

Chapter 7. The Glassy State and Glass Transition

- The origin of glass transition

The behaviour of amorphous polymers at low temperatures corresponds with the glassy state described in Chapter 9. Because the system contracts on cooling the free volume becomes insufficient for long range correlations between the small movements which the individual chain segments can make. Thus the diffusional displacements of whole sections of chains are completely suppressed and the polymeric character of the molecules is no longer apparent.

1. Motion of small molecules; free volume and thermal expansion

Consider a model of a liquid that consists of n rather small molecules contained in volume V . Each of these molecules will occupy a volume $v = V/n$ at some temperature T . This volume per molecule will consist partly of free space, since the molecules will be vibrating about their equilibrium position and will consequently exclude other molecules from taking up positions too close to them. In addition, there is the possibility that, under their random thermal motion, some of the molecules may pull apart in such a way as to open a void or hole in the liquid.

An average amount of free volume $v_f (= V_f/n)$ may be assigned to each of the n molecules. As a crude model, assume that each piece of free volume comes in a spherical shape of radius b and that the energy of the free volume is just a surface-tension energy $4\pi\epsilon b^2$. To a first approximation, ϵ may be con-

sidered the surface energy per unit area; numerically it would then equal the surface tension of the liquid.

According to the Boltzmann distribution law, the chance that a particular molecule will have associated with it a hole of radius b will be proportional to $\exp(-4\pi\epsilon b^2/kT)$. The average size of a hole in the liquid will therefore be obtained from the following expression:

$$v_f = \frac{\int_{b=0}^{\infty} (\frac{4}{3})\pi b^3 \exp(-4\pi\epsilon b^2/kT) db}{\int_0^{\infty} \exp(-4\pi\epsilon b^2/kT) db} \quad (4.1)$$

After the indicated operations are performed,

$$v_f = (1/6\pi)(kT/\epsilon)^{1.5} \quad (4.2)$$

This leads to the following expression for the volume of a liquid that has volume V_0 at $T = 0$:

$$\begin{aligned} V &= V_0 + V_f \\ &= V_0 + (n/6\pi)(k/\epsilon)^{1.5} T^{1.5} \end{aligned} \quad (4.3)$$

Since the volume coefficient of expansion of a liquid (α) is by definition $(1/V_0)(dV/dT)$,

$$\alpha \cong (n/4\pi)(k/\epsilon)^{1.5} T^{0.5} \quad (4.4)$$

where V_0 has been taken as unity, and variation of n with temperature has been neglected. Since the value α is usually regarded as essentially independent of T , Eq. (4.4) may seem in error because of the factor $T^{0.5}$; however, the value of α actually does increase with T for most liquids. In fact, the expansion of straight-chain paraffin hydrocarbons, to mention one instance, is far better represented by an α varying as in Eq. (4.4) than by a constant α . In addition, the numerical value given for α by Eq. (4.4) is not unreasonable.

2. Motion of small molecules: Jump frequency at large T

A molecule will be able to jump to a new equilibrium position provided: (1) there is enough free volume available to make such a jump possible; (2) the molecule has enough energy to break loose from its neighbors and move into the hole; and (3) the molecule is moving in the proper direction at just the right time to enter the hole. Of these three factors, only the first will be highly temperature-sensitive. Free volume can only be obtained by opening a void in the liquid. This will require considerable thermal energy to be localized in a small region of the liquid if the hole is to be of molecular dimensions.

The energy needed for the molecule to break loose from its neighbors and move into the hole will usually be only a small fraction of the energy needed to produce the hole; consequently, this factor should be a much less critical function of the temperature than is the first. Similarly, a molecule will ordinarily be vibrating in its equilibrium cell with such a high frequency that, if the first condition is satisfied and a hole is present, the molecule

will eventually vibrate in the proper direction for entering the hole. Therefore, one may approximate the true situation by stating that the probability that a molecule will jump to a new equilibrium position is equal to a constant multiplied by the probability that a large hole is adjacent to the molecule. If the hole must have a volume v^* or larger if a molecule is to jump into it, the fraction of the total number (n) of holes having volumes larger than v^* must be found. Since the probability of finding a hole of radius b is proportional to $\exp(-4\pi\epsilon b^2/kT)$, the following expression results for the number of holes larger than v^* (assuming each hole to be independent):

$$\frac{n \int_{b^*}^{\infty} \exp(-4\pi\epsilon b^2/kT) db}{\int_0^{\infty} \exp(-4\pi\epsilon b^2/kT) db} \quad (4.5)$$

