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The glass transition in linear polymers

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It is suggested that polymeric materials undergo the glass transition when the energy contained in the scissoring modes of vibration of the polymer backbone becomes comparable with the van der Waals forces restraining the end of a vibrating segment. As the temperature is raised the vibrating segments gradually increase in length, causing large changes in the macroscopic properties. It is shown that for certain polymers the glass transition temperature may be calculated from first principles. The glass transition temperature depends upon molecular weight and the change in specific heat at this temperature may be quite accurately calculated.

1. Introduction

Many polymers undergo a change of state called the glass transition when their temperature is raised sufficiently above the absolute zero and the transition is identified by substantial changes in the properties of the polymer. The phenomenology of the transition and an introduction to the previous theoretical approaches are described in two review articles by Shen and Eisenberg [1, 2].

In this paper, a mechanism is suggested which accounts for some of the qualitative characteristics of the glass transition, and which also enables one to estimate the numerical value of the glass transition temperature for a simple polymer.

2. The mechanism of the glass transition

Consider a cube of amorphous polymeric material, of mass 1 g. Let the polymer be linear and have two different types of carbon atom alternately along its backbone (the calculations could thus refer say to polyvinyl chloride but not to polyethylene or polydiancarbonate). Assume initially that all the polymer molecules have the same number of atoms, and that the cube is at some temperature remotely below the material's glass transition point.

If the geometrical arrangement of the individual polymer molecules in the cube was examined in detail, most of the carbon atoms would most certainly be found to be bound to neighbours by van der Waals forces. However, because of the amorphous nature of the material it seems clear that a number of chain segments would be found where constituent atoms are either unbound or only weakly bound to their neighbours. "Segment" in this context means a number of repeat units in the polymer backbone.

A schematic representation of an unbound segment is shown in Fig. 1. A number of carbon atoms in the chain are shown as being so arranged that they lie outside the potential wells of their neighbours. The terminal atoms A and B are bound and the segment is counted as being

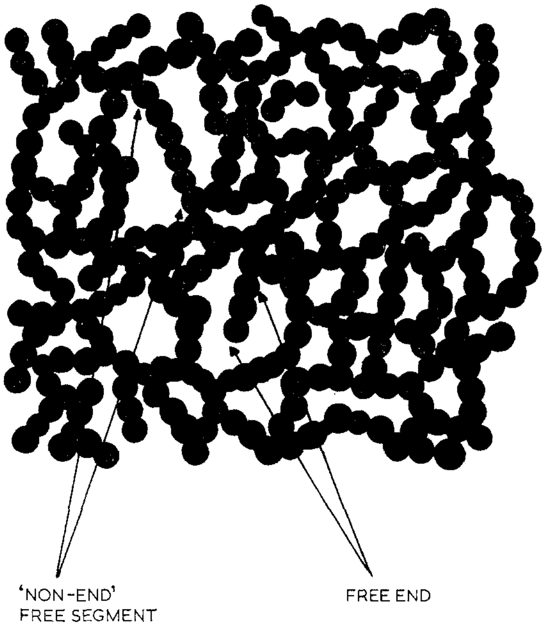


Figure 1 A section taken through a polymer sample showing in stylized form how a free segment might look.

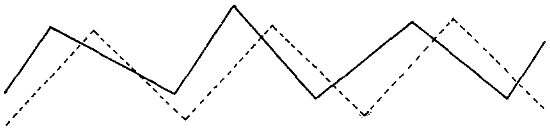


Figure 2 Illustration of the scissoring mode.

$N + 2$ atoms in length. This segment is able to take up certain longitudinal modes of vibration; one of these, the scissoring or "accordion" mode, is shown in Fig. 2. In both classical and quantum mechanics, the normal frequencies of vibration and, hence, the energy at a temperature TK can be calculated.

We suggest that if the temperature (and, therefore, the vibrational energy) becomes sufficiently large, then the van der Waals forces constraining an end atom, A, to remain near its neighbour, A′, will be insufficiently large to maintain the configuration. The vibrating segment will then increase its length. If the temperature is increased sufficiently, a time will come when the test cube consists wholly of vibrating segments, rather than containing only a few. Such a change will clearly be reflected in gross changes of the measurable physical properties of the bulk sample.

It is easy to determine that the vibrational energy for short segments at say 250K is a few times 10^{-14} erg. This is exactly the order of magnitude of the van der Waals forces holding the polymer chains together.

