Note on the Monomeric Friction Coefficient of Poly-n-butyl Methacrylate in Diethyl Phthalate

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From dynamic mechanical measurements encompassing the glass to rubber transition region Saunders et al.⁽¹⁾ have recently shown that the monomeric friction coefficient ζ_0 (in dyne sec./cm.) of poly-*n*-butyl methacrylate in diethyl phthalate at 0°C varied with the polymer concentration c (in g./ml. of solution), according to the relation:

$$\zeta_0 = 5.8 \times 10^{-10} \exp(24c) \qquad (1)$$

They state that there appears to be no theoretical expectation for the form of this relation. The purpose of the present communication is to show that their ζ_0 data can be interpreted reasonably in terms of a free volume theory described recently by Fujita and Kishimoto⁽²⁾, if the original theory is modified so that the diluent concentration C (in grams of diluent per gram of dry polymer) is replaced by the volume fraction of diluent v⁽³⁾. Thus, the starting assumption of the modified theory is that the fractional free volume, f, in the polymer-diluent mixture at a fixed temperature T is a linear function of v, i.e.

$$f = f(T,\ 0) + \beta'(T)v \qquad (2)$$

where $f(T,\ 0)$ is the free volume fraction in the pure polymer at temperature T and

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1) P. R. Saunders, D. M. Stern, S. F. Kurath, C. Sakookim and J. D. Ferry, *J. Colloid Sci.*, **14**, 222 (1959).

2) H. Fujita and A. Kishimoto, *J. Polymer Sci.*, **28**, 547 (1958).

3) The modification of the original theory, involving derivations of the new equations, and applications of the modified theory to viscosity data on concentrated polymer solutions will be described in detail in a forthcoming publication.

$\beta'(T)$ is a parameter (dependent on temperature) similar in nature to the parameter β defined previously²⁾. The physical meaning of the new parameter β' will be given in a forthcoming article³⁾.

If one starts with Eq. 2 and uses a similar procedure to that described in Ref. 2, one can derive the relation:

$$-\frac{2.303[f(T,\ 0)]^2\log a_v}{1+2.303f(T,\ 0)\log a_v}=\beta'(T)v \qquad (3)$$

Here a_v is the concentration shift factor with the pure polymer as a standard and may be evaluated, in a manner described previously²⁾, from appropriate viscoelastic measurements obtained as a function of diluent concentration. Eq. 3 may be rewritten in the form:

$$-(1/\log a_v)=2.303f(T,\ 0) + \{2.303[f(T,\ 0)]^2/\beta'(T)\}(1/v) \qquad (4)$$

This indicates that plots of $-1/\log a_v$ vs. $1/v$ form a straight line and $f(T,\ 0)$ and $\beta'(T)$ can be determined from its slope and intercept at $1/v=0$.

Under the assumption that all the relaxation mechanisms—at least, those contributing to the mechanical behavior in the particular region concerned—have the same dependence on diluent concentration in the polymer, the shift factor a_v may be evaluated from the ratio of the monomeric friction coefficient of the mixture at diluent concentration v to that of the pure polymer ($v=0$) at the same temperature. The authors calculated a_v for the system poly-n-butyl methacrylate+diethyl phthalate at 27°C (this is the glass transition temperature of pure poly-n-butyl methacrylate⁴⁾) from the ζ_0 data of Saunders et al.¹⁾ and of Child and Ferry⁴⁾. The latter study gives the ζ_0 values for the pure polymer at 27°C. The former data, which were originally given for the temperature 0°C have been converted to the desired temperature by using the WLF equation⁵⁾ with the numerical constants recorded in Table II of Ref. 1. Fig. 1 shows the plot of $-1/\log a_v$ vs. $1/v$ obtained from these data. It is seen that the plotted points follow a straight line reasonably well, in agreement with the prediction of Eq. 4. From the solid line drawn one finds that $f(T_g^0,\ 0)=0.023$ and $\beta'(T_g^0)=0.05_0$; here T_g^0 denotes the glass transition temperature of the pure polymer. It is of interest to see that the value of $f(T_g^0,\ 0)$ obtained, which was denoted by f_g^0 in Ref. 2, is quite close to the approximately) universal value 0.025.

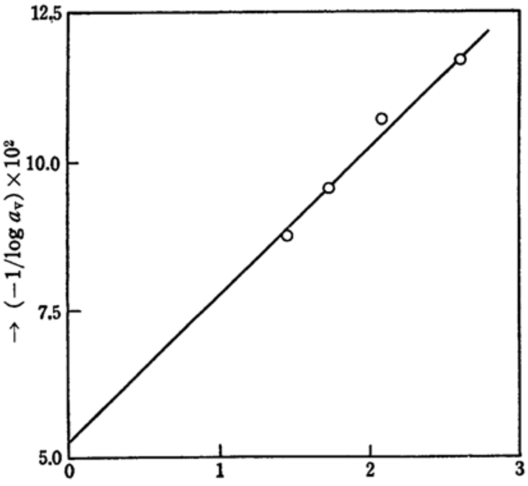

Fig. 1. Plot of $-1/\log a_v$ vs. $1/v$ for the system poly-n-butyl methacrylate + diethyl phthalate at 27°C; v is the volume fraction of diethyl phthalate in the mixture.

Eq. 4 may be used to evaluate $f(T,\ 0)$ and $\beta'(T)$ when the steady-flow viscosity, η, of the polymer-diluent mixture is known as a function of diluent volume fraction v. In this case the shift factor a_v may be taken as the ratio $\eta/[(1-v)\eta_0]$, where η_0 is the value of η for the pure polymer at the same temperature T. The authors applied Eq. 4 to Bueche's data⁶⁾ for the steady-flow viscosity on the system polymethyl methacrylate+diethyl phthalate at 100°C, the glass transition temperatue of this polymer⁷⁾. A very satisfactory straight line was obtained between $-1/\log a_v$ and $1/v$ and yielded $f(T_g^0,\ 0)=0.017$ and $\beta'(T_g^0)=0.051$, where $T_g^0=100$°C. This low value of f_g^0 is consistent with a similar low value obtained previously⁷⁾ for this methacrylate polymer. Of interest is the result that the β' value derived here is very close to the one obtained above from the analysis of the friction coefficient data for the poly-n-butyl methacrylate+diethyl phthalate system. Although the definite conclusion must be reserved, it appears that to a first approximation the parameter $\beta'(T)$ is characteristic of the diluent

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4) W. C. Child, Jr. and J. D. Ferry, *J. Colloid Sci.*, **12**, 327 (1957).

5) M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

6) F. Bueche, *J. Applied Phys.*, **26**, 738 (1955).

7) H. Fujita and A. Kishimoto, *J. Colloid Sci.*, **13**, 418 (1958).

species, when camparison is made at T_g of respective polymers.

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