# Isothermal thickening and thinning processes in low molecular weight poly(ethylene oxide) fractions crystallized from the melt:
## 2. Crystals involving more than one fold

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The existence of a non-integral folding chain (NIF) crystal in a poly(ethylene oxide) fraction with molecular weight of 7100 can be proved by differential scanning calorimetry and time-resolved synchrotron small angle X-ray scattering experiments. At this molecular weight, the fraction can crystallize to a final form comprised of integral folding chain (IF) crystals with extended ($n = 0$), once-folded ($n = 1$), twice-folded ($n = 2$), and even triply-folded ($n = 3$) chain crystals. The fold length of NIF crystals increases with crystallization temperature. When this fold length is between those of IF($n = 2$) and IF($n = 1$) crystals, the NIF crystal can be thickened into the IF($n = 1$) crystal, or thinned into the IF($n = 2$) crystal. In the same way, if the fold length of NIF crystal lies between those of IF($n = 1$) and IF($n = 0$) crystals, similar isothermal thickening and thinning processes can also be observed. Which process occurs depends upon the thermodynamic driving force between the NIF and IF crystals and upon kinetic effects. Detailed kinetic maps of the fold length changes with time will be discussed.

**(Keywords: crystal melting; crystallization; fold length; integral folding; isothermal thickening; isothermal thinning; kinetic effect; morphology; non-integral folding; poly(ethylene oxide); thermodynamic driving force; time-resolved synchrotron small angle X-ray scattering)**

## INTRODUCTION

Non-integral folding chain (NIF) crystals formed in low molecular weight poly(ethylene oxide) (PEO) fractions have been experimentally observed[1–5]. These NIF crystals are recognized as transient states during crystallization, and act as initial precursors of the crystal growth. The final integral folding chain (IF) crystal observed by Kovacs *et al.*[6–10] resulted from transitions of NIF to IF crystals through an isothermal thickening or thinning process. This phenomenon is not unique to low molecular weight PEO fractions. In fact, the pioneering work for the observation of NIF crystals involved pure *n*-alkanes crystallized from both solution and the melt, as reported by Keller's research group[11–13]. They found that the crystallization must be a compromise between the thermodynamic driving force and kinetic pathway.

Prior to this investigation, two molecular weight fractions of PEO have been studied: PEO(MW = 3000) and PEO(MW = 4250). Their average extended chain lengths are 19.0 nm and 26.9 nm, respectively. For these two molecular weights, the IF crystals observed represent either extended chain crystals, IF($n = 0$), or once-folded chain crystals, IF($n = 1$). At low crystallization temperatures, the NIF crystal is thermodynamically the least stable crystalline state, yet it grows the fastest. The majority of the NIF chain molecules undergo an isothermal thinning process to form IF($n = 1$) crystals even though the fold length of NIF crystal is thicker than that of the IF($n = 1$) crystal. On the other hand, with increasing temperature, the fold length of NIF crystal increases continuously, as does its thermodynamic stability. At a certain temperature, the thermodynamic stability of the NIF crystal equals that of the IF($n = 1$) crystal. Above that temperature, the NIF crystal still exists, but a transition from the NIF to IF($n = 0$) crystals is identified through an isothermal thickening process[5].

In PEO fractions, kinetics of the transition from the NIF to IF crystals are critically dependent upon thermodynamic driving force and chain motion either along the crystallographic *c*-axis in the solid state at low temperatures, or on the growth surface at high temperatures. Although only two IF crystals are observed during the crystallization of these two fractions, isothermal thickening and thinning processes should be more hampered with increasing chain length. Furthermore, for chain lengths of sufficient magnitude, IF crystals involving more than one fold can be observed[6–10]. Therefore, the focal points of our ongoing research are: (1) with increasing chain length, how seriously will the

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transition kinetics be hampered for a fixed fold number $n$?; (2) before the final formation of IF crystals with a fold number larger than one, do NIF crystals exist and if so, what are the transition kinetics from NIF to IF crystals?; (3) it is well known that in high molecular weight polymer crystals thermodynamic stability is proportional to lamellar thickness and as a consequence, isothermal thinning is not possible; therefore where is the molecular weight boundary above which the isothermal thinning process is impossible?

In this paper we report our recent differential scanning calorimetry (d.s.c.) and time-resolved synchrotron small angle X-ray scattering (SAXS) results on one PEO fraction with MW = 7100. This fraction may exhibit IF crystals up to triply-folded chain crystals ($n = 3$). It is our intention to investigate the roles that NIF crystals play in the crystal growth under conditions where these final IF crystals exist.