This expression may be integrated in terms of the error function. Then, if the critical energy defined by

$$\epsilon^* = 4\pi\epsilon b^{*2}$$

is much greater than kT , as it ordinarily will be, Eq. (4.5) yields

$$n(\pi\epsilon^*/kT)^{1/2} \exp(-\epsilon^*/kT) \quad (4.6)$$

The jump frequency ϕ will be proportional to the quantity given by expression (4.6) and will also be proportional to the time required for the local liquid structure about a molecule to change its energy appreciably. This time will ordinarily be much shorter than the time between jumps, since it will depend primarily on the vibrational collisions of adjacent molecules. For this reason, it should not be highly temperature-sensitive. In addition, the jump frequency should depend upon various geometrical factors mentioned previously; hence,

$$\phi = \phi_0 \exp(-\epsilon^*/kT) \quad (4.7)$$

where the quantity ϕ_0 defined by Eq. (4.7) is far less temperature-sensitive than the exponential.

An order of magnitude for ϕ_0 can be obtained by noting that if the temperature is very high the exponential factor in Eq. (4.7) becomes unity, and thus ϕ_0 is equal to ϕ . In this limit, there should be a very large number of holes present; accordingly, the jump frequency ϕ should be very close to the reciprocal of the time necessary for the molecule to cross its cell. This value will be of the order of the vibration frequency of the molecule, which will be in the range 10^{12} to 10^{14} . Since ϕ is always much smaller than this, as will be shown later, it is clear that $\epsilon^* \gg kT$ at ordinary temperatures.

Equation (4.7) may be substituted in Eq. (3.3) to give the diffusion constant:

$$D = (\phi_0 \delta^2 / 6) \exp(-\epsilon^*/kT)$$

3. Motion of polymer molecule segments at large T

Substitution of Eq. (4.7) in Eq. (3.8) yields the following expression for the segmental friction factor f_0 :

$$f_0 = (6kT/\phi_0\delta^2) \exp(\epsilon^*/kT) \quad (4.9)$$

This value can then be used in Eq. (3.11) to obtain the diffusion constant of a polymer molecule:

$$D = (\phi_0\delta^2/6N^*) \exp(-\epsilon^*/kT) \quad (4.10)$$

Again it may be seen that an Arrhenius plot can be used to find ϵ^* , provided Eq. (4.10) is valid. Later in this chapter it will be seen that Eq. (4.10) is often a poor approximation for polymers unless ϵ^* is allowed to vary. The reasons for this are related to the fact that the various pieces of free volume, that is, the holes, were assumed to act independently of each other when Eq. (4.5) was derived.

Similarly, Eq. (4.9) can be substituted into Eq. (3.16) to obtain an expression for the viscosity of polymers:

$$\eta = (\rho NkT/6\phi_0\delta^2)(R^2/M)N^* \exp(\epsilon^*/kT) \quad (4.11)$$

This equation predicts that an Arrhenius plot of $\ln(\eta/T)$ vs. $(1/T)$ should give a straight line with slope ϵ^*/k . As in the case of Eq. (4.10), experimental data for polymers show Eq. (4.11) to be applicable only if ϵ^* is allowed to vary with temperature.

Typical Arrhenius plots for two polymers at various plasticizer contents are shown in Figures 18 and 19. The apparent value of ϵ^* at any temperature can be found from the slope of the curve at that temperature. Obviously, the slope and therefore ϵ^* increases as the temperature or the plasticizer content is lowered. At very high temperatures or with large plasticizer contents, the value of ϵ^* is close to 15 Kcal/mole for most polymers. The value of ϵ^* becomes very large at temperatures near the glass temperature, and values in excess of 200 Kcal/mole have been reported (38,48). Figure 20 shows the values for pure poly-methyl methacrylate at various temperatures.

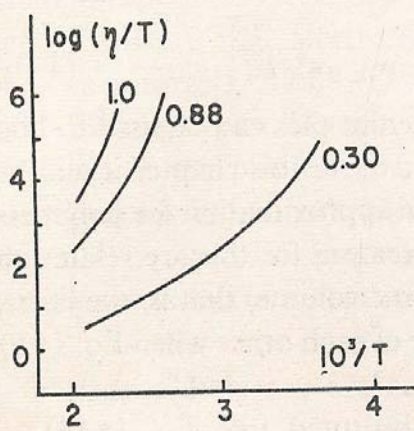


Figure 18. The viscosity of polystyrene-dibenzyl ether solutions as a function of temperature at the weight fraction of polymer shown on the curves (42).