3. Calculation of vibrational energies

Consider a segment similar to that of Fig. 1. Let there be $2N$ free carbon atoms having alternately masses m_1 and m_2, with $m_1 > m_2$. The normal frequencies of vibration, ω_i, must first be found and then the energy is calculated from these using [3]

$$W = \sum_i \frac{h\omega_i/2\pi}{[\exp(h\omega_i/2\pi kT) - 1]} \text{ ergs per segment.} \quad (1)$$

The problem of the normal modes of different types of chain have been discussed by a number of authors, amongst whom Born [4], Brioullin [5], Smith [6], Wallis [7], Rosenstock [8], Genensky and Newell [9], Stockmayer and Hecht [10], Kirkwood [11] and Zbinden [12] all make points relevant to the present discussion.

Before discussing the zig-zagged chain it is convenient to recall the result for a linear chain such as that schematized in Fig. 3. Let the spring constant be γ dyn cm^{-1}. By writing the equations of motion for each particle and imposing suitable boundary conditions, one can solve these equations [4, 12] to obtain the frequencies ω_s of the normal modes. ω_s is given by

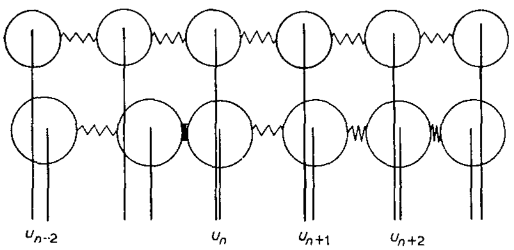


Figure 3 Linear diatomic chain, showing the equilibrium and displaced positions.

$$\omega_s^2 = \xi \pm \left[\xi - 4\alpha\beta \sin^2\left(\frac{2s\pi}{N}\right)\right]^{\frac{1}{2}} \quad (2)$$

with

$$\alpha = \gamma / m_1 \quad \beta = \gamma / m_2 \quad \xi = \alpha + \beta$$
$$s = 1, \ldots, N/2 .$$

For each value of s, there are two values of frequency: those corresponding to the positive sign are said to be on the *optical branch*; the remainder (negative sign) on the *acoustic branch*. The situation is shown in Fig. 4.

The case of a tetrahedral zig-zagged chain is similar, but is considerably more complicated in calculational detail. Kirkwood [11] derived the form for the normal frequencies for the case where $m_1 = m_2$. Zbinden [12] extended this calculation to cover the case $m_1 \neq m_2$. Unfortunately, Zbinden's calculation does not

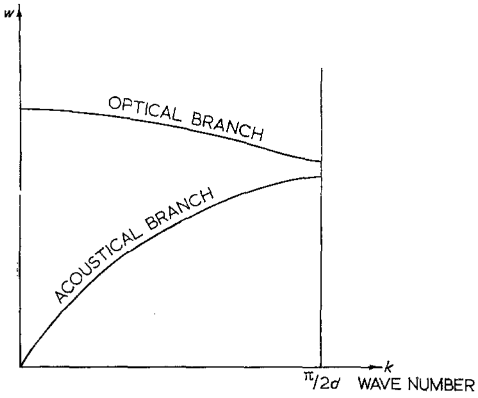


Figure 4 Frequency versus wave number for a diatomic linear chain.

yield such a simple formula as Equation 2: there are two acoustic branches, and two optical branches and for any given value of s, the frequencies are the solution of a fourth order equation having rather complicated coefficients.

Numerical calculation of the normal frequencies [13] using Zbinden's method is simple and, hence, the energies of vibration at any temperature can be obtained. However it is necessary to assume that the energy of a distorted chain is the same as that of a fully extended one [11].

4. The distribution of unbound segments

In Section 2 it was explained that, because of the amorphous nature of the polymer, one should expect to find short segments of chains whose members were not bound to their neighbours. It it were not so, it would be rather difficult to imagine how the sample cube could not be crystalline. The problem is to determine what distribution of free segments there are at low temperatures. The result will be described as a distribution $D(1)$, $D(2)$ . . . . . . $D(N)$, in which $D(i)$ is the number of free segments of length, i, in a 1 g test cube.

The experimental observations can be explained by assuming two types of free segment: first the *ends* of the polymer molecules must be free. This is almost demanded by the phenomenology. Studies of the molecular weight dependence [15] of the glass transition temperature (T_g) show that, to a good approximation, T_g (M_w) behaves as

$$T_g\,(M_w) = T_g\,(M_w = \infty) - \frac{\text{constant}}{M_w} \cdot \quad (3)$$

It is agreed by most authors that the form of Equation 3 implies that the chain ends play an important role. Bueche [15] has epitomized these arguments, but until recently, it has not been clear what is special about the chain ends. Wallis [7], however, in a very careful analysis, has shown that the atoms at the end of a chain have large displacements, and it is reasonable to interpret the results as meaning that as a polymer is cooled from its molten state the vibrating ends carve out a small cavern in which they remain free to vibrate even at very low temperatures. An end probably involves two or three atoms.