## EXPERIMENTAL

### *Materials*

The PEO fraction used in this study was purchased from Polymer Laboratory as a standard material, and refractionated in our laboratory. Its molecular weight is 7100 with a polydispersity of 1.04. The extended chain length of this fraction can be calculated[6] using the equation $l = \mathrm{MW}/158.2$. For this fraction, therefore, the average extended chain length is 44.9 nm, the average once-folded chain length is 22.4 nm, the average twice-folded chain length is 15.0 nm, and the average triply-folded chain length is 11.2 nm.

### *Instrumentation and experiments*

All methods used in this study are similar to those carried out in the study of the PEO(MW = 4250) fraction. They have been described in detail in part 1 of this series[5]. Very briefly, our d.s.c. measurements were performed in a Dupont 9900 thermal analysis system, calibrated with standard materials. Isothermal crystallization experiments were carried out through a self-seeding technique[6]. After isothermal crystallization, two heating rates of 0.5°C $\mathrm{min}^{-1}$ and 5°C $\mathrm{min}^{-1}$ were used during successive periods of heating.

Time-resolved SAXS measurements were conducted at the Oak Ridge National Laboratory beamline[14], X-14, at the National Synchrotron Light Source (NSLS). The monochromator was tuned to 8.000 keV, which is equivalent to a wavelength of 0.15498 nm. A Mettler hot stage (FP-52) was mounted on a Huber goniometer with the positional sensitive proportional counter (PSPC) at a distance of 1.232 m. The same self-seeding technique was adopted. The shortest time for data collection was approximately 0.9 min. Lorentz correction of the SAXS data was applied by multiplying the intensity $I$ (counts per second) by $s^2$ ($s = 2\sin\theta/\lambda$, where $\lambda$ is the wavelength of the synchrotron X-ray). The crystal fold length was directly obtained through long spacings determined by SAXS without further correction. Integration of the intensity in a certain $s$ region was carried out after first subtracting the base line of background scattering without any PEO sample.

## RESULTS

### *Crystal melting and crystallization*

*Figure 1* shows the relationship between melting temperature, $T_m$, and crystallization temperature, $T_c$, of the PEO(MW = 7100) fraction. The data were collected from d.s.c. heating traces at heating rates of 5°C $\mathrm{min}^{-1}$ and 0.5°C $\mathrm{min}^{-1}$. *Figure 2* gives a set of these d.s.c. traces at 0.5°C $\mathrm{min}^{-1}$ for the crystal melting after isothermal

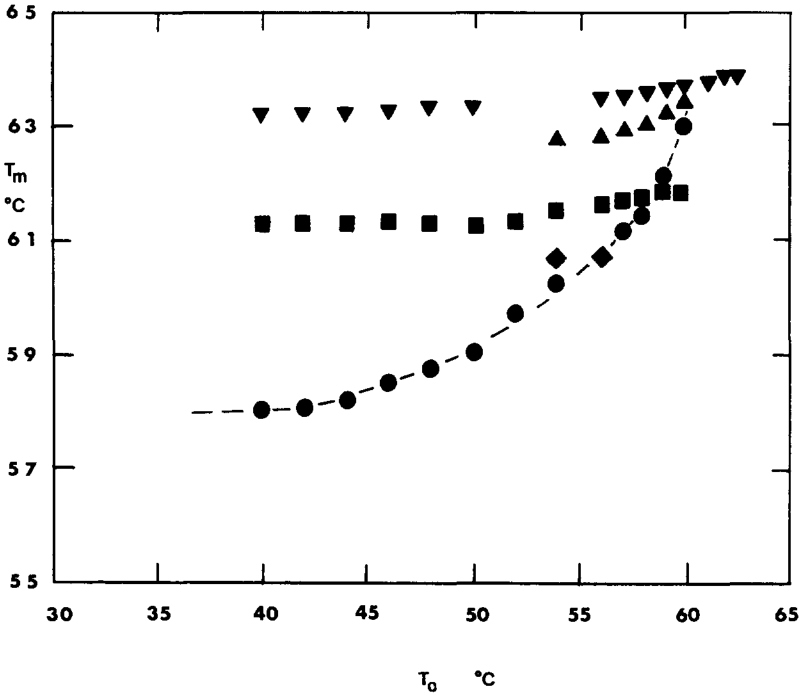

**Figure 1** Relationships between crystallization temperature ($T_c$) and melting ($T_m$) temperatures for the PEO(MW = 7100) fraction crystallized from the melt. ▼, IF($n = 0$); ■, IF($n = 1$); ◆, IF($n = 2$); ●, fold length of NIF crystals; ▲, intermediate crystal melting (see text)

