Segmentwise Diffusion in Molten Polystyrene

INTRODUCTION

The temperature and concentration dependences of mutual and self-diffusion coefficients in concentrated polymer solutions can rather satisfactorily be predicted and correlated using the free-volume theory of transport.[1-4] However, at least one important aspect of the theory which needs resolution is the manner in which the size, shape, and flexibility of the solvent influence the diffusion process. In the free-volume theory proposed by Vrentas and Duda,[1-4] the mutual diffusion coefficient D and the self-diffusion of the solvent D_1 are given by the following expression in the limit of zero solvent mass fraction:

$$D = D_1 = D_{01} \exp\left[- \frac{\gamma \hat{V}_2^* \xi}{V_{FH}(0)} \right]$$

(1)

Here, γ is an overlap factor which is introduced because the same free volume is available to more than one molecule, D_{01} is a preexponential factor, $\hat{V}_{FH}(0)$ is the specific hole free volume of the pure polymer at the temperature of interest, and $\hat{V}_2^*$ is the minimum local hole free volume per gram of polymer required for displacement of a polymeric jumping unit.

The parameter ξ is defined as follows

$$\xi = \frac{\tilde{V}_1^*}{\tilde{V}_2^*}$$

(2)

where $\tilde{V}_1^*$ is the minimum or critical hole free volume per mole of solvent jumping units required for displacement of a solvent jumping unit and $\tilde{V}_2^*$ is the critical hole free volume per mole of polymer jumping units required for displacement of a polymer jumping unit. Clearly, one way in which solvent size influences the diffusion process is through the quantity ξ, and, hence, it is possible to investigate possible mechanisms for solvent transport in amorphous polymers by measuring ξ for a wide variety of solvents diffusing in the same polymer.

The principal objective of this note is to present data which can be used to further test a proposed mechanism for the process by which a solvent molecule moves through the polymer matrix. A secondary objective is to present new diffusivity and solubility data for n-alkane diffusion in amorphous polystyrene. The proposed mechanism for solvent self-diffusion is discussed in the second section of the paper, and data for testing this mechanism are presented and interpreted in the third section of the paper.

PROPOSED MECHANISM FOR SOLVENT SELF-DIFFUSION

In the free-volume theory of transport formulated by Vrentas and Duda,[1-4] the following picture of molecular motion is proposed. Fluctuations in local hole free volume occur by a general recession of the molecules surrounding a particular molecule, and the molecule or jumping unit of the solvent, for example, moves to fill the expanded hole which is created. This leaves a similar hole at the initial position of the solvent which is then diminished in size by a process essentially opposite to that which increased the size the original hole. For this proposed mechanism, the critical volume required for displacement of a solvent jumping unit is identical to the actual size of the solvent jumping unit. In this picture of the self-diffusion process, the solvent and polymer jumping units are intrinsic properties of the solvent and polymer, respectively, and the size of the polymer jumping unit is not in any way influenced by solvent size and shape.

Since the volume occupied by a solvent molecule can be estimated by equating it to its equilibrium liquid volume at 0 K, it is convenient to define the parameter ξ_L as follows:

$$\xi_L = \frac{\tilde{V}_1^0(0)}{\tilde{V}_2^*} \tag{3}$$

where $\tilde{V}_1^0(0)$ is the molar volume of the equilibrium liquid solvent at 0 K. For relatively small or spherically shaped penetrant molecules, it is reasonable to expect that the entire molecule will perform a jump. Consequently, for such solvents, $\xi = \xi_L$, and ξ will be a linear function of $\tilde{V}_1^0(0)$ regardless of solvent size as long as the entire solvent molecule is the solvent jumping unit. A plot of ξ vs. the molar volume at 0 K of the entire solvent molecule will thus be a straight line through the origin for all solvents which jump as single units. Other solvents (for example, flexible chain solvents of sufficient length) may move in a segmentwise manner with jumping units which constitute only a portion of the solvent molecule. The molecular shape and flexibility of a solvent, as well as the total molecular volume, may thus be important in the self-diffusion process. It appears reasonable to suppose that a single-size jumping unit of the solvent molecule has a substantially greater probability for jumping than a jumping unit of any other size and that such jumping units can exhibit reasonably independent movement over small distances. In such cases, $\xi/\xi_L < 1$ and the quantity ξ/ξ_L need not be the same for two given solvents, each of which does not move as a single unit.