In addition to the free end segments a number of "non-end" free segments must also be present such as shown in Fig. 1, but a logical method for determining their number is not forthcoming. Fortunately, the precise distribution chosen has little effect on the results given here. Table I gives the particular distribution of (non-end) free segments used in these calculations and this distribution is assumed to be a material property for all amorphous polymers. The relationship of "non-end" to "end" free segments will be discussed further in conjunction with the specific heat results, at a later stage.

TABLE I

Length of segment	No. of such segments
1	2.8×10^{22}
2	5.0×10^{17}
3	3.8×10^{17}
4	1.8×10^{17}
5	5.2×10^{16}
6	9.1×10^{15}
7	9.6×10^{14}
8	6.1×10^{13}
9	2.3×10^{12}
10	5.6×10^{10}
11	8.0×10^{8}
12	6.9×10^{6}

5. Method of calculation of the glass transition temperature

The summation procedures implicit in Equation 1 necessitate the numerical calculation of all answers. The calculations are simple but rather long, and therefore the program used, together with an explanation of the symbols and method, have been deposited at the National Lending Library [13, 14].

In order to determine the position of the transition temperature, some measurable material property must be calculated. Glass transition temperatures are normally found by measuring the shear modulus [16], refractive index [17], coefficient of expansion [16] or by observation of the specific heat [16]. Accurate calculation of the modulus and refractive index is difficult; however, the specific heat is easily obtained from Equation 1.

$$C_p = \frac{\partial w}{\partial T} = \frac{h^2}{2\pi kT^2}$$

$$\sum_i \frac{w_i^2 \exp\,(hw_i/2\pi kT)}{[\exp\,(hw_i 2\pi kT) - 1]^2}\ \text{erg segment}^{-1}\,\text{K}^{-1} \quad (4)$$

Consider a free segment of length N repeat units at 0 K. When the temperature is raised to T its energy is $E_N\,(T)$. This energy is thought to be available to undo the "knots" at the end of the segment. If $E_N(T)$ becomes greater than the van der Waals energy ν^1 tying either A or B (see Fig. 1) to its neighbour, the segment would extend by one repeat unit. $[E_{N+1}(T) - \nu^1]$ erg are then available to undo the next knot, of ν^{11} erg. Assigning an average interaction energy $\bar{\nu}$, the quantities

$$\epsilon_2 = E_{N+2}(T) - 2\bar{\nu}$$
$$\epsilon_3 = E_{N+3}(T) - 3\bar{\nu}$$
$$\epsilon_l = E_{N+l}(T) - l\bar{\nu}$$

can be calculated. Determination of l for which ϵ_l becomes less than $\bar{\nu}$, the new length of a segment at temperature T can be found. Finally, by evaluating C_p using Equation 4, the specific heat of the scissoring vibrations as a function of temperature can be found. The qualitative behaviour as shown in Fig. 5, is always found.

By such a procedure, the change in specific heat at the glass transition temperature can be found, and this is independent of any $\bar{\nu}$. The glass transition temperature for a given polymer can therefore be determined using its $\bar{\nu}$ which is already known.

The glass transition temperature is also dependent on molecular weight. In the following sections the theoretical and experimental results for several real systems will be compared.

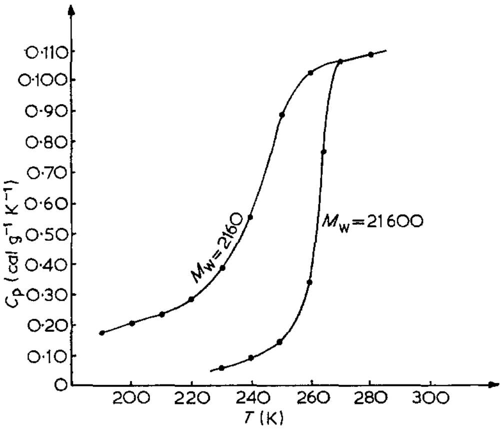


Figure 5 Specific heat versus temperature near T_g. Only the specific heat contribution from longitudinal vibrations are shown. The figure shows values for polypropylene for both low and high degrees of polymerization.

