

# Transition Points of Polymers

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## SYNOPSIS

As a model for polymers, the pseudocrosslink of various sizes is proposed. The size of links, lengths of connected chains, and the times  $\tau$ 's for their translation or relaxation are derived. According to the size, four transition temperatures ( $T$ 's) are proposed such as the linking for the smallest size  $A$  ( $T_A$ ), that for the largest one  $B$  ( $T_B$ ), the melting point ( $T_m$ ), and the glass transition point ( $T_g$ ). The equation for  $T_g$  is derived with an assumption that the cooling time  $t$  is equal to the relaxation time of the segment at  $T_g$  and  $T_g$  is found to be about 50°C higher than  $T_A$ .  $T_g$  decreases with  $t$ .  $T_B$  is twice as much as  $T_A$ .  $T_g/T_B$  is 2/3 in the general case and 1/2 for hindered polymers.  $T_m$  is very close to  $T_B$ , but somewhat lower than it when the cohesion heat is large. Related problems are discussed: The thermal expansion coefficient above  $T_g$  is about 1/10  $T_g$ . The rebound resilience of rubber at temperature  $T$  is given by a ratio of  $(T - T_g)/(T - T_A)$ . The sound velocities in glassy plastics and rubber are 2000 and 50–100 m/s, respectively, depending on the elasticity. The temperature-shift factor for the stress-relaxation spectrum is derived directly from the equation for the relaxation time without use of the thermal expansion coefficient. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

A polymer is usually classified and characterized by transition temperatures, e.g., the melting temperature  $T_m$  for crystalline polymer, the softening temperature  $T_B$  (according to the transition point in the relaxation spectrum), and the glass transition temperature  $T_g$  for the noncrystalline one.  $T_m$  is the thermodynamical transition temperature, whereas the latter two are affected more or less by the rheological condition such as the rate of cooling or that of deformation.  $T_g$  is a second-order transition temperature. However, they are also associated with thermodynamical conditions and  $T_g$  runs parallel to  $T_m$  or  $T_B$  in most cases.

The author<sup>1,2</sup> proposed a pseudocrosslink model, in which various sizes of links and various lengths of chains exist, and they are determined by thermodynamical conditions. This article deals with transition temperatures in terms of a thermodynamical point of view.

## THEORY

### Pseudocrosslink Model

A pseudocrosslink is formed by the entanglement of polymer chains with the aid of the cohesion of segments in chains. It resembles the association of molecules but they differ in size from an ordinary association because segments in a polymer chain form links of various sizes by the zipperlike nature of a polymer chain. The outline of the proposed theory is described as follows:

A chain consisting of  $n$  segments forms a spherical coil of a diameter proportional to  $n^{1/2}$  and is entangled with overlapping coils. The total volume of the entangled coils is given by a square of the volume of a coil given by  $n^{2(3/2)}$  in a segmental unit and its entropy is  $R \ln n^3$ . A pseudocrosslink of size  $b$  is connected with a chain of a length of  $n_b$  and the following equation holds in the equilibrium condition:

$$bH_0 = RT \ln n_b^3, \quad (1)$$

where  $H_0$  is a cohesion heat of a unit link composed of two segments.

After the dissociation of a link of  $b$  segments, it translates to the next equilibrium position apart by a distance of  $n_b^{1/2}$ . It is induced by an elastic force of the chain whose energy is  $(\alpha^2/2)RT$ ,  $\alpha$  being the elongation expressed by a ratio of the increased end-to-end distance of a chain to the initial one. In the successive dissociation of a link, the elongation of a chain is assumed to attain its ultimate elongation in each stage and  $\alpha$  becomes  $n_b^{1/2}$ . Accordingly, it follows that

$$n_b = b^2 \quad (2)$$

From eqs. (1) and (2),  $b$  or  $n_b$  are given as a function of temperature  $T$  as

$$b/\ln b = 6RT/H_0 \quad (3)$$

Equation (3) indicates that  $b$  becomes 1–4 and 16 at  $T_A$  and  $T_B$ , respectively, as explained later. It is graphically approximated to

$$b \cong 12T/T_A - 8 \quad (3')$$

where  $T_A$  is a transition temperature of a link  $A$ .  $b$  is 4 and 16 at  $T_A$  and  $2T_A$  or  $T_B$ , and  $n_b$  is 16 and 256, respectively.

