.36	0.20	0.44
0.4	33	0.67	0.25	0.17	0.58
0.8	48	0.51	0.11	0.10	0.79
1.2	59	0.41	0.06	0.07	0.87
2.0	72	0.29	0.02	0.05	0.93

[a] Molar ratio $C_6H_5{\cdot}CH{\cdot}CH_2/CH_2Cl_2$. [b] From ref 11 and 13. [c] Estimated from self-diffusion data as described in the text. [d] Obtained by difference; see eq 1.

at the higher polymer concentrations.) First, use of a Lennard-Jones potential (instead of a hard-sphere model) introduces *a priori* a factor of 1.15 into eq 2.[14] Secondly, a more realistic diffusion model, allowing intermolecular relaxation by translational jumps of the order of a molecular diameter rather than by many small-distance translational displacements,[12] introduces a factor of approximately 1.3.[13] Thirdly, the neglect of *inter*molecular rotational motion of adjacent CH_2Cl_2 molecules probably introduces an additional factor of 1.2;[15] this correction arises from the fact that the spins are not located at the centers of the molecules.[15] Hence, the sum of all these corrections would introduce a factor of the order of 1.8; in other words, using the simple eq 2 we may have, at worst, underestimated $(T_1^{-1})_{ss}$ by a factor of about 2. Finally, $(T_1^{-1})_{sp}$ is determined from the measured spin–lattice relaxation times, T_1, by difference (see eq 1).

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Experimental Procedures

(A) Materials and Sample Preparation. Spectrograde methylene chloride and atactic polystyrene (Arro Laboratories, Joliet, Ill.) were used. Series of narrow molecular weight 3600 (35 monomeric units per chain, weight average/number average <1.10) and 97,200 (935, $W_w/W_n < 1.06$) were examined over a concentration range of R = 0–2.5, where R is the number of monomeric segments to molecules of methylene chloride. This is equivalent to a range of 0–75 wt % polymer or 1–0.24 fractional volume of solvent.

The sample tubes were deaerated by the standard freeze–pump–thaw technique and flame sealed. Complete dissolution was speeded by warming. Residual atmosphere was subsequently removed by pumping *via* a previously attached breakseal, ensuring complete removal of oxygen. Some tubes were filled with about 0.2 atm of He.

(B) Proton Spin–Lattice and Spin-Echo Measurements. The proton spin–lattice relaxation and spin-echo data were obtained on modified Varian A-60 and DA-60 equipment.[16,17] The absolute values of the diffusion coefficients are based on $D = 2.5 \times 10^{-5}$ cm² sec⁻¹ (water, 30°). The measurements (which were 95–97% reproducible over periods of months) are shown in Figures 1 (relaxation data) and 2 (self-diffusion), together with the corresponding data of the system CH_2Cl_2–ethylbenzene (the "monomeric analog"). Only one solvent peak was observed (fast exchange). Our data, unless otherwise remarked, refer to about 35°.

(C) Activation Energy, Density, Specific Volume, and Thermal Expansion Coefficient. Activation energies of T_1 of CH_2Cl_2 in the polymeric medium were measured with the help of the Varian V-6040 attachment. The corresponding Arrhenius plots gave satisfactory straight lines through four to five temperature points. The results are shown in Figure 3 by the solid lines.

The required densities of the solutions were measured by standard procedures and the specific volumes calculated from these data.

The thermal expansion coefficient of a solution of composition $R \sim 2$ was measured to be 0.0008 ± 15% deg⁻¹, which is of sufficient accuracy for our purposes.

(D) Viscosity Measurements. The solution viscosities (molecular weight 3600) and their activation energies were determined according to standard practice[18] with calibrated Cannon viscometers in a closed system to avoid CH_2Cl_2 evaporation. The activation energies, together with those of pure CH_2Cl_2,[19] are displayed in Figure 3 by the dashed line.