6. The specific heat change

A plot of specific heat, C_p, of polyisobutylene as a function of temperature, is shown in Fig. 6 [18]. Similar results are observed in almost all polymers, and ΔC_p lies in the range 0.040 to 0.120 cal g^{-1} K^{-1}. Wunderlich [19], by considering the data available on many polymeric and monomeric glass formers deduced that

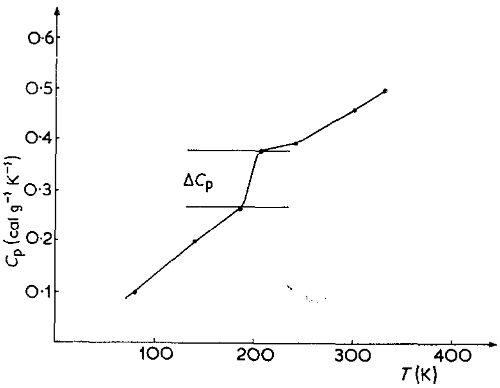


Figure 6 The observed dependence of specific heat for polyisobutylene.

$$M\Delta C_p \simeq 5.4 \text{ cal K}^{-1} \qquad (5)$$

where M is the molecular weight of a repeat unit, e.g.

$$\text{—CH}_2 - \text{CHCl—}$$

in polyvinylchloride. Wunderlich and Jones [20] subsequently attempted to derive this relation by considering the vibrational energies of the polymer chain; other methods of obtaining this will be shown in this section and the constant may be calculated to be very close to that deduced by Wunderlich.

The total specific heat of a polymer is mainly the sum of the incoherent vibrations of the repeat units in the van der Waals fields of their neighbours, and the longitudinal vibrational energy of the polymer chains, as discussed in Section 2. In practice further contributions from, for example, rotation of side groups, may be seen but these will be ignored as being relatively unimportant. The incoherent vibrations will form a background steadily increasing with temperature. Numerical calculation shows that below the glass transition temperature, the specific heat contribution from the longitudinal vibrations is small, being in the order of 10^{-3} cal g^{-1} K^{-1}. As the polymer is taken through the transition temperature, the individual polymer molecules become free to vibrate longitudinally so that a sharp rise in the vibrational specific heat is observed.

The specific heat contribution due to the longitudinal vibrations of a single segment was derived as (Section 5)

$$C_{\mathrm{p}} = \frac{h^2}{2\pi kT^2}\phi \text{ erg segment}^{-1}\,\mathrm{K}^{-1}$$

where

$$\phi = \sum_i \frac{w_i^2 \exp(hw_i/2\pi kT)}{[\exp(hw_i/2\pi kT) - 1]^2},$$

h = Planck's constant, k = Boltzman's constant. The summation is taken over all the normal frequencies see [4-6].

Since C_{p} is small below T_{g},

$$\Delta C_{\mathrm{p}} = C_{\mathrm{p}}\,.$$

Where C_{p} is slightly higher than T_{g}, say T_{g} + 20°C, thus

$$\Delta C_{\mathrm{p}} = \frac{C_n\, h^2}{2\pi JkT^2}\phi \text{ cal g}^{-1}\,\mathrm{K}^{-1}$$

where J is the mechanical equivalent of heat and C_n is the number of polymer molecules per gram.

$$C_n = \frac{2N_0}{M}$$

N_0 = Avogadro's number and M is the molecular weight of a repeat unit.

Therefore,

$$M\Delta C_{\mathrm{p}} = \frac{2N_0\,\mathrm{h}^2}{2\pi JkT^2}\phi\,.$$

For the polymer chains to have energies in the order of 100 × 10^{-4} erg (necessary to undo the van der Waals knots), hw/kT must be small enough for $\exp(hw/kT) = 1 + hw/RT$ to be a good approximation. In this case,

$$M\Delta C_{\mathrm{p}} = \frac{2N_0 k}{J}(1 - hw/2\pi kT)$$

yielding, roughly, $M\Delta C_{\mathrm{p}} \simeq 5.3$ cal K^{-1} which agrees well with Wunderlich's value of 5.4 cal K^{-1}.

It is not necessary, however, to employ this algebraic calculation to obtain values of ΔC_{p} for different polymers. The energies and specific heats may be calculated numerically as shown in [13] and [14]. Table II shows a comparison of experimental and calculated values of ΔC_{p} while Table III gives predicted ΔC_{p} values for polymers where no suitable experimental data has been published. Values of $M\Delta C_{\mathrm{p}}$ may be obtained from the calculated values of ΔC_{p}, giving an average value, $M\Delta C_{\mathrm{p}} \simeq 5.11$ cal K^{-1}, which agrees well with Wunderlich's value.

The calculated values of ΔC_{p} refer to completely amorphous materials. Partially crystalline materials will normally have values of ΔC_{p} reduced to not more than $X.\Delta C_{\mathrm{p}}$ where X is the weight fraction of amorphous material.

