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A Theory of Pseudo Cross-Link

1. Viscosity of Polymers in Molten States and in Concentrated Solution

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Summary

It is assumed that the polymer forms a sphere coil and overlapped with other coils. Pseudo crosslinking takes place by a temporary association of segments. The calculation result shows that pseudo cross-link is proportional to $(n_0/n_B)^3$, n_0 being the degree of polymerization of the molecule and n_B that of the chain. Since the rate of flow is inversely proportional to $(n_0/n_B)^{3.5}$ the viscosity is proportional to $(n_0/n_B)^{3.5}$. It is also proportional to C^n, C being the concentration and n being more than 2. Diffusion is inversely proportional to $(n_0/n_B)^2$. Branched polymer shows low viscosity, proportional to $s(n_0/s)^{3.5}$, s being the number of branch.

Introduction

It is well-known that polymers in the molten state or in the concentrated solution exhibit very high viscosity proportional to the 3.5th power of the molecular weight and more than 2nd power of the concentration. Moreover, the polymer shows visco-elastic behavior depending on the temperature and the rate of deformation. In order to interprete the above behavior, a pseudo cross-link structure of the polymer has been proposed by the several authors[1~3] A pseudo cross-link is defined as a temporary cross-link forming between two segments by an intermolecular force and changing its position during deformation of the molecular chain. This sort of concept seems to be useful for explanation of the elastic behavior of the polymer but not always for the viscous nature. Instead, another model such as reptation[4] or tube model[5] was proposed which gave an interpretation of high viscosity of the molten polymer, but the scope of the model is at present limited only to the viscous region or a box-type relaxation spectrum.

The author investigated the nature of the pseudo cross-bond and extended the model to the viscosity of the polymer network[6]. This paper describes a summary of the further study.

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Theory

1 Pseudo cross-link

The formation of the pseudo crosslink resembles a temporary association of the ordinary molecule except that the segments of the polymer form a chain. The temporary association of the molecule can be expressed by the difference between the association and dissociation. Let us suppose that ν molecules are associated among N molecules in a unit volume, i.e. 1 cm^3, to form $\nu/2$ links, then the change $d\nu/dt$ is expressed by an equation (1).

$$\frac{d\nu}{dt} = k(N - \nu)^2 - 2k'(\nu/2) \qquad (1)$$

Where k and k' are respectively a bimolecular reaction constant of the association and a unimolecular one of the dissociation giving two free molecules. An equilibrium number of associated molecules for a small ν is

$$\nu = \frac{k(N - \nu)^2}{k'} = \left(\frac{kN}{k'}\right) N = KN \qquad (2)$$

where K is an equilibrium constant of the association and expressed as an exponential function of the exthothermal heat of association, ΔH, and entropy loss of a segment, ΔS. Both ΔH and ΔS are of negative value.

$$\frac{\nu}{N} = K = \exp\left\{\frac{-\Delta H}{RT} + \frac{\Delta S}{R}\right\} \qquad (3)$$

For large ν value equation (3') is to be used, instead of equation (2).

$$\frac{\nu}{N} = \frac{K}{1 + K} \qquad (3')$$

In case of the polymer a similar equation to (3) is applicable, if the mobility of the segments is not limited, but actually the region of the segmental motion is limited to the volume of a sphere of the coiled molecule as shown in figure 1. Consequently, the number of collision of the segments is different from that of ordinary molecules, the latter of which is proportional to N^2. A molecule composed of n_0 segments whose diameter is ℓ forms a coiled sphere whose diameter is $(n_0^{1/2}\ell)$ and whose volume is $(n_0^{3/2}\ell^3)$. The collision occurs in a region V overlapping two coils and the number of collision of segments is proportional to the square of concentration of segments in a coil, i.e. $(n_0/n_0^{3/2}\ell^3)$ and the number of combination of segments between two molecules, i.e. n_0^2,

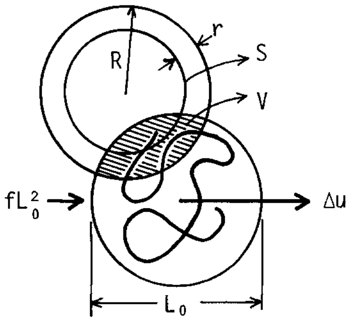

Fig. 1 Coiled sphere moving

and therefore, the equilibrium value of cross-linked segments, ν, is

$$\nu \backsim (n_0/n_0^{3/2}\ell^3)^2 (n_0^2)\ K \qquad (4)$$

Since the collision of segments takes place in an overlapped volume, V, of two coiled spheres, the number of available sites for the collision is multiplied. V is given as a function of overlapping distance, r, by

