Polymer Bulletin 7, 31–37 (1982)

Polymer Bulletin

A Theory of Pseudo Cross-Link
2. Transitions and Relaxation Spectra

Junji Furukawa

Department of Applied Chemistry, Aichi Institute of Technology, Yakusa-cho,
Toyota, 470-03 Japan

Summary

A theory of pseudo cross-link model suggests the existence of multiple links of various size composed of 1~16 segmental units. They possesses the heat and entropy of various magnitude giving various transition temperature, T_A for the cross-link composed of 4 segments and T_B for that of 16 segments. The glass-transition point T_g and the melting point T_m are defined by the different size of lateral multiple links. Relationships, $T_m = 2T_A$ and $T_g = (2/3)T_m = (4/3)T_A$, are derived. A wedge-type relaxation spectrum is obtained as a distribution of size of cross-links. For temperature dependence the WLF-equation is obtained.

Theory

In the preceding paper the author discussed on the viscosity and the diffusion of the polymer in the molten state or in the concentrated solution with emphasis on the effect of a molecular entanglement due to a segmental interaction which is proportional to the third power of molecular weight as is expressed by equation (1).

$$\nu/N = n_0^3 K \varepsilon \qquad (1)$$

Where ν and N are the number of cross-linked segments and that of total segments existing in 1 cm^3, respectively. n_0 is the number of segments in a molecule proportional to the molecular weight. K is a fractional equilibrium constant for the cross-linking and expressed as an exponential function of the heat, ΔH and the entropy, ΔS, of cross-linking.

$$K = \exp\left\{\frac{-\Delta H}{RT} - \frac{\Delta S}{R}\right\} \qquad (2)$$

Equation (1) is n_0^3-times larger than the value for the ordinary association given by equation (3), if a factor ε is taken to be unity

$$\nu/N = n_0^3 K \qquad (3)$$

This is because that equation (1) involves the calculation of coordination factor of the molecular coils, which is overlapped to each others and this

0170-0839/82/0007/0031/$01.40

effect is canceled by the rapid configurational change of the molecule or the rapid relaxation of the cross-link. Under the condition of complete melting the rapid configurational change of the molecule is allowed to occur to the difinite size of the molecule, i.e. n_B , and ε is to be

$$\varepsilon = 1/n_B^3 \qquad (4)$$

Accordingly, equation (1) is rewritten as

$$\nu/N = (n_0/n_B)^3 K \qquad (5)$$

However, the configurational change of a molecule is a rate process and ε is a function of the rate of deformation and the temperature. After gelation the chain length n is to be taken instead of the molecular length, n_0, and consequently,

$$\nu/N = n^3 K\varepsilon$$

Since n is to be N/ν in the gel, it follows that

$$\nu/N = K^{1/4}\,\varepsilon^{1/4} \qquad (6)$$

In fact,the vulcanization of rubber shows that the elasticity was found to be proportional to $t^{1/4}$, t being a time of vulcanization[1]. This fact is derived from the following equations with a rate constant k.

$$\frac{d(\nu/N)}{dt} = k\left(\frac{N-\nu}{\nu}\right)^3 \varepsilon \cong k(N/\nu)^3\,\varepsilon \qquad (7)$$

or

$$\nu/N = (kt\varepsilon)^{1/4} \qquad (8)$$

1. Flow temperature

Since the collision of segments in a chain composed of n_B segments is proportional to n_B^2, the configurational entropy obtained by the dissociation of a cross-link is $R \ln n_B^2$ and the activation free energy of configurational change, ΔF^*, for a chain is

$$\Delta F^* = E^* - R \ln n_B^2 \qquad (9)$$

where E^* is the activation heat of the dissociation equal to $-\Delta H$. The condition at which ΔF^* becomes zero gives a transition, above which the molecular flow occurs.

$$E^*/RT_B = 2 \ln n_B \qquad (10)$$

On the other hand, a chain possessing n_B segments, i.e. the B-chain, is linked with one cross-link in the gel condition and therefore,

$$n_B = N/\nu_B \qquad (11)$$

where ν_B is a number of the B-cross-link in 1 cm^3. Substituting equations (2) and (3) into equation (11), it follows that

$$n_B = \exp\left\{\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right\} \qquad (12)$$

and from equations (10) and (12), T_B is obtained as follows

$$T_B = \frac{3}{2}\frac{\Delta H}{\Delta S} \qquad (13)$$

Here, $\Delta H/\Delta S$ implies another transition temperature, T_A or

$$T_A = \Delta H/\Delta S \qquad (14)$$

T_B is 1.5 times higher than T_A.