Wunderlich and Jones in [20] attempted to calculate the total heat capacity of the polymer, using an ingenious addition scheme enabling them to make a good estimate of the total specific heat at a given temperature even though certain necessary information was not available. Here, this difficulty in calculating the specific heat of the incoherent vibrations is not relevant as only the part which is of immediate interest has been calculated.

7. Van der Waals energies

In order to calculate the glass transition temperature $\bar{\nu}$ must be known. The calculations here are sensitive to $\bar{\nu}$, in that a change of a factor of 2 in $\bar{\nu}$ alone changes the transition temperature by approximately 100K.

It is interesting to note that the Gibbs-DiMarzio theory [1, 2, 21] of glass transition is

TABLE II

	ΔC_{p} (cal $\mathrm{g}^{-1}\,\mathrm{K}^{-1}$)		
Material	Calculated	Observed	Reference
Polystyrene	0.059	0.060	[23, 24]
Polyisobutylene	0.072	0.080	[18, 25]
Polyvinylchloride	0.086	0.086	[26, 27]
Polymethylmethacrylate	0.060	0.081	[20, 34]
Polypropylene	0.101	0.116	[20, 34]
Poly(4-methylpentene-l)	0.062	0.092	[35]
Poly-α-methyl styrene	0.057	0.076	[36]
Poly-l-pentene	0.065	0.0925	[37]
Poly-l-butene	0.081	0.0855	[37]

TABLE III

Material	ΔC_p (cal g^{-1} K^{-1})	Wunderlich constant
Polyvinylidenechloride	0.049	4.7
Polyacrylonitrile	0.113	6.0
Polymethacrylonitrile	0.088	5.9
Polyvinylalcohol	0.123	5.4
Polyacrylic acid	0.083	5.9

insensitive to $\bar{v}$, where $\bar{v}$ may equal infinity without adverse effect. However, this does not agree with observations in [1]. Examination of the transition temperatures of polymers with two different carbons (to which the present results relate), it is immediately clear that polyolefins ($\bar{v} \simeq 2.5 \times 10^{-14}$ erg) exhibit transition temperatures lying about 100 K below hydrogen bonded polymers ($\bar{v} \simeq 5.0 \times 10^{-14}$ erg). The approximate sizes of the van der Walls wells for some of the polymers under consideration can be set within quite narrow ranges. Consider two polymer repeat units lying close to each other (e.g. Fig. 7a). These are bound by van der Waals forces, having a potential energy, separation diagram of the qualitative form shown in Fig. 7b. In order to separate the two groups $\bar{v}$ erg, on average, must be expended. $\bar{v}$ for short range van der Waals forces may be obtained from the corresponding values for small molecules. Extensive investigations of these forces have been made and are explained in [22]. For polyolefins and polyethers $\bar{v}$ lies in the range 2.0×10^{-14} to 3.0×10^{-14} erg, while for hydrogen bonded materials $\bar{v} \simeq 5 \times 10^{-14}$ erg. This value is obtained assuming the strength of hydrogen bonds to be around 3 kcal per mole of bonds. This corresponds to a well depth of $\sim 20 \times 10^{-14}$ erg. In a two carbon polymer A-B-A-B-A-B, where a hydrogen bond can be formed between A-A but not between A-B, B-B etc, there are four possible bonding patterns: AA, AB, BA, BB of which the AA bonds are by far the largest. The average must therefore be about 5×10^{-14}.

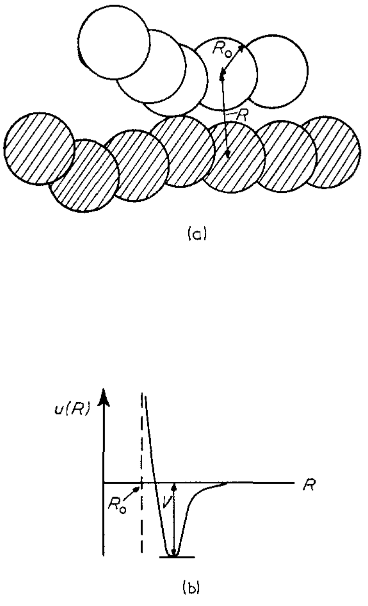


Figure 7 Van der Waals forces holding the separate chains together.

For polar materials such as polyvinyl chloride, and certain others, e.g. polystyrene the value of $\bar{v}$ is not accurately known. These materials are further complicated by the knowledge that the well depth of Fig. 7b is probably not equal to $\bar{v}$, since the polar forces are relatively long range. In the following section the glass transition temperatures for polyolefins and hydrogen bonded materials are calculated with the values of $\bar{v}$ given above. $\bar{v}$ for the remaining materials has been found by trial and error and will be used subsequently to discuss the molecular weight dependence.

