Rotational isomerization by stretching takes place predominantly in C—C(CH_3)═CH—C bond sequences for *cis*-PIP and in CH_2—CH_2 bonds for *trans*-PIP chains.

The *a priori* probability for the trans state for CH_2–CH_2 bonds is considerably greater for PIP chains than for PBD chains owing to the second-order interdependence of rotations imposed by $\omega \ll 1$. Rotational isomerization about these bonds takes place to a greater degree for PIP chains than for PBD chains. For example, with $\sigma = 1.0$ we obtain $p_t = 0.455$, $n'\delta_{t;2} = 1.38$, and $\Delta_{t;2} = 0.63$ for *trans*-PBD chains, whereas for *trans*-PIP, $p_t = 0.592$, $n'\delta_{t;2} = 1.74$, and $\Delta_{t;2} = 1.03$.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Contract No. F 44620-69-C-0058.

Appendix

Anisotropies of Group Polarizability Tensors. The only modifications required for the adaptation of expressions for PBD chains given in the Appendix of the previous paper are the replacement of $\chi = \pi - \angle$C═CH by $\chi' = \pi - \angle$C═C—CH_3 and of $\Delta\alpha_{C-H}$ by $\Delta\alpha_{C-CH_3}$ in the previous eq 62 for $\hat{\alpha}_d$.[5] Thus $\hat{\alpha}_d$ is given by eq 17. The tensor $\hat{\alpha}_2$ for the second bond is identical with $\hat{\alpha}_d$ given by this equation.

$$\hat{\alpha}_d = \begin{bmatrix} (2/3)\Delta\alpha_{C=C} + (1/2)[\cos 2\chi' + 1/3]\Delta\alpha_{C-CH_3} & -(1/2)(\sin 2\chi')\Delta\alpha_{C-CH_3} & 0 \\ -(1/2)(\sin 2\chi')\Delta\alpha_{C-CH_3} & -(1/3)\Delta\alpha_{C=C} - (1/2)[\cos 2\chi' - 1/3]\Delta\alpha_{C-CH_3} & 0 \\ 0 & 0 & -(1/3)\Delta\alpha_{C=C} - (1/3)\Delta\alpha_{C-CH_3} \end{bmatrix} \tag{17}$$

Modified Free-Volume Theory of Penetrant Diffusion in Polymers

H. L. Frisch,[1a] **D. Klempner,**[1b] **and T. K. Kwei***[1c]

State University of New York at Albany, Albany, New York 12203,
The Polymer Science Center, University of Massachusetts, Amherst,
Massachusetts 01002, and Bell Telephone Laboratories, Incorporated,
Murray Hill, New Jersey 07974. *Received December 21, 1970*

ABSTRACT: Fujita's formulation of the free-volume theory of penetrant diffusion is modified by introducing a reference temperature and reference free volume which need not coincide with those for the viscosity. The modified theory, unlike its predecessor, can accommodate data for small as well as large penetrant molecules and also accounts for some earlier empirical correlations.

The application of free-volume theory to the interpretation of diffusion of large organic molecules in polymers has met with notable success.[2] Specifically, it has been shown that the dependence of the diffusion coefficient on temperature and concentration can be described by the same type of equation which represents the dependence of viscosity on these two variables. However, the predicted interrelations between the diffusion and the viscosity data did not hold for penetrant molecules of small size, *e.g.*, poly(vinyl acetate)–water and poly(methyl acrylate)–water.[3] The reason for this discrepancy can be rationalized by the consideration that the diffusion of small molecules requires a portion of the free-volume distribution different from that involved in the diffusion of large molecules comparable in size to the chain segment. In this paper, we would like to formulate this concept in an expression which contains a reference point for the free volume of diffusion not necessarily identical with that of viscous flow.

Let us first summarize Fujita's[2] derivations (Fujita's notation is used in the text with the exception that φ represents the volume fraction of diluent)

$$D(\varphi, T) = A_d \exp[-B_d/f_d(\varphi, T)] \tag{1}$$

$$f_d(\varphi, T) = f_d(0, T) + \beta_d(T)\varphi \tag{2}$$

and

$$D_0(T) = D(0, T) = A_d \exp[-B_d/f_d(0, T)] \tag{3}$$

In these equations, the subscript d refers to the diffusion process, A is a frequency factor, B corresponds to the minimum hole size for the jump process, f is the average fractional free volume of the system, and β describes the effectiveness of the diffusant molecules for increasing the free volume of the give polymer. The viscosity of the system is expressed in a similar manner with the use of subscript v

$$\eta_0(T) = A_v \exp[B_v/f_v(0, T)] \tag{4}$$

Combination of eq 1 and 4 yields

$$\ln D_0(T) = C - \frac{B_d f_v(0, T)}{B_v f_d(0, T)} \ln \eta_0(T) \tag{5}$$

If the condition given by eq 6 is met

$$f_v(0, T) = f_d(0, T) \tag{6}$$

then

$$\begin{aligned} \ln D_0(T) &= C - (B_d/B_v) \ln \eta_0(T) \\ &= C' - (B_d/B_v) \ln a_T \end{aligned} \tag{7}$$

---

[1] (a) State University of New York; (b) University of Massachusetts; (c) Bell Telephone Laboratories.