Taking  $\nu_b$  and  $N$  as the number of linked segments and total one in a unit volume or  $1 \text{ cm}^3$ , respectively, the equilibrium is given as

$$\nu_b/N = n_b^3 K \quad (4)$$

where  $K$  is an equilibrium constant and is expressed with the heat  $\Delta H$  and the entropy  $\Delta S$  of linking. In equilibrium among all sizes of links and all lengths of chains,  $n$  is replaced by  $N/\nu$  as the average and

$$\nu/N = K = \exp[(\frac{1}{3})(-\Delta H/RT + \Delta S/R)]$$

This means the formation of small links in the large coil under the control of the large link. In other words, there is a hierarchy of the network structure between  $A$  and  $B$ . The links higher than  $n_B$  do not exist, because in the next higher hierarchy  $C$ ,  $b$  becomes 64 and  $n$  is  $10^{2.4 \times 4}$  or  $10^{9.6}$ , which are too large to exist except for crosslinked polymers. Taking  $H_0$  as the cohesion heat of a segment, the equation is

$$\nu_b/N = \exp[b(-H_0/RT + \Delta S_0/R)] \quad (5)$$

$H_0$  is about 0.8 kcal for hydrocarbon polymers and  $\Delta S_0$  is  $2R$ . Below  $A$ ,  $H_0/2RT$  is less than unity and the link smaller than  $A$  is not recognized except in

extremely rapid or impact deformation. As a result, the size of the actual link lies between  $A$  and  $B$ .  $T_1$ ,  $T_A$ , and  $T_B$  are the transition or melting temperature of the unit link, the link  $A$ , and the link  $B$ , respectively. According to eq. (3'), the transition temperatures for the size of  $b$  of 2, 3, 4, 10, and 16 are 0.962, 0.910, 0.962, 1.45, and 1,962 times  $T_A$ , respectively. Between sizes 1 and 4, there is no difference. They are expressed as

$$T_{1-4} = T_0 = T_A = H_0/2R \quad (6)$$

and

$$T_{16} = T_B = 2T_A = H_0/R \quad (7)$$

Another fundamental equation is that of the relaxation time  $\tau$  for the translation of a link or a chain in a molecular coil. According to Eyring's equation for viscosity,<sup>3</sup>  $\tau$  for a single molecule is

$$\tau = (h/kT)\exp(E^*/RT)$$

where  $h$  and  $k$  are the Planck's and Boltzmann's constants, respectively, and  $h/kT$  implies a time for a collision or  $10^{-13}$  s.  $E^*$  is an activation energy for translation of a molecule migrating in a distance equal to a molecular diameter  $l$ .  $E^*$  is taken to be one-third of the heat of vaporization and is of about 10 kcal/mol. As a result, an exponential factor is  $10^2$  and  $\tau$  becomes about  $10^{-11}$  s.

On the contrary, the translational motion of a segment in a chain differs from that of a simple molecule, because the former is limited in a coil of a polymer chain and also the local motion is much hindered by the neighboring segment.

The translational process involves dissociation and translation of the pseudocrosslink. The time for the process, i.e., the relaxation time, is of a function of size  $b$  and is denoted by  $\tau_b$ . It is expressed as

$$\tau_b = \tau_0 \exp\{(\frac{2}{3})(bH_0/RT)\} n_B^{0.5} \quad (8)$$

where  $\tau_0$  is the relaxation time of a unit segment translating in a distance  $l$  or the length of a segment. The exponential factor is a fraction of the dissociation of  $b$  size link of an activation energy  $bE_b^*$ , which is taken to be  $\frac{2}{3}$  of the cohesion heat  $bH_0$  (see the Appendix).  $n_B^{0.5}$  is a distance for the relaxation and is equal to the diameter of the largest  $B$  coil composed of  $16^2$  or  $10^{2.4}$  segments. The exponential factor is replaced by  $n_b^2$  by using eq. (1) and eq. (8) becomes

$$\tau_b = \tau_0 n_b^2 n_B^{0.5} \quad (8')$$

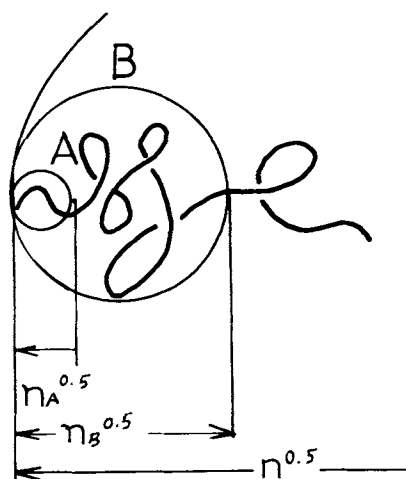


Figure 1 Hierarchies in polymer coil.

Equation (8') is applied to express the segmental motion in a coil or the configurational change of a chain smaller than the chain of a length  $n_B$ .

For a large deformation such as the viscous flow of a molecular chain of a length of  $n$ , it is necessary to account for the factors of the entanglement of coils and the prolonged distance of relaxation. They are  $(n/n_B)^3$  and  $(n/n_B)^{0.5}$ , respectively. Accordingly, eq. (8') is modified to

$$\tau = \tau_0 n_B^{2.5} (n/n_B)^{3.5} = \tau_0 n_B^{-1} n^{3.5} \quad (9)$$

For an oligomer of small molecular length  $n$  less than  $n_B$ ,

$$\tau = \tau_0 n^{2.5} \quad (10)$$

Equations (9) and (10) express the relaxation time of the whole molecule, whereas eq. (8'), that of the link or chain  $b$  in a molecular coil. The melt viscosity  $\eta$  is expressed by a product of the elasticity  $E$  and the relaxation time  $\tau$ .  $E$  is inversely proportional to  $n$ , and, therefore,  $\eta$  of the polymer and oligomer are proportional to  $n^{3.5}$  and  $n^{1.5}$ , respectively.

