Diffusion in a Polymer Matrix

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ABSTRACT: Self-diffusion of benzene in polydimethylsiloxane (PDS) and of chloroform in poly(ethylene oxide) (PEO) has been studied at fixed concentration and temperature as a function of polymer molecular weight (MW). The diffusion coefficient of these solvents is sensitive to polymer molecular weight at low values, but is insensitive at high molecular weight of polymer. Self-diffusion has also been measured in 9:1 mixtures of PDS, each component being a sharp fraction. Molecular weights of the two components are varied separately over a range 162 to 800,000. It is found that the diffusion coefficient of the minor component decreases with increasing molecular weight of the major component when the latter is low, but becomes insensitive for MW(major) $\gg$ MW(minor). The measurements were made by nmr spin echo, employing a pulsed field gradient.

The diffusion of small molecules in polymers has been studied extensively, usually as a function of the specific chemical natures of polymer and solvent or as a function of temperature or solvent concentration.[1] Here we wish to focus on the effect of the molecular weight (MW) of the polymer in hindering solvent motion.

It is generally found that solvent diffusion is independent of polymer molecular weight;[1] however, there must be a limit to this independence as the molecular weight of the polymer becomes very small, since it is well known from studies of two-component systems of small molecules that the diffusion coefficient of either component is strongly dependent on what substance is chosen as the other component. Thus an increase in the diffusion coefficient of a small solvent molecule is to be expected as the mobility of the polymer chain becomes appreciable at very low molecular weight.

The value of the polymer molecular weight where this begins to occur is in itself interesting, since it is related, among other things, to the number of polymer segments which must move aside in unison to let the solvent molecule past.

The polymer–solvent systems chosen were (1) $CHCl_3$ in poly(ethylene oxide) (PEO) and (2) C_6H_6 in polydimethylsiloxane (PDS). These two polymers were chosen partly because of the availability of sharp fractions, partly because their long T_2's allow easy determination of the diffusion coefficient of the polymer[2] as well as of the solvent, and also because nmr relaxation studies in this laboratory have given us some understanding of the mobility of these polymers.[3]

As part of this same study we have measured the diffusion of polymer in polymer, using 9:1 mixtures of two sharp fractions of PDS. In this way the diffusion of large molecules in a polymer matrix can be studied as a function of matrix molecular weight.

It would have been interesting to study also the diffusion of large *rigid* molecules in a polymer matrix, but solubility limitations and the short T_2's characteristic of such molecules would make a study of this kind difficult.

Experimental Section

Spectroquality $CHCl_3$ and C_6H_6 from Matheson Coleman and Bell were employed as solvents.

The low molecular weight PEO samples were Union Carbide materials of the Carbowax series. These have been shown in a previous study[4,5] to be of low polydispersity ($\bar{M}_w/\bar{M}_n \approx 1.1$). A sample of Polyox WSR-301 was crudely fractionated by precipitation to obtain a material of high molecular weight. The polydispersity was estimated by gel permeation chromatography[2,4] to be of order 2.2.

All of the Carbowax materials studied here are terminated by hydroxyl end groups on both ends except for the Carbowax 550. In this last polymer, one end of the chain is terminated with a methoxy group.

Low molecular weight analogs of PEO having both types of end groups were employed. The di-, tri-, and tetraethylene glycols were from Aldrich and from Dow Chemical Co. Samples of bis(2-methoxyethyl) ether, $(CH_3OC_2H_4)_2O$, and triethylene glycol dimethyl ether, $(CH_3OC_2H_4OCH_2)_2$, were obtained from Aldrich Co. All of the PEO solutions were made at a concentration of 50 ± 2 g/dl.

The PDS materials were furnished by O. K. Johannsen and R. Buch of the Dow-Corning Laboratories, where the molecular weights and polydispersities were determined. They found in all cases $\bar{M}_w/\bar{M}_n \approx 1.1$. Solutions of 90% by weight PDS in 10% benzene were prepared. The PDS mixtures were 10% by weight of one molecular weight and 90% in the other molecular weight, no other substance being present.

The diffusion measurements were performed by nmr spin echo, using a pulsed-field gradient.[6] With the most viscous substances it was advantageous to observe the stimulated echo, because of the short T_2's.[7]

The solvent and polymer signals were readily resolved because of the difference in chemical shift. Using weak rf pulses,[8] resonance was set for the desired component. The remaining signal of the unwanted component was eliminated by adjusting the length of the second rf pulse[9] and by filtering the detected output.

Separation of the two diffusion coefficients in the PDS mixtures was easy in most cases, where the ratio of the two values of D was large. In some cases the differences between the T_2's were sufficient to aid in resolving the diffusion coefficients.