$$T_B = 1.5\ T_A \qquad (15)$$

T_B is regarded as a transition temperature above which the B-cross-link is capable of dissociation. The viscous flow results in by the successive dissociation of the B-cross-links, and it is a rate process requiring a relaxation time τ. Accordingly, in a time t shorter than τ the complete change of the molecular configuration of the B-chain does not occur, and

at t=0

$$\left(\frac{\nu_B}{N}\right)_{t\to o} = n_B^3 K \qquad (16)$$

and at $t > \tau$

$$\left(\frac{\nu_B}{N}\right)_{t>\tau} = K \qquad (17)$$

In general, ν_B is expressed as a function of time as follows,

$$\nu_B/N = (1 + n_B^3\ e^{-t/\tau})\ K \qquad (18)$$

Below T_B,

$$(\nu/N)_{t\to o} = n^3K = (N/\nu)^3K \qquad (19)$$

or

$$(\nu/N)_{t\to o} = K^{1/4} = \exp\left\{\frac{1}{4}\left(\frac{-\Delta H}{RT} + \frac{\Delta S}{R}\right)\right\} \qquad (20)$$

Equation (20) suggests that the B-cross-link possesses a free energy of the formation smaller than that at the equilibrium condition. In other words, the B-cross-link is a multiple link and coexists with a smaller link having one fourth of the free energy of formation. The latter is denoted by ν_A and expressed by

$$\nu_A/N = \exp\left\{\frac{1}{4}\left(\frac{-\Delta H}{RT} - \frac{\Delta S}{R}\right)\right\} = \exp\left\{\frac{-\Delta H_A}{RT} + \frac{\Delta S_A}{R}\right\} \qquad (21)$$

where ΔH_A and ΔS_A are the heat and entropy of the formation of the A-cross-link, respectively and they are one fourth of those of the B-cross-link. Equation (21) is also obtained by the statistical calculation. Since the probability of formation of the B-cross-link is given by the successive formation of the A-cross-links,

$$\frac{\nu_B}{N} = \left(\frac{\nu_A}{N}\right)^4\left(1 - \frac{\nu_A}{N}\right) = \left(\frac{\nu_A}{N}\right)^4 = \exp\left\{4\left(\frac{-\Delta H_A}{RT} + \frac{\Delta S_A}{R}\right)\right\} \qquad (22)$$

Here, ν_A/N and $(1 - \nu_A/N)$ are the probability of crosslinking of the A-cross-link and that of non-crosslinking.

In a simmilar way, the A-cross-links coexist with the smaller cross-links, whose population is ν_0/N.

$$\frac{\nu_0}{N} = \left(\frac{\nu_A}{N}\right)^{1/4} = \exp\left\{\frac{1}{16}\left(\frac{-\Delta H}{RT} + \frac{\Delta S}{R}\right)\right\} \qquad (23)$$

It is likely assumed that there are multiple cross-links of various size. The population of the b-cross-link composed of b segments is given by

$$\frac{\nu_b}{N} = \exp\left\{\frac{b}{16}\left(\frac{-\Delta H}{RT} + \frac{\Delta S}{R}\right)\right\} \qquad (24)$$

Obviously b is distributed in a range between 1 and 16, as shown in figure 1.

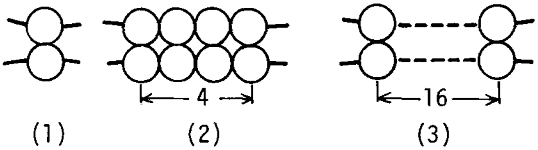

Fig.1 Multiple cross-links : (1) Single link (2) A-link , (3) B-link

The unit cross-link is estimated from the heat of crosslinking. In the crystallization one segment is linked with other segments of the solid and looses a configurational entropy equal to R (the gas constant) on the formation of one link, whose heat or the heat of crystallization is ΔH_m. On the contrary, in the formation of a cross-link, two segments are involved loosing an entropy of 2R for one cross-link. Accordingly, the heat, ΔH_0 and the entropy, ΔS_0, of cross-linking for one segment are respectively