In summary, the polymer chain forms a coil and it involves small coils of various sizes and the hierarchies  $A$  and  $B$  are formed as illustrated in Figure 1. The upper hierarchy is that of  $B$ , but in the cross-linked polymer, the chains larger than chain  $B$  exist, forming the hierarchies higher than  $B$ . The relaxation of stress or strain of each chain occurs by the translation through the stage of hierarchies. Such a process is observed in the creep of polymeric materials.

As another feature of the polymer chain, it is also noticed that a polymer chain is composed of many segments and the translational motion of a segment

is much hindered by the neighboring segments and the relaxation time of the unit segment  $\tau_1$  becomes very long, as much as  $10^{-7.8}$  s as compared with that of the free molecule, i.e.,  $10^{-11}$  s. It is caused by the entrainment effect of the accompanied segments in a chain, as is illustrated in Figure 2. With this effect, the polymer chain exhibits various characteristic properties such as the glass transition.

### Entrainment Effect<sup>2</sup>

Calculation of the entrainment effect may be very complicated and, instead, a simple assumption is adopted such that the retardation effect is replaced by the cohesion effect of the neighboring segment, because it is connected chemically and is located in a position to bring about a cohesive force to the segment. Since the cohesion heat is shared by two segments, the translational energy  $RT$  is diminished by one-half of the cohesion heat  $H_0/2$ , which is equal to  $RT_0$  or  $RT_A$  and

$$RT - H_0/2 = R(T - T_A) \quad (11)$$

The equation may be too simple to estimate the hydrodynamic effect but it affords an approximate magnitude. For hydrocarbon segments,  $T_A$  is about 200 K and the actual translational energy is about  $RT/3$  at 300 K. Equation (11) is an origin of the glass transition and also is concerned with various rheological phenomena, such as the thermal expansion of polymeric materials, the rebound resilience of rubber, and the temperature shift of the stress-relaxation spectrum. As a result, the time for the unit segment translating a distance  $l$  is

$$\tau_0 = (h/kT) \exp[(z-2)(H_0/3)/(z)R(T - T_A)]$$

where the vaporization heat is replaced by  $(z-2)H_0$ ,  $z$  being a coordination number of 8–10 for a free

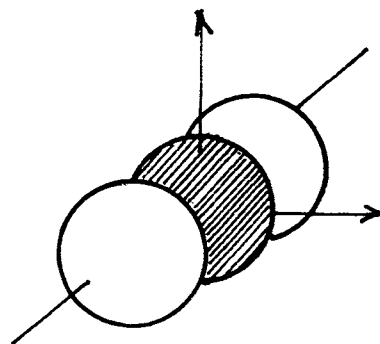


Figure 2 Entrainment in chain.

segment and that for the segment in a chain is less than a simple molecule by 2. Also, the segmental motion is limited to two directions perpendicular to the main chain and the translational energy becomes  $\frac{2}{3}$  of that of the free segment. Consequently,  $RT$  is replaced by  $(\frac{2}{3})R(T - T_A)$ .

Taking  $10^{-13}$  per second as  $h/kT$ ,  $2RT_A$  as  $H_0$ , and 8 as  $z$ , it follows that

$$\tau_0 = (h/kT)\exp[(z - 2)T_A/(T - T_A)] \quad (12)$$

At 300 K,  $\tau_0$  is of an order of  $10^{-7.8}$  s and  $10^3$  times larger than that of a simple molecule. The relaxation time of the unit segment translating a distance  $n_B^{0.5}$  is

$$\tau_1 = \tau_0 n_B^{0.5} = 10^{-6.6} \text{ s}$$

For  $\tau_A$  and  $\tau_B$ ,

$$\tau_A = \tau_1 n_A^2 = 10^{-4.2} \text{ s}$$

and

$$\tau_B = \tau_1 n_B^2 = 10^{-1.8} \text{ s}$$

These relaxation times are to be applied to hydrocarbon polymers at room temperature and to other polymers at the temperature about 50°C higher than  $T_g$ .

### Glass Transition

For a polymer, the translational motion of a segment is not recognized when the time of cooling or deformation  $t$  is less than  $\tau_A$  and the glass transition takes place at this condition. At the condition that  $\tau_A = t$  in eqs. (6), (8), and (12), it follows that

$$T_g - T_A = (z - 2)T_A \{ \ln(h/tkT) + \ln(n_A^2 n_B^{0.5}) \}$$

Taking 6 for  $z - 2$ ,  $10^{13}$  for  $h/tkT$ ,  $10^{1.2} \text{ s}^{-1}$  for  $n_A$ , and 1 s for  $t$  as a standard, it becomes

$$T_g - T_A = 0.27T_A(1 - 0.11 \log t)$$

or

$$T_g = 1.27T_A = 0.64T_B \quad (13)$$

Thus,  $T_g$  is about  $(\frac{2}{3})T_B$  and it is a standard relation but is affected by the steric hindrance, e.g., of polyvinylidene halide. The glass transition is difficult to occur at  $T_g$  and, instead, the apparent glass transition temperature is  $T_A$  or  $(\frac{1}{2})T_B$ . Thus,  $T_g/T_B$  is  $\frac{2}{3}$  or  $\frac{1}{2}$ .

