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A Theory of Pseudo Cross-Link
6. Polymer Melt, Dilute Solution and Semi-Dilute Solution

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Summary

The calculation of entanglement is reexamined and it is expressed by two factors nc^2 and n^2c^2, n and c being the length of the polymer and its concentration, respectively. Both factors are concerned with the inter-coil interaction revealing in the melt viscosity η so that η is proportional to $n^{3.5}c^{4.5}$. At the melt temperature T_B, a critical chain length n_B is 256 and T_B is twice as high as T_A, i.e. a liquid-solid transition. At T_B the entropy of cross-linking becomes 2/3 times of that at T_A. The osmotic pressure increases in the semi-dilute solution by a factor of $(c/c^*)^{4/3}$, c^* being a critical concentration for overlapping. In the dilute solution in θ-solvents the cohesion of segments enables the independent coil to form an intra-coil linking even below c^* and induces the coil-globule transition at the θ-point to give rise to self-coaguration.

Introduction

It was known that the polymer coils overlap to each others in the semi-dilute solution when the concentration c is larger than a critical one c^*. And the osmotic pressure π in good solvents is larger than that of the dilute solution by the overlapping factor $(c/c^*)^a$. The exponent a is derived from the scaling law to be $1/(3\nu_D - 1)$ and 1.33 taking a parameter ν_D proposed by de Gennes to be 0.585[1].

On the other hand, the dilute solution in θ-solvents shows the clouding below the θ-point in spite of very dilute solution and the coil is known from the viscosity measurement to be collapsed to a globule by lowering the temperature.

These phenomena, especially the meaning of the exponent a and the reason for the transition are not completely elucidated. The author proposes an explanation based on a theory of pseudo cross-link[2]. In this connection, the nature of the polymer melt is reexamined.

1. Overlapping of coils

The critical concentration c^* is given as follows: The volume of a cube-shaped coil is $n^{3/2}v_0$, and the concentration of the polymer coil is c/nv_0, where n is the segmental molecular length, c is a fractional concentration and v_0 is the volume of a segment. In a closed packing,

$$(c^*/nv_0)(n^{3/2}v_0) = 1 \quad (1) \qquad \therefore\ c^* = 1/n^{1/2} \quad (2)$$

The ratio c/c^* is called as a degree of overlapping. The effect of overlapping can be discussed by a theory of pseudo cross-link as described previously: The association of simple molecules is expressed as

$$\nu = c^2N^2k/k' \quad (3) \qquad \text{or} \qquad \nu/N = c^2K \quad (4)$$

where ν and N are the number of associated and total molecules in 1 cm^3, respectively and K is a fractional equilibrium constant. For long chain molecules the following overlapping factors are multiplied.

(i) Square of the concentration of a molecule in a coil, i.e.

$$(n/n^{3/2}v_0)^2 = 1/nv_0^2$$

(ii) Number of combination of segment for the cross-link between two chain molecules, i.e. n^2

(iii) Number of coils existing in a volume of 1 cm^3, i.e. c/n

(iv) Sum of the overlapping volume of surrouding coils, i.e.

$$c(n^{3/2})^2 = cn^3v_0$$

The product of the factors (i) and (ii), i.e. c^2n is concerned with the intra-coil overlapping giving the number of collisions of segments in a coil and the latter is concerned with the inter-coil overlapping giving the number of collisions when the coil is rotating. For the calculation of osmotic pressure the total number of collisions of segments is given by the product of the former and the number of coils; $c^2n \times Nc/n$ or c^3N. For the calculation of the elasticity E the pseudo cross-link ν is proportional to the products of both factors and the equilibrium constant of the pseudo cross-link K and is expressed as

$$\nu = n^3c^4NK \qquad (5)$$

Therefore, the elasticity E is given by

$$E = n^3c^4NK\,kT \qquad (6)$$

However, each factors disappear when the time t is larger than the relaxation time of the rotation τ_r and that of the translation τ_t and the remaining link is

$$\frac{\nu}{N} = \frac{c^4n^3K}{1 + c^2n^2(1 - e^{-t/\tau_r}) + c^4n^3(1 - e^{-t/\tau_t})} \qquad (7)$$

The link becomes K, c^2nK and c^4n^3K when t is $t > \tau_t$, $\tau_t > t > \tau_r$ and $\tau_r > t$, respectively. And with increasing c, ν/N becomes c^4n^3K, $c^2n/(1 - e^{t/\tau_r})$ or $K/(1 - e^{-t/\tau_t})$. In fact, the elasticity of hydrogel was known to be proportional to c^4 in dilute solution, whereas to c^2 in concentrated solution[3].