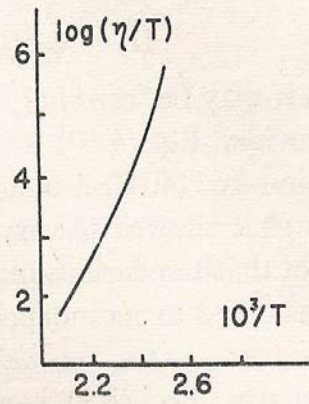


Figure 19. The viscosity of a polyisobutylene of 134,000 molecular weight as a function of temperature (47).

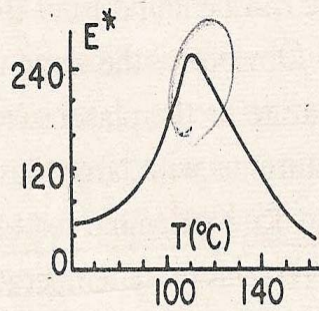


Figure 20. Variation of ϵ^* (Kcal/mole) as a function of temperature for polymethyl methacrylate (38).

4. Segmental motion near the glass temperature

There is good reason to believe that the energy term will not vary too much with the mode of arrangement of the N holes provided that N , and hence V_f , is held constant. This proceeds from the following considerations. The surface energy per unit volume of a hole, the energy density of a hole, will be $4\pi a^2\epsilon/(\frac{4}{3}\pi a^3)$, or $3\epsilon/a$; thus it is evident that small holes have a higher energy density than large holes. However, it was indicated above that small holes have a greater tendency to share surfaces than do large holes, an effect that would lower the energy density for small holes. It is hoped that these and other similar effects will cancel each other, thereby resulting in the same energy density for all size combinations of the N holes. This assumption is actually made in the present approach to the problem; consequently, the energy term in the free energy is ignored.

For the present it will be assumed that the free volume V_f

consists of n packets, one for each molecule or segment. The correct treatment (51) does not assume these packets to be of equal size. For simplicity, however, it will be assumed here that each packet has the same size (v_f); consequently, $V_f = nv_f$.

The chance that a particular molecule (or segment, in the case of polymer chains) will have q packets associated with it is

$$p(q) = [1 - (1/n)]^{n-q} (1/n)^q \{n!/q!(n-q)!\} \quad (4.12)$$

This expression is derived through the following reasoning. Consider n boxes into which one throws n balls at random. The chance that a given ball will go into a given box is $1/n$, while the chance that it will not go into this box is $1 - (1/n)$. Hence, the chance that a particular box will contain q balls is the product of the chance that q balls will go into the box, or $(1/n)^q$, and the chance that $(n - q)$ balls will not go into the box, or $[1 - (1/n)]^{n-q}$. But this only accounts for one way of obtaining q of the n balls in one box. There are $n!/(n - q)q!$ ways of permuting n objects of which q are the same; therefore, the factor containing the factorials also enters into Eq. (4.12).

Since n will be a very large number that will be considered to be much larger than q ,

$$[1 - (1/n)]^{n-q} \cong e^{-1} \quad (4.13)$$

Also,

$$\begin{aligned} n!/q!(n-q)! &= (n)(n-1) \cdots (n-q+1)/q! \\ &\cong n^q/q! \end{aligned} \quad (4.14)$$

Hence,

$$p(q) \cong e^{-1}(1/q!) \quad (4.15)$$

If q is not too small (and it will be seen later that it is of order 40 or larger), by Sterling's approximation for the factorial,

$$p(q) \cong (1/2\pi q)^{1/2} \exp[-q(\ln q - 1) - 1] \quad (4.16)$$

But since $q = v'_f/v_f$, where v'_f is the actual amount of free volume associated with the molecule, one has the following for the probability that a molecule has a free volume v'_f associated with it:

$$p(v'_f) = (v_f/2\pi v'_f)^{1/2} \exp[-\beta v'_f/v_f] \quad (4.17)$$

where $\beta = (\ln q - 1)$ and unity has been neglected in comparison to q .

For a molecule or segment to jump to a new position, more than a critical amount of free volume (v^*) must be associated with it. Therefore, the probability that a molecule can jump to a new position will be proportional to the integral of $p(v'_f)$ over $v^* < v'_f < \infty$. As will be seen later, v'_f/v_f is much larger than unity in this range; and since β is a slowly varying function of v'_f , as is the term in front of the exponential,

$$\int p(v'_f) dv'_f \cong (\text{constant}) \exp[-\beta^* v^*/v_f] \quad (4.18)$$

Proceeding as in Sec. 4 of this chapter, one has the following value for the jump frequency of the segment or molecule:

$$\phi = \phi_0 \exp[-\beta^* v^*/v_f] \quad (4.19)$$

where

$$\beta^* \equiv \ln(v^*/v_f) - 1$$

It should be noticed that β^* will not be too far from unity for reasonable values of the ratio v^*/v_f . Since v^* itself is not well known, the quantity β^* may for many purposes be considered

as unity.

