Effect of Polymer Side Chains on the Infinite Dilution Diffusion Coefficients of Volatile Liquids in Poly(methyl Methacrylate) and Poly(ethyl Methacrylate) at Elevated Temperatures

It has been established that the presence of polymer side chains influences the solubility of volatile solutes in polymers. Saeki et al.[1] investigated the solubility of nonpolar and polar solutes in the homologues of poly(methacrylates) and poly(acrylates), namely, poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), and poly(n-butyl acrylate) (PNBA). They have found that values of the Flory-Huggins interaction parameter of organic solutes at infinite dilution were smaller for polymers having long side chains than for polymers having little or no side chains. They have concluded that, for nonpolar solutes, this is attributable to the shielding of the acrylate group by the polymer side chains and that, for polar solutes, the polymer side chains have a relatively small influence on the values of the interaction parameter. Karim and Bonner[2] also have investigated thermodynamic parameters (e.g., heat of solution, Flory-Huggins interaction parameter, and specific interaction parameter) of a number of aromatic and aliphatic solutes at infinite dilution in PEMA, using gas-liquid chromatography. However, little has been reported in the literature that deals with the effect of polymer side chains on the diffusivity of volatile solutes in molten polymers at elevated temperatures.

In our previous paper,[3] we have reported measurements made of infinite dilution diffusion coefficients of volatile liquids in polystyrene (PS) and poly(vinyl acetate) (PVAc) at elevated temperatures, using inverse gas chromatography (IGC). As part of our continuing effort on enhancing our understanding of the relationships between the structure of a polymer and the diffusivity of a solute in the polymer, we very recently made measurements of infinite dilution diffusion coefficients of volatile liquids in poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) at elevated temperatures, using IGC. The purpose of the study was to investigate the effect, if any, of the polymer side chains on the diffusivity of volatile liquids in amorphous polymers at elevated temperatures. In this paper, we shall report the results of the investigation.

EXPERIMENTAL

In the present investigation, inverse gas chromatography (IGC) was used. Specifically, packed chromatographic columns were used to obtain data of the variation of the plate height with the average gas velocity, which was then used to determine diffusion coefficient with the aid of the van Deemter equation.[4] The details of the apparatus and experimental procedures employed are described in our previous study.[3] In the present investigation, the polymers used were poly(methyl methacrylate) (PMMA) (Rohm and Haas) and poly(ethyl methacrylate) (PEMA) (Polysciences). The reasons these polymers were chosen are that, in contrast to PS and PVAc, they have side chains and their glass transition temperatures (105°C for PMMA and 65°C for PEMA) lie in the same range as those for PS (100°C) and PVAc (29°C). As volatile liquids, toluene, benzene, ethylbenzene, and n-decane were used. All these liquids used were reagent grade.

The experimental conditions employed (i.e., temperature and glass bead size) are given in Table I. Several columns were prepared, having a coverage ratio of 0.5%, with a polymer loading of approximately 0.25 g. The choices made of glass bead size were primarily dependent upon the temperatures at which experimental runs were to be made. Specifically, as the temperature was increased, larger glass beads had to be used.

The IGC method requires an analysis of the variation of the plate height H with the average gas velocity u, and diffusion coefficients are determined by the use of the van Deemter equation:[4]

$$H = A + B/u + Cu \qquad (1)$$

TABLE I
Experimental Conditions Employed for Determining Diffusion Coefficients

Solute	Temperature (°C)	Glass bead diameter (mm)
(a) Poly(methyl methacrylate)		
Toluene	140 – 180	0.3, 0.4, 0.6, 1.0
Ethylbenzene	150 – 180	0.4, 0.6, 1.0
n-Decane	150 – 160	0.3, 0.6
(b) Poly(ethyl methacrylate)		
Benzene	110 – 139	0.3, 0.6
Toluene	110 – 160	0.3, 0.4, 0.6
n-Decane	120 – 160	0.3, 0.4, 0.6