For a low polymer or oligomer, it is given by eq. (10) and

$$\begin{aligned} T_g - T_A &= (6/2.3 \cdot 7.8)T_A \\ &\times (1 - 0.12 \log t + 0.12 \cdot 2.5 \log n) \\ &= 0.33T_A(1 - 0.12 \log t + 0.3 \log n) \end{aligned}$$

or

$$T_g(n) = T_g(1 - 0.029 \log t + 0.062 \log n) \quad (14)$$

According to eq. (14),  $T_g$  decreases with time and increases with the molecular weight or  $n$  for an oligomer.

### Temperature Effect on Relaxation Spectrum

The relaxation time decreases as the temperature increases and the shift factor  $a_T$  is expressed by a product of two factors; one is the decrease of the relaxation time  $\tau_0$  of the unit segment and the other is that of elasticity  $E$  and

$$\log(\tau/\tau_g) = \log(\tau_0/\tau_{0g}) + 2 \log(E/E_g)$$

Since  $\tau_0$  and  $E$  are expressed, respectively,

$$\ln \tau_0 \sim E^*/R(T - T_A) \quad \text{and} \quad \log E \sim E^*/RT$$

The latter is smaller by a factor of  $(T - T_A)/T$  or  $\frac{1}{4}$ – $\frac{1}{5}$ . Consequently,

$$\begin{aligned} \log\left(\frac{\tau}{\tau_g}\right) &= \frac{1.5(z - 2)T_A}{2.3(T_g - T_A)} \cdot \frac{-(T - T_g)}{(T_g - T_A) + (T - T_g)} \\ &= \frac{-C_1(T - T_g)}{C_2 + T - T_g} \end{aligned} \quad (15)$$

The coefficients  $C_1$  and  $C_2$  become 16° and 50°, respectively, and they are very close to 17.44 and 51.6 of the empirical equation of Williams, Landel and Ferry.<sup>4</sup> In the latter case,  $a_T$  is taken as a ratio of viscosity  $\eta/\eta_g$ , which is equal to  $(\tau/\tau_g)^{1.5}$ .

In relation to the thermal expansion the Doolittle's equation<sup>5</sup> of viscosity,  $\eta$  is derived from eq. (12), taking  $V$  as the segment volume and  $N_A$  as the Avogador's number:

$$\begin{aligned} \eta &= (N_A h/V)\exp\{E^*/R(T - T_A)\} \\ &= (N_A h/V)\exp(1/f) \end{aligned} \quad (16)$$

Equation (16) may be used at near  $T_g$ .

Usually, the Doolittle's equation is employed for derivation of the equation of the temperature-shift factor for the dynamic relaxation spectrum, and, therefore, the shift factor involves the free-volume fraction  $f$  and the thermal expansion coefficient  $\alpha$  as variables. It is to be noticed that  $f$  and  $\alpha$  are not universally constant but depend on the type of polymer.

### Thermal Expansion of Polymer<sup>2</sup>

Thermal expansion is caused by the expansion of the free volume. For a simple molecule, the free volume  $V_f$  or its fraction  $f$  are given by Eyring et al.<sup>3</sup> as

$$f^{1/3}H = RT \quad (17)$$

This is derived from a geometrical requirement and is to be valid for the solid state. Above  $T_g$  or in the liquid state, the following equation may be more suitable from the mode of dynamic motion of a segment:

$$fH = R(T - T_A) \quad (18)$$

In eq. (18),  $f$  is about 10% at room temperature but becomes a constant value of 2.3% at  $T_g$  as

$$f_g = R(T - T_A)/H = (T_g - T_A)/2T_A(z - 2) = 0.023$$

The molecular volume  $V$  is given by the sum of the core volume  $V_s$  and the free volume  $V_f$  as

$$V = V_s(1 + f)$$

$V_s$  is equal to the molar volume in the solid state. The thermal expansion coefficient  $\alpha$  is the sum of that of solid ( $s$ ) and that of liquid ( $l$ ) and is expressed as

$$\alpha = dV/VdT = d \ln V_s/dT + (df/dT)/(1 + f) = \alpha(s) + \alpha(l)$$

and  $\alpha(l)$  for  $z$  of 8 is

$$\alpha(l) = R/H = R/(z - 2)(2RT_A) = \frac{1}{9}T_g \quad (19)$$

In other words,  $\alpha$  is inversely proportional to  $T_g$  or the heat of cohesion. The value  $\alpha$  of polymers is almost same as that of the corresponding simple molecule.