A more exact treatment which does not assume uniform size of the free-volume packets but which neglects surface-energy effects has been carried through by Cohen and Turnbull (51). Their result is essentially the same as Eq. (4.18), but with a somewhat different value for β^* . Therefore Eq. (4.19) may be used with confidence, provided that β^* is considered to be a constant approximately equal to unity.

Equation (4.19) can be substituted in Eq. (3.3) to obtain the diffusion constant for small molecules, with the result that

$$D = (\phi_0 \delta^2 / 6) \exp(-\beta^* v^* / v_f) \quad (\text{small molecules}) \quad (4.20)$$

This equation has been tested for various small-molecule liquids and found to give reasonable results even at low temperatures.

Similarly, Eq. (4.19) can be used in Eqs. (3.8), (3.11), and (3.16) to give the following expressions applicable to polymer molecules:

$$\left. \begin{aligned} f_0 &= (6kT / \phi_0 \delta^2) \exp(\beta^* v^* / v_f) & (4.21) \\ D &= (\phi_0 \delta^2 / 6N^*) \exp(-\beta^* v^* / v_f) & (4.22) \\ \eta &= (\rho N k T / 6 \phi_0 \delta^2) (R^2 / M) N^* \exp(\beta^* v^* / v_f) & (4.23) \end{aligned} \right\} (\text{polymers})$$

In these equations, the quantities ϕ_0 , δ , v^* , and v_f refer to polymer segments, not to the molecule as a whole, of course. A discussion of the applicability of these equations to actual experimental results will be deferred until after a consideration of the glass temperature.

5. WLF equation

Consider first Eq. (4.23) for the viscosity of a polymeric liquid. All the factors except the quantity $(T / \phi_0) \exp(\beta^* v^* / v_f)$ are essentially independent of temperature. Even the factor T / ϕ_0 will be relatively constant in comparison to the large changes usually observed for viscosity as a function of temperature. Consequently, for a given polymer system and to a good approximation,

$$\eta = B \exp(\beta^* v^* / v_f) \quad (4.24)$$

Equation (4.24) has been known for some time to be an exceptionally good representation for the viscosity of molten paraffins as well as many other liquids (56,57). It is often called the “Doolittle equation,” since it was Doolittle who first proposed it as an empirical representation. Of course, its use depends upon the proper choice of free volume v_f , which will now be investigated.

Consider the viscosities of a liquid at two different temperatures, T_1 and T_2 . From Eq. (4.24),

$$\eta_1/\eta_2 = \exp [(\beta^*v^*/v_{f1}) - (\beta^*v^*/v_{f2})] \quad (4.25)$$

Or after taking logarithms of each side,

$$\ln (\eta_1/\eta_2) = (\beta^*v^*) [(1/v_{f1}) - (1/v_{f2})] \quad (4.26)$$

If a molecule or chain segment has a total volume v_1 associated with it at T_1 , it is reasonable to define the free volume at T_2 by the following relation (53):

$$v_{f2} = v_{f1} + \alpha v_1(T_2 - T_1) \quad (4.27)$$

where α is the expansion coefficient for the gross liquid minus

the expansion coefficient for the glass; that is, $\alpha = \alpha_l - \alpha_g$. This merely says that the free volume increase as the temperature is raised from T_1 to T_2 is equal to the thermal expansion in excess of the van der Waals' expansion of the glass. Hence it is assumed that the free volume effective in promoting molecular motion is only that portion which is in large enough packets so that it does not equilibrate readily at low temperatures. The reason for taking α as being $\alpha_l - \alpha_g$ rather than α_l will become apparent when the results for the variation of glass temperature with molecular weight are discussed in the next chapter.