$$\Delta H_0 = \Delta H_m/2 \qquad (25)$$

and

$$\Delta S_0 = R \qquad (26)$$

Since ΔH_m for hydrocarbon polymers is about 700 cal/mole of CH_2-unit, ΔH_0 is 350 cal/mole which is smaller than the thermal energy, RT, at room temperature. In other words, the cross-link denoted by ν_0 is not observable and the A-cross-link is taken to be as the smallest size of cross-link. Under the above assumption, it follows that ΔH_A is 1.4 Kcal and ΔH_B is 5.6 Kcal. The A-cross-link and the B-cross-link are composed of the units of $(CH_2)_4$ and $(CH_2)_{16}$, respectively.

2 Transition temperature

There are various transition temperatures, T_A, T_B or T_m. They correlate with each others as follows

$$T_A = \Delta H/\Delta S \qquad (26) \qquad\qquad T_B = 1.5\ T_A \qquad (27)$$

and

$$T_m = 2\ T_A \qquad (28)$$

The crosslinks at the corresponding temperatures are given by

$$\frac{\nu_A}{N} \doteq \exp\left\{\frac{\Delta S_A}{R}\left(1 - \frac{T_A}{T_A}\right)\right\} = \exp\left(1 - \frac{T_A}{T_A}\right) = 1 \qquad (29)$$

$$\frac{\nu_B}{N} = \exp\left\{\frac{-\Delta S_B}{R}\left(1 - \frac{T_B}{T_A}\right)\right\} = \exp\ (-16/3) = 10^{-2.3} \qquad (30)$$

The elasticities at T_A and T_B, i.e. E_A and E_B, respectively, are expressed as

$$E_A = \frac{\nu_A}{N} \cdot \left(\frac{N_0}{V}\right)kT = \left(\frac{\nu_A}{N}\right)\frac{RT}{V} \qquad (31)$$

and

$$E_B = \left(\frac{\nu_B}{N}\right)\frac{RT}{V} \qquad (32)$$

where N_0 is Avogadro's number and V is the molar volume of segment. Taking 4 x 14 cm^3 for V, E_A and E_B are $10^{8.5}$ and 10^6 dyne/cm^3. They do not depend on the value of ΔH, although thier temperatures are shifted as shown in figure 2. At the transition point T_A, the cross-link occurs between two segments and in the glassy state a lateral multiple cross-link composed of more than two segments may be formed. For example, the crosslink is formed among three segments by two crosslinks as shown in figure 3. The glass-transition may be induced by such a lateral multiple bond and in this case the heat and the entropy, i.e. ΔH_g and ΔS_g per one segment are

$$\Delta H_g = 2/3 \cdot \Delta H_m \qquad (33)$$

$$\Delta S_g = R \qquad (34)$$

From equations (33) and (34), the glass-transition temperature, T_g is expressed

$$T_g = \frac{\Delta H_g}{\Delta S_g} = \frac{2}{3}\,T_m = \frac{4}{3}\,T_A \qquad (35)$$

It is well-known that Tg is two thirds of T_m and T_g is a little higher than the transition T_A.

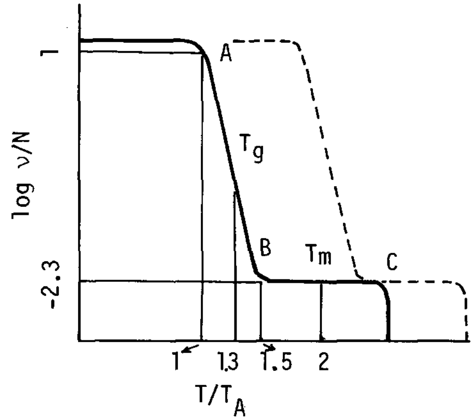

Fig.2 Temperature spectrum

The dotted line indicates a spectrum for the polymer of higher ΔH than that denoted with a solid line.