where A, B, and C are constants. At sufficiently high values of u, the second term in Eq. (1) can be neglected and therefore the slope of a plot of H versus u permits one to determine the constant C. Note that the constant C accounts for mass transfer in the stationary polymer phase and is related to the diffusion coefficient D as follows:

$$C = \frac{qkf_m}{(1 + k)^2 D} \qquad (2)$$

where q is a shape factor accounting for the nonuniformity of the liquid film in the packed column, f_m is the film thickness at its deepest point, and k is the mass distribution ratio of the solute between the gaseous and liquid phases. The readers are referred to our previous paper[3] discussing the details of the procedures for analyzing the data obtained using IGC.

RESULTS

As pointed out in our previous paper,[3] IGC is an indirect method for determining the infinite dilution diffusion coefficient of solutes in molten polymers. Therefore, one must have information on the diffusion coefficient that has been determined by other independent methods, such as sorption methods. Such information will then allow one to determine the geometric factor q, appearing in Eq. (2), that is associated with the use of packed chromatographic columns, and consequently values of the infinite dilution diffusion coefficient D.

There is scarcity of experimental data available in the literature, reporting the infinite dilution diffusion coefficient of volatile solutes in either PMMA or PEMA at temperatures above their glass transition temperatures (T_g). In our investigation, we had to extrapolate to infinite dilution the finite-concentration diffusion coefficient data of toluene in PMMA at 140°C, that was presented, on a logarithmic scale, by Ju et al.,[5] who used a sorption method. We were fully aware of the fact that extreme caution was necessary when performing such an extrapolation. Using the extrapolated value of the infinite dilution diffusion coefficient $D = 2.3 \times 10^{-9}$ cm²/s at 140°C, and experimentally determined values for the average glass bead radius r of 0.015 cm and film thickness f_m of 2.47×10^{-4} cm, we determined the value of the geometric factor q to be 0.105.

The experimental values of the diffusion coefficient obtained in this study are presented in Table II. Using this experimental data, plots of log D versus $1/(K_{22} + T - T_{g2})$ are given in Figure 1 for PMMA and PEMA, with the four solutes benzene, toluene, ethylbenzene, and n-decane. Note that the plots given in Figure 1 are based the Vrentas-Duda free-volume theory:[6]

$$\ln D = \ln D_0 - \frac{E}{RT} - \frac{\gamma \hat{V}_2^* \xi / K_{12}}{K_{22} + T + T_{g2}} \qquad (3)$$