For solvents in a homologous series of compounds which can move in a segmentwise manner, it seems likely that at least the larger members of the series have the same size jumping unit and, hence, that ξ is the same for all of these penetrants. Consequently, a leveling of the parameter ξ with increasing solvent size for flexible chain solvents of sufficient length may be interpreted as evidence of segmentwise movement for this series of solvents. Alternatively, Ferguson and von Meerwall[5] have suggested that the size of the polymer jumping unit is not an intrinsic property of the polymer but rather reflects an adjustment to the size of the diluent molecule. In this picture of the self-diffusion process, a leveling of the parameter ξ is a consequence of the adjustment of $\tilde{V}_2^*$ to the size of the diffusing solvent molecule, and there need not be segmental mobility for a homologous series of solvents. Consequently, if a common value of ξ is observed for a homologous series, further data are needed to decide if the common ratio between polymer jumping unit size and the size of the penetrant jumping unit arises from diluent segmental motion or from adjustment of the size of the polymer jumping unit. In particular, a ξ value should be determined for a rigid, bulky solvent which must jump as a single unit and which has a $\tilde{V}_1^0(0)$ value comparable to or greater than those for the solvents in the homologous series.

Data for diffusion of a homologous series of solvents have been reported for a number of amorphous polymers. A leveling of the parameter ξ with solvent molar volume for n-alkyl acetate diffusion in poly(methyl acrylate) was attributed to segmentwise motion of the n-alkyl acetates owing to the apparent flexibility of these penetrants.[6] This conclusion was based on the observation that the ξ value for benzene was approximately 20% larger than that for the n-alkyl acetates, even though benzene has a lower molar volume than the larger members of this homologous series of penetrants. This evidence for concluding that the leveling of ξ is caused by the inception of segmentwise motion at a certain penetrant size is perhaps not as strong as might be desired since this interpretation is based on the assumption that the 20% difference in ξ values for benzene and the n-alkyl acetates cannot be attributed entirely to experimental error. In the same study,[6] it was concluded that a possible interpretation of diffusion data for polyisobutylene–solvent systems was the existence of segmentwise diffusion of sufficiently large and sufficiently flexible penetrants. However, the absence of data for a rigid, bulky solvent with relatively large molar volume does not allow a definitive interpretation of the observation that there is a leveling of ξ values for solvent diffusion in polyisobutylene. Finally, Chen and Ferry,[7] Rhee et al.,[8] and von Meerwall and Ferguson[9] reported self-diffusion data for n-alkanes in rubbery polymers and concluded that there was a leveling of ξ values with increasing solvent size. It was also shown that D_1 in the limit of zero solvent mass fraction was, in general, inversely proportional to the number of carbon atoms or to the molecular weight of the n-alkane chain. A somewhat different dependence of D_1 on penetrant length was reported by von Meerwall and Ferguson[9] for one of their rubber samples, but it

appears that these data are not as reliable as the diffusion data for the sample which showed the behavior described above. Although some data for rigid, bulky solvents were reported in these investigations, it appears that there is insufficient evidence for definitively concluding that there is segmentwise movement of the linear penetrant molecules.