On the other hand,  $\alpha(s)$  is derived from eq. (17):

$$\alpha(s) = df/dT = 3(R/H)T^2 = 3(R/H)f^{2/3}$$

Taking  $f_g$  or 0.023 as  $f$ , it follows that

$$\alpha(s) = 0.25\alpha(l) \quad (20)$$

Thus, the thermal expansion of solid is one-quarter of that of liquid.

### Effect of Vulcanization

For an oligomer,  $T_g$  increases with increasing the molecular length  $n$  and also  $n$  increases to  $n'$  with chemical crosslinks whose number is  $\nu_1$  or degree of vulcanization is  $\nu_1/N$  as

$$N/n' = (N/n) - \nu_1$$

or

$$n' = n(1 + n\nu_1/N)$$

Therefore, eq. (14) is modified as

$$T_g(n) = T_g[1 + 0.062 \log n + 0.062 \log(1 + n\nu_1/N)] \quad (21)$$

Equation (19) for the thermal expansion coefficient becomes

$$\alpha(l)(\nu_1) = \alpha(l)[1 - 0.062 \log(1 + n\nu_1/N)] \quad (22)$$

For the solid state, however, the situation is somewhat different, because the thermal expansion in the liquid state is trapped by the glassification and retards the shrinkage due to the glassification. The internal strain trapped reveals an increasing effect on thermal expansion of polymer glass. Thus,  $\alpha(s)$  increases by vulcanization:

$$\begin{aligned} \alpha(s)(\nu_1) &= \alpha(s)[1 + \{\alpha(l)/\alpha(s)\}0.062 \log(1 + n\nu_1/N)] \\ &= \alpha(s)[1 + 0.24 \log(1 + n\nu_1/N)] \end{aligned} \quad (23)$$

Consequently, the nature of the glass is much affected by the condition of glassification or the rate of cooling.

### Rebound Resilience and Sound Velocity in Rubber<sup>6</sup>

The rebound resilience ( $RR$ ) of rubbery material is expressed by a ratio of the rebound height to the

falling distance. It may be difficult to calculate hydrodynamically, but it is thermodynamically given by a ratio of energy revealed at the rebound to that given by impact deformation and it follows that

$$RR = (T - T_g)/(T - T_A) - RR_0 \quad (24)$$

where  $RR_0$  is another energetical factor due to the steric hindrance in the chemical bond.

The sound velocity  $c$  in rubber is given as

$$c = (E/\rho)^{1/2} = [(\nu_1 + \nu_b)kT/\rho]^{1/2} \quad (25)$$

The frequency of sound lies between 0.1 to 0.001  $s^{-1}$  and, therefore, the rubberlike elasticity  $E$  is a controlling factor.  $E$  is a function of the size of pseudocrosslinks  $b$  or the length of chains  $n_b$  and at  $T_B$ :

$$E = (N/n_B)kT = 10^{-2.4}E_0$$

This means that the sound velocity in rubber is very small as compared with plastics and increases with increasing  $T_g$ . Plastics are used in the glassy state and the elasticity is almost constant at  $E_0$  or  $10^9$  dyne/cm<sup>2</sup> and the sound velocity is about 2000 m/s in contrast to 50 m/s in rubber.

### Softening and Melting Point<sup>7</sup>

The melting point,  $T_m$ , is defined as a point of the solid-liquid transition. For crystalline polymers, the transition of polymer crystal to melt takes place at  $T_m$ . However, for polymers of noncrystallization, two points are measured and used, i.e.,  $T_A$  or  $T_g$ , and the softening one  $T_B$ .

They depend on the rheological conditions but are also correlated with thermodynamical conditions. According to the pseudocrosslink model,  $T_A$  is a critical point for translation of the link of the smallest size and  $T_B$  is that of the largest one.  $T_g$  gives the brittle point, whereas  $T_B$  gives the flow point of the polymer melt.

At  $T_B$ , the unit link is composed of two segments but one of them is involved in the solids and, therefore,  $T_B$  is given by  $H_0/R$  as shown in eq. (7).

On the other hand, the melting point for crystalline polymer  $T_m$  is given by the ratio of the heat of fusion  $\Delta H$  to the entropy  $\Delta S$ . Here,  $\Delta H$  may be equal to  $bH_0$ . Also,  $\Delta S$  is proportional to  $\Delta H$ , because  $\Delta S$  is concerned with the molar volume  $V$  proportional to the cohesion energy or is  $cH_0$ ,  $c$  being a constant. Since the crystallization propagates successively, the entropy of the first unit is  $R$  but that of the successive unit is  $R/2$  and

$$\Delta H = bH_0$$

$$\Delta S = b\{R + (R/2)(cH_0)\}$$

Therefore,

$$T_m = (H_0/R) / \{1 + (cH_0)/2\} \quad (26)$$

Hence,  $T_m$  is somewhat lower than is  $T_B$ . Moreover, the crystallization is much affected by orientation and  $T_m$  is changed from the above equation. A linear correlation is expected between  $\Delta H$  and  $\Delta S$ . It will be discussed in a later article.

