Polymer crystallization at large supercoolings: 1. Change in fold length with crystallization temperature in nylon-6 and nylon-6,6 crystallized from dilute solutions

Hiroshi Kiho and Yoshihisa Miyamoto
Department of Physics, College of Liberal Arts, Kyoto University, Kyoto 606, Japan

and Hideki Miyaji
Department of Physics, Faculty of Science, Kyoto University, Kyoto 606, Japan

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Crystallization from dilute solution of nylon-6 and nylon-6,6 is examined. The crystallization temperatures are determined by turbidity of solutions and the crystallization temperature dependence of the fold length is studied especially at large supercoolings. Two models are proposed for the change in the fold length with crystallization temperature in connection with the fact that at large supercoolings the growth surfaces are rough so that secondary nucleation is no longer the rate-determining process. One is based on a kinetic theory with the probability of chain folding; the probability is attributed to the entropy due to the diversity of conformation of a polymer chain in solution. The other is based on the idea of Rault; the fold length is initially determined by the size of polymer chains just before crystallization and increases through the thickening process which is an activation process.

(Keywords: crystallization; large supercooling; fold length; nylon-6; nylon-6,6)

INTRODUCTION

The fold length L of crystalline polymers decreases with decreasing crystallization temperature, and its invariance with the crystallization temperature at large supercooling has been reported for isotactic polystyrene[1] and nylon-6,6[2,3]. The empirical equation for the dependence of the fold length L on the supercooling ΔT is of the form:

$$L = \delta L + A_0/\Delta T \qquad (1)$$

where A_0 and δL are constants.

There are two current ideas on the factors which determine the fold length. According to the classical kinetic theory, the fold length increases up to infinity at high supercooling, which is well known as the 'δL catastrophe'. This δL catastrophe has never been observed. Lauritzen and Hoffman introduced the effects of physical adsorption on the growth surfaces prior to crystallization and lowered the δL catastrophe temperature beyond the experimental temperature range[4,5]. In order to avoid the δL catastrophe, Point introduced the opportunity to fold back at every stage of deposition of a segment along the stem direction[6]. DiMarzio and Guttman argued Point's process analytically[7].

On the other hand, Allegra proposed a new model in which the fold length is determined by the size of molecular loops in melt or solutions; these loops are associated with the formation of nuclei[8]. Rault insisted further that the limiting length δL is related to the conformation of polymer chains in the liquid state just before crystallization[9] and that the temperature dependence of the fold length is a result of annealing near the growth faces for a short time[10]. Recently, Sadler and Gilmers calculated the temperature of the fold length by a Monte Carlo method, imposing simple restrictions of the connectivity of segments on crystallization[11]. Their results show that the temperature dependence of the form of equation (1) holds only at low supercoolings and the fold length slowly decreases with increasing ΔT even at large supercoolings.

In the present paper, we carefully re-examine the temperature dependence of the fold length of nylon-6 and nylon-6,6 crystallized from dilute solutions; in these two polymers it has been reported that the limiting thickness was observed. Possible mechanisms of crystallization of polymers at high supercoolings will be proposed and discussed.

EXPERIMENTAL

The materials used are nylon-6 ($M_w = 42\,000$, $M_w/M_n = 1.4$) and nylon-6,6 ($M_w = 32\,000$, $M_w/M_n = 2.0$). Crystallizations were carried out from 0.05% 1,4-butanediol solutions. The pellets were dissolved at 200°C for nylon-6 and 220°C for nylon-6,6 under nitrogen atmosphere and the solution was transferred by nitrogen gas pressure to a vessel in the crystallization bath kept at quenching temperature T_q (ref. 12). For nylon-6, T_q ranges from 15°C to 120°C and for nylon-6,6 from 70°C to 150°C. Crystallization was observed by detecting a decrease in intensity of a transmitted laser beam with a phototransistor. The crystallization temperature was measured with a thermocouple dipped in the vessel. At

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the highest temperatures, the self-seeding technique was adopted. The suspension was suction-filtered at T_q. After the residual solvent was substituted by ethanol, the resulting mats were dried. The substitution and drying were always carried out at temperatures below T_q in order to prevent annealing effects.

Small-angle X-ray scattering (SAXS) photographs were taken with Ni-filtered CuKα radiation incident parallel to the mat surface. The high-power X-ray source (Rigaku RU-1000), operated at 60 kV and 1 A, was used to obtain distinct patterns. The long spacings were measured visually. The crystal form was found to be α-form for both nylon-6 and nylon-6,6 by wide-angle X-ray diffraction. The morphology of the crystals was examined by transmission electron microscopy.