$$V = \frac{1}{3}\pi r^2 (3R - r) \qquad (5)$$

The overlapping zone of the same volume V is locating on a sphere surface S, which is given by

$$S = 4\pi (R - r)^2 \qquad (6)$$

The total number of coordination sites is given by the integration of VS with respect to r varying from zero to 2R or $n_0^{1/2}\ell$, and divided by the square of segment volume, v_0^2,

$$\Sigma VS/v_0^2 = \int_0^{2R} \frac{4}{3}\pi^2 r^2 (3R - r)(R - r)^2 dr / [4/3\pi(\ell/2)^3]^2$$

$$\doteq 0.9\ n_0^3 \qquad (7)$$

Equation (7) is to be multiplied by the number of coils per unit volume, i.e. N/n_0 and divided by the total number of sites in a unit volume for the calculation of the configurational efficiency for overlapping coils.

$$\nu \backsim \left(\frac{N}{n_0}\right)\left(\frac{\Sigma VS}{v_0^2 N}\right)\left(\frac{n_0}{n^{3\ 2} v_0}\right)^2 n_0^2 K \qquad (8)$$

Since v_0 is a volume of a segment and is equal to 1/N, equation (8) becomes

$$\nu \backsim 0.9\ n_0^3 KN \qquad (9)$$

Equation (9) is larger than equation (2), because equation (9) involves overlapped calculation of volume V. If the motion of the segments of a molecules is not limited, the factor n_0^3 in equation (9) may be varnished. However, the configurational change of the polymer molecule may be a rate process and the rapid change is limited to a finite value of polymer length, n_B. Consequently, equation (8) is to be multiplied by a factor ε, which is equal to $1/n_B^3$.

$$\frac{\nu}{N} = n_0^3 K\varepsilon = \left(\frac{n_0}{n_B}\right)^3 K = z^3 K \qquad (10)$$

or $\varepsilon = 1/n_B^3$, and $z = n_0/n_B$

In other words, a polymer molecule is divided into z unit coils having n_B segments. The number of pseudo cross-links is larger by a factor z^3 than the value calculated for the simple molecule and this implies that the relaxation of links is not so fast as a simple molecule and z^3- times relaxation phenomena occur for the transition of one molecule in the viscous flow. Since equation (10) is derived based on the network structure, equation (10) is applicable to the polymer, whose degree of polymerization and concentration are larger than their limited values, n_B and C_B. Gelation occurs under the condition, that the number of cross-links is larger than the number of molecule, and consequently

$$\frac{N C_B}{n_B} = \nu = \left(\frac{n_B}{n_B}\right)^3 C_B^2 K$$

or

$$n_B C = 1/K \qquad (11)$$

2 Viscosity of the molten polymer

Viscous flow of the polymer is caused by the shear force, which is given by the force f acting on a unit area multiplied by the cross-sectional area A_0 and divided by the unit bottom area A_0. The velocity difference Δu exists between two coils, whose distance is given by an average distance of two coils, i.e. $L_0/2$ and $\Delta u/L_0$ gives a velocity gradient. The viscosity η is defined by equation (12).

$$\frac{\Delta u}{L_0/2} = \frac{f}{\eta} \qquad (12)$$

For the polymer, f is given by an elastic force, i.e.

$$f = \nu k T (\lambda - 1) \qquad (13)$$

where k is the Boltzmann constant and $(\lambda - 1)$ is the elongation ratio of a chain. If the dissociation of a pseudo cross-link is a rate-determining step, which is followed by the rapid shrinkage of a chain and by the reformation of a new pseudo crosslink at a new position apart. Provided that the rate-determining step of flow is the dissociation of a pseudo cross-link whose rate constant is k', the relaxation time, τ of the molecule, is z^3- times larger than that of a chain, i.e. 1/k' and Δu is given by a product of $1/\tau$, L_0 and its elongation ratio $(\lambda - 1)$. The velocity gradient is

$$\frac{\Delta u}{L_0} = \frac{k' L_0 (\lambda - 1)}{L_0 z^3} = \left(\frac{n_B}{n_0}\right)^3 k'(\lambda - 1) \qquad (14)$$

The viscosity of the polymer, η, is derived from equations (12), (13) and (14),

$$\eta = \frac{f}{2\Delta u/L_0} = \left(\frac{n_0}{n_B}\right)^3 \nu_B k T/2 k' \qquad (15)$$

where k' is given as an exponential function of the activation energy of flow E^*

$$k' = \left(\frac{kT}{h}\right) e^{-E^*/RT} \qquad (16)$$

where k and h are the Boltzmann's and Planck's constant, respectively. Since the elasticity E is given by ν_B, the Avogadoro's number N_0 and the molar volume of a segment V,

$$E = \nu_B k T = \frac{\nu_B}{N} \cdot \frac{N_0 k T}{V} = \frac{\nu_B}{N} \cdot \frac{R T}{V} \qquad (17)$$

the relaxation time, τ, is

$$\tau = \frac{\eta}{E} = \frac{1}{2}\left(\frac{n_0}{n_B}\right)^3\left(\frac{h}{kT}\right) e^{E^*/RT} \tag{18}$$