where D_0 is a pre-exponential factor, E is the critical energy per mole needed to overcome attraction forces, R is the universal gas constant, T is the absolute temperature, K_{22} is a free volume parameter, T_{g2} is the glass transition temperature of the polymer, and $\gamma \hat{V}_2^* \xi / K_{12}$ are properties of the polymer-solute system. The precise definitions and physical significance of these
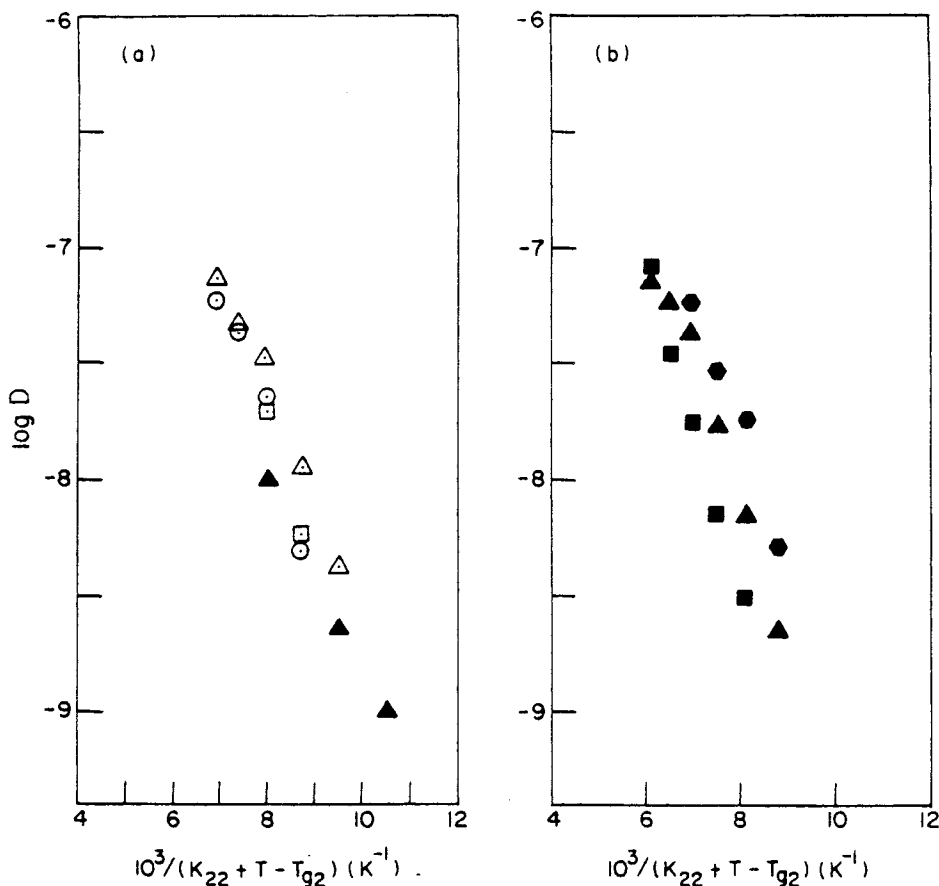
Fig. 1.   Log D versus $1/(K_{22} + T - T_{g2})$. (a) PMMA with: (⊙) ethylbenzene; (▲) toluene; (▢) n-decane; (▲) toluene (Ref. 5). (b) PEMA with: (▲) toluene; (■) n-decane; (●) benzene.

parameters are described in a paper by Vrentas and Duda.[7] In preparing Figure 1 with the aid of Eq. (3), the values of K_{22} used are 73.0 K for PMMA and 65.0 K for PEMA, and the values of T_{g2} used are 108°C for PMMA and 65°C for PEMA. In Figure 1 the dependence of D on the structure of solute is seen, especially for PEMA.

With the same experimental data as those used in Figure 1 (see Table II), we have prepared plots of ln $D\zeta$ versus $1/T_{RF}$ and they are displayed in Figure 2 for PMMA and PEMA, with the four solutes employed. Note that the plots given in Figure 2 are based on a *generalized* Vrentas-Duda free-volume theory:[3]