RESULTS

Crystallization was isothermal above 70°C for nylon-6 and above 130°C for nylon-6,6; above this temperature the crystallization temperature T_c equals T_q. Below this temperature, T_c is taken as the temperature at which the rate of decrease in intensity of the transmitted laser beam is maximum. The half-time of crystallization $t_{1/2}$ is taken as the time required for one-half of the total amount of decrease in intensity of the laser beam. The temperature dependence of $t_{1/2}$ is shown in *Figure 1*. The crystallization behaviours for nylon-6,6 are very similar to those reported by Dreyfuss and Keller[2]. The yield decreases appreciably above 145°C for nylon-6,6. No maximum in the crystallization rate against crystallization temperature was observed, contrary to the case of polystyrene. Transmission electron microscopy shows that the morphology of the crystals was leaves or sheaves under the present crystallization conditions; no facet was observed.

Figure 2 shows the long spacing, L, determined by SAXS as a function of the crystallization temperature T_c. The results for nylon-6,6 are similar to those reported hitherto[2,3,13]; but in the temperature region below 130°C where constant fold length was reported in previous work, a slight decrease in L is observed with decreasing T_c. A similar decrease is also seen for nylon-6. No stepwise change in L by a repeating unit is seen in *Figure 2*, but the curves are smooth both for nylon-6 and nylon-6,6.

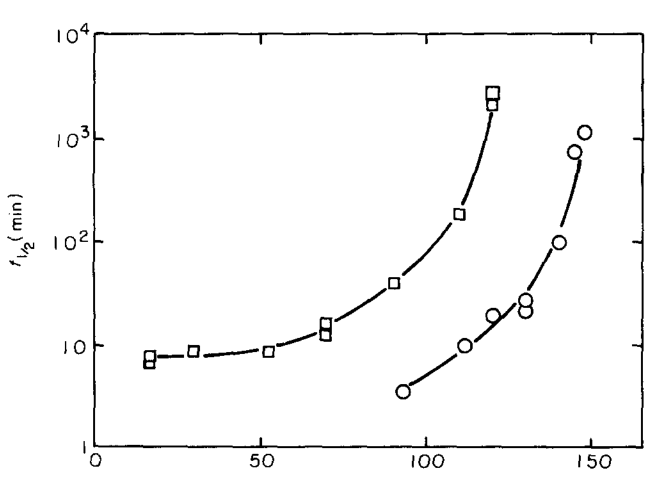

Figure 1 Dependence of the half-time of crystallization $t_{1/2}$ on crystallization temperature T_c: ■, nylon-6; ○, nylon-6,6. Concentration is 0.05%

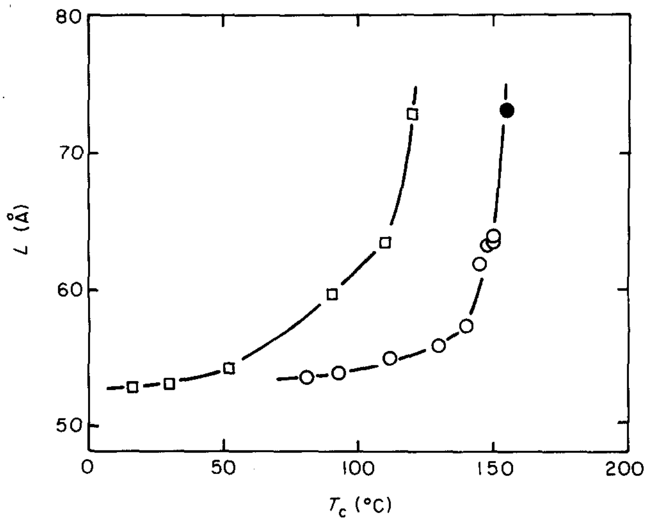

Figure 2 Dependence of the fold length L on crystallization temperature T_c: symbols are the same as those in *Figure 1*; ●, crystallization by self-seeding

DISCUSSION

The rate of crystallization largely depends on crystallization temperature T_c (*Figure 1*). The growth rate in adhesive growth mode of a rough surface varies much more slowly with T_c. Therefore, the T_c dependence of $t_{1/2}$ is attributed to that of the primary nucleation rate. In fact, the self-seeding method decreased the crystallization time greatly.