8. The glass transition temperatures

Consider polypropylene. From Section 7 $\bar{v}$ lies in the range 2.0×10^{-14} to 3.0×10^{-14} erg. The glass transition temperatures calculated as in Section 5 and given in detail in [13] and [14], are $T_g = 240°C$ and $T_g = 300°C$. For the hydrogen bonded polyvinyl alcohol the best results are $\bar{v} = 4.5 \times 10^{-14}$ to 5.5×10^{-14} erg ,$T_g = 390$ to 440 K. However, it is likely that $\bar{v}$ is the same for all polyolefins and therefore the value, $\bar{v} = 2.3 \times 10^{-14}$ erg, giving $T_g = 263$ K for polypropylene may be chosen and from this the glass transition temperatures for the other polyolefins may be calculated. These are given in Table IV. The results in Fig. 8 show quite reasonable correlation. It must, however, be noticed that the

TABLE IV

Material	T_g calculated	T_g observed
Polypropylene	263	263
Poly-l-butene	252	250
Poly-l-pentene	244	235
Poly-l-hexene	234	225
Poly-l-octene	221	210
Polyvinylmethylether	249	255
Polyvinylethylether	244	250
Polyvinyl-*n*-butylether	233	220

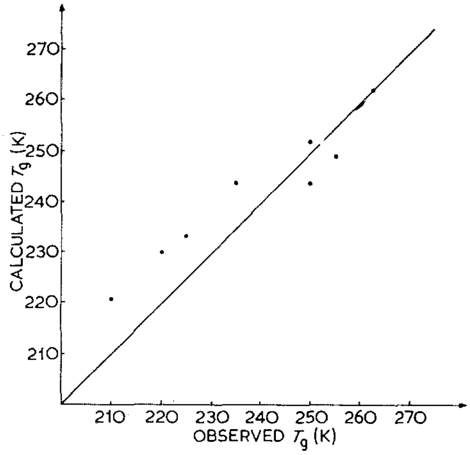


Figure 8 Calculated and observed values of T_g for a group of weakly bound polymers. $\bar{\nu}$ is taken to be 2.3×10^{-14} erg. The 45° line should contain all the points if the theory were exactly correct.

isomeric polyisobutylene and poly-l-butene have different observed transition temperatures whilst the theory demands that they should be exactly equal.

TABLE V

Material	$\bar{\nu} \times 10^{14}$
Polystyrene	4.75
Polymethylmethacrylate	4.75
Poly-α-methylstyrene	6.50
Polyvinylchloride	4.0
Polyacrylonitrile	4.25

Table V gives the effective values of $\bar{\nu}$ for those polymers for which a reasonable estimate cannot be made. The values fall between those of the polyolefins (low) and the hydrogen bonded polymers (high), as do the values of T_g.

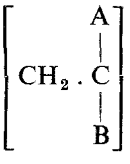
9. The effect of molecular weight on T_g

The calculations used previously may also be employed to determine the molecular weight dependence of the transition temperature. This dependence will first be examined qualitatively.

In Section 1 it was suggested that an amorphous polymer undergoes the glass transition when the thermal energy of vibration becomes greater than the van der Waals energies holding a polymer chain to its neighbours. It was seen how, with rising temperature, the free ends of the chain gradually extend themselves finally leaving the chain essentially disconnected from the surroundings.

Consider a particular molecule from a bulk sample, of e.g. 100 carbons long. At low temperatures, two or three carbons at each end of the chain are free. In order for the whole molecule to become free, each "end" must attain enough thermal energy to undo (100/2) – 2 = 48 van der Waals "knots"; similarly, each end of a molecule 500 carbons long would have to gain enough energy to undo 248 knots. Therefore the polymer sample containing the longer molecules will have to be raised to a higher temperature before it undergoes the glass transition. The glass transition temperature is, therefore, dependent upon the length of the molecule, and the role of the chain ends is now quite clear.

The glass transition temperature as a function of molecular weight may now be calculated, given an approximate value of $\bar{\nu}$, the average intermolecular force. Some values of $\bar{\nu}$ are known, whereas others are set artificially by finding a value of $\bar{\nu}$ which gave the correct transition temperature for infinite molecular weight (see Section 8 and Table V). Using these values of $\bar{\nu}$, T_g (P) may be calculated. P is the degree of polymerization, i.e. the number of



$$\left[\mathrm{CH_2}\,.\,\overset{\displaystyle\mathrm{A}}{\underset{\displaystyle\mathrm{B}}{\mathrm{C}}}\right]$$

units in the chain.