2. Viscosity

The relaxation times τ_r and τ_t are respectively given by

$$\tau_r = (h/kT)n^2c^2\exp(E^*/RT) \qquad (8)$$

and

$$\tau_t = (h/kT)n^2c^2(nc^2/n_B)(n/n_B)^{0.5}\exp(E^*/RT)$$
$$= (h/kT)n_B^2c^4(n/n_B)^{3.5}\exp(E_B^*/RT) \qquad (9)$$

where n_B is the length of the critical chain B having no viscous resistance for deformation. For the chain longer than the B-chain the time for escaping of the molecule from a coil is proportional to the product of (c^2n/n_B) and $(n/n_B)^{0.5}$. The factor $(n/n_B)^{0.5}$ is the ratio of the end-to-end distance of a molecule to that of a chain and is taken into consideration for calculation of the time of escaping a whole molecule.

The viscosity η can be derived from the product of the elasticity and the relaxation time and is expressed as

$$\eta = E \times \tau = (Nh)n_Bc^{2\sim 4}(n/n_B)^{3.5}\exp(E_B^*/RT) \qquad (10)$$

Thus, the viscosity of the polymer in the molten state is proportional to $n^{3.5}c^4$. However, in the oligomer whose chain length n is less than n_B, it becomes

$$\eta = (Nh)nc^2\exp(bE_0^*/RT) \qquad (11)$$

In other wprds, the viscosity of the oligomer is proportional to nc^2 and the activation energy of the flow is less than that of the polymer E_B^* but b-times larger than that of liquid E_0^*, b being $4 \sim 16$.

It is also pointed out that the viscosity of branched polymers is calculated by taking the entanglement and is same as that of the linear polymer whose chain length is n/f, f being the number of arms[4].

$$\nu/N = (n/f)^3c^4K \qquad (12)$$

But the activation energy and entropy for relaxation are doubled due to the simultaneous break-down of two links locating in two neighboring coils, and the relaxation time τ and the viscosity η becomes respectively

$$\tau = (h/kT)n_B^2\{(n/n_B)^{3.5}\exp(E_B/RT)\}^2 \qquad (13)$$

and

$$\eta = (Nh)n_B(n/n_B)^7\exp(2E_B/RT) \qquad (14)$$

A similar equation to (14) has recently been derived by Ngai et al.[5] from their coupling theory.

3. Melting temperature T_B

For exhibiting the snappy elasticity the activation energy of pseudo cross-link is larger than the sum of the activation energy of the translation of the segments in the chain, since the translation of the links after their break-down is accompanied by the flow of each segments of the chain. Consequently, the activation energy of the link of a size b is balanced with the sum of that of the component segments in a chain in the flow direction i.e. $n_b^{1/2}E_o^*$, where n_b is the chain length of the b-chain bounded by the cross-link of a size b. The critical chain length n_B is given by the following equation taking b to be 16 as shown in figure 1.

$$E_B^* = 16E_o^* = n_B^{1/2}E_o^* \qquad (15)$$

or $n_B = 16^2 = 256 = 10^{2.4}$

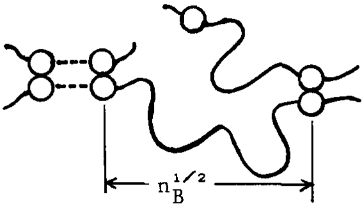

Fig.1

The critical chain length n_B is very important for the determination of the elasticity of the rubbery zone of unvulcanized rubber and the diameter of the blob in the molten state. For example, the former becomes

$$E_B = (\nu_B/N)(RT/v_o) = 10^9\cdot10^{-2.4} \text{ or } 10^{6.6} \text{ dyne/cm}^2 \qquad (16)$$

The latter becomes $n_B^{1/2}$ or $10^{1.2}$ Å and it may be reflected on the lateral thickness of the folded crystal for crystallizable polymer, i.e. $n_B^{1/2}$ or 250/2 Å.