Results and Discussion

(A) Translational Solvent Mobility. The results of the T_1 and the spin-echo measurements, evaluated as described above, are shown in Figure 4. We have removed from T_1^{-1} the natural dependence on the spin concentration,[12] designating by N_s the number of CH_2Cl_2 protons per cubic centimeter and by N_p the number of polystyrene protons per

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(19) "International Critical Tables," Vol. 7, McGraw-Hill, New York, N. Y., 1930.

cubic centimeter. The solid circular (triangular) dots thus show this "reduced" intermolecular relaxation rate $(T_1^{-1})_{ss}/N_s$ due to the relative motion between CH_2Cl_2 molecules in the solutions employing polystyrene of 35 (935) monomeric units. On the other hand, the open circular and triangular points show the corresponding data, $(T_1^{-1})_{sp}/N_p$, for the relative motion between a CH_2Cl_2 molecule and a polystyrene segment. Introducing a correlation time $\tau \equiv 6a^2/D$, where a is the molecular diameter and D the translational diffusion coefficient, we can express T_1^{-1} by (see eq 2)

$$(T_1^{-1})_{ss}/N_s \approx C_s\tau_{ss}$$
$$(T_1^{-1})_{sp}/N_p \approx C_p\tau_{sp} \quad (3)$$

where C_s and C_p are essentially constant factors of about equal value.[20] Therefore, the data in Figure 4 describe the concentration dependence of the times it takes a CH_2Cl_2 molecule to diffuse a molecular diameter away from an adjacent CH_2Cl_2 molecule (τ_{ss}) and from an adjacent polystyrene segment (τ_{sp}). We thereby obtain an indication of the degree of the intermolecular forces in the medium. However, since C_p is not accurately defined,[20] we cannot expect to obtain meaningful *absolute* values for τ_{sp}.

The results in Figure 4 then lead to the following conclusions. (1) The times τ_{ss} as well as τ_{sp} increase monotonically and in a parallel fashion with increasing polymer concentration. Within the accuracy of our data, we therefore do not observe any abrupt change of diffusional behavior which might conceivably occur in the regions of higher polymer concentrations ("second-order transition"). At the highest polymer concentrations investigated (about 0.76 volume fraction of polystyrene), the correlation times have increased by a factor of about 50–100 over their values in pure CH_2Cl_2. Taking $\tau_{ss} = 0.085 \times 10^{-10}$ sec for pure CH_2Cl_2,[13] this value would then have increased to about 4×10^{-10} sec. (2) In contrast to this, the values of τ_{ss} and τ_{sp} vary insignificantly in the corresponding monomeric CH_2Cl_2–ethylbenzene system (lower curves in Figure 4). (3) There is a small but significant rise in the correlation times τ_{ss} and τ_{sp} when the polymer molecular weight is increased from 3600 to 97,200 (35 to 935 units per chain). This rise is greater the greater the polymer concentration.

The main points to be drawn from this are as follows. (1) The polystyrene molecules considerably increase the times for significant CH_2Cl_2 displacements (distance of the order of a molecular diameter) or, differently expressed, increasing amounts of polymer induce the medium to "trap" a solvent molecule for increasing times. Furthermore, since $1 \lesssim \tau_{sp}/\tau_{ss} \lesssim 2$, there is probably *no* significant difference between the time a CH_2Cl_2 molecule spends near another CH_2Cl_2 molecule or near a polystyrene chain segment. In other words, there exists essentially only one "solution environment" at a given composition. (2) This solution environment is more "rigid" in the higher molecular weight medium, be it on account of an inherently different chain conformation, increased intermolecular forces between chains, the diminished effect of the polymer end groups,[21] or a combination of these; we have no definite conclusions. (3) The increase in the molecular trapping times (as defined just above) of CH_2Cl_2 with increasing polymer concentrations is solely due to the chain molecules (and not due to some property of the monomeric chain segment, say specific interactions between CH_2Cl_2 and the π system of a benzene ring), since no change of τ_{ss} and τ_{sp} with concentration is discernible in the CH_2Cl_2–ethylbenzene system.

It is useful to remark here that the macroscopic solution viscosity is not a meaningful parameter with which to relate the increase in the τ's. This is immediately evident from the results in Figure 4 when, for instance, we compare any value of T_1^{-1} for the 3600 molecular weight with the 97,200 molecular weight series at the same value of R. Although the increase in the solution viscosity is as much as several orders of magnitude, the solvent mobility is decreased only by a factor of about 1.2. (In the following section, we shall see

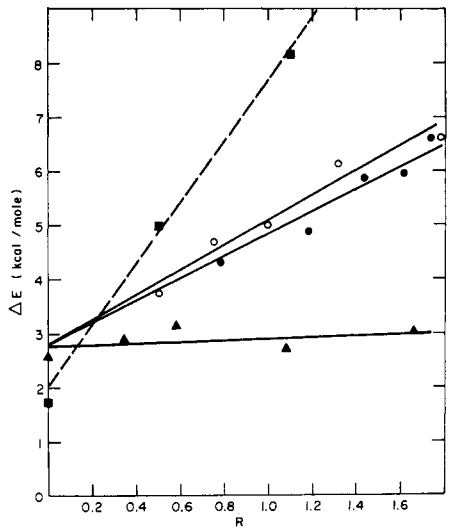

Figure 3. Activation energies of T_1 of CH_2Cl_2 in the system CH_2Cl_2–polystyrene (●, 35 monomer segments per chain; ○, 935 monomer segments per chain) and CH_2Cl_2–ethylbenzene (▲); ■, activation energies of solution viscosity (35 segments per chain).