In this paper we present new mutual diffusion data for molten polystyrene which we believe is reasonably strong evidence for segmentwise diffusion of a homologous series of flexible solvent molecules. Diffusion data are presented for four members of the n-alkane series and also for a rigid, bulky solvent, triisopropylbenzene, which is presumed to move as a single unit and which has a molar volume at 0 K larger than the four members of the homologous series. It was shown previously,[10] using solvent diffusion data for polystyrene, that ξ is a linear function of $\bar{V}_1^*(0)$ for all solvents which should jump as single units. This set of solvents included the solvent triisopropylbenzene which has a molar volume significantly larger than that of the polymeric jumping unit and also larger than the jumping units of two penetrants which appeared to exhibit piecewise movement. These two penetrants were dye molecules with a rigid, rodlike structure, and the piecewise movement in this case refers to the possibility that only part of the rod is effectively displaced in a direction parallel to its axis. Here, we use data for flexible chain solvents to conclude that a homologous series of such compounds undergoes segmentwise movement.

RESULTS AND DISCUSSION

Diffusivity data were collected as a function of concentration at 155 and 165°C using a quartz spring balance for the diffusion of n-octane, n-decane, and n-dodecane in amorphous polystyrene. Mutual diffusion coefficients and solubility data from these experiments are presented in Tables I and II. Data for the n-pentane–polystyrene system were reported previously.[11,12] It was not possible to obtain reliable diffusivity data for higher members of the series using the vapor sorption method because of the low vapor pressures. Values of ξ for the n-alkane series were derived from estimated values of the diffusivity at zero solvent mass fraction using a procedure described elsewhere.[10,12] The error in a computed value of ξ was estimated to be less than 10%.

Values for the parameter ξ for the four members of the n-alkane series and for four compounds which should jump as single units are presented in Figure 1 as a function of solvent molar volumes at 0 K. All of the diffusion data presented in this figure for polystyrene–solvent systems were collected in this laboratory. It is evident from this figure that a straight line through the origin provides a good representation of the four solvents which should jump as single units. Furthermore, all four of the members of the n-alkane series have essentially the same value of ξ. The relatively small differences in the ξ values are probably due to errors introduced in estimating D at zero mass fraction of solvent. It is clear from Figure 1 that the

TABLE I
Mutual Diffusion Coefficients for n-Alkane–Polystyrene Systems

Solvent	Temperature (°C)	Wt% solvent	$10^7\ D\ (cm^2/s)$
n-Octane	155	0.531	1.09
		1.43	2.55
	165	0.450	1.48
		1.37	2.96
n-Decane	155	0.912	0.600
		2.18	1.57
	165	0.868	1.00
		2.42	3.08
n-Dodecane	155	1.42	0.548
		3.09	1.25
	165	1.29	0.890
		2.99	1.97

TABLE II
Solubility Data for n-Alkane—Polystyrene Systems

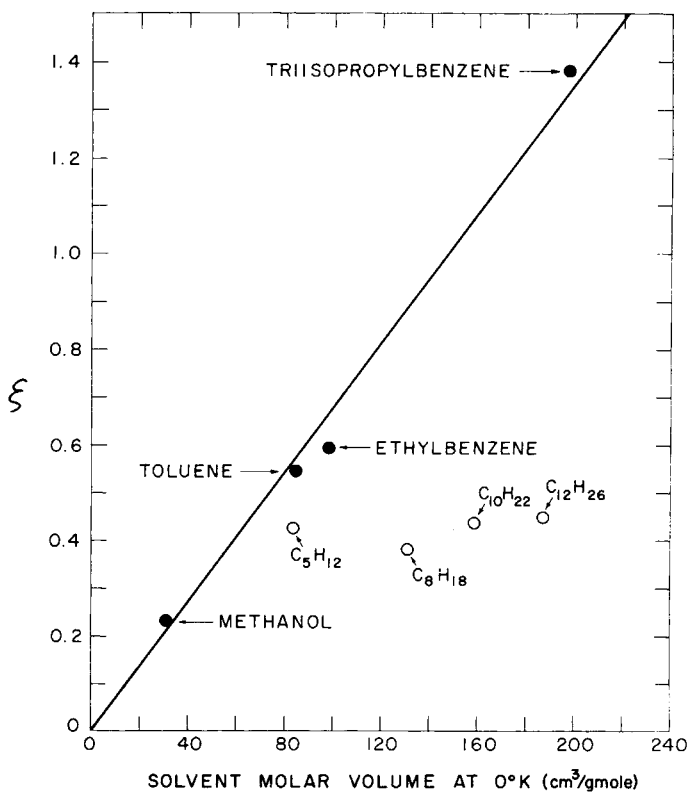| Solvent	Temperature (°C)	Pressure (mm Hg)	Wt% solvent
n-Octane	155	206	0.758
		412	1.71
	165	195	0.643
		453	1.68
n-Decane	155	90	1.30
		160	2.64
	165	120	1.24
		230	2.94
n-Dodecane	155	45	2.03
		66	3.54
	165	50.5	1.85
		81	3.48

