Polymer crystallization at high supercoolings: 2. Molecular-weight dependence of lamellar thickness in isotactic polystyrene

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

Yoshihisa Miyamoto and Hiroshi Kiho
Department of Physics, College of Liberal Arts, Kyoto University, Kyoto 606, Japan
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We have examined the dependence of the lamellar thickness (l) on the crystallization temperature (T_c) and on the molecular weight for isotactic polystyrene (i-PS) crystallized at high supercoolings. The temperature dependence is expressed by the formula $l=\delta l+A\exp(-B/T_c)$ with $A=27\,000$ (Å) and $B=3200$ (K) for i-PS. The molecular-weight dependence, which is not a function of the equilibrium dissolution temperature, is reported for crystallization from dilute solution for the first time. The molecular-weight dependence of l is attributed to that of the limiting thickness δl. This result is explained by the molecular-weight dependence of the average length of loops created by folding.

(Keywords: crystallization; lamellar thickness; isotactic polystyrene; high supercoolings; molecular weight)

INTRODUCTION

In the crystal growth of polymers from dilute solution, there have been few papers published for high supercoolings. Experimentally, many polymers cannot be crystallized isothermally at high supercoolings because of the fast growth rate. Theoretically, the nucleation theory of Lauritzen and Hoffman[1] is only valid at low supercoolings. The nucleation theory gives the dependence of lamellar thickness l on the crystallization temperature T_c (or supercooling ΔT) as:

$$l=\delta l+A_0/\Delta T \tag{1}$$

wher A_0 is a constant, $\Delta T=T_d^\circ-T_c$ (T_d° is the equilibrium dissolution temperature) and δl is the limiting thickness. This equation is supported by experiments at low supercoolings[1]. Furthermore, the growth rate at low supercoolings is represented satisfactorily in terms of the nucleation theory[2]. In the case of high supercoolings, Kiho *et al.* have proposed rough surface growth[3]; because of the disappearance of the free-energy barrier for two-dimensional nucleation, the growth face is not a flat surface but a rough surface at the molecular scale. Therefore, this case is beyond the scope of nucleation theory. Their temperature dependence of the lamellar thickness at high supercoolings is given by:

$$l=\delta l+A\exp(-B/T_c) \tag{2}$$

where A and B are constants. They showed that the lamellar thickness of nylon-6 and nylon-6,6 can be expressed by equation (2)[3].

In this report, we first examine equation (2) for isotactic polystyrene (i-PS), which was another polymer reported to crystallize isothermally at high supercoolings[4]. The main object of this paper is, secondly, to clarify the origin of δl. The molecular-weight dependence of δl was found in i-PS. Discussion of the factors that determine δl will be made in the light of the statistical mechanics of a polymer chain at the growth face; the statistical average of molecular loops is compared with the δl value obtained experimentally.

EXPERIMENTAL

The isotactic polystyrene (i-PS) used is a commercial one (General Science Corporation). The weight-average molecular weight is $M_w=1.57\times10^6$ ($M_w/M_n=6.4$), and the tacticity is 97.2% isotactic triad. We use dimethyl phthalate (DMP) as solvent. At high dissolution temperatures (higher than 200°C), polystyrene suffers oxidative degradation, resulting in chain scission even under a nitrogen atmosphere because of residual oxygen in the solvent; the molecular weight decreases after dissolution. The molecular weight was determined by gel permeation chromatography on crystallized samples. *Table 1* shows the weight-average molecular weight (M_w) and polydispersity (M_w/M_n) of five samples. Even in the i.r. absorption spectra of severely degraded samples, there is no sign of degradation except for the absorption peak due to an acetophenone-type structure around $1690\,\mathrm{cm}^{-1}$; the end of the degraded chain is of acetophenone type after chain scission[5]. Therefore, we do not take the effect of degradation into consideration except for the decrease in the molecular weight.