In conclusion, viscosity is to be proportional to the third power of the degree of polymerization or the molecular weight, but actually to the 3.4 ~ 3.5-th power. The latter relation is obtained if the flow distance in equation (14) is taken to be a chain distance, $n_B^{1/2}\,\ell$, instead of a molecular distance $n_0^{1/2}\,\ell$, it follows that

$$\eta = \left(\frac{n_0}{n_B}\right)^{3.5}\nu_B\, k\,T/\,2\,k' \tag{19}$$

Equation (14) is assumed to be affected by the applied force or the rate of shear. Since the polymer network is extended to the direction of stretching, the unit network is deformed. When it is stretched by λ, the actual cross-sectional and bottom areas of the unit network are $1/\lambda$- and $(1/\sqrt{\lambda})\mathrm{x}\lambda$-times larger than the original one and hence, the actual viscosity η is proportional to $\lambda^{-3/2}$. In addition, the activation energy for the dissociation of cross-links is also lowered by the applied force. The work done, W, is given by a product of the force, f, acting on a unit cross-sectional area of the chain , L_B^2, and the loosening distance of cross-bond, $\delta\ell$,

$$W = f\,L_B^2\,\delta\ell = \nu_B\, k\,T(\lambda - 1)\left[\left(\frac{N}{\nu_B}\right)^{1/2}\ell\right]^2\delta\ell = k\,T(\delta\ell/\ell)(\lambda - 1) \tag{20}$$

Since the density difference between solid and liquid is in general nearly 1.1, the value of $\delta\ell/\ell$ is to be 0.03, namely

$$\frac{\ell^3}{(\ell + \delta\ell)^3} = \frac{1}{1 + 3\;\delta\ell/\ell} = \frac{1}{1.1} \tag{21}$$

Consequently, it follows that

$$\eta \propto \lambda^{-3/2}\ \exp\left\{\frac{E^*/N_0\ -\ W}{kT}\right\} = \lambda^{-3/2}\ \exp\left(\frac{E^*}{RT}\right)\ \exp\{-\ 0.03(\lambda - 1)\} \tag{22}$$

It can be concluded that the effect of loosening of the cross-bond is neglegible as compared with that of deformation of the network and the viscosity is

$$\eta \propto \lambda^{-1.5} = \left\{\frac{1}{(f/\nu_B\, k\,T)\ +\ 1}\right\}^{1.5} \tag{22}$$

3 Viscosity of the concentrated solution

In the solution, the concentration of the polymer, C mole of segment in N mole of segments, is involved in the calculation in equation (8). The number of coils, N/n_0, and the total number of coordination $\Sigma VS/\ell^6$ are multiplied by C, respectively, but the concentration of segments in a coiled shpere is remained unchanged, because the coil involves always one polymer molecule concerned, although other sites in a coil are occupied by the solvent instead of other polymer segments. As a result, equation (8) is rewritten as

$$\nu \propto \left(\frac{N\,C}{n_0}\right) (C\,\Sigma VS/\ell^6)(1/N) \left(\frac{n_0}{n_0^{3/2}\,\ell^3}\right)^2 n_0^2\,K$$

$$\propto n_0^3\,C^2\,K \qquad (23)$$

However, if the solvation of the segments takes place, the dissocation of a pseudo cross-link is enhanced by solvation which is proportional to the number of cross-bond, the concentration of solvents, i.e. N(1 - C) and the rate constant of solvation, k_s'. Accordingly, an equilibrium value of ν is calculated

$$\frac{d\nu}{dt} = k\,n_0^3 NC^2 - 2k'\nu/2 - 2k_s'(\nu/2)N(1 - C) = 0 \qquad (24)$$

or

$$\frac{\nu}{N} = \frac{k\,N\,n_0^3 C^2}{k' + 2k_s' N(1 - C)} \qquad (25)$$

Equation (20) suggests that the viscosity is proportional to the concentration of the order higher than two.