Fig. 1. Dependence of ξ on solvent molar volume at 0 K for eight solvents diffusing in polystyrene: (●) solvents which might be expected to move as single units; (○) four members of the n-alkane series.

leveling of the ξ values for the n-alkane series is not due to an adjustment of the size of a polymeric jumping unit to the size of the solvent jumping unit since triisopropylbenzene has a ξ value which is approximately three times as large as the common value for the n-alkanes. Hence, it seems reasonable to attribute the leveling of the ξ values for this homologous series to segmentwise movement of the n-alkane chains. The size of the common jumping unit for these compounds is of the order of four carbon atoms. Data for n-alkane diffusion in polyisobutylene[6] also indicate that the solvent jumping unit consists of four carbon atoms.

Although there is not a large amount of new data presented in this paper, these data are such that it is possible to easily distinguish between two possible mechanisms for the leveling of ξ values for a homologous series of solvents diffusing in an amorphous polymer. Furthermore, it is evident from Figure 1 that the difference in ξ values between the n-alkane series and the solvent triisopropylbenzene is many times the estimated error for ξ. Hence, the conclusion that there is reasonable evidence for the segmentwise movement of the n-alkane chains is not clouded by experimental uncertainty. It is also important to emphasize that the ξ values reported here are effectively equivalent to other parameters measured in the study of the diffusion of a homologous series of solvents. For example, it is easy to show that ξ is simply related to the activation energy for diffusion at zero solvent concentration[6] so that the leveling of activation energy values reported by Chen and Ferry[7] is entirely equivalent to the leveling of ξ values. Furthermore, Rhee et al.[8] and von Meerwall and Ferguson[9] utilized a procedure for comparing the diffusional characteristics of two solvents which was based on measuring friction coefficients of the two penetrants in a number of polymers in the limit of zero solvent concentration. If this procedure is applied using eq. (1), then it is easy to show that a unit slope on their friction coefficient plot implies equal ξ values for the two penetrants. Hence, this equality of ξ values for two penetrants is equivalent to the equality of B_d values reported previously.[8,9] Clearly, the phenomenon of segmentwise movement of penetrants can be studied either by measuring the temperature dependence of diffusion coefficients[6,7] in a single polymer or by measuring diffusion coefficients in at least two polymers at a single temperature.[8,9] A comparison of the relative merits of these approaches is beyond the scope of this paper.

Since all four members of the homologous series have effectively the same value of ξ, it is clear from eq. (1) that the dependence of D_1 or D at zero solvent concentration on penetrant length or molecular weight is dictated by the nature of the preexponential term. For polymer molecules, which, of course, have a large number of jumping units, Bueche[13] has shown that D_1 should be inversely proportional to molecular weight if there are no entanglements. It might thus be expected that D_1 for the homologous series of n-alkanes would be inversely proportional to solvent molecular weight or to the number of carbon atoms in the chain for sufficiently large members of the series. As noted above, this type of molecular weight dependence has been reported for n-alkane diffusion in rubbery polymers for members of the series with at least eight carbon atoms. For the small members of the n-alkane series, it is conceivable that the dependence on carbon number is more complex since the derivation of Bueche is based on the assumption that all jumping units have the same jumping frequency. This may not be true for short chains. Indeed, if the data of Prager et al.[14] for n-butane and n-pentane diffusion in polyisobutylene are examined for *all* three temperatures reported, then it is evident that D_1 is generally not inversely proportional to carbon number for these short chains. Finally, for very long n-alkane chains, it is possible that reptation mechanisms may be present so that D_1 will be inversely proportional to the square of the number of carbon atoms.[15]