The temperature dependence of the long spacing of chain folded crystals is expressed by equation (1) at low and moderate supercoolings. This equation is derived from the kinetic theory: secondary nucleation and growth. The term $A_0/\Delta T$ in equation (1) is explicitly written as

$$\begin{aligned} A_0/\Delta T &= 2\sigma_e/\Delta f \\ &= 2\sigma_e T_d^0/\Delta h \Delta T \end{aligned} \tag{2}$$

where σ_e is the fold surface free energy, Δf the free energy difference between the crystal state and the liquid state, T_d^0 the equilibrium dissolution temperature and Δh the heat of fusion. The length $2\sigma_e/\Delta f$ corresponds to the value at the saddle point of a free energy map of secondary nucleation and is the smallest length of a secondary nucleus which can go on to grow. The first term in equation (1), δL, is the additional stabilizing length which assures the finite growth rate at T_c.

The activation energy F^* for the formation of the secondary nucleus generally decreases as ΔT increases. When F^* becomes comparable to kT, secondary nucleation becomes less important. Accordingly, the temperature dependence of the fold length may be different from equation (1) at supercooling higher than a certain value ΔT^*, where $F^*(\Delta T^*) = kT$. In dilute polymer solutions, ΔT^* is usually of the order of several tens of degrees. In such high supercoolings, it is reasonable to consider that the rate of formation of crystallites with thickness L depends on the number of fluctuations which lead to a crystallite with thickness L from random coil chains. The activation energy is given by

$$F^*(\Delta T) = -kT \ln \Omega \qquad \text{for } \Delta T > \Delta T^* \tag{3}$$

where Ω is the partition function of the fluctuations; F^* is essentially due to the entropy of fluctuations. Since chains are still in the liquid state or the adsorbed state at this activated state F^*, the fold length L will depend on the conformation of chains just before crystallization, as pointed out by Rault.

In the light of the above considerations, we propose two models describing polymer crystallization at high supercoolings.

Kinetic approach

The process considered below is an extension of Point's model. At high supercoolings, the growth faces are rough and should have many steps; in fact, electron microscopy shows no facets for the crystals. The chains can crystallize at various sites on steps without forming an extra surface by folding back with loop length v (*Figure 3*). In this case, the probability for the folding process would hardly depend on the thickness of the substrate. The temperature dependence of the fold length may be naturally different from that determined by the thermodynamic nature of the secondary nucleus.

A stem made of j segments with a cilium of N segments (a) crystallizes in the stem direction to become a stem of $j+1$ segments or (b) attaches to steps by folding with a loop length v. Let A be the rate constant for the process (a) and B that for the reverse process. Let C_j be the overall net rate constant for the folding process (b). These rate constants can be expressed as

$$A = K\alpha$$
$$B = K\exp(-\beta\Delta T) \tag{4}$$
$$C_j = K[\alpha\gamma_j - D\exp(-\beta\Delta T)]$$

where

$$\beta = abl_0\Delta h/kTT_d^0$$

Here K is the jump frequency including diffusion process, $\alpha(<1)$ is a parameter restricting the crystallizable conformations of a cilium at the root on the crystal surface. D is a factor due to an excess free energy by formation of end surfaces, γ_j is the probability of chain folding from a stem of j segments, a is the width of the segment, b is the thickness of the segment and l_0 is the length of the segment in crystals. The expressions for A and B are the same as those for crystallization of simple materials with rough surfaces except for factor α. In the expression for C_j, the second term corresponds to dissolution of the segment formed by the folding process. We neglect the end surface energy without the work of folding, so that D is equal to unity. Since chain–chain interactions are negligible in dilute solutions, γ_j is given by

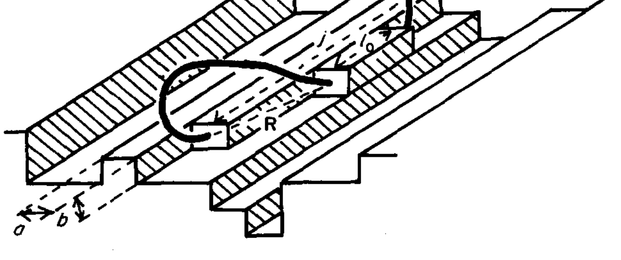

Figure 3 Schematic illustration of chain folding in a dilute polymer solution. A cilium segment crystallizes with a v-segment loop on a step at a distance R from the root of the cilium

$$\gamma_j = \sum_{\mathbf{R}} \sum_{v=v_{\min}}^{N} \Omega(v,\mathbf{R})\Omega(N-v)abl_0/\Omega(N) \tag{5}$$

where $\mathbf{R}$ is the distance between the roots of a loop, $v_{\min}$ the minimun loop length determined by $\mathbf{R}$, $\Omega(v,\mathbf{R})\mathrm{d}^3\mathbf{R}$ the partition function of the loop whose length is v segments and the interroot distance is $\mathbf{R}$ and

$$\Omega(N) = \int_{\text{semi-space}} \mathrm{d}^3\mathbf{R}\,\Omega(N,\mathbf{R}) \tag{6}$$