Crystallization was carried out from 0.1 wt% DMP solutions. After dissolution, the solution was transferred

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Table 1 The weight-average molecular weight (M_w), polydispersity (M_w/M_n) and long period (L). L is the value for the samples crystallized at 80°C, measured by small-angle X-ray scattering

Sample	$M_w/10^4$	M_w/M_n	L (Å)
I	45	3.8	75
II	44	3.7	74
III	18	2.4	72
IV	9.3	2.0	69
V	6.3	1.8	67

by nitrogen gas pressure to a vessel in a bath kept at the crystallization temperature T_c from 20 to 130°C. Crystallization was observed by measuring the intensity of the transmission of a He–Ne laser. Temperature was measured by a Pt resistance thermometer dipped into the bath. After crystallization had finished, the suspension was suction filtered at T_c to obtain a mat of crystals. Since DMP is not volatile, residual solvent was substituted by methyl ethyl ketone. The mat thus obtained was dried at room temperature.

The long period L was measured by small-angle X-ray scattering. The X-rays were Ni-filtered Cu Kα radiation, and a photographic method was employed. The peak position was measured visually. The camera length was 411 mm.

The temperature dependence of L is examined for samples II and IV. For samples I, III and V, crystallization was performed only at 80°C, and we examined the molecular-weight dependence of L for five samples. The morphology of the crystals was examined by transmission electron microscopy.

RESULTS

Electron microscopy of the crystals showed that there are no isolated lamellar crystals. Crystals aggregated to form large clusters; lamellar crystals could be observed at the edge of clusters. A lamella has an irregular shape; it is far from the hexagonal shape that was observed on crystallization from other solvents[6]. These morphological observations suggest rough surface growth at high supercoolings.

The crystallization rate was highest around $T_c = 70$°C. Even at 70°C, crystallization is slow enough to assume isothermal crystallization. *Figure 1* shows the half-time of crystallization $t_{1/2}$ when the intensity of transmission of the laser falls to half the intensity at $t = 0$. The inverse of $t_{1/2}$ can be considered as the crystallization rate. The crystallization rate is higher for samples of higher molecular weight.

Figure 2 shows the long period L as a function of T_c. In the temperature range where Jones *et al.*[4] observed a constant long period, L still decreases slowly with decreasing T_c. *Figure 2* also shows that i-PS of higher molecular weight has a larger long period. The two curves in *Figure 2* coincide with each other after a shift along the vertical axis. Therefore, the difference between the two curves is the difference in δl; in fact, $l - \delta l$ plotted against T_c is independent of the molecular weight (*Figure 3*). The values of δl are calculated by subtracting 3 Å from the long period obtained by crystallization at 80°C (*Table 1*), on the basis of the fact that, at 80°C, the difference between L ($T_c = 80$°C) and δl is 3 Å (see discussion). *Figure 4* shows the molecular-weight dependence of δl. The limiting thickness δl increases with molecular weight. This dependence of δl on the molecular weight has never been reported and is the main issue in the present report.

DISCUSSION

Figure 5 shows schematically the growth face of a polymer single crystal growing at high supercooling. Because of the disappearance of the free-energy barrier for nucleation, the growth face is rough. The uncrystallized part of a crystallizing molecule forms a dangling cilium on the growth face; the cilium crystallizes at its root on the growth face. A dangling cilium can fold with a certain probability to create a new loop and a shorter cilium. *Figure 5* shows the loop of ν segments and the cilium of

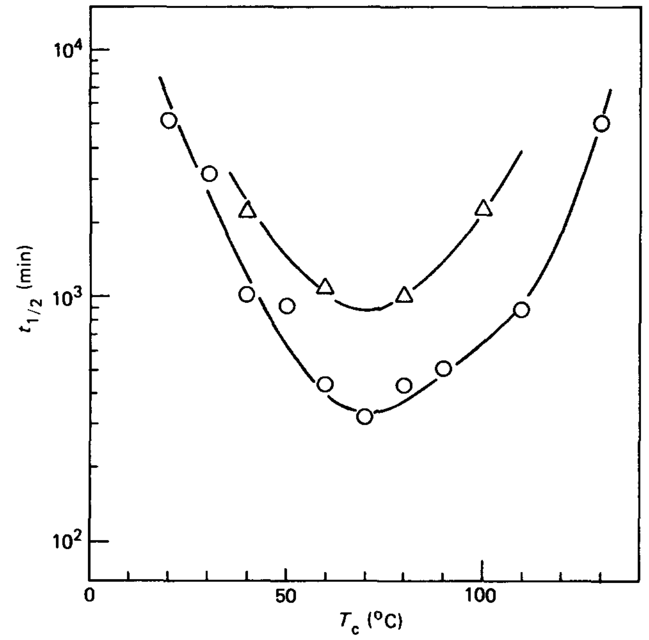

Figure 1 Half-time of crystallization $t_{1/2}$ plotted against the crystallization temperature T_c: (○) $M_w/10^4 = 44$; (△) $M_w/10^4 = 9.3$