The specific heat for the scissoring modes of polystyrene is shown in Fig. 9 as a function of temperature using the degree of polymerization as a parameter. From this type of diagram, a graph of T_g versus molecular weight may be obtained. The graph for polystyrene is shown in Fig. 10. Clearly

$$T_g = T_g(\infty) - A/p$$

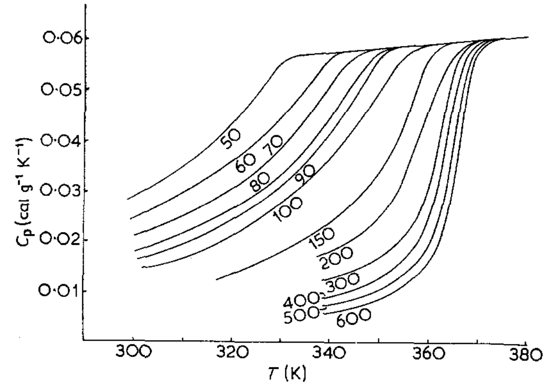


Figure 9 Specific heat of scissoring mode for polystyrene. The parametrizing number is the number of carbons in the backbone.

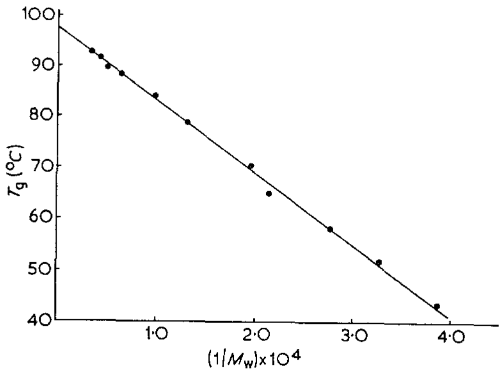


Figure 10 Glass transition temperature plotted against $1/M_w$. The glass transition temperatures are found from Fig. 9 by visually locating the point of maximum slope.

and $A = 1.5 \times 10^5$°. Calculation for all the other polymers of Table V, gives the results shown in Table VI.

Additional calculations demonstrate the qualitative effect of changing m_2/m_1 and $\bar{\nu}$ upon the value of A. Beginning with polystyrene ($m_1 = 14$; $m_2 = 90$; $\bar{\nu} = 4.75$) and changing m_2 and $\bar{\nu}$, the values of A given in Table VII are obtained. These show that A increases both with m_2/m_1 and $\bar{\nu}$. The values of A calculated by this method do not agree in detail with the experimental values, however, they are of the correct order of magnitude.

TABLE VII

m_2/m_1	$A \times 10^{-5}$	
	$\bar{\nu} = 2.3 \times 10^{14}$ (ergs)	$\bar{\nu} = 4.75 \times 10^{14}$ (ergs)
16/14	0.39	0.48
90/14	0.75	1.50

From Fig. 9 (for polystyrene), it is seen that for very low degrees of polymerization the specific heat curve has relatively high values of C_p immediately below the transition temperature, and that the whole transition region is rather smooth. It is not clear whether this corresponds with experimental observation or not. The model for this paper, with all the ends free and being 2 to 3 atoms long, together with a number of non-end free segments, was established in Section 4. The distribution of non-end free segments was fixed by taking a reasonable estimate and checking that the values of T_g and C_p were insensitive to the precise distribution chosen. It was assumed that this model was a fixed material property regardless of molecular weight and type of polymer. However, the distributions may depend weakly on molecular weight and the low molecular weight curves of Fig. 9 may be unnecessarily spread out, but at the moment the assumption used in Section 4 seems to be simplest. Further evidence may be found, in due course, to enable the distribution to be discussed more quantitatively.

TABLE VI

	$A \times 10^{-5}$		
Material	Calculated	Observed	Reference
Polypropylene	0.58	0.86	[28]
Polyvinylchloride	1.10	0.80	[29]
Polyacrylonitrile	1.20	2.80	[30]
Polymethylmethacrylate	1.40	2.10	[17, 31]
Polystyrene	1.50	1.00	[32]
Poly-α-methylstyrene	1.94	3.60	[33]

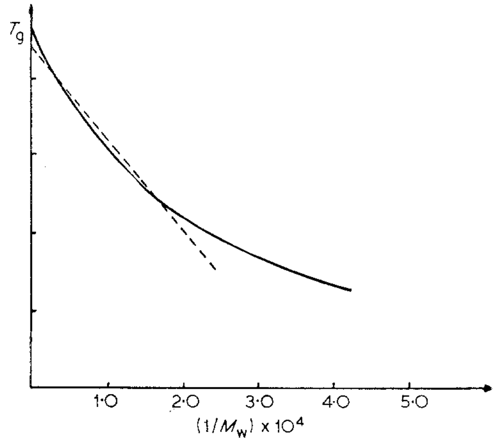


Figure 11 Experimentally observed behaviour of T_g versus $1/M_w$ (after Cowie and Toporowski). Full line – observed behaviour; dotted line – apparent behaviour if very low molecular weights are ignored.