The folding probability γ_j is nearly independent of j, except for adjacent re-entry loops of smaller j where γ_j increases with j. We assume C_j (i.e. γ_j) is independent of j as a rough approximation. Then the rate equations are formally the same as those solved by DiMarzio and Guttman[7], though the rate constants are different from those derived from energetic considerations. The temperature dependence of the fold length at high supercooling, where $\exp(-\beta\Delta T) \ll 1$, is obtained by inserting the present rate constants A, B and C_j into equation (2-64) in ref. 7:

$$L = l_0[\bar{v} + 1 + 1/\gamma + \exp(-\beta\Delta T)/\alpha(1+\gamma)] \tag{7}$$

where $\bar{v}$ is the average number of segments in a loop. Since β includes the factor $1/T$, L is given in the form:

$$L = \delta L + A_1\exp(-B_1/T) \tag{8}$$

where A_1 and B_1 are given by

$$A_1 = l_0\exp(abl_0\Delta h/kT_d^0)/\alpha(1+\gamma) \tag{9}$$

$$B_1 = abl_0\Delta h/k \tag{10}$$

In the following discussion, we assume that $\bar{v}$ and γ are independent of temperature; $\delta L = l_0(1+\bar{v}+1/\gamma)$ is constant.

Although the invariance of fold length is not observed in *Figure 2*, we assume that δL is 52 Å for nylon-6 and 52.5 Å for nylon-6,6 taking account of a slight decrease in L at low temperature. *Figure 4* shows a test of equation (8). The linear relation between the logarithm of $(L-\delta L)$ and the inverse of crystallization temperature is seen at high supercoolings. Agreement with the experimental results is satisfactory. The supercooling at which the experimental results deviate from the straight line roughly corresponds to ΔT^*. The data by Jones *et al.*[1] for isotactic polystyrene are plotted in *Figure 5*. Equation (8) also holds for polystyrene. The coefficients A_1 and B_1 in equation (8) are listed in *Table 1* for nylon-6, nylon-6,6 and isotactic polystyrene. From the values of B_1 in *Table 1*, the lengths of the segment in crystallization process are estimated as 12.5 Å for nylon-6, 12.8 Å for nylon-6,6 and 14.5 Å for polystyrene. The values of parameters used are as follows[14]: $\Delta h/\text{mole} = abc\Delta hN_A = 5.1$ kcal and c (monomer unit length) = 8.62 Å for nylon-6; 10.1 kcal

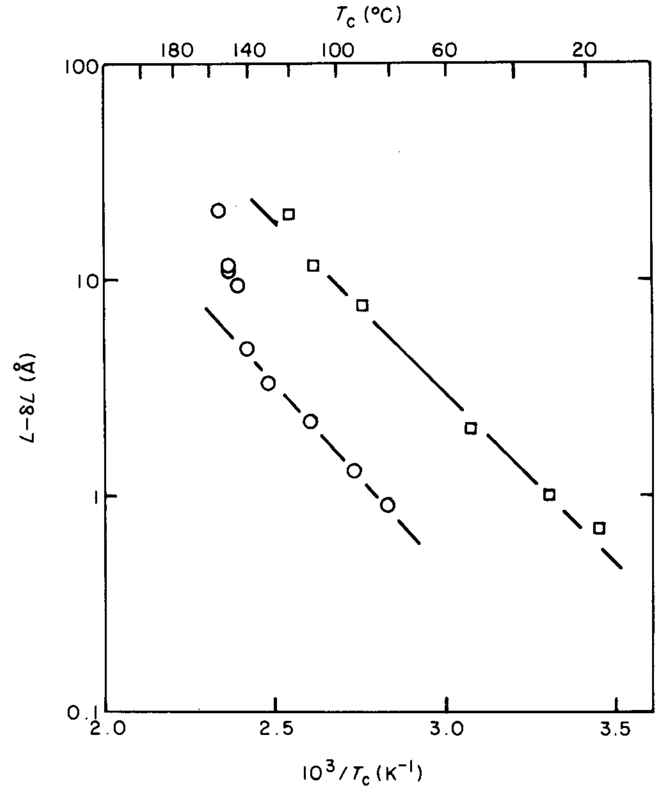

Figure 4 Plots of $\log(L-\delta L)$ *versus* the inverse of crystallization temperature for nylon-6 (■) and nylon-6,6 (○)