## DISCUSSION

### Pseudocrosslink Model

The pseudocrosslink model was proposed long ago by several authors: Tobolsky et al.,<sup>8</sup> Yamamoto,<sup>9</sup> Lodge,<sup>10</sup> and the author.<sup>11</sup> They assumed the formation of temporary links for the explanation of viscoelastic phenomena. The author<sup>1</sup> proposed later the links of various sizes from the thermodynamical concept by which the distribution of the size of links together with the length of the chains connected with the links are predicted. Links form and dissociate with various relaxation times lying between  $10^{-7}$  and  $10^7$  s and the change is reversible but not temporary in this sense. The size of the link is also correlated with transition temperatures.

### Link Size and Chain Length

In this model, the multisize links and their distribution are assumed. It is in contrast to other models. In this model, a segmental motion in a molecular coil is dealt with for the viscoelastic region and the motion of the molecular coil for the viscous flow. Therefore, the translational motion of a segment is allowed for two directions except that along the molecular chain.

In contrast to this, in the tube model of Doi and Edwards,<sup>12</sup> the motion of the molecule is dealt with and, therefore, the translational motion of the segment is allowed only along the molecular chain. Accordingly, the tube model seems to be applied mostly for the viscous region.

### Transition Temperatures

$T_g$  is derived from the equation for relaxation times and found to be about 50° higher than  $T_A$  and this

is compatible with the prediction of Gibbs and DiMarzio.<sup>13</sup> The proportionality between the melting point and the glass transition point is known in the literature: In most cases, a ratio of  $T_g/T_m$  is 2/3, but for polyvinylidene compounds, it is 1/2. Since the heat of fusion  $\Delta H$  is proportional to the cohesion heat,  $T_m$  and  $T_g$  are proportional to the cohesion heat  $H_0$ .

It is interesting to note that eq. (13) also holds for glasses of simple organic compounds. Figure 3 is obtained from data of  $T_g$  of Seki<sup>14</sup> and  $T_m$  of conventional handbooks. Seki succeeded in the formation of glass by rapid cooling with liquid helium. Alcohol and even propylene are glassified. However, the glassification of ordinary liquids is, in general, difficult as compared with the corresponding polymers. There is a possibility of the formation of a chain structure before glassification for ordinary liquid. But it is only an assumption at present.

The glass transition temperature is affected by the rate of cooling and also by the molecular weight of the polymer. The latter is regarded as the effect of the terminal segment having a larger free volume and  $T_g$  is linearly correlated with the number-average molecular weight  $M_n$  as<sup>15</sup>

$$T_g = T_g + K/M_n$$

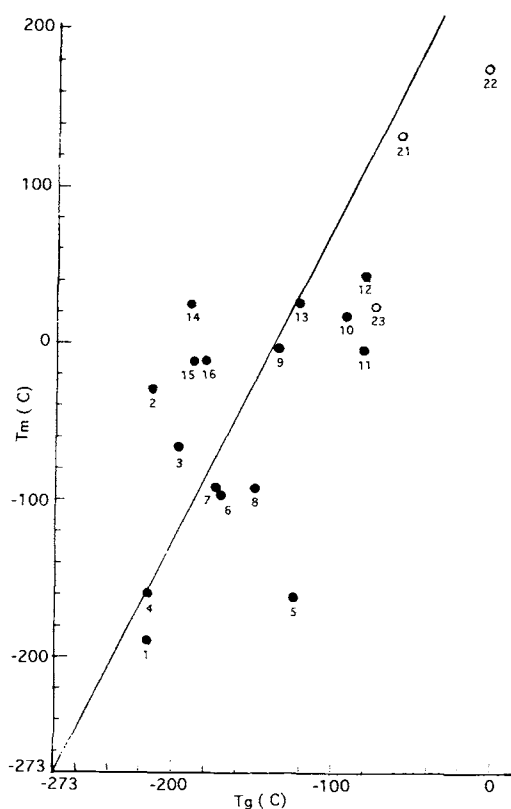
The terminal effect is important for polymers of high molecular weight.

However, the region of low molecular weight  $T_g$  seems to be affected by another origin. The plot of  $T_g$  against  $1/M_n$  in the range of  $(1-5)10^{-5}$  or  $n$  of  $(1-5)10^3$  does not always afford a straight line and gives curved ones for polymers of  $\alpha$ -methylstyrene and poly(methyl methacrylate) (PMMA). This range is rather of oligomer and eq. (13) or

$$T_g - T_A = A[1 + B \log n]$$

affords straight lines. The constants  $A$  are 440 and 390 K and the slopes  $B$  are 0.19 and 0.11, respectively.  $B$  is 2-3 times larger than the theoretical one and it seems to correlate with the cooling rate, because the freezing of the state requires a sufficient time at the end of polymer chains. The small value of  $B$  for PMMA may be explained by a steric hindrance giving a large kinetic segmental length and  $B$  becomes smaller. The cooling rate in glassification may be important for the precise determination of  $T_g$ .