Results and Discussion

Diffusion coefficients of polymer and of solvent in the PEO solutions and in the PDS solutions are presented in Figure 1, together with the viscosities of the PEO solutions. The

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Table I

Diffusion Coefficients (cm²/sec) in PDS Mixtures

Mol wt of 90% component	9:1 Mixtures[a] Mol wt of 10% component: 162	746	4600	40,000	115,000	800,000
162	3.6×10^{-5}		3.5×10^{-6}	3.8×10^{-7}	1.0×10^{-7}	3.1×10^{-9}
746		2.2×10^{-6}	3.4×10^{-7} (1.9×10^{-6})	9.5×10^{-8} (1.4×10^{-6})	2.0×10^{-8}	
4,600	(1.9×10^{-7})	8.3×10^{-7} (1.5×10^{-7})	1.2×10^{-7}	1.9×10^{-8} (1.3×10^{-7})	5.5×10^{-9} (7.4×10^{-8})	
40,000	(5.5×10^{-9})	4.8×10^{-7} (4.3×10^{-9})	6.8×10^{-8} (3.9×10^{-9})	3.9×10^{-9}		
115,000	(9×10^{-10})			4.9×10^{-9}	4.8×10^{-10}	
800,000		5.8×10^{-7}	8.2×10^{-8}	3.6×10^{-9}		

Various Concentrations of Dimer

% polymer	19	29	33	42	42	59	61	67	67	84
D(dimer)	1.7×10^{-5}	1.7×10^{-5}	1.2×10^{-5}	1.1×10^{-5}	8.2×10^{-6}	6.5×10^{-6}	8.2×10^{-6}	2.4×10^{-5}	6.3×10^{-6}	4.1×10^{-6}
MW(polymer)	115,000	40,000	746	4600	800,000	40,000	115,000	746	4600	4600
D(polymer)			5×10^{-5}					1.1×10^{-5}		

Other

10% of MW 800,000 in heptamer, $D = 8.0 \times 10^{-10}$

10% of MW 40,000 in tetramer, $D = 1.9 \times 10^{-7}$ and 1.7×10^{-6}

[a] Value for major component in parentheses.

significant features of the results are apparent—the diffusion coefficient of the solvent is proportional to that of the polymer when the polymer has a low molecular weight. At higher molecular weight of polymer, the diffusion coefficient of the solvent becomes less sensitive and finally independent of the molecular weight of the polymer. The viscosities of the PEO solutions parallel the diffusion coefficients of the polymer rather than of the solvent where these differ.

The importance of hydrogen bonding between molecules is evident from the diffusion and viscosity data, comparing the triethylene glycol and tetraethylene glycol solutions with the methoxy-terminated species of approximately the same molecular weight. All the measurements indicate lower mobility in the glycol solutions.

The fact that the diffusion coefficients and viscosities are the same for the tri- and tetraethylene glycols in solution is rather puzzling, since the diffusion coefficients of glycols in bulk decrease monotonically with increasing molecular weight. The values for the first four members of this series are $D = 1.5 \times 10^{-6}$, 9.3×10^{-7}, 6.3×10^{-7}, and 3.6×10^{-7} cm²/sec, respectively. Dilution with a common solvent would be expected to decrease this variation with molecular weight, but not to the extent observed.

The diffusion constants of the major and minor components in the PDS mixtures are presented in Table I. The diffusion coefficient of each component shows the same basic features in its dependence on the molecular weight of the other component, but as expected, the effect of the molecular weight of the major component on the diffusion of the minor component is much more striking than the other way around. Therefore, the diffusion coefficients of the minor component (10%) are presented graphically in Figure 2. A few of the values plotted were not measured directly, but were obtained by extrapolation from measurements at other concentrations, as given in Table I.

The results are quite similar to the previous results with diffusion of solvent in polymer solution. The diffusion co-

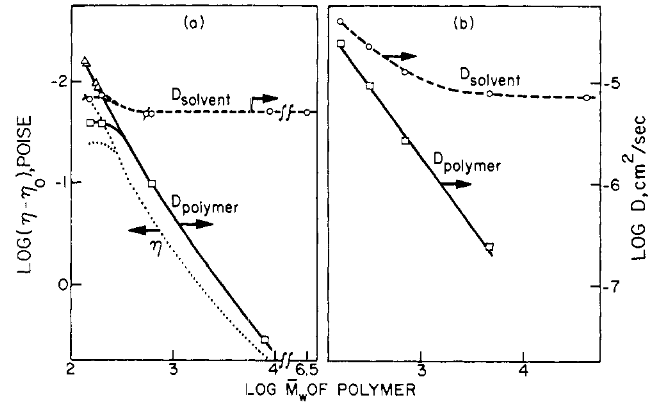

Figure 1. Self-diffusion and viscosity in polymer–solvent mixtures: (a) □, D(PEO), hydroxy terminated; ○, D(CHCl$_3$) in hydroxy-terminated PEO; ⌀, D(CHCl$_3$) in Carbowax 550; △, D(CHCl$_3$), D(PEO), methoxy-terminated PEO; (b) ○, D(C$_6$H$_6$); □, D(PDS).