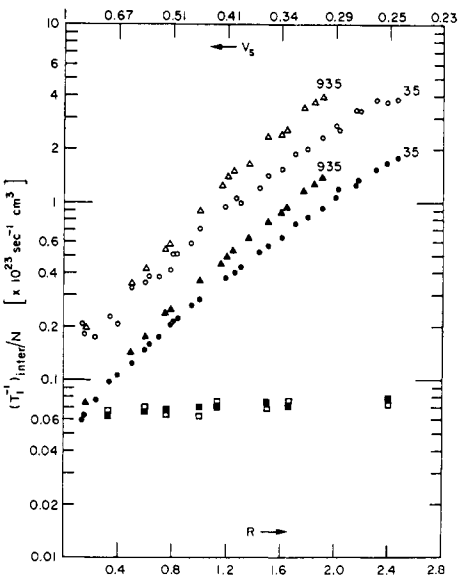

Figure 4. Reduced intermolecular relaxation rates (sec^{-1} cm^3) for the relative translational motion between CH_2Cl_2–CH_2Cl_2 (●, ▲) and CH_2Cl_2–polystyrene (○, △) as function of solution composition R (=number of monomeric chain segments per molecule CH_2Cl_2). The number of monomer segments per chain molecule is indicated. □, ■, corresponding values for the CH_2Cl_2–ethylbenzene system. V_S = the fractional volume of CH_2Cl_2.

(20) C_p differs from C_s by a factor of 2 (solvent molecules diffuse much faster than the polymer chains), by an additional factor of $^2/_3$ (relaxation between spins on unlike molecules), and by the ill-definable meaning of d (see eq 2), the "closest distance of approach" (see ref 12).

(21) The polystyrene chain contains one butyl end group from the initiator.

TABLE II
ACTIVATION ENERGIES, CRITICAL VOLUME, AND NUMBER OF POLYMER SEGMENTS INVOLVED IN THE TRANSLATIONAL MOBILITY OF POLYMER AND SOLVENT MOLECULES IN THE SYSTEM CH_2Cl_2–POLYSTYRENE[a]

R	E, kcal/mol		v*, Å^3		n = v*/v_f[e]	
	Solution viscosity	Solvent diffusion	Solution viscosity	Solvent diffusion	Solution viscosity	Solvent diffusion
2.1[b]		7.1		500		9
1.1[c]	8.1	5.0	570	350	12	8
0.5[d]	5.0	3.8	275	210	8	6

[a] Molecular weight of polystyrene 3600 (about 35 monomeric segments per chain). [b] About twice as many $C_6H_5 \cdot CH \cdot CH_2$ units as CH_2Cl^2 molecules. [c] About equal numbers of monomeric segments and solvent molecules. [d] About twice as many CH_2Cl_2 molecules as $C_6H_5 \cdot CH \cdot CH_2$ units. [e] van der Waals diameter taken from R. A. Svehla, NASA Technical Report No. R-132, 1962.

that it is more significant to compare the solvent mobility with the *activation energy* of the solution viscosity.)

We can compare the CH_2Cl_2–polystyrene system with other solvent–polymer systems, namely, one in which there are very strong specific interactions between solvent and polymer, the other where slow concentration fluctuations have been invoked. The $CHCl_3$–polyvinylpyrrolidinone system is an example for the first type: here the hydrogen atom of $CHCl_3$, in the neighborhood of the chains, is directed preferentially toward a peptide group.[8] The benzene–poly(methyl methacrylate) system is an example for the second type: evaluation of Anderson and Liu's data[6] (their Figure 3) shows that the translational correlation times for benzene–polymer diffusion are shorter than those for benzene–benzene diffusion by a factor of $\sim$3.