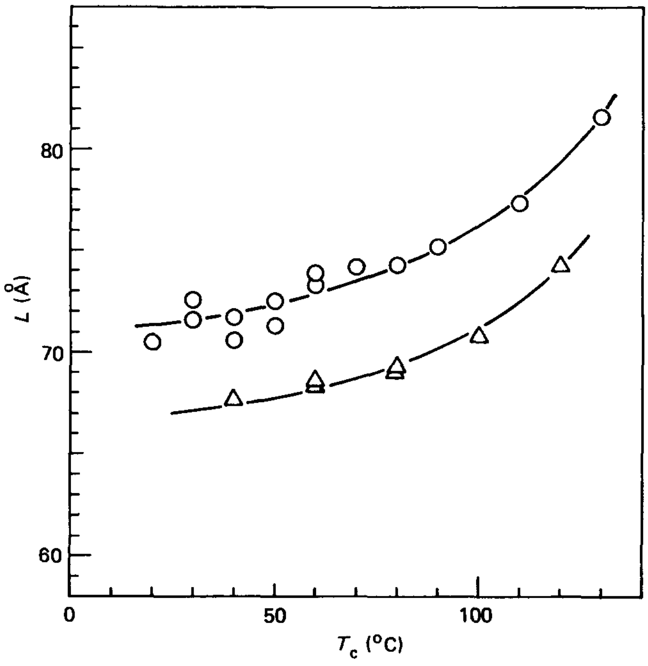

Figure 2 Long period L plotted against the crystallization temperature T_c: (○) $M_w/10^4 = 44$; (△) $M_w/10^4 = 9.3$

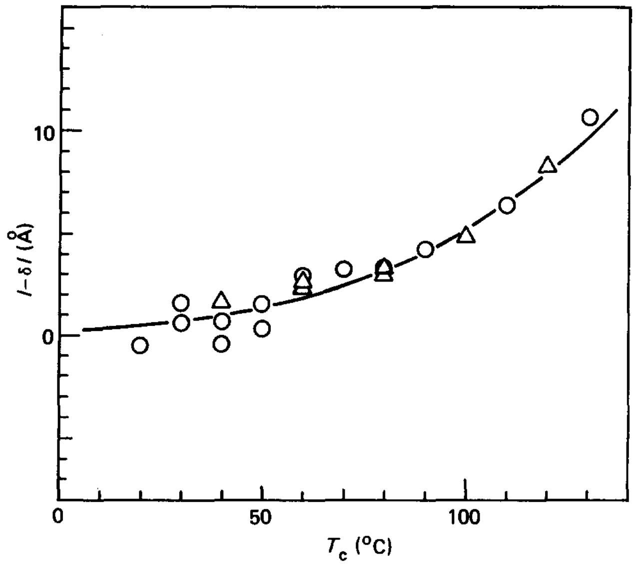

Figure 3 Plot of $l-\delta l$ against the crystallization temperature T_c (for the determination of δl, see text): (○) $M_w/10^4=44$; (△) $M_w/10^4=9.3$; (——) calculated by the formula $l-\delta l=A\exp(-B/T_c)$ with $A=27000$ (Å) and $B=3200$ (K)