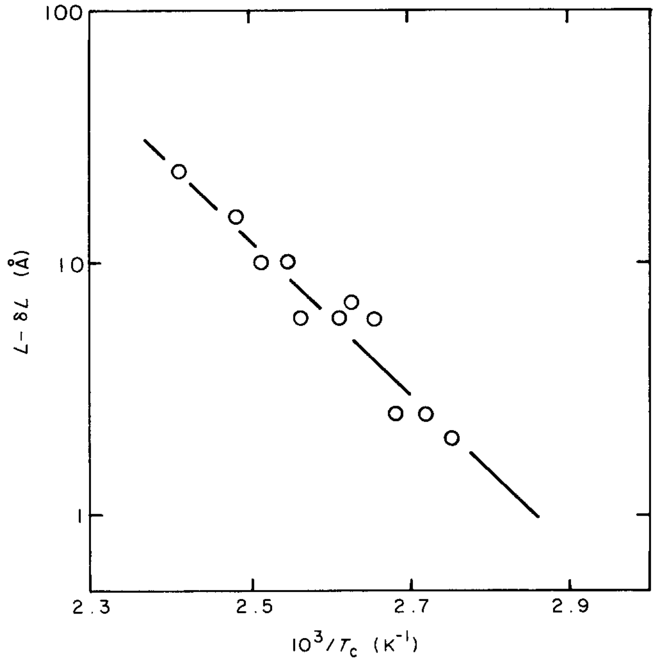

Figure 5 Plots of $\log(L-\delta L)$ *versus* the inverse of crystallization temperature for polystyrene (Jones *et al.*[1])

and 17.2 Å for nylon-6,6; and 2.2 kcal and 2.22 Å for polystyrene, respectively.

Approach in terms of reorganization model

Another interpretation is possible of equation (8) which explains the experimental results well. According to Rault, the lamellae thicken by annealing just after crystallization. He considered that annealing is an activated process and that the activation energy for thickening is proportional to the stem length L, and he obtained the temperature dependence of L in the form of equation $(1)^{10}$.

Table 1 Experimental values of δL, A_1 and B_1 in equation (3) and segment length l_0. The activation energy for γ relaxation H_γ is listed for comparison[15]

	δL (Å)	A_1 (Å)	B_1 (K)	l_0 (Å)	H_γ (K)
Nylon-6	52	14	3600	12.1	4200
Nylon-6,6	52.5	98	4100	13.9	4000
Polystyrene[a]	70	59	7100	14.2	17000[b]

[a] Jones *et al.*[1]
[b] Atactic polystyrene

There is, however, no explicit factor of ΔT in equation (8), which means that the associated activation energy is independent of L. Reorganization may occur only in some region near the growth face; the depth of the reorganization region is denoted Δx. As the growth rate G becomes larger, Δx will be larger. The time interval of annealing Δt which is equal to $\Delta x/G$, may be considered constant at large supercooling, although at low supercooling Δx is so small that it is comparable to a monolayer depth b. Then the thickening rate dL/dt is proportional to $\exp(-B_1/T)$ at large supercooling. In connection with these considerations, the coefficients A_1 and B_1 in equation (8) are expressed as follows:

$$A_1 = f l_0 \Delta t \exp(\Delta S^*/k) \tag{11}$$

and

$$B_1 = \Delta H^*/k \tag{12}$$

where f is a frequency factor, and ΔS^* and ΔH^* are the activation entropy and the activation enthalpy for the thickening process of segments, respectively. It is interesting to note that the values of the activation enthalpy B_1 listed in *Table 1* are comparable to those of γ relaxation process which is attributed to the local mode relaxation or the crankshaft motion of polymer chains.

The value of the limiting thickness δL is determined by the conformation of adsorbed chains on the growth faces or by the chain conformation in solution in either model, which will be described by the persistence length at the crystallization temperature. Since the coil relaxation time is much smaller in dilute solutions than in the melt, in dilute solutions the chain conformation just before crystallization should depend on the crystallization temperature rather than on the high temperature before quenching as in the case of crystallization from the melt. Knowledge about the behaviour of chains in highly supercooled solution is necessary to be able to discuss the temperature dependence of δL, which we have neglected in this paper.

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