$$\ln D\zeta = a + b/T_{RF} + c/T_R \tag{4}$$

where

$$a = \ln D_0 \zeta \tag{5}$$

$$b = \zeta \hat{V}_2^* \xi / K_{12} T_c \tag{6}$$

$$c = -E/RT_c \tag{7}$$

$$T_{RF} = (K_{22} + T - T_{g2})/T_c \tag{8}$$

$$T_R = T/T_c \tag{9}$$

$$\zeta = M^{1/2}/T_c^{1/2} V_c^{1/3} \tag{10}$$

TABLE II
Summary of the Diffusion Coefficients Determined

T (°C)	$\dfrac{1}{T_R}$	$\dfrac{10^3}{(K_{22} + T - T_{g2})}$	$\dfrac{1}{T_{RF}}$	log D	ln $D\zeta$
		(a) PMMA/Toluene			
140	1.432	9.505	5.624	− 8.383	− 22.154
150	1.398	8.681	5.136	− 7.961	− 21.180
160	1.366	7.987	4.726	− 7.484	− 20.082
170	1.335	7.396	4.376	− 7.332	− 19.732
180	1.305	6.887	4.075	− 7.137	− 19.281
		(b) PMMA/Ethylbenzene			
150	1.458	8.681	5.357	− 8.315	− 21.997
160	1.425	7.987	4.929	− 7.639	− 20.445
170	1.392	7.396	4.565	− 7.355	− 19.791
180	1.362	6.887	4.251	− 7.226	− 19.493
		(c) PMMA/n-Decane			
150	1.458	8.681	5.361	− 8.234	− 21.839
160	1.426	7.987	4.933	− 7.691	− 20.587
		(d) PEMA/Benzene			
110	1.467	8.795	4.944	− 8.284	− 21.913
120	1.429	8.084	4.544	− 7.743	− 20.668
130	1.394	7.479	4.204	− 7.534	− 20.186
139	1.364	7.008	3.939	− 7.275	− 19.589
		(e) PEMA/Toluene			
110	1.544	8.795	5.204	− 8.649	− 22.763
120	1.505	8.084	4.783	− 8.163	− 21.644
130	1.467	7.479	4.425	− 7.788	− 20.782
140	1.432	6.959	4.132	− 7.388	− 19.860
151	1.395	6.464	3.825	− 7.211	− 19.454
160	1.366	6.108	3.614	− 7.162	− 19.339
		(f) PEMA/n-Decane			
120	1.571	8.084	4.993	− 8.495	− 22.439
130	1.532	7.479	4.619	− 8.155	− 21.658
140	1.495	6.959	4.298	− 7.764	− 20.756
150	1.459	6.506	4.018	− 7.475	− 20.092
160	1.426	6.109	3.773	− 7.095	− 19.217

Note in Eqs. (6) to (10) that T_c is the critical temperature, M is the molecular weight, and V_c is the critical volume of the solute. It should be pointed out that $D\zeta$ may be considered to be *reduced* diffusion coefficient and T_{RF} is a dimensionless temperature.

A comparison of Figure 1 with Figure 2 indicates the quality of correlation is much improved when the experimental data were correlated using the variables $D\zeta$ and $1/T_{RF}$.

DISCUSSION

It is seen in Figure 2 that two linear regions appear to exist, separated by a certain critical value of $1/T_{RF}$. The critical value of $1/T_{RF}$ may be obtained by extrapolating the two linear
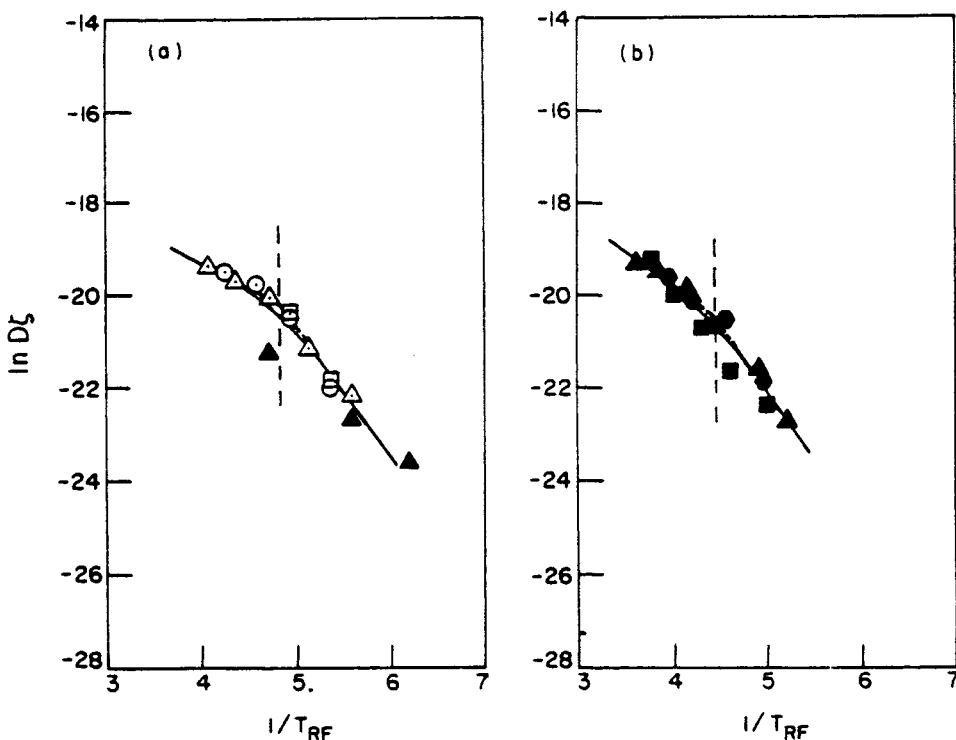
Fig. 2. ln $D\zeta$ versus $1/T_{RF}$ for: (a) PMMA and (b) PEMA. Symbols are the same as in Figure 1.