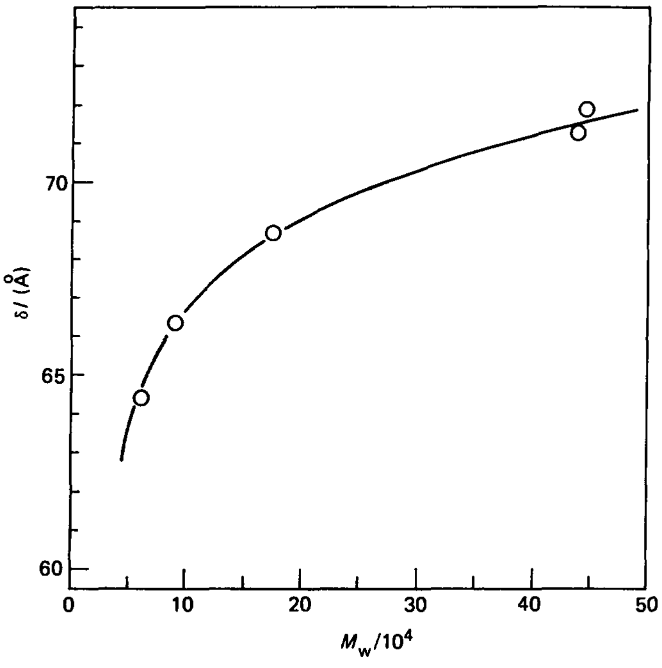

Figure 4 Plot of δl against the average molecular weight M_w

$(N-\nu)$ segments created by folding of a cilium of N segments. It was shown that, if these loops are able to crystallize to form tight folds by zippering, the average length of the loop on the top and bottom fold surfaces contributes to the lamellar thickness (loop crystallization)[3]. This average length is determined by the conformation of a molecular chain in solution just before crystallization. Therefore, the lamellar thickness can be expressed as the sum of two terms: the average length of the loops and the term determined by kinetic equations. Though the loop length is broadly distributed, the fold surface of the lamellar crystal can be smoothed by local rearrangement during crystallization. The concept of loop crystallization was originally proposed by Allegra[7].

Dependence of lamellar thickness on crystallization temperature

The dependence of the lamellar thickness on the crystallization temperature is given by following equations[3]:

$$l=\delta l+A\exp(-B/T_c) \tag{3}$$

with

$$\delta l=s\bar{\nu}+l_0(1+1/\gamma) \tag{4}$$

$$A=\frac{l_0}{\alpha(1+\gamma)}\exp\left(\frac{B}{T_d^\circ}\right) \tag{5}$$

$$B=abl_0\Delta h_f/k \tag{6}$$

where s is the segment length* in solution[8], l_0 is the length of the crystallizing unit introduced by Point[9], $\bar{\nu}$ is the average number of segments in a loop, γ is the probability of chain folding, $\alpha(<1)$ is a parameter restricting the crystallizable conformations of a cilium at the root on the crystal, ab is the cross-section of one chain in the crystal (a is the width and b is the thickness), Δh_f is the heat of fusion per unit volume, T_d° is the equilibrium dissolution temperature and k is the Boltzmann constant. (Though s is assumed to be l_0 in ref. 3, s is generally independent of l_0.) The first term in (4), i.e. $s\bar{\nu}$, is the term from loop crystallization. The contribution due to the detailed structure of the fold is independent of $\bar{\nu}$. This contribution has no effect on the molecular weight dependence of δl and is expected to be small enough to be neglected. The second term in (3) expresses the temperature dependence of lamellar thickness. Since T_d° is almost constant in high-molecular-weight materials, this term is independent of molecular weight, in agreement with the present experimental result. The full curve in *Figure 3* is calculated from equation (3) with $A=2.7\times10^4$ (Å) and $B=3200$ (K). The value of l_0 is calculated from B to be 6.9 Å with the values $ab=70.5$ (Å^2) and $\Delta h_f=9.11\times10^8$ (erg cm^{-3}) for i-PS[10]. The value of 6.9 Å is reasonable for

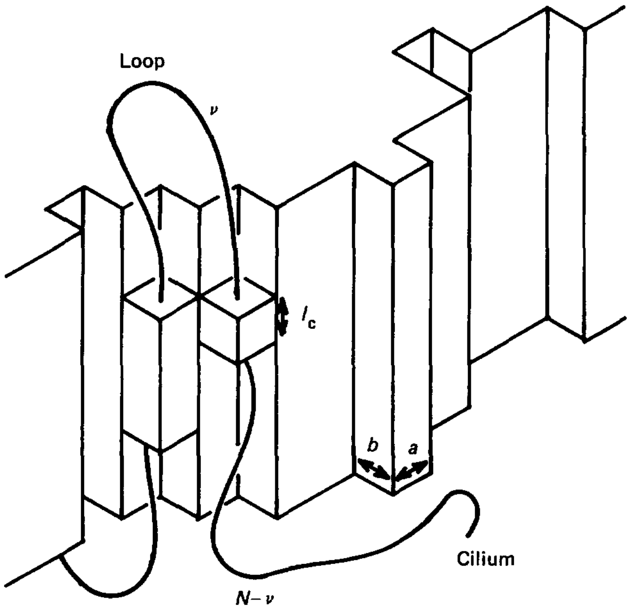

Figure 5 Schematic illustration of a rough growth face. A loop of ν segments and a cilium of $(N-\nu)$ segments are represented