In any event, if Eq. (4.27) is substituted into Eq. (4.26), one has after some rearrangement,

$$\ln (\eta_1/\eta_2) = (\beta^*v^*/v_{f1})(T_2 - T_1)/[(v_{f1}/v_1\alpha) + (T_2 - T_1)] \quad (4.28)$$

This relation is very interesting because it is of the same form as a semiempirical relation proposed by Williams, Landel, and

Ferry (the so-called “WLF equation”) to explain the temperature dependence of viscosity and other rate processes in glass-forming liquids (49). They found that, if T_1 is taken to be the glass temperature of the material, then Eq. (4.28) agrees with experiment in the temperature range $T_g < T < T_g + 120$, provided that

$$(\beta^*v^*/v_{f1}) = 40 \quad \text{and} \quad (v_{f1}/v_1\alpha) = 52 \quad (4.29)$$

One therefore has the following equation, denoted the WLF equation,

$$\ln(\eta_0/\eta) = 40(T - T_g)/[52 + (T - T_g)] \quad (4.30)$$

where η_0 is the viscosity at the glass temperature. This equation has been tested against data for many noncrystalline polymers, as well as for other glass-forming liquids. Typical of these are silicates, boron trioxide, *n*-propanol, glycerol, and many others (49). They all appear to obey Eq. (4.30) very well within the range $T_g < T < T_g + 120$; therefore it may be concluded that the molecular ideas leading to Eq. (4.28) are probably valid.

It is interesting to examine the meaning of the relation in Eq. (4.29). If one takes $\beta^* = 1$, then $v_{f0} = v^*/40$; or, approximately 40 times as much free volume is needed for a segment or molecule to jump as is found on the average for each segment at the glass temperature. Hence, great aggregation of free volume must occur at low temperatures if a segment or molecule is to be able to move. Also, from Eq. (4.29), $v_{f0} = (52)(v_g\alpha)$. Since $\alpha = \alpha_l - \alpha_g$ is about 5×10^{-4} per °C in the case of most liquids, $v_{f0} = v_g/40$. In other words, about $1/40$ of the volume at the glass temperature is free volume. It should also be noticed that since v_{f0} was shown above to be about $v^*/40$, it appears that the hole needed for a molecule or segment to jump must be about equal to the size of the molecule or segment itself. This observation is entirely reasonable, of course.

Although Eq. (4.30) is nearly universal for glass-forming liquids, discrepancies do arise. First, the equation begins to depart from experiment if the temperature is raised too far above T_g . Each liquid behaves somewhat differently at these high

temperatures. Such deviations are not unexpected, since the relations of Eq. (4.29) cannot be expected to be completely temperature-insensitive. It is well known that the expansion coefficient of a liquid will vary with temperature; accordingly, α —and hence the quantity 52—will change at high temperatures. Also, there is no absolute assurance that β^*v^* will be rigidly constant as a function of temperature. In addition, the quantity preceding the exponential in Eq. (4.24) is certainly not fully constant as assumed.

There are also indications that some materials would agree better with Eq. (4.29) if slightly different constants were used. This modification is not completely unreasonable from a theoretical standpoint; however, the difficulty of making measurements at temperatures near T_g still leaves much doubt as to whether or not these constants should change somewhat. Since a 10° temperature change near T_g can cause the viscosity to change by a factor of several hundred, experimental difficulties become quite influential near T_g . Also, as will be seen later, small amounts of impurity greatly influence the exact value

measured for T_g .

Since measurements near T_g are difficult to make, Williams, Landel, and Ferry suggest that a different reference temperature be taken (49). They take as reference a temperature T_s that is roughly 50°C above T_g . In terms of this new reference temperature Eq. (4.30) becomes

$$\ln(\eta_s/\eta) = (20.4)(T - T_s)/[102 + (T - T_s)] \quad (4.31)$$

They further suggest that T_s be obtained empirically by fitting the equation to the experimental data. However, if T_g is known, it would appear that the relation $T_s = T_g + 50$ will be accurate enough for most purposes.

Before concluding this section, it should be pointed out that Eq. (4.26) has been tested for several monomeric liquids that are not ordinarily regarded as glass-forming systems (51). Molten metals, for example, are found to conform reasonably well with Eq. (4.26). In addition, a simple extension of Eq. (4.26) can be used to predict accurately the variation of molecular motion as

6. Chemical structure and T_g

The presence of highly polar groups along the polymer chains has the effect of increasing the intermolecular forces which pull the chains closer together. This reduces the free volume. Polar polymers therefore have relatively high glass temperatures. However, a more important factor is the steric effect of the chain substituent groups. Stiff and bulky side groups, which inhibit the free rotation of the chain segments, increase T_g , whereas flexible side groups, which serve to hold the chains apart, free their motions and decrease T_g . The interplay of these two factors can best be illustrated by a study of the data in Table 10.1. These have been collected from the work of Wiley and his colleagues, who used the refractometric method of determining T_g , so that the values in the table represent a strictly comparable series. This list of glass temperatures is by no means exhaustive, but it suffices to illustrate the effects of the size and polarity of the main types of side groups on the transition temperatures.

