

dually. A series of such plates is presented in *Figure 2*.

It is important to note that the residual ultimate strength of the polyesters after the water-boil treatment increased with the bromine content – consistent with the inhibition of craze formation².

We do not have, as yet, a sufficient explanation of the craze-preventive action by the bromine. It is impossible that the bulkiness of the bromine atom results in increasing the free volume of the polyester. Thus, penetration of more water molecules is allowed before the swelling stresses

which gradually build up match the yield stress of the polymer and cause crazing.

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Glass transition temperatures and molecular weight*

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(Received 12 March 1979)

In a recent paper, it was shown that the dependence of the glass transition temperature, T_g , on the molecular weight, M , was given by an equation of the form (1)

$$T_g = T_{g,\infty} - \frac{A}{M+B} \quad (1)$$

where $T_{g,\infty}$ is the limiting glass transition temperature of the polymer of infinite molecular weight and A and B are parameters whose values depend on the chemical structure of the polymer. It was demonstrated that this expression was applicable to several liquids over wide ranges of molecular weight, including the low molecular weight region, using a single value for each of the parameters A and B .

Since the publication of ref 1, it was found that earlier work by both Fox and Loshaek² and by Kanig³ also led to an equation of the same form as equation (1). We should now like to discuss these two approaches in turn and point out that although the equations are of the same form, the assumptions used in the derivations are incorrect since they lead to physically impossible situations.

The equation of Fox and Loshaek can be expressed as:

$$T_g = T_{g,\infty} \frac{\alpha_\infty - C - \frac{(m+m_e)\Delta v_0}{T_{g,\infty}M}}{\alpha_\infty - C + \frac{(m+m_e)\Delta\alpha}{M}} \quad (2)$$

where α_∞ is the slope of the volume-temperature response for a polymer with infinite molecular weight, C is a constant for a given polymer, m and m_e are the molecular weights of the repeating unit and the two chain ends, respectively, Δv_0 is defined as $v_0(1) - v_0(\infty)$ where $v_0(1)$ and $v_0(\infty)$ are

the specific volumes of the liquid having one monomer unit and an infinite number of monomer units at $T = 0$, respectively and $\Delta\alpha = \alpha_1 = \alpha_\infty$ where α_1 is the slope of the V, T response for the liquid containing one monomer unit.

Simple manipulation of equation (2) leads to

$$T_g = T_{g,\infty} - \frac{A}{M+B}$$

which is identical to equation (1). Here, A has the value

$$A = \left(\frac{m+m_e}{\alpha_\infty - C} \right) \left(\Delta v_0 + \Delta\alpha T_{g,\infty} \right) \quad (3)$$

and B can be expressed as

$$B = \frac{m+m_e}{\alpha_\infty - C} \Delta\alpha \quad (4)$$

Using these results the ratio A/B becomes

$$\frac{A}{B} = \frac{\Delta v_0}{\Delta\alpha} + T_{g,\infty} \quad (5)$$

Thus, by examining the ratio rather than the individual values themselves it is possible to eliminate the parameter B whose value is generally unknown. This last expression can be rearranged to yield:

$$\frac{\Delta v_0}{\Delta\alpha} = \frac{A}{B} - T_{g,\infty} \quad (6)$$

The fit of equation (1) to the experimental T_g, M data for several series of liquids permit one to obtain values of A , B and $T_{g,\infty}$ and thus from these values the ratio $\Delta v_0/\Delta\alpha$ can be calculated. The requisite data are given in *Table 1* which is obtained from ref 1. From the values of $A/B - T_{g,\infty}$ listed

* This paper represents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration

Table 1 Values of $T_{g,\infty}$, A and B for various liquids

Liquid	$T_{g,\infty}$ (K)	A (kg/mol)	B (g/mol)	$A/B - T_{g,\infty}$	m_e (g/mol)
Poly(dimethyl siloxane)	149	7580	42.8	+28.1	23
n-Alkanes	184	30 200	195	-29.1	-31
Polypropylene	270	49 800	267	-83.5	-83
Poly(vinyl chloride)	351	85 800	382	-126	-138
Polystyrene	373	100 000	378	-109	-110
Poly(methyl methacrylate)	387	270 000	2880	-293	-2180
Polycarbonate	436	259 000	1270	-232	-676
Poly(α -methystyrene)	446	448 000	2400	-259	-1400

in the Table it may be seen that with the sole exception of the siloxane liquids these values are negative, i.e. $\Delta v_0/\Delta\alpha < 0$.

We now enquire whether this result is reasonable.

The full form of this ratio may be expressed as:

$$\frac{\Delta v_0}{\Delta\alpha} = \frac{v_0(1) - v_0(\infty)}{\alpha_1 - \alpha_\infty} \quad (7)$$

From direct measurement, it is found that α invariably decreases as the molecular weight increases², and hence $\alpha_1 - \alpha_\infty > 0$ always. By the same token, the specific volume of a liquid at a given temperature invariably decreases as the molecular weight increases² and hence $v(1) - v(\infty) > 0$ always. This is true at any temperature in the liquid range and since there is no reason to suppose that the V, T response for members of a family of liquids interset, then $v(1) - v(\infty) > 0$ for the hypothetical liquid at $T = 0$ and thus we have $v_0(1) - v_0(\infty) > 0$. Since both numerator and denominator of equation (7) are positive the ratio will also be positive.

It has been shown that the right hand side of equation (7) is greater than zero while the data in Table 1 show that the left hand side of the equation is less than zero. This is an impossible situation and hence the values of A and B cannot have the physical significance that the Fox and Loshaek treatment would attribute to them.

Using an entirely different approach, Kanig³ derived a relationship between T_g and the degree of polymerization, P , which was originally cast as

$$\frac{1}{T_g} = \frac{a}{P} + b \quad (8)$$

where a and b are parameters with the units moles of monomer per mole of polymer chain and reciprocal absolute temperature, respectively, and whose precise meanings are of no

concern here. This expression can be readily transformed into:

$$T_g = T_{g,\infty} - \frac{A}{M + B}$$

where now A is given by:

$$A = maT_{g,\infty}^2$$

and

$$B = maT_{g,\infty} - m_e$$

Hence, the relationship can be derived that m_e , the molecular weight of the end-groups, is given by:

$$m_e = \frac{A}{T_{g,\infty}} - B \quad (9)$$

which contains only quantities whose values have already been estimated from the fit of equation (1) to the experimental data. The final column in Table 1 contains the values of m_e calculated according to equation (9). With the exception of the siloxane fluids, the required m_e values aside from their inappropriate magnitudes are all negative which again is a physically impossible situation. It can easily be shown, in common with the Fox and Loshaek treatment that a positive value of m_e will lead to values of the quantity $A/B - T_{g,\infty} > 0$.

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The generality of the plastic fracture process

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(Received 10 July, 1979)

In uniaxial tension, the post-yield fracture of several glassy polymers is known to be initiated from 'diamond shaped' cavities which grow from defects in the drawn material. Previously the materials examined were PVC^{1,2}, nylon fibres³, and at elevated temperatures poly(ether sulphone)⁴,

polycarbonate⁴, PMMA⁴ and polystyrene⁵. It is now known that poly(ether sulphone)⁶ and polycarbonate produce diamonds at room temperature. Also several other polymers can be added to this list. Figure 1 shows diamonds in five polymers drawn at 25°C. The polymers in question are