regions as indicated by the dotted lines in Figure 2. It should be mentioned that actually there would be *no* discontinuity in the slope of ln $D\zeta$ versus $1/T_{RF}$ plots; transition would be smooth as indicated by the solid line in Figure 2. The critical value of $1/T_{RF}$ is seen to be insensitive to the type of solute and the type of polymer used. This observation is in agreement with that made in our previous investigation that dealt with the diffusion of the same solutes benzene, toluene, ethylbenzene, and n-decane in PS and PVAc. We have determined the critical value of $1/T_{RF}$ to be 4.97 for PMMA and PEMA, which is very close to the value 4.87 for PS and PVAc obtained in our previous investigation.[3]

Having observed two distinct regions in the ln $D\zeta$ versus $1/T_{RF}$ plots, let us consider each region separately. In the lower linear region, namely, at values of $1/T_{RF}$ above the critical one, Eq. (4) may be expressed as

$$\ln D\zeta = \alpha + b/T_{RF} \tag{11}$$

We have determined in the present investigation that the values of b are -3.0 for PEMA and -2.85 for PMMA, and from our previous investigation,[3] we have $b = -1.25$ for PS and $b = -2.54$ for PVAc. Therefore we have the following relationship:

$$|b(\text{PS})| < |b(\text{PVAc})| < |b(\text{PMMA})| < |b(\text{PEMA})| \tag{12}$$

In view of the fact that the value of b (i.e., the slope of the ln $D\zeta$ versus $1/T_{RF}$ plots) is insensitive to the type of solute and dependent only upon the structure of the polymer, and, in view of the fact that the glass transition temperature (T_g) of a polymer is a structural parameter, we have tried to see if there is any correlation between values of b and the T_g's. For the four polymers under consideration, we have

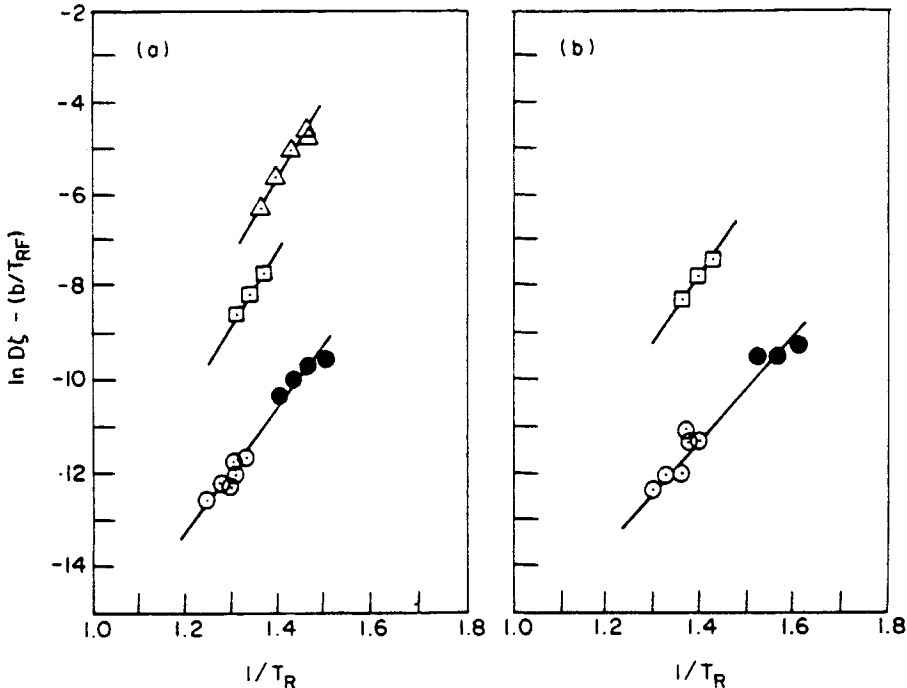$$T_g(\text{PVAc}) < T_g(\text{PEMA}) < T_g(\text{PS}) < T_g(\text{PMMA}) \tag{13}$$