A point we wish to stress here is that the hindering effect of polymer molecules on solvent mobility is, generally, twofold. First, there is solvent–polymer interaction through any reactive group built into the monomeric chain units (for instance, the hydrogen bonding of $CHCl_3$ to –CO–N< of polyvinylpyrrolidinone[8]). Such specific effects should also be apparent, with comparable intermolecular forces, in a corresponding solvent–monomer system, say $CHCl_3$–ethylpyrrolidinone. Second, there is the hindering effect on solvent mobility arising from the presence of the long *chain* molecules, a purely polymeric effect.

(B) Solvent Mobility, Activation Energy of Solution Viscosity, and Polymer Segmental Motion. The activation energies of T_1 of CH_2Cl_2 and of the solution viscosity, shown in Figure 3, are now combined with the measured expansion coefficient on the basis of Cohen and Turnbull's theory of molecular transport.[22] As discussed by Kumins and Kwei,[23] this theory lends itself well to an estimate of molecular parameters relevant to solvent mobility and polymer segmental motion of a "nonspecific" solvent–polymer system such as that studied here.

In this theory, the average free volume available to the solvent molecule is given by

$$v_f = v_m - v_0 = \alpha v_m(T - T_0) \quad (4)$$

where v_m and v_0 are the average (from the density) and the van der Waals volumes of the molecule, respectively, and α is the total thermal expansion coefficient. Setting $T_0 = 0$, we obtain[22,23]

$$E/k \approx v^*/\alpha v_m \quad (5)$$

where E is the activation energy of the molecular transport process and v^* is a critical volume permitting this process to occur. Results of this analysis, yielding v^* and the number $n = v^*/v_f$ of polymer segments involved, are collected in Table II for three solution compositions.

It is clear that the values are estimates only. For instance, we have set $T_0 = 0$ (out of ignorance); this is certainly not correct.[23] Furthermore, T_0 for viscosity is not necessarily the same as T_0 for diffusion.[24] Assuming that T_0 for solution viscosity is higher than T_0 for solvent diffusion,[25] the number of polymer segments permitting chain slippage would be increased more than the number required for solvent diffusion. For instance, setting T_0(viscosity) $\sim$ 150°K and T_0(diffusion) $\sim$ 100°K, we find for the solution R = 1.1 in Table II the values n = 24 and 12 instead of 12 and 8. This, therefore, shows that slippage of polymer chains in the system requires the cooperative motion of more, but *not* exceedingly more, polymer segments than does solvent diffusion. In contrast to the orientational motion of CH_2Cl_2 molecules in polystyrene,[11] the translational motion of CH_2Cl_2 is correlated with the macroscopic solution viscosity in the manner described here.

Conclusions

Defining different solution environments by the different observable trapping times (translational correlation times) they exert on diffusing molecules, there seems to exist only one such solution environment in the CH_2Cl_2–polystyrene system at each solution composition. In other words, as explained in the text, a diffusing CH_2Cl_2 molecule spends about the same time in the neighborhood of another CH_2Cl_2 molecule as in the vicinity of a polystyrene chain segment. This assumes that the formalism which connects the respective intermolecular relaxation rates with the corresponding correlation times—a formalism derived for liquids of relatively rigid molecules[12]—is applicable to the solvent–polymer system.

Within the polymer molecular weight range of 3600–97,200, there is a significant increase in solvent trapping times with increasing molecular weight, all other factors being equal.[26]

(22) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, 31, 1164 (1959).
(23) C. A. Kumins and T. K. Kwei, "Diffusion in Polymers," J. Crank and G. S. Park, Ed., Academic Press, New York, N. Y., 1968, Chapter 4.
(24) H. L. Frisch, D. Klempner, and T. K. Kwei, *Macromolecules*, 4, 237 (1971).
(25) The free volume of the polystyrene chains must be smaller than that of the CH_2Cl_2 molecules; this is just a different way of saying that the self-diffusion coefficient of the solvent decreases with increasing polymer concentrations.
(26) O. F. Bezrukov, V. P. Budtov, and V. P. Fokanov, *Vestn. Leningrad. Univ., Fiz., Khim.*, No. 22, 57 (1970), claim on the basis of their spin-echo measurements of toluene in polystyrene that there is no molecular weight dependence of solvent diffusion in the range of molecular weights 10^3–10^7. However, the authors base this conclusion on observations of solutions where the diffusion coefficient (relative to pure solvent) has dropped to only about 0.95 (approximately 5% polymer). According to our data (see Figure 1), this may be too little polymer to show any effect.