On the other hand, the melting of the B-link is accompanied by the rotation of the coil whose entropy is $R\ln n_B^2$, and therefore, the activation energy of flow E_B^* is balanced with $RT_B\ln n_B^2$ at the melting temperature of B-link, T_B and

$$16E_o^* = RT_B\ln n_B^2 \qquad (17)$$

In the previous paper E_o^* is taken to be equal to $-\Delta H_o$, but it is more likely that E_o^* is equal to $(2/3)\times(-\Delta H_o)$ and if so

$$T_B = \{16\times(2/3)\times(2RT_A)\}/(R\ln 16^4) \cong 2T_A \qquad (18)$$

The flow temperature T_B is twice as high as T_A and is equal to the melting point T_m, if the polymer is crystallizable. Taking $-\Delta H_o$ to be 0.8 Kcal, E^* is estimated for polyethylene to be $E^*=16E_o^*=16\times(2/3)(-\Delta H_o) = 8.4$ Kcal.

4. Entropy of pseudo cross-linking

The entropy loss ΔS_o for cross-linking is $-2R$ at T_A as reported previously, but ΔS_o at T_B is different from that calculated by the following equation.

$$1/n_B = \nu_B/N = \exp\{-16(\Delta H_o/RT_B + \Delta S_o/R)\} \qquad (19)$$

or

$$\Delta S_{o(B)}/R = -2RT_A/2RT_A - (\ln 256)/16 = -1.34$$
$$= (2/3)(\Delta S_{o(A)}/R) = -4/3 \qquad (20)$$

In other words, ΔS_o at T_B is 2/3 times smaller than ΔS_o at T_A. This may be due to the tendency that the pseudo cross-link still possesses a translational motion at T_B, i.e., $(1/3)\Delta S_{o(A)}$ unlike that at T_A. The entropy of linking ΔS_o may decrease with raising the temperature due to the increase of the remaining entropy of pseudo cross-links. In general, the following equation may hold.

$$\Delta S_{o(T)} = \beta\Delta S_{o(A)} \quad , \quad \beta = 1 - (T - T_A)/(T + T_A) = 2T_A/(T + T_A) \qquad (21)$$

In equation (21) β is 1, 0.86 or 2/3 at T_A, T_g or T_B, respectively.

From these results, equations for the relaxation spectrum and the WLF-equation proposed in the report 2 are to be revised as follows: From the equation, i.e.,

$$\nu_b/N = \exp\{b(-\Delta H_o/RT + \Delta S_o/R)\}$$

and $\tau = (h/kT)n_B^2 \exp(bE_0^*/RT)$

the relaxation spectrum is

$$\log(E/E_0) = \log(\nu/\nu_0) = (3/2)\{1 - T/(\Delta H_0/\Delta S_0)\} \times \log(\tau/\tau_0) \qquad (22)$$

The slope at temperature below Tg, $\Delta H_0/\Delta S_0$ is taken to be T_A and

$$(3/2)\{1 - T/(\Delta H_0/\Delta S_0)\} = (3/2)(1 - T/T_A) \qquad (23)$$

which becomes -1/2 at T_g. Above Tg the slope is

$$(3/2)[1 - (T/T_A)\{2T_A/(T + T_A)\}] = -(3/2)\{(T - T_A)/(T + T_A)\} \qquad (24)$$

which also becomes -1/2 at T_B. Consequently, the slope is almost equal to -1/2 between Tg and T_B. The WLF-equation for the time-temperature relation becomes, taking E/E_0 to be 10^{-2}, T_A to be 200°C and Tg/T_A to be 4/3,

$$\log\frac{\tau}{\tau g} = \frac{2\log E/E_0}{Tg/T_A - 1}\,\frac{T - Tg}{(Tg - T_A) + T - Tg} = \frac{-12(T - Tg)}{66 + T + Tg} \qquad (25)$$