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TABLE 10.1
Glass temperatures of various polymers

Polymer	T_g °C	Ref.
Polybutadiene	-85	22
Polyisobutene	-77	22
Natural rubber	-75	22
Neoprene	-50	22
GR-S (78% butadiene, 22% styrene)	-67	22
Copolymers of butadiene with acrylonitrile (T_g varies linearly with % acrylonitrile from 0% acrylonitrile to 52% acrylonitrile)	-85 -16	23 23
Polystyrene	75*	25
Polyvinyl acetate	29	24
Polymethyl acrylate	0	25
Polyethyl acrylate	-23	25
Poly-n-propyl acrylate	-51	25
Poly-n-butyl acrylate	-63	22
Polycetyl acrylate	35 (m.p.)	25
Polymethyl methacrylate	72	25
Polyethyl methacrylate	47	25
Poly-n-propyl methacrylate	33	25
Poly-n-butyl methacrylate	17	25

* 100°C is a more frequently accepted value for polystyrene of high molecular weight.

At the top of Table 10.1 is a group of elastomers which have very low glass temperatures. It is noticeable that, apart from neoprene, they are hydrocarbons which have very weak intermolecular forces. Polybutadiene, which has no side groups at all on the chains, has the lowest T_g , whereas polyisobutylene and natural rubber, both with methyl side groups, have slightly stiffer chains and transition temperatures approximately 10 degC higher than polybutadiene. In neoprene the methyl side groups of natural rubber are replaced by chlorine atoms. These are slightly larger than the methyl groups and have much stronger dipolar forces. It can be seen that they increase T_g by almost 25 degC.

Polystyrene is a hydrocarbon polymer with only weak van der Waals forces between the chains. Nevertheless the bulky nature of the side groups makes the rotation of the chains very difficult and polystyrene is a hard plastic with a glass transition at 100°C. The side groups in polyvinyl acetate have a similar arrangement and about the same molecular volume as the phenyls in polystyrene. They have however an internal flexibility and despite their extra polarity obstruct the rotation of the chain segments less than

(i) Tg of copolymer

In many cases a plot of T_g against composition by weight for a series of copolymers lies below the straight line joining the transition temperatures of the two homopolymers [32, 33, 34]. By assuming that each type of monomer unit retains its characteristic free volume in the copolymer above T_g and using the iso-free volume criterion for the glass transition, it is easy to derive [34].

$$\frac{1}{T_g} = \frac{1}{(w_1 + Bw_2)} \left[\frac{w_1}{T_{g_1}} + \frac{Bw_2}{T_{g_2}} \right] \quad (6)$$

Here w_1 and w_2 are the weight fractions of the two monomers, whose homopolymers have transitions at T_{g_1} and T_{g_2} , expressed in °K, and B is a constant for the pair of monomers. B is specified by the theory but is difficult to predict numerically; it is however never far from unity. The success of eq. (6) in describing the data is illustrated in Fig. 10.8. When B is exactly unity, eq. (6) reduces to the very simple, but non-linear form

$$1/T_g = w_1/T_{g_1} + w_2/T_{g_2} \quad (7)$$

The data for many pairs of vinyl monomers fit eq. (7) fairly well.

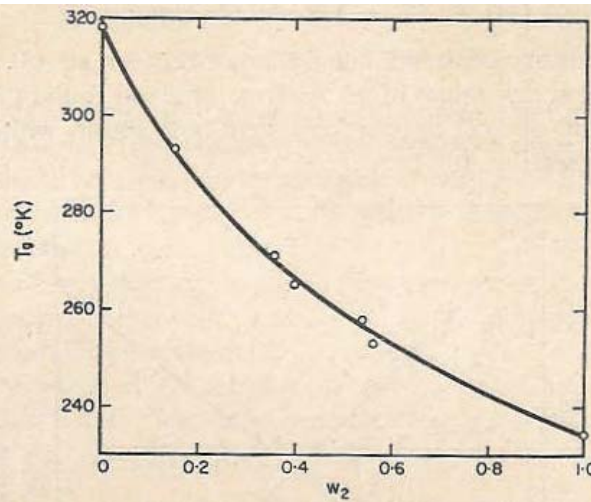


FIG. 10.8 Glass temperatures T_g of copolymers of polychlorotrifluoroethylene with polyvinylidene fluoride plotted against the weight fraction w_2 of the latter. The curve is the theoretical eq. (6) with $B = 1.75$ (see Wood [29]). (Data from L. Mandelkern, G. M. Martin and F. A. Quinn, *Journal of Research of the National Bureau of Standards* [34].)