Recently some very careful results of T_g versus M_w have appeared, in which very low molecular weight samples have been included. These results show a noticeable deviation from the straight line relationship discussed above.The real situation is shown in Fig. 11. This low molecular weight deviation is not contained in the present calculation, and it is not explicable as an artefact associated with the finite molecular weight range of the experimental sample. It seems most likely that the effect is linked with conformational changes, and the discussion in Section 11 may be relevant here.

10. Some qualitative considerations

10.1 Side chains

It has frequently been noted that the addition of an alkyl chain to a vinyl polymer causes a reduction of the glass transition temperature. In the present model this is an immediate consequence. Increasing the mass ratio m_2/m_1 for fixed $\bar{\nu}$ causes the transition temperature to drop. This is, of course, only valid as long as the carbon and its side chain can be regarded as a point mass. The longer the alkyl side chain, the less accurate this approximation will be since the vibration of the side chain will rapidly get out of phase with that of the parent carbon. Thus, it is expected that increase in length of a pendant chain will cause an initial decrease in the glass transition temperature, which becomes less marked as the chain length is increased.

10.2 Plasticizers

It is possible that one mode of operation of a plasticizer is by being adsorbed in some way on to the main polymer chain. Therefore, it is possible to imagine that not only are the number of polymer-polymer van der Waals "knots" reduced, but that the effective mass distribution in the backbone might be altered in the direction of increasing m_2/m_1. Both these effects would lead to the lowering of the transition temperature. Unfortunately reasonably numerate calculations appear to be difficult to perform.

10.3 Crosslinking

For any theory of the glass transition to be valid the effects of crosslinking should be taken into consideration, however, because of the complexity of the experimental situation, this will be discussed in a subsequent paper. In order to give comparison between as many experimental and theoretical results as possible, certain inorganic glasses, in addition to carbon-based networks, will be discussed.

11. Discussion

In this paper some of the consequences of a particular model of the glass transition process have been examined numerically but these must be seen in their proper context. It was postulated that the energy contained in the scissoring motion of the polymer backbone is an important factor in the glass transition. By using Zbinden's calculation it was possible to examine some of the numerical consequences of the model.

Previous ideas about the glass transition emphasized various conformational changes of the polymer. "Stiffness of the chain" or "the flexibility" of a certain group are frequently referred to in the references. It is clear that the ability of the chain to change its conformation must play some part in the glass transition, as the small but very well established kinetic effects at the transition temperature could not otherwise occur.

Kinetic effects are certainly not contained in the scissoring mode model. It is suggested that here the scissoring energy is the major process and that conformational effects are of secondary importance. Taking this as a working hypothesis, most of the features observed in simple linear polymers may be understood in qualitative terms at least. This hypothesis has the additional advantage of avoiding an important conceptual difficulty about how segments in the polymer can be free to rotate. Some authors have discussed the glass transition in terms that imply that quite large elements of the polymer backbone are able to rotate in the bulk state. This idea is difficult to reconcile with geometrical considerations. Examination of space filling models seems to imply that if any such rotations can take place, then quite a large segment must be involved. This, in turn, implies a large expenditure of energy, so that even in solution this sort of process would tend to be unlikely at the relatively low temperatures under consideration.

In the bulk, where there are many interfering neighbours, rotations seem even more unlikely, and would also seem to imply a much larger change in specific volume than is in fact observed.

Finally, the relation between the present calculations and the free volume theories must be discussed. It can be seen, at least qualitatively, that the coefficients of expansion of the polymer below and above the glass transition temperature will be substantially different. The precise calculation of the coefficients of expansion leads to some difficulty. Calculations of these quantities require some knowledge of the anharmonicity of the potential wells. The method of estimating the coefficient of expansion of a zig-zagged chain, without introducing some adjustable parameter is not, at present, clear. Nevertheless, below the transition temperature the coefficient of expansion will reflect the incoherent vibrations of the chains in the van der Waals wells of their neighbours, whilst above it there will be additional terms reflecting the scissoring mode. Thus it is expected that on a specific volume-temperature plot a change in slope taking place over a temperature range corresponding to the range over which C_p changes, i.e. about 20°C will be found. This is in accordance with observation. Given these weakly restrictive assumptions the relation of the present calculations to the free volume formation, may be understood qualitatively.

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