It is conceivable that the solvent residence time is slightly shorter in regions near polymer chain ends because their larger flexibility engenders faster local segmental motion. However, that this could be (if at all) the sole reason for the observed effect is conjecture. The mobility data do not indicate that, at the higher polymer concentrations, the system passes through a glass transition, but our measurements are not accurate enough to make a definite decision. We have shown, on the basis of a temperature study, that the number of polymer segments necessary to permit slippage of the (low molecular weight) chains is not exceedingly higher than that involved in solvent diffusion.

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Properties of Poly(dimethylsiloxane) Networks Prepared in Solution, and Their Use in Evaluating the Theories of Rubberlike Elasticity

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ABSTRACT: Poly(dimethylsiloxane) networks were prepared by γ irradiation of solutions of the polymer in cyclohexane; concentrations employed corresponded to volume fractions $v_{2,S}$ of polymer ranging from 0.3 to 1.0. The moduli of these networks were obtained by stress–elongation measurements on the extracted, dried networks, and the relative degrees of cross-linking were obtained by swelling equilibrium experiments. These data were used to calculate the dependence of the modulus on the volume at which the cross-linking had been carried out. Comparison of experimental and theoretical values of this quantity lends strong support to the theory of rubberlike elasticity developed by Flory and coworkers. In addition, for samples having equal moduli, deviations from the form of the theoretical stress–elongation relationship decrease with decreasing $v_{2,S}$, with the strongest such dependence apparently occurring at small values of this volume fraction. In contrast, nonequilibrium effects exhibited by these networks also decrease with decreasing $v_{2,S}$, but the largest change is observed at large values of $v_{2,S}$. At constant $v_{2,S}$, increase in degree of cross-linking seems to *increase* the cited deviations from theory but to *decrease* nonequilibrium behavior. These additional results suggest that such deviations from theory can be, at most, only partially due to nonequilibrium effects.

Although the basic features of the phenomenon of rubberlike elasticity have been well established in the molecular theories of James and Guth,[1,2] Flory and coworkers,[2,3] and Hermans,[2,4] there are still a number of unresolved issues in this area. One of the most interesting points of contention, because of its connection to the very foundations of statistical mechanics, involves the existence and magnitude of a volume-dependent contribution to the entropy and free energy of network deformation.[1–5] Since extensive discussion of the theoretical basis and magnitude of such a term has not resolved the disagreement, experiments designed to discriminate among the three theories assume particular importance. Unfortunately, however, such experiments[6] have thus far yielded results of considerable ambiguity.

Since the equations which relate the extent of swelling of a network in equilibrium with a solvent to its density of cross-links are significantly different in these theories, measurements of both the extent of equilibrium swelling and the elastic modulus of a network should permit one to establish which of the theories is most nearly correct. Of particular interest in this approach to the problem are networks prepared from polymers in solution since, in this case, the differences among the predictions of the several theories are maximized.[5] Results of such a study[5] on networks of poly(*cis*-1,4-butadiene) which had been prepared from both the bulk polymer and from its solutions in benzene were not, however, in agreement with any of the theories. In this investigation, it was concluded that the disagreement between experiment and theory was probably due to the fact that the cross-linking procedures carried out in solution involved such low polymer concentrations that there was considerable inhomogeneity in cross-linking in the resulting networks. It is quite conceivable that in such networks an estimate of cross-link density from swelling equilibrium measurements would not be appropriate, for example, in the interpretation of the elastic modulus of the same sample in uniaxial extension.[5]

It is therefore the purpose of the present study to investigate the elastic properties of networks prepared from solutions having sufficiently high polymer concentration to minimize complications due to network inhomogeneities. Poly(dimethylsiloxane) was chosen for the preparation of such networks for a variety of reasons. As shown in a previous study,[7] cross-linked samples are relatively easy to prepare, are readily extensible at room temperature, are very stable over long periods of time, and show relatively small deviations from the form of the stress–elongation relationship[1–4] predicted by the statistical theories of rubberlike elasticity. In addition,

(1) See, for example, H. M. James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).
(2) An extensive collection of references to the development of the molecular theory of rubberlike elasticity may be found in ref 5.
(3) See, for example, P. J. Flory, *Trans. Faraday Soc.*, **57**, 829 (1961).
(4) See, for example, J. J. Hermans, *J. Polym. Sci.*, **59**, 191 (1962).
(5) J. E. Mark, *J. Amer. Chem. Soc.*, **92**, 7252 (1970).
(6) For a recent review of earlier experimental studies as well as theoretical aspects of this problem, see K. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969); see also ref 5.
(7) J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).