[2] H. Fujita, *Fortschr. Hochpolym-Forsch.*, **3**, 1 (1961).

[3] (a) A. Kishimoto, E. Maekawa, and H. Fujita, *Bull. Chem. Soc. Jap.*, **33**, 988 (1960); (b) H. Fujita and A. Kishimoto, *J. Polym. Sci.*, **28**, 547 (1958).

where

$$C' = C - (B_d/B_v)\ln \eta(0, T_r) \tag{8}$$

is a new constant, with T_r the characteristic reference temperature for the bulk viscosity of the pure polymer.

According to eq 6, a plot of $\ln D_0(T)$ *vs.* $\ln a_T$ would result in a straight line of slope $-B_d/B_v$.[2] The terms B_d and B_v have the meanings of critical volumes of the jump processes and are expected to be nearly the same if the size of the penetrant approaches that of a chain segment. In fact, the experimental slopes are reasonably close to the predicted value of -1. This is shown most clearly by the plot for the hydrocarbons of various chain lengths in ref 4.

Now, let us examine the possibility that $f_d(0, T)$ is not related to $f_v(0, T)$ in a simple manner. As mentioned previously, the physical meaning of such an arguemnt is that the portion of the free-volume distribution which contributes to the diffusion of small molecules is ineffective in the flow process. For this reason, it is more general to adopt a reference temperature for diffusion, T_D, and a corresponding free-volume fraction f_D as shown in eq 9. The reference point

$$f_d(0, T) = f_D + \alpha'(T - T_D) \tag{9}$$

T_D may be considered as the temperature below which the mobility of the smallest increment of free volume in the polymer decreases drastically. T_D and f_D are no longer identical with T_g and f_g. However, it is still true that T_D will represent a characteristic reference temperature for diffusion and can thus be related to T_g by

$$T_D = T_g - T^* \tag{10}$$

where T^* represents a universal shift in temperature. A linear relation between $\ln D_0(T)$ and $\ln a_T$ will still be valid since eq 5 can also be written as

$$\ln D_0(T) = C'' - \frac{B_d f_v}{B_v f_D}\ln a_T \tag{11}$$

However, it is clear that D and η will not have the same concentration dependence if β_d in eq 2 is different from its counterpart β_v.

One can now rewrite eq 3 as

$$D_0 = A\exp[-B_d/\{f_D + \alpha'(T - T_D)\}] \tag{12}$$

In order for eq 12 to be equivalent to the usual Arrhenius expression

$$D_0 = A_d\exp[-E_d/RT] \tag{13}$$

the following relations must hold

$$f_D \cong \alpha' T_D \tag{14}$$

and

$$E_D/R = B_d T_D/f_D \tag{15}$$

The term B_d, which is a measure of the critical volume for diffusion, is sensitive to the size of the penetrant. The parameter f_D, in analogy to f_g, is expected to be approximately the same for many different polymers. Further, it probably does not vary a great deal as long as the penetrant size is much smaller than that of a chain segment.

Equation 15 is consistent with the well-known observation that the activation energy of diffusion of nearly spherical gas molecules can be factored into a product of two functions, the first one characterizing solely the gas and the second function characterizing solely the polymer.[5,6] An empirical correlation was previously obtained for the factorization scheme[7]

$$E_D/R = \frac{d^2}{a}(T_g - T^*) \tag{16}$$

where d is the diameter of the gas molecule, a is a constant area of 0.33 Å^2, and T^* has the value 106°K. Equation 16 is in perfect agreement with the predictions of eq 10 and 15. It represents very well the diffusion data of He, H_2, O_2, and N_2 in many rubbery polymers. It is, of course, recognized as a limiting case for small spherical molecules just as Fujita's treatment is for large molecules.

Acknowledgment. H. L. Frisch wishes to acknowledge the support of Grant No. 3519-C 5,6 from the Petroleum Research Fund, administered by the American Chemical Society.

---

(4) H. L. Frisch and C. E. Rogers, *J. Polym. Sci.*, *Part C*, **12**, 297 (966).

(5) H. L. Frisch, *ibid., Part B*, **1**, 581 (1963).

(6) T. K. Kwei and W. M. Arnheim, *ibid., Part A*, **2**, 957 (1964).

(7) H. L. Frisch and T. K. Kwei, *ibid., Part B*, **7**, 789 (1969).