4 Diffusion of polymer

Diffusion of the simple molecule was discussed by Eyring[7] in terms of his theory of rate processes. In a similar way, the diffusion coefficient D is defined by the following equation (26),

$$ds = -\,DA\,\frac{dC}{dx}\,dt \qquad (26)$$

where ds is the quantity of the polymer that crosses a boundary of cross-section A in the time dt when the concentration gradient is dC/dx, the distance x being measured in the direction of diffusion. The polymer molecule moves by a distance between the successive equilibrium position equal to the diameter of the molecular coil, i.e. L_0. The diffusion rate, ds/dt, is also proportional to the moving velocity of the coil, Δu.

$$\frac{ds}{dt} = A\,N\left(L_0\frac{dC}{dx}\right)\Delta u \qquad (27)$$

Combining equations (26) and (27) gives

$$D = L_0 \Delta u \qquad (28)$$

Here, Δu is similar to that in equation (14), but does not involve a factor arising from the chain elongation, λ.

$$\Delta u = \left(\frac{n_B}{n_0}\right)^3 k'\,L_0 \qquad (29)$$

Let L_0 be equal to $n_0^{1/2}\ell$, it follows that

$$D = \frac{n_B^3\ell^2}{n_0^2}k' = \left(\frac{n_B}{n_0}\right)^2 (n_B^{1/2}\,\ell)^2 \left(\frac{kT}{h}\right) e^{-E^*/RT} \qquad (30)$$

Equation (30) leads us to a conclusion that the diffusion rate is inversely proportional to the square of molecular weight, which is similar to that derived from the reptation or tube model.

5 Branched polymer

Star-shaped polymers form a coil of smaller size than linear polymers. The diameter of coiled sphere of the polymer having s arms is $(2n_0/s)^{1/2}\ell$. Putting this value into equation (8) gives the same equation as equation (8)

$$\nu \propto \left(\frac{N}{n_0}\right)(2n_0/s)^{\frac{3}{2}\times 2}\left(\frac{1}{N}\right)\left[\frac{n_0}{(2n_0/s)^{3/2}\ell^3}\right]^2 n_0^2 k/k'$$

$$= n_0^3 N K \qquad (31)$$

In the case (a) the molecule is assumed to be enough large to form a coil involving a whole molecule. In other case (b), each branches form thier independent coils, although they are linked to each others as illustrated in figure 2. Another equation is obtained : the length of molecule is decreased by 1/s but the s coils are linked, and consequently

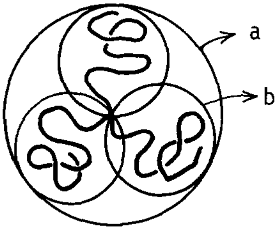

Fig.2 3-Branched polymer coils involving a whole molecule (a) and a chain (b)

$$\nu \propto \left(\frac{N}{n_0}\right)\left[s\left(\frac{n_0}{s}\right)^{3/2}\right]^2\left(\frac{1}{N}\right)\left[\frac{n_0/s}{(n_0/s)^{3/2}\ell^3}\right]^2 (n_0/s)^2 k/k'$$

$$= s\left(\frac{n_0}{s}\right)^3 N K \qquad (32)$$

Equation (32) implies that the number of pseudo cross-links and the viscosity of the branched polymer are lower than those of the linear polymers of the same molecular weight. However, it is assumed that independent coils tend to unite each others when the molecular weight of branched chain increases due to increase of chain flexibility and equation (31) is used. Consequently, the melt viscosity is given by equation (33)

$$\eta \propto s\left(\frac{n_0}{s}\right)^{3.5} \sim n_0^{3.5} \qquad (33)$$

6 Rigid rod-like polymer

In a rigid rod-like polymer, the diameter of the coil is larger than that of a flexible polymer, but this effect is canceled in the calculation of coordination number of coils and the concentration of molecule in a coil. The most influential effect arises from the ability of configurational change of a molecule in a coil, which is much smaller than the flexible polymer, and consequently, the factor n_0^2 is decreased to 1 for the complete rigid polymer. Accordingly, the order of molecular weight dependency of the pseudo cross-link and the viscosity becomes nearly unity.

$$\frac{\nu}{N} = \left(\frac{N}{n_0}\right)(n_0^3)^2(1/N)\left(\frac{n_0}{n_0^3 \ell^3}\right)^3 \text{ x } \varepsilon K = n_0 K\varepsilon \qquad (34)$$

The effect of the concentration seems to be somewhat complicated, because the ability in configurational change of the molecule in a coil and a factor ε may be increased with dilution of the polymer.

In summary, a pseudo cross-link hypothesis seems to be useful for explanation of viscous property of molten polymer or concentrated polymer solution in relation to thier polymer structure. So far as viscosity and diffusion of molten polymer or concentrated solution concern, the results is almost same as that from the reptation or tube model. It seems that the segmental motion inside and outside of the unit B-coil corresponds, respectively, to those of the "tube". Accordingly, the size of the B-coil or tube is very important and it will be discussed in the following paper.

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