(ii) Molecular weight and T_g

$$1/T_g = 1/T_g^\infty + A/M \quad (8)$$

where T_g^∞ is the glass temperature of polymer of infinite molecular weight. A is a positive constant, which was 0.515 in this case.

With the same definition of free volume as has been used in this book and with the assumption that all molecular weight fractions have an equal free volume at their glass temperatures, Fox and Flory [20, 43] have derived

$$T_g = T_g^\infty - K/M \quad (9)$$

where K is a positive constant. The deviation between eq. (8) and eq. (9) is noticeable only at low values of M . At large M it was found that plots of T_g against $1/M$ and of $1/T_g$ against $1/M$ were both linear, within the experimental errors, (see Fig. 10.9).

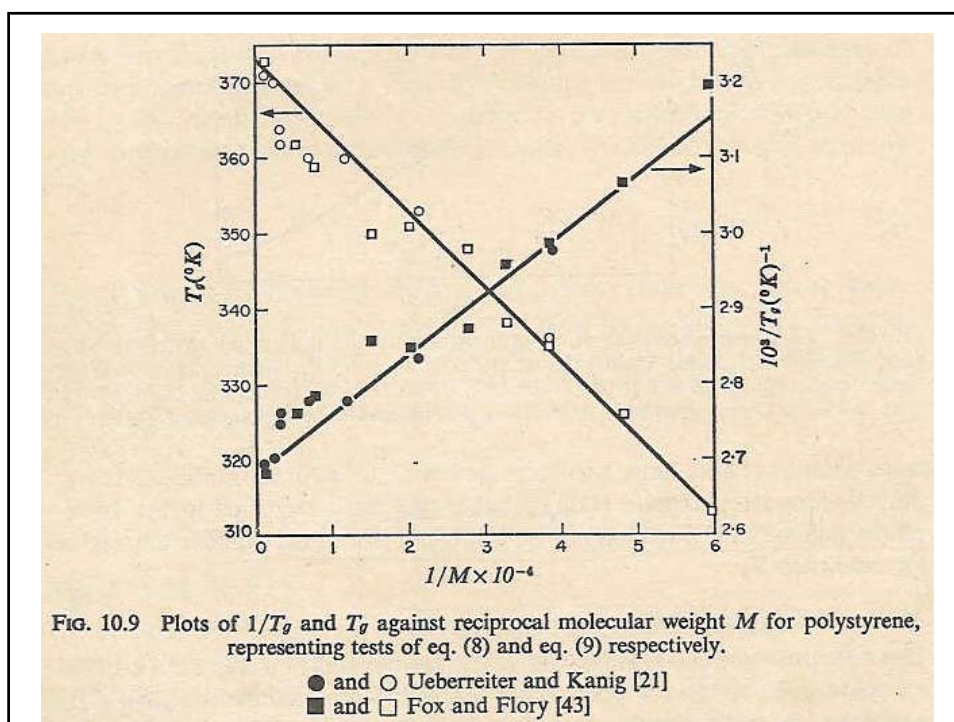


FIG. 10.9 Plots of $1/T_g$ and T_g against reciprocal molecular weight M for polystyrene, representing tests of eq. (8) and eq. (9) respectively.

● and ○ Ueberreiter and Kanig [21]
 ■ and □ Fox and Flory [43]

(iii) Branaching, crosslinking and T_g

The idea that chain ends introduce extra free volume also enables the effect of branching to be foreseen. Imagine two polymer molecules of molecular weights M_1 and M_2 . If they are coupled end-to-end they give a molecule of weight $(M_1 + M_2)$ with two chain ends, but if one molecule is T -joined to the other to form a branched molecule of weight $(M_1 + M_2)$ this has three chain ends. In general a linear molecule with $(\omega - 2)$ branches attached along its length has ω chain ends. If the total molecular weight is M , the glass temperature is given by a simple modification of eq. (9) [11]. This is

$$T_g = T_g^\infty - K\omega/2M \quad (10)$$

Thus branching lowers T_g below the value it would have for an unbranched polymer of the same molecular weight. It seems practicable to use measurements of T_g and M with eq. (10) to determine the degree of branching. In this connection it is noteworthy that it is the number average molecular weight which is appropriate in eqs. (9) and (10).

