

Free Volume and Ionic dc Conductivity in Polymers

The free volume V_f of a given molecule is defined by the volume within its cage less the volume of the molecule. The average free volume per molecule, V_f , can be written as¹

$$V_f = V - V_0$$

where V is the average volume per molecule in the liquid and V_0 is the van der Waals volume of the molecule.

Electrical conduction in polymers depends upon the mobility of electrons, holes, and ions. Frenkel² stressed on the important role of free volume in molecular transport. In a previous paper an attempt was made to correlate the conductivity of polymers with temperature by using the free volume concept,³ in which Doolittle's equation⁴ was used:

$$V_f = V_g [0.025 + \alpha(T - T_g)] \quad (1)$$

where V_g is the volume at the glass transition temperature and α is the difference between the thermal expansion coefficient of the liquids and the glass.

In this paper an attempt has been made to correlate the dc conductivity σ in polymers with the free volume by using the concept of fluidity ϕ . Fluidity is correlated with free volume by Batschinski⁵ in this way:

$$\phi = A \exp(-b V_0/V_f) \quad (2)$$

where b is a constant.

The diffusion coefficient D , related to free volume by Cohen and Turnbull,¹ based on the fluidity relation, is

$$D = ga^+U \exp(-\gamma V^+/V_f) \quad (3)$$

where a^+ is approximately equal to molecular diameter, u is $(3kt)^{1/2}/m$, γ is a constant, and g is a geometric factor. T is the temperature ($^{\circ}\text{K}$), m is the mass of the molecule, and k is Boltzmann's constant. Killis et al.⁶ have defined the conductivity by the relation

$$\sigma = (D/RT) cq^2 \quad (4)$$

where c , q , R , and T are defined there. Since ionic conductivity depends on the diffusion of ions, which, in turn, depends on the free volume. So the expression for ionic conductivity can be written as

$$\sigma = (ga^+u/RT) cq^2 \exp(-\gamma V^+/V_f) \quad (5)$$

If $(ga^+u/RT) cq^2$ is assumed a constant, B then eq. (5) can be written as

$$\sigma = B \exp(-\gamma V^+/V_f) \quad (6)$$

where V is a constant and V^+ is of the order of $10V^1$. Now, if V_f/V^+ is proportional to the fractional free volume (FFV), eq. (6) may be written as

$$\sigma = B \exp(-\gamma^*/\text{FFV}) \quad (7)$$

γ^* is a new constant.

For testing the validity of this correlation [eq. (7)], a large number of conductivity data at 25°C of different polymers are plotted with $1/\text{fractional free volume}$ in Figures 1 and in 2, which gives a very good fit.

In Figure 1, the fractional free volume at T_R , which is the reference temperature, is defined in a previous paper,⁷ and in Figure 2 the fractional free volume of polymers at T_g is plotted.

Using regression analysis, equations for the variation of $\log \sigma$ with fractional free volume at T_R and at T_g for Figures 1 and 2 can be written as follows:

For $[\text{FFV}]_{T_R}$

$$\log \sigma = -12.18 - 0.55/[\text{FFV}]_{T_R} \quad (8)$$

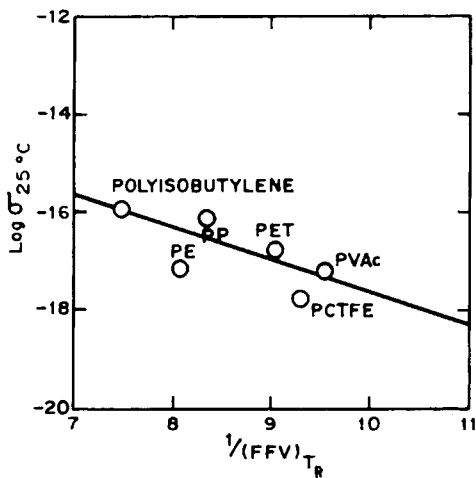


Fig. 1. The $\log \sigma$ variation with $1/[FFV]_{T_g}$ for PE (polyethylene), PET (poly(ethylene terephthalate)), PCTFE [poly(chlorotrifluoroethylene)], PVAc [poly(vinyl acetate)], PP (polypropylene) data from Refs. 3 and 7.

and for $[FFV]_{T_g}$

$$\log \sigma = -17.02 - 0.02/[FFV]_{T_g} \tag{9}$$

This free volume dc conductivity correlation can be used for determining the dc conductivity of polymer with the fractional free volume. Also the fractional free volume can be estimated in a similar fashion.

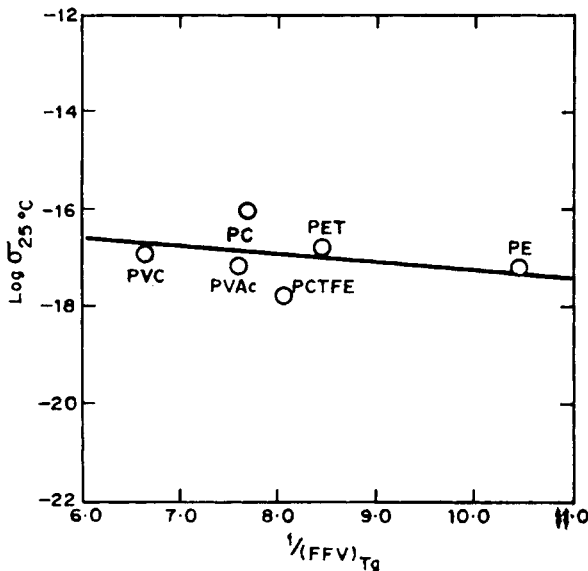


Fig. 2. The $\log \sigma$ plot with $1/[FFV]_{T_g}$ for polymers. Abbreviations are same as above except PC (polycarbonate) data from Refs. 3 and 7.

References

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