Fig. 3.   ln $D\zeta - (b/T_{RF})$ versus $1/T_R$. (a) Toluene in: (▲) PEMA; (▣) PMMA; (◯) PS; (●) PVAc. (b) Ethylbenzene in: (▣) PMMA: (◯) PS; (●); PVAc.

If we restrict our attention to PS and PVAc only, it appears that an inverse relationship exists between values of b and the T_g's. Thus, PVAc, having a T_g lower than that of the PS, has a value of b larger than that of the PS. However, such a relationship fails when we include PMMA and PEMA into our consideration. It can then be concluded that the use of the T_g of a polymer cannot explain why the PMMA and PEMA, having higher T_g's than the PVAc, also have larger values of b than the PVAc. We therefore speculate that the flexibility of the polymer side chains must be included to explain the dependence of b on the type of polymer (i.e., polymer structure). Note that both PMMA and PEMA have side chains, whereas both PVAc and PS do not, and that PEMA has longer side chains and thus is more flexible than PMMA. This now seems to explain why the PEMA has a value of b larger than PMMA, which in turn has a value of b larger than PVAc and PS, as observed in Eq. (12). We therefore conclude that the parameter b in Eq. (4) (i.e., the slope of $D\zeta$ versus $1/T_{RF}$ plots) also represents the flexibility of a polymer due to the presence of side chains.

Let us now consider the upper linear region of ln $D\zeta$ versus $1/T_{RF}$ plots, given in Figure 2. In order to facilitate our discussion, we have prepared plots of ln $D\zeta - (b/T_{RF})$ versus the reciprocal of the reduced temperature $1/T_R$ (see Eq. (9) for the definition of T_R) and they are displayed in Figures 3 and 4. Note in these figures that ln $D\zeta - (b/T_{RF})$ represents the difference between the actually measured values of diffusivity (ln $D\zeta$) and the values of diffusivity (b/T_{RF}) obtained from the extrapolation of the lower linear region in the ln $D\zeta$ versus $1/T_{RF}$ plots to temperatures above the critical value. For comparison purposes, the data of PS and PVAc (see Figures 12 and 13 of Ref. 3) are included in Figure 3 and 4. Two observations are worth noting in Figure 3 and 4: (1) values of ln $D\zeta - (b/T_{RF})$ vary with the type of solute; (2) PEMA has values of ln $D\zeta - (b/T_{RF})$ larger than PMMA, which in turn has values of ln $D\zeta - (b/T_{RF})$ larger than those PS and PVAc. Note that PS and PVAc have essentially the same values of ln $D\zeta - (b/T_{RF})$.