It is important to note that, since the value of ξ is effectively the same for all four members of the n-alkane series, the dependence of D_1 on penetrant length or molecular weight is not dependent on the form of the free-volume expression for the transport process. Bueche[13] has related D_1 to molecular weight by determining the distance traveled by a molecule and also by computing the force needed to pull the molecule through its surroundings. The dependence on molecular weight is the same for both models, and free-volume theory is used only to compute a jump frequency of a segment for the first model and a segment friction factor for the second model. In the reptation model, the molecular weight dependence is determined by the proposed reptation mechanism, and free-volume theory is used only to compute the diffusion coefficient of a single segment.[16]

Estimates of D_1 at zero solvent mass fraction were obtained for the n-alkanes for 8, 10, and 12 carbon atoms, and these results are plotted vs. the number of carbon atoms in Figure 2.
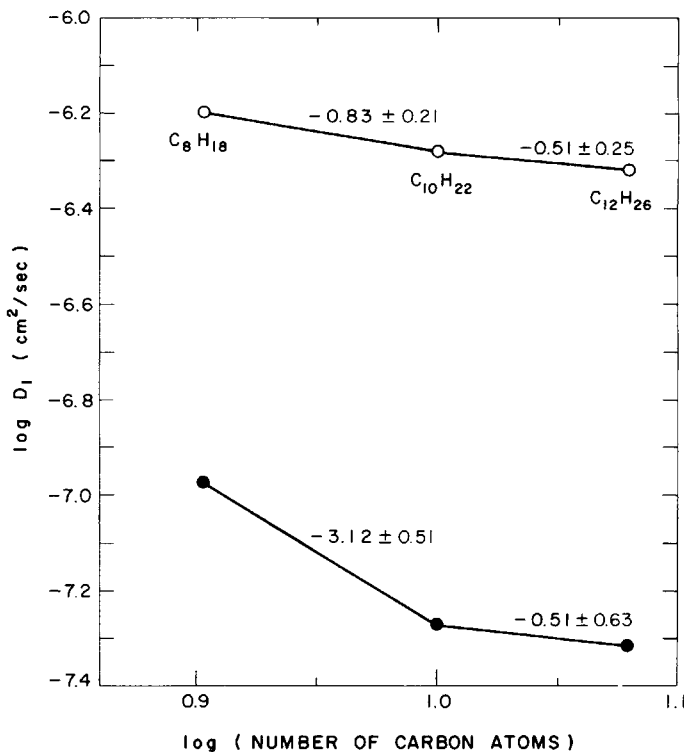
Fig. 2. Dependence of D_1 at zero solvent mass fraction on the number of carbon atoms for three members of the n-alkane series: (●) data of this study for diffusion in polystyrene at 165°C; (○) data of von Meerwall and Ferguson[9] for diffusion in cis-polyisoprene at 51°C. Numbers on the straight lines indicate slopes.

The slopes of the two straight lines formed from these data are clearly significantly different from −1, and, in one case, the difference cannot be attributed to experimental error. Hence, the simple dependence on the number of carbon atoms proposed above does not appear to be valid for such short chains. This conclusion might appear to be in disagreement with results reported by von Meerwall and Ferguson,[9] who found that D_1 was inversely proportional to diluent molecular weight for n-alkanes ranging from 8 to 36 carbon atoms. However, if data for the three lowest members of the series are considered (with 8, 10, and 12 carbon atoms), it is evident from Figure 2 that slopes significantly different than −1 are obtained, and, in one case, the difference between the calculated slope and the expected slope of −1 cannot be attributed to the reported experimental error. Consequently, the segmentwise movement for short n-alkane chains may involve a significantly more complex mechanism than that for longer chains.

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