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* The segment length s is determined so that s multiplied by the number of segments ν is equal to the length of a fully extended chain in the crystal

the length of the crystallizing unit. Therefore, equation (3), on the basis of rough surface growth, can describe the temperature dependence of lamellar thickness at high supercoolings in crystallization of i-PS as well as nylon-6 and nylon-6,6[3].

Molecular-weight dependence of limiting thickness

At low supercoolings, the effect of the molecular weight on the lamellar thickness is taken into account through the molecular-weight dependence of T_d°, especially for low molecular weight. Therefore, plots of l vs. ΔT given by (1) for different molecular-weight samples are represented by the same curve[11,12]. However, *Figure 2* shows that, at high supercoolings, the two curves for the different molecular weights cannot coincide in the plot of l vs. ΔT; in fact, the two curves can coincide with each other after a shift along the vertical axis as shown in *Figure 3*. Therefore, we can conclude that δl depends on molecular weight. In equation (4) (the expression for δl), s and l_0 are independent of molecular weight. Therefore the average loop length $\bar{\nu}$ and the probability of folding γ should depend on molecular weight. Both $\bar{\nu}$ and γ are determined by the conformation of a polymer chain in solution just before crystallization. Since we can reasonably assume that the relaxation time of a chain is so short that a chain always has the equilibrium conformation, $\bar{\nu}$ and γ are calculated by statistical mechanics.

Here, we define a cilium and a loop. A cilium is that part of one molecule one end of which is fixed on the growth face; a loop is that part for which both ends are fixed. We write the partition functions of a cilium and a loop, which contain N segments, as $\Omega_{\rm cilium}(N)$ and $\Omega_{\rm loop}(N)$ respectively. When a cilium of N segments folds and divides into a loop of ν segments and a cilium of $(N-\nu)$ segments, the partition function is assumed to be the product of each partition function, $\Omega_{\rm loop}(\nu)\Omega_{\rm cilium}(N-\nu)$. Then, we can calculate the average loop length ν_N and the probability of folding γ_N for a cilium of N segments as:

$$\nu_N=\frac{\sum_{\nu=\nu_0}^{N}\nu\Omega_{\rm loop}(\nu)\Omega_{\rm cilium}(N-\nu)}{\sum_{\nu=\nu_0}^{N}\Omega_{\rm loop}(\nu)\Omega_{\rm cilium}(N-\nu)} \qquad (7)$$

$$\gamma_N=\frac{1}{\Omega_{\rm cilium}(N)}\sum_{\nu=\nu_0}^{N}\Omega_{\rm loop}(\nu)\Omega_{\rm cilium}(N-\nu) \qquad (8)$$

where ν_0 is the minimum loop length required for folding. Further, to get $\bar{\nu}$, we need the average with respect to N. Therefore:

$$\bar{\nu}=\textstyle\sum_N \nu_N P_N \qquad (9)$$

where P_N is the distribution function of cilia of N segments. We introduce P_N to take into account the molecular-weight distribution and the shortening of a cilium by folding.

For further calculation, we first assume a reflecting wall: chains cannot penetrate into the crystal through the growth face. Secondly, we regard the chains as Gaussian chain:random walk (RDW), not self-avoiding walk (SAW). Thirdly, we take into account only the loop whose end-to-end distance is nearly zero; the loop whose end-to-end distance is large cannot crystallize. Then, we can write the expression of the partition functions[13]:

$$\Omega_{\rm loop}(N)=Z^N\pi s^2\left(\frac{3}{2\pi Ns^2}\right)^{5/2}\int\exp\left(-\frac{3r^2}{2Ns^2}\right)b\,{\rm d}r^2 \qquad (10)$$

$$\Omega_{\rm cilium}(N)=Z^N 2\left(\frac{3}{2\pi N}\right)^{1/2} \qquad (11)$$

where Z is the partition function of one segment. These two equations are the asymptotic formulae for large N. Substituting (10) and (11) into (7) and (8), we get ν_N and γ_N, respectively.