According to eq. (13), the constant  $A$  is same as  $T_g$  for the largest oligomer  $B$ , above which  $T_g$  is not affected by the molecular weight.



**Figure 3** Linear relationship between  $T_m$  and  $T_g$  for organic liquid: (1) propene; (2) carbon tetrachloride; (3) chloroform; (4) isopentane; (5) ethanol; (6) methanol; (7) toluene; (8) vinyl acetate; (9) water; (10) propylene glycol; (11) glycerol; (12) diethylphthalate; (13) phenyl salicylate; (14) cyclohexanol; (15) cycloheptene; (16) cyclohexene. Polymers: (21) polyethylene; (22) polypropylene; (23) natural rubber.

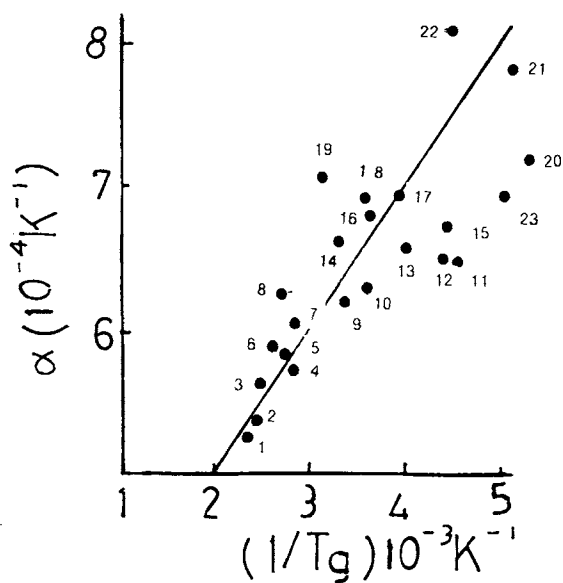
### Thermal Expansion

Figure 4 shows the relationship between the thermal expansion coefficient  $\alpha$  and the glass transition temperature  $T_g$  and it is compatible with eq. (19). The effect of the chemical crosslink  $\nu_1$  is interesting to note. The thermal expansion coefficient  $\alpha$  at 190-250°C decreases with increasing  $\nu_1$ , whereas at 50-140°C,  $\alpha$  increases according to Kinjo et al.<sup>16</sup>

Above  $T_g$ , the decreasing effect is due to the increase in  $T_g$ . However, below  $T_g$ , the coefficient for solid  $\alpha(s)$  is smaller than  $\alpha(l)$  by a factor of 1/4, as expected from eq. (20). Also,  $\alpha(s)$  increases with crosslinks according to eq. (23).

### Effect of Vulcanization

The increasing effect of vulcanization on  $T_g$  was pointed out and explained in terms of the effect on



**Figure 4** Relation between thermal expansion and  $T_g$ : (1) poly(*o*-methyl styrene); (2) poly(*p*-methyl styrene); (3) polysulfone; (4) poly(vinyl chloride); (5) polystyrene; (6) poly(methyl methacrylate); (7) poly(cyclohexyl methacrylate); (8) polycarbonate; (9) poly(*n*-butyl methacrylate); (10) poly[bis(chloromethyl oxyethylene)]; (11) *trans*-polyisoprene; (12) poly(ethylene oxide); (13) poly(methyl vinyl ether); (14) polychlorofluoroethylene; (15) *trans*-polybutadiene; (16) polymethylacrylate; (17) polypropylene; (18) poly(vinyl acetate); (19) poly(ethylene terephthalate); (20) poly(tetramethylene oxide); (21) poly(propylene oxide); (22) poly(vinylidene fluoride); (23) polyoxymethylene.

the free volume or the segmental motion in the literature.<sup>17</sup> The  $T_g$  of epoxy resin, polyurethane, alkyd resin, and natural rubber increases with increasing degree of vulcanization  $\nu_1$  and follows

$$T_g = A + B \log \nu_1$$

The slope  $B$  is high, about 180 K in most cases. As compared with eq. (21), the expression is somewhat different but of the same order. The above relation was observed at small degree of  $\nu_1$  as  $10^{-2}$ – $10^{-3}$ , corresponding a semivulcanization of the oligomer. Conventional vulcanized rubber of high molecular weight is known to have good low-temperature properties below  $-50^\circ\text{C}$  for hydrocarbon rubber.

Below  $T_g$ , the phenomena are complicated due to the condition of glassification. The contraction of free volume on cooling may be retarded by the elastic deformation caused by the formation of crosslinks. Such a negative effect is trapped in the glass by quenching and remains as an internal strain. It decreases  $\alpha$  from the thermodynamical value. In fact, the molar volume  $V$  increases but the elasticity  $E$

decreases with increasing the degree of vulcanization in contrast to the vulcanized rubber.