When a network polymer is prepared by using a small amount of divinyl comonomer two cases have to be distinguished. If the divinyl compound is very different in structure and molar volume from the main vinyl monomer, the product has to be regarded as a copolymer. If however the monomers are very similar the copolymer may be treated as a simple cross-linked polymer and the iso-free volume theory applied [44]. The result for fairly low degrees of cross-linking is

$$T_g = T_g^\infty - K/M + K_x \nu \quad (11)$$

where K_x is a constant for the particular polymer, ν is the number of cross-links per gram and M would be the molecular weight if all the cross-links were severed. This equation has been shown to fit the data for polystyrenes cross-linked with divinyl benzene [45] and for polymethyl methacrylate cross-linked with ethylene glycol dimethacrylate [46].

For very much higher degrees of cross-linking Ueberreiter and Kanig [45] have shown that T_g rises more rapidly than the cross-linking density and when there are only two chain units between each pair of cross-links the network is no longer capable of being thermally activated into the leathery state. It was also found, using plots of ν against T to locate T_g , that the width of the transition region (range of curved ν versus T) increased as the degree of

(iv) The effect of diluents on T_g

The effect of adding a low molecular weight substance to a polymer is to lower its glass temperature. This effect has been well known for a long time and is exploited in practice when relatively involatile diluents such as dibutyl phthalate or tricresyl phosphate are mixed as plasticizers with polyvinyl chloride to give flexible products.

By postulating that the free volumes of the separated polymer and diluent are additive in the mixture and that the free volume fraction has a critical value ϕ_g which is the same for the pure polymer, the diluent and their mixtures at their respective glass temperatures, it is a relatively straightforward matter to derive a relation between T_g and composition [48]. The latter is most conveniently expressed in terms of the volume fractions of polymer ν_p and diluent ν_d .

Referring back to eq. (1) it can be seen that the free volume ϕ_g associated with ν_p cm³ of polymer at the glass temperature T_g of the mixture of polymer

and diluent is

$$\phi_p = v_p[\phi_g + (\alpha_i - \alpha_g)(T_g - T_{gp})] \quad (13)$$

Similarly for v_d cm³ of the diluent the free volume ϕ_d is

$$\phi_d = v_d[\phi_g + \alpha_d(T_g - T_{gd})] \quad (14)$$

since for a simple liquid the whole of the thermal expansion may, to a first approximation, be regarded as contributing extra free volume. Thus for 1 cm³ of the mixture the free volume fraction at T_g , i.e. ϕ_g , is given by $(\phi_p + \phi_d)$. Hence adding eqs. (13) and (14) and rearranging gives

$$T_g = \frac{v_p T_{gp}(\alpha_i - \alpha_g) + v_d T_{gd} \alpha_d}{v_p(\alpha_i - \alpha_g) + v_d \alpha_d} \quad (15)$$

By setting $(\alpha_i - \alpha_g)$ equal to $4.8 \times 10^{-4} \text{ deg}^{-1}$ for all polymers [28], Kelley and Bueche [48] showed that eq. (15) gave an excellent representation of the variation of T_g with composition of the systems polystyrene + diethyl benzene and polymethyl methacrylate + diethyl phthalate (Fig. 10.10).

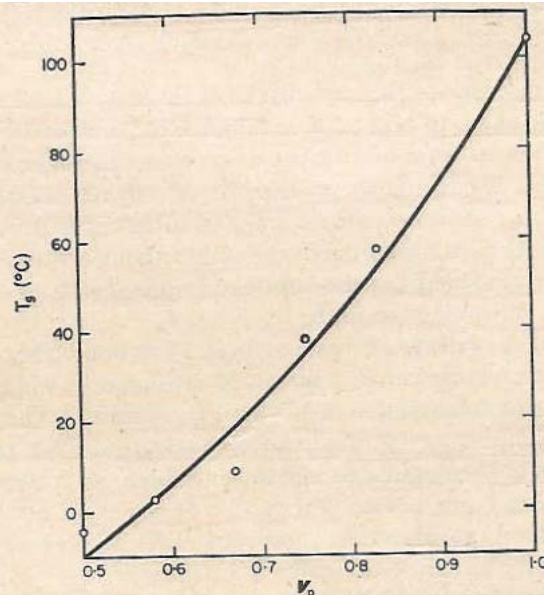


FIG. 10.10 Plot of glass temperature T_g against volume fraction of polymer v_p for mixtures of polymethyl methacrylate with diethyl phthalate. The curve represents eq. (15) with $\alpha_d = 10 \times 10^{-4}$ and $T_{gd} = -65^\circ\text{C}$ as estimated from viscosity measurements. (Data from F. N. Kelley and F. Bueche, *Journal of Polymer Science* [48].)