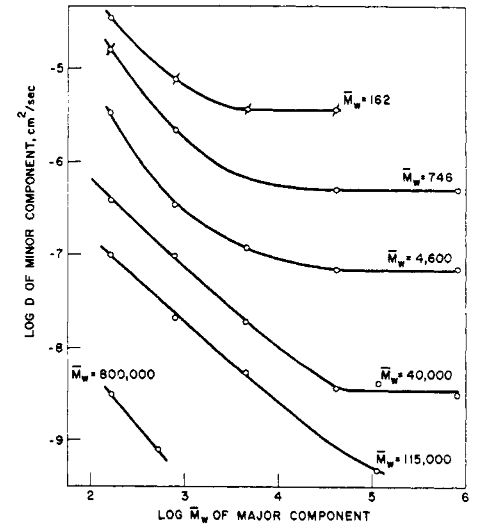

Figure 2. Self-diffusion of minor component in 9:1 PDS mixture. Each curve is a separate MW of minor component: ○, measured directly; ⌀, obtained by extrapolation.

efficient of the minor component decreases with increasing molecular weight of the major component, but when the latter is large enough, the diffusion coefficient levels out and becomes insensitive to it.[10] Chloroform, benzene, and hexamethyldisiloxane (HMS) are small molecules, and thus their diffusion becomes independent of polymer molecular weight at relatively low molecular weight. However, as the molecular weight of the minor component increases, its motion remains sensitive to the molecular weight of the other (polymer) component up to much higher values.

It is interesting to note that the increase in molecular weight of the major component to which the diffusion of the minor component is sensitive is not as great as the increase in molecular weight of the minor component itself. Whereas the ratio MW(major)/MW(minor) at the turning or leveling-off point is greater than 10 for low molecular weight of minor component, this ratio approaches unity at the highest molecular weights studied. It would be interesting to see what happens to this ratio at the turning point for a still higher molecular weight of the minor component, but the measurements made represent the limit of our capabilities with the spin-echo method.

A pictorial explanation of most of the above results can be given as follows. For two polymer molecules to become disentangled and to move out of each others' way, the entire length of the small molecule as well as a roughly equal portion of the larger molecule must move in a coordinated fashion. The motion of this portion of the larger molecule is expected to be independent of how far away the chain ends are, at least beyond a certain minimum distance. Thus the ease of motion of the smaller molecule is determined by its own size, but not by the size of the larger molecule.

On the other hand, diffusion of the large molecule is determined not only by the difficulty of disentangling from a given small molecule, but by the number of small molecules with which it is entangled. This is in turn proportional to its length. Thus the ease of diffusion of the large molecule is determined by the lengths of the chains of both components.

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[10] The fact that the self-diffusion coefficient of a polymer is independent of the molecular weight of a matrix polymer when the latter is much greater has also been observed in the case of polystyrene, molecular weight 80,000, in a radiotracer study by F. Bueche, *J. Chem. Phys.*, **48**, 1410 (1968).

Studies on the Stress Relaxation of Polystyrenes in the Rubbery Flow Region. II

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ABSTRACT: An empirical equation for stress relaxation in the rubbery flow region has been applied to commercial and narrow-distribution polystyrenes. The parameters involved have been mathematically related to the shear viscosity, η_s, and steady-state shear compliance, J_e^0. Relationships between the parameters and the molecular weight averages of the samples are also presented. An extrapolation to a completely monodisperse species is performed and its implications are discussed.

In the first paper of this series,[1] the empirical time-dependent modulus equation

$$E_r(t) = E_r(0)e^{-(t/\tau)^B} \qquad (1)$$

of DeBast and Gilard[2] was presented as adequately describing the rubbery plateau, rubbery flow, and terminal regions of the time-dependent modulus of narrow distribution polystyrenes. In this three-parameter equation, $E_r(0)$ is the value of the rubbery plateau modulus, τ is the time parameter which determines the length of the rubbery plateau, and B is the rate-of-decay parameter which influences the shape of the rubbery flow region. The previous paper[1] fitted eq 1 to the experimental modulus–time curves by a least-squares technique which allowed all three parameters to vary. The result was approximately constant values for $E_r(0)$ and B, while τ was found to follow the following relation when expressed in seconds for modulus curves at 115.0°

$$\tau = (1.4 \times 10^{-14})M^{3.4} \qquad (2)$$

This relationship shows the strong molecular weight dependence of the length of the rubbery plateau region, as has been observed by others.[3,4] The shape of the rubbery flow region has been observed to be pronouncedly affected by the breadth of the molecular weight distribution. The shape determines the value of B in eq 1, which must be chosen so as to accommodate the much broader rubbery flow region observed for polydisperse samples.[5] Therefore, B would appear to be a function of the heterogeneity of the polymeric material. Of course, we are aware that a distribution of molecular weights cannot be defined by a single variable, and thus at best B might be some function of a quantity relatable to the molecular weight distribution. We must also be aware that, because we are using a single parameter, B, to describe the shape of the modulus curve, we are restricted to describing the time-dependent modulus behavior of unimodal or close to unimodal distributions of molecular weights. The work done on

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