The property  $P$  in the solid state such as  $E$ ,  $V$ , and  $\alpha$  is expressed by Kinjo et al.<sup>18</sup> as

$$P = A + B \log \nu_1$$

The effect denoted by  $B/A$  is calculated. It seems rather smaller than that for  $T_g$ ,  $\alpha(l)$  and  $\alpha(s)$  (above  $T_g$ ) are  $-0.047$  and  $0.125$ , respectively, and almost of the same order as that of the theoretical ones.

For  $V$  and  $E$ ,  $B/A$  is  $0.018$  and  $0.5$ , respectively. Theoretically, the molar volume is a function of free volume or thermal expansion and the effect of vulcanization runs parallel to the effect on the thermal expansion.

A very large decrease in elasticity may be due to the increase of the free volume. The elasticity is expressed as an exponential function of the free-volume fraction similarly to the viscosity and eq. (16) may be used also for elasticity.

### Rebound Resilience of Rubber

Poly(vinyl ether) of various alkyl groups showed a relationship like that of eq. (24) in the literature.<sup>19</sup> A similar relation is roughly recognized from literature data of several kinds of rubbers, despite that of different conditions of vulcanization.

### Sound Velocity in Rubber

As compared with plastics, the sound velocity of rubber is very low,<sup>20</sup> because the former is glassy whereas the latter is rubbery. However, the softening temperature  $T_B$  is proportional to  $T_g$  and, therefore, rubbers of high  $T_g$  show high elasticity  $E$  and the sound velocity  $C$ . In fact,  $C$  and  $E$  tend to be in parallel to  $T_g$  in most cases. Rubbers having high steric hindrance such as polyisobutene, silicone rubber, and chlorosulfonated polyethylene show high velocity. A high value of *cis*-polybutadiene is due to a low  $T_g$  as compared with other rubbers such as natural rubber, styrene-butadiene rubber, polychloroprene rubber, and acrylonitrile-butadiene rubber.

### CONCLUSION

The glass transition and softening of polymers are concerned with rheological factors, but are expressed thermodynamically with aid of a concept of the pseudocrosslinks of various sizes. The melting point



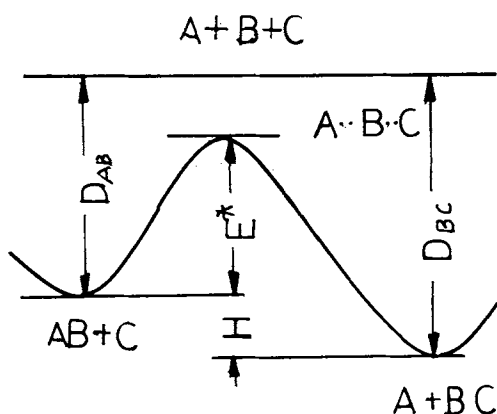
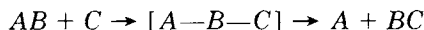


Figure 5 Schematic reaction path.

of the crystalline polymer and its relationship with the glass transition temperature is roughly discussed. As related problems, the thermal expansion, the rebound resilience of rubber, and the sound velocity in polymers are predicted. The temperature shift factor for the relaxation spectrum is derived.

## APPENDIX<sup>21</sup>

Let us consider the following reaction process as shown in Figure 5:



The energy levels of each stage are expressed as functions of the bond energies  $D$ 's of the compounds, i.e.,  $AB$ ,  $BC$ , and the activated intermediate  $[A-B-C]$  as  $D_{AB}$ ,  $D_{BC}$ , and  $D_{[A-B-C]}$ , respectively.  $D_{[A-B-C]}$  is assumed to be equal to an arithmetic mean of the initial, final, and nonbonded stages or  $A + B + C$  and the contribution of each stage is assumed to be all equal to  $1/3$ . Then, the activation energy  $E^*$  is given as

$$\begin{aligned} E^* &= D_{AB} - \left(\frac{1}{3}\right)(D_{AB} + D_{BC} + D_{A+B+C}) \\ &= \left(\frac{2}{3}\right)D_{AB} - \left(\frac{1}{3}\right)D_{BC} \end{aligned} \quad (\text{A.1})$$

because  $D_{A+B+C}$  is zero. Since the heat of reaction  $H$  is given as the difference  $D_{BC} - D_{AB}$ ,  $E^*$  becomes

$$E^* = \left(\frac{1}{3}\right)D_{AB} - \left(\frac{1}{3}\right)H \quad (\text{A.2})$$

which indicates that  $E^*$  decreases with decreasing the stability of the compound  $AB$  and with increas-

ing the heat of reaction  $H$ . For the decomposition reaction,  $D_{BC}$  is zero and  $E^*$  becomes  $\left(\frac{2}{3}\right)D_{AB}$  and it corresponds to the calculation of the activation energy in the case of eq. (8). On the other hand, in the viscous flow, the initial and final stages are both on the same level or  $H$  is zero and  $E^*$  becomes  $\left(\frac{1}{3}\right)D_{AB}$ . It corresponds to eq. (12).

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