In our previous paper,[3] we have indicated that energy effects play an important role in determining the infinite dilution diffusion coefficients of volatile solutes in rubbery polymers, at temperatures above a certain critical value (i.e., in the upper linear region of ln $D\zeta$ versus $1/T_{RF}$ plots). On the basis of this interpretation, it appears from Figures 3 and 4 that energy effects are greater in PEMA than in PMMA, and that they are much greater in PEMA than in PS and PVAc. Note in Figures 3 and 4 that the slope of ln $D\zeta - (b/T_{RF})$ versus $1/T_R$ plots varies with
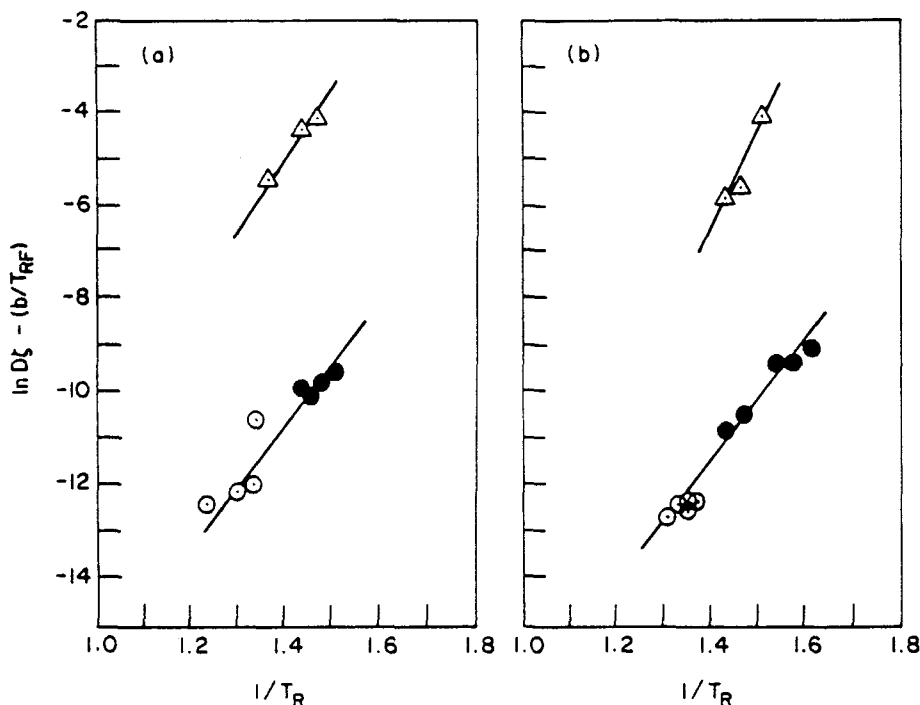
Fig. 4. In $D\zeta - (b/T_{RF})$ versus $1/T_R$. (a) Benzene in: (▲) PEMA; (⊙) PS; (●) PVAc. (b) n-decane in: (▲) PEMA; (⊙) PS; (●) PVAc.

the type of solute. This seems to suggest to us that energy effects are dependent upon both the type of solute and the structure of the polymer. We therefore speculate tentatively that energy effects are greater in polymers having side chains (e.g., PEMA and PMMA) than in polymers having little or no side chains (e.g., PS and PVAc). The validity of this speculation can be tested if data of the infinite dilution diffusion coefficient of solutes in rubbery polymers, having very low T_g's, are available over a wide range of temperature, including temperatures well above the T_g's of such polymers. Further experimental study is needed to test the speculation made above.

References

1. S. Saeki, J. C. Holste, and D. C. Bonner, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 2049 (1983).
2. K. A. Karim and D. C. Bonner, *Polym. Eng. Sci.*, **19**, 1174 (1979).
3. D. S. Hu, C. D. Han, and L. I. Stiel, *J. Appl. Polym. Sci.*, **33**, 551 (1987).
4. J. J. van Deemter, F. J. Zuiderweg, and A. Klinkenberg, *Chem. Eng. Sci.*, **5**, 271 (1956).
5. S. T. Ju, H. T. Liu, J. L. Duda, and J. S. Vrentas, *J. Appl. Polym. Sci.*, **26**, 3735 (1981).
6. J. S. Vrenta, and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1085 (1979).
7. S. T. Ju, L. Duda, and J. S. Vrentas, *Ind. Eng. Chem. Prod. Res. Dev.*, **20**, 330 (1981).

DAVID S. HU
CHANG DAE HAN

Department of Chemical Engineering
Polytechnic Institute of New York
Brooklyn, New York 11201