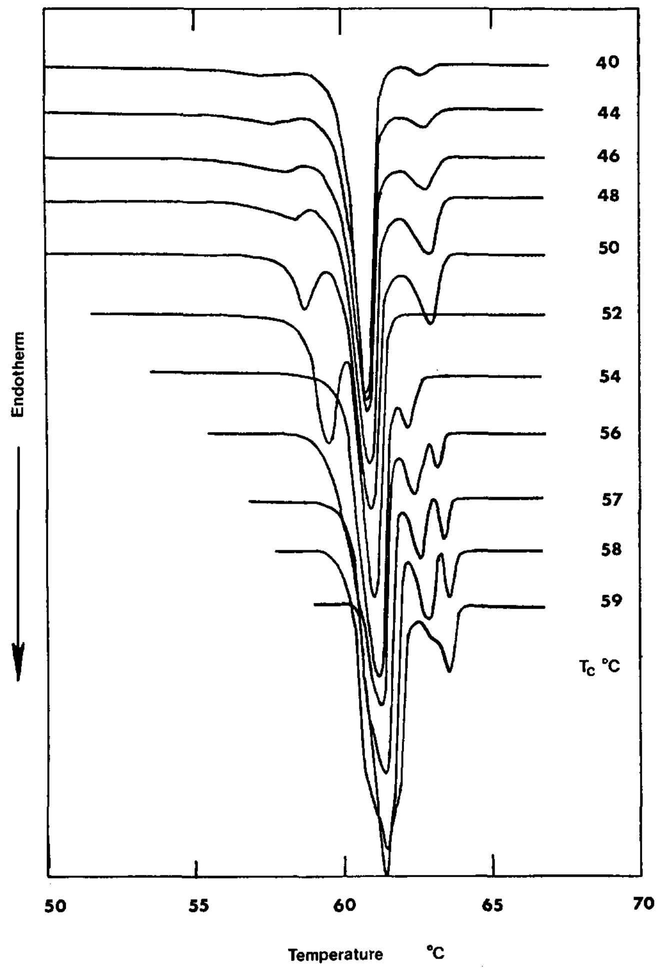

**Figure 2** Set of d.s.c. heating traces of crystal melting at a heating rate of 0.5°C min$^{-1}$ after isothermal crystallization at different temperatures

crystallization at different temperatures. The reason for such slow heating is to increase the resolution of these heating traces. Nevertheless, one must consider annealing effects on the crystals during slow heating (see below). The crystal melting behaviour of this fraction is rather complicated, as shown in *Figures 1* and *2*. Below $T_c$ = 52°C, three melting peaks can be distinguished, with an additional shoulder (around 60.5°C) at the low temperature side of the main melting peak. The lowest $T_m$ is most dependent on $T_c$. As much as 2°C variance in this $T_m$ can be found for a $T_c$ range between 40°C and 52°C. At $T_c$ = 52°C, it is interesting to find that the highest melting peak has disappeared, leaving only two melting peaks. With increasing $T_c$ to 54°C, another melting peak is developed at 62.8°C, which is between the original two high $T_m$ values as shown in *Figures 1* and *2*. For $T_c$ = 56°C, the highest melting peak reappears at 63.7°C. The newly developed melting peak is now at 62.9°C, with the main melting peak at 61.7°C. Interestingly, the shoulder at the low temperature side of the main melting peak is clearer at this $T_c$, positioned at 60.5°C. This is due to a slight increase of the main melting peak temperature with $T_c$ (it reaches 62°C at $T_c$ = 60°C), while this shoulder remains at almost constant melting temperature. Further increase in $T_c$ leads to a slight shift of the highest melting peak towards 64°C when above $T_c$ = 61.0°C. On the other hand, the newly developed peak merges with the highest $T_m$ at this $T_c$. The main melting peak gradually decreases its heat of fusion, and vanishes above about $T_c$ = 61°C. The peak at 60.5°C cannot be observed above about $T_c$ = 57°C.

It is perhaps most important that the lowest $T_m$ continuously increases with $T_c$ (dashed line in *Figure 1*). It merges with several melting peaks at various $T_c$ values, and finally, at high $T_c$, it can still be observed between two melting peaks with $T_m$ = 64°C and 62°C.

### *Isothermal thickening and thinning processes at constant temperatures*

*Figure 3* shows time-resolved synchrotron SAXS data for the PEO(MW = 7100) fraction crystallized at $T_c$ = 40°C. At an initial crystallization time, $t_c$, of 0.9 min, a fold length of 18.2 nm is observed. This is between the IF($n$ = 1) (22.4 nm) and IF($n$ = 2) (15.0 nm) crystals, and is therefore assigned as a NIF crystal. With increasing time, it is obvious that the scattering peak width becomes increasingly broad, indicating that there are multiple overlapping scattering peaks. At $t_c$ = 17 min, a second scattering peak appears at around 22.4 nm. Increasing $t_c$ further leads to a gradual decrease in intensity of the 18.2 nm scattering peak accompanied by a slight shift of the scattering angle towards a higher $s$ value, as shown in *Figure 3*. Starting at $t_c$ = 46 min, a scattering peak of 15.0 nm is evident. Therefore, the change from 18.2 nm scattering peak to 15.0 nm corresponds to an isothermal thinning process, and from 18.2 nm scattering peak to 22.4 nm corresponds to an isothermal thickening process.