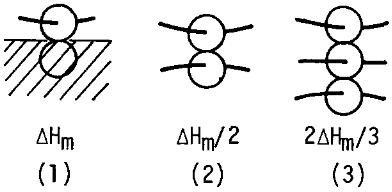

Fig.3 Lateral multiple crosslink with heat of formation (1) on the crystal (2) single link (3) three-segmental link

3 Relaxation spectra

The cross-link possesses different heat of crosslinking and therefore, different heat of activation for the dissociation depending on its size. The relaxation is determined by the rate of dissociation and consequently, the relaxation time, τ, is expressed as an exponential function of the activation energy of bond dissociation proportional to its size b.

$$\tau_b = \frac{h}{kT} \exp\left\{ b \cdot \frac{E_0^*}{RT} \right\} \qquad (36)$$

where h is the Planck constant. E_0^* is an activation energy for the dissociation of the unit cross-link. Eliminating b from equations (24) and (36), it follows that

$$\log \frac{E_b}{E_A} = \log \frac{\nu_b}{\nu_A} = \left(1 - \frac{T}{T_A}\right) \log \frac{\tau_b}{\tau_A} \qquad (37)$$

Since ν_b/ν_A is proportional to the ratio of the elasticity E_b/E_A, equation (37) gives a linear relation between log E and log τ, or a wedge-type relaxation spectrum as shown in figure 4. The slope is given by $(1 - T/T_A)$ which is about -1/2 in a range between Tg and T_B i.e. 1.3 T_A and 1.5 T_A, respectively. The relation is compatible with the experimental relation.

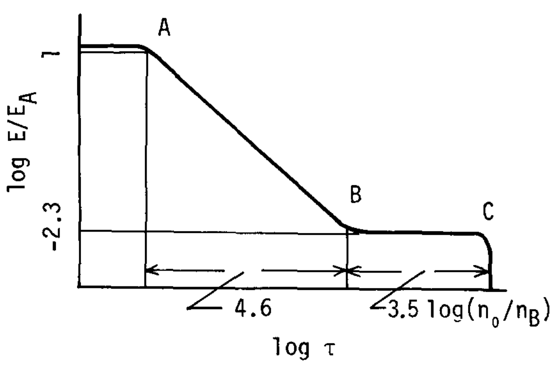

Fig.4 Relaxation spectrum

Equation (37) also suggests that the elasticity is much changed by the temperature. Taking E_b constant, the relation between T and τ is obtained. For example, Tg and τ_g are correlate as

$$\log \frac{E_b}{E_A} = \left(1 - \frac{T_g}{T_A}\right) \log \frac{\tau_g}{\tau_A} \qquad (38)$$

Combining equations (37) and (38), it follows that

$$\log \frac{\tau_b}{\tau_g} = \left(\log \frac{E_b}{E_A}\right) \left\{ \frac{1}{1 - T/T_A} - \frac{1}{1 - Tg/T_A} \right\}$$

$$= \frac{\log E_b/E_A}{T_g/T_A - 1} \; \frac{T - T_g}{(T_g - T_A) + (T - Tg)} \qquad (39)$$

Equation (39) gives an equation for a shift factor with respect to temperature proposed by Williams, Landel and Ferry.[2] Taking -3 for $\log(E_b/E_A)$, 1.33 for T_g/T_A and 50°C for $T_g - T_A$, equation (39) becomes

$$\log \frac{\tau}{\tau_g} = \frac{-10(T - T_g)}{50 + T - T_g} \qquad (40)$$

Equation (40) is similar to the WLF-equation, although the coefficient is not completely identical. More detailed consideration may be necessary for the simultaneous formation of lateral multiple bonds together with that of longitudinal ones.

Equation (35) is to be applicable to the temperatures between T_A and T_B

and above T_B, the spectra are shifted according to equation (36) and also the factor arising from the molecular weight or n_0 of the polymer, since the relaxation time is also a function of n_0, namely,

$$\tau = \left(\frac{h}{kT}\right) e^{E_B^*/RT} \cdot \left(\frac{n_0}{n_B}\right)^{3.5} \qquad (41)$$

and

$$E \doteq \frac{\nu_B}{N} \frac{RT}{V} \qquad (42)$$

Equation (42) gives a box-type relaxation spectrum.

References

1. FURUKAWA, J., ONOUCHI, Y., INAGAKI, S. and OKAMOTO, H., Rubber Processing and Applications, 1 , 173(1982)
2. MILLIAMS, M. L., LANDEL, R. F. and FERRY, J. D., J. Amer. Chem. Soc., 77, 3701(1955)

Received and accepted March 8, 1982