5. Osmotic pressure of the semi-dilute solution

In the semi-dilute solution the polymer molecule is completely solvated with solvents and the effect of pseudo cross-link is not significant. However, the molecular coils overlap to each others and the collision of the segments is much enhanced to increase the osmotic pressure. The critical concentration c*, where the overlapping begins, is given by the following relation: Taking c as the fractional concentration and supposing cube-shaped coils, then

$$c^*(n^{3/2}/n) = 1 \quad \text{or} \quad c^* = 1/n^{1/2} \qquad (26)$$

The osmotic pressure π of the coiled molecule in dilute solution is expressed as $\pi = (c/n)RT$ (27)

And in the semi-dilute solution the value is to be multipled by the overlapping factor, i.e., nc^2. However, the effect of overlapping depends on the temperature, because the temporary link should have different entropies depending on the temperature. Consequently,

$$\pi = (c/n)RT(nc^2)^{\beta} \qquad (28)$$

It is likely assumed that the segment in the solution collides to form a temporary link whose entropy is $\Delta S_{0(B)}$ or $(2/3)\Delta S_{0(A)}$. In the words, the exponent β is to be 2/3. As a result, equation (28) is transformed to

$$\pi = (c/n)RT(c/c^*)^{4/3} \qquad (29)$$

For the concentrated solution the correction for the excluded volume of the polymer is necessary, that is equal to Zc, Z being a coordination number of the segment or about 6, because the molecule is solvated with Z solvent-molecules. Equation (29) is modified as

$$\pi = (c/n)RT(c/c^*)^{1.33}/(1 - Zc) \qquad (30)$$

The upper critical concentration c** is

$$c^{**} = 1/Z = 1/6 \qquad (31)$$

In fact, the literature indicated that the upper critical concentration c** is almost 15 %irrespective of the kind of solvents.

6. Dilute solution in θ-solvents

In θ-solvents no significant solvation is possible but instead, the cohesion of segments may play an important role. The coil-globule transition takes place when the temperature is lowered to the θ-point even at very low concentration, at which no overlapping of coils is possible and the coil exists rather independently. It seems that the intra-coil formation of pseudo cross-link takes place to give rise to the self-coaguration. In this case, the correction due to the interaction of coils is necessary, that is given by a product of an actual cohesion heat ΔH of the segment and the volume of a coil, viz. $\Delta H \times n^{3/2} \times (c/n)^2$. Thus, the van der Waals-type equation becomes

$$\{\pi - (c/n)^2 n^{3/2}\Delta H\}\{1 - (c/n)n^{3/2}\} = (c/n)RT$$

or

$$\pi = (c/n)RT\{1 + (c/c^*)(1 + \Delta H/RT)\} \qquad (32)$$

Here, ΔH is an actual cohesion heat or the sum of the cohesion heat ΔH_0 and the heat of mixing ΔH_{mix}, the former being negative whereas the latter being positive

$$\Delta H = \Delta H_0 + \Delta H_{mix} < 0$$

and

$$\theta = \Delta H/\Delta S_0(B) = T_B - \Delta H_{mix}/(4/3)R \qquad (33)$$

Consequently, θ is regarded as a transition temperature for the self-coaguration. Below this point the volume of the coil V decreases from the original one V_0 by lowering temperature and the coil is collapsed to a globule. Since the volume of a coil V is expressed by a product of the number cross-link on a chain, i.e., ν/n and the volume of a coiled chain, i.e., $(n/\nu)^{3/2}$, the volume of a coiled molecule becomes $(n/\nu)^{1/2}$. Consequently, the change of volume below θ-point is expressed by

$$\begin{aligned}\ln(V/V_0) &= (-1/2)\ln(\nu/\nu_0) = (\Delta H/2R)(1/T - 1/\theta)\\ &= (\Delta H/2R\theta T)(\theta - T) \qquad (34)\end{aligned}$$

where V_0 is a volume of a coiled molecule at θ. Since ΔH is negative the volume is decreasing with lowering temperature. Equation (34) seems to coincide with the experiment in literature[6]. On the contrary, the dilute solution in good solvent the volume of a coil is decreasing with increasing temperature by desolvation in contrast to the case of poor solvents.

Conclusion

The concept of the pseudo cross-link is extended to the explanation of the osmotic pressure in the semi-diluted solution and also the coil-globule transition in θ-solvents.

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