The calculated results are shown in *Figure 6*. The change in γ_N with N is small; γ_N is assumed to be independent of N. This result confirms the assumption under which (3) is derived; probability of folding is independent of N. Therefore, the molecular-weight dependence of δl is attributed to $\bar{\nu}$. The full curve in *Figure 6* represents $\bar{\nu}$ calculated with the assumption that the length of cilia is distributed uniformly up to the length corresponding to the average molecular weight because of the shortening of a cilium; P_N is constant. The molecular weight dependence of δl is shown in *Figure 6*. To compare the calculated $\bar{\nu}$ with δl obtained in the experiment, we use the following parameters: $s=10$ Å, number of styrene monomers in one segment in solution is 5, $\nu_0=2$ and $l_0(1+1/\gamma)=13$ (Å). These values are determined to get good agreement between the calculation and the experiment. These calculations, which are based on several assumptions, show that the molecular-weight dependence of δl to such high molecular weight as $M_w=45\times10^4$ for i-PS is explained by the molecular-weight dependence of the average loop length $\bar{\nu}$. It should

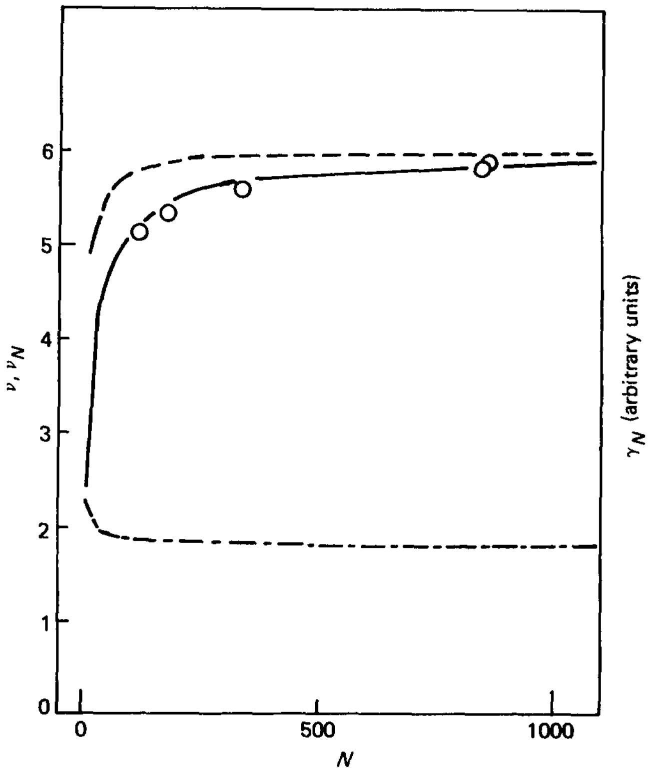

Figure 6 Calculated curves for $\bar{\nu}$ (———), ν_N (– – –) and γ_N (–·–·–); (○) δl obtained from experiment. For the parameters used in the calculations, see text

be noted that, without the reflecting wall, in both cases of RDW and SAW, we cannot fit the data with reasonable parameters. Therefore, the existence of a reflecting wall is essential.

CONCLUSIONS

The lamellar thickness of i-PS crystals was examined at high supercoolings from dilute solution: the temperature dependence and the molecular-weight dependence of lamellar thickness were studied. For the dependence of lamellar thickness on crystallization temperature, we confirmed that (3) is applicable for i-PS and we obtain the parameters $A = 2.7 \times 10^4$ (Å) and $B = 3200$ (K). For the molecular-weight dependence, we obtain the remarkable result that the limiting thickness δl depends on the molecular weight. The main part of δl is determined by the average loop length $\bar{\nu}$. The calculated $\bar{\nu}$ depends on the molecular weight and agrees with the experimental result. Therefore, we can conclude that, on crystallization at high supercoolings, polymers crystallize on a rough surface and the limiting thickness is determined by the average loop length and the probability of chain folding.

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