*Figure 4* displays another set of synchrotron SAXS data for this fraction at $T_c$ = 44°C. It is evident that an isothermal thinning process occurs from a fold length of 18.5 nm at $t_c$ = 0.9 min to 15.7 nm at $t_c$ = 408 min. At the same time, an isothermal thickening process leads to

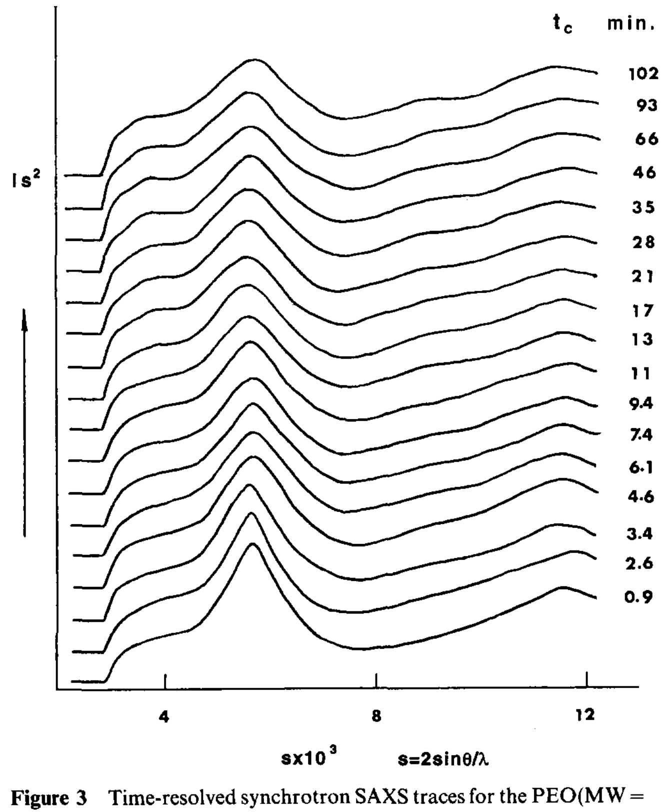

**Figure 3** Time-resolved synchrotron SAXS traces for the PEO(MW = 7100) fraction at $T_c$ = 40°C

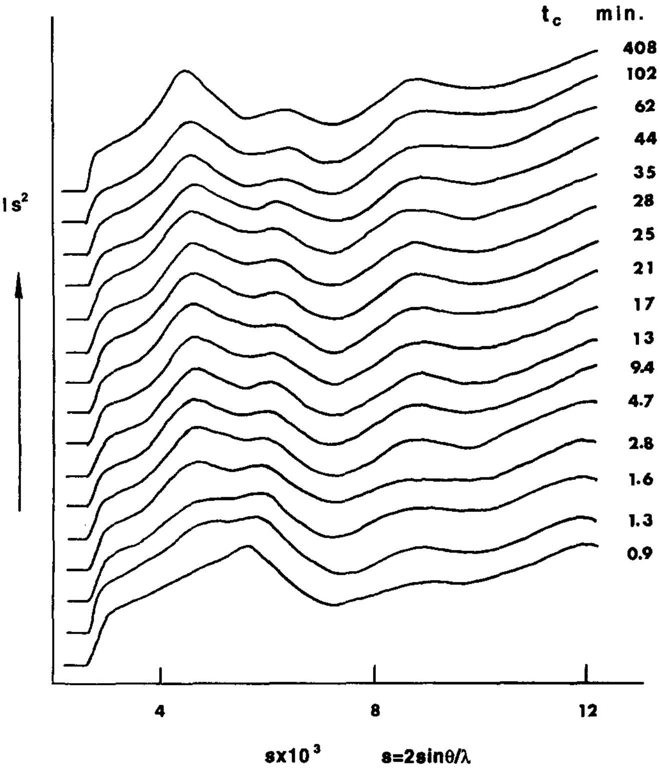

**Figure 4** Time-resolved synchrotron SAXS traces for the PEO(MW = 7100) fraction at $T_c = 44$°C

growth of a scattering peak at 22.4 nm. With increasing $t_c$, this peak increases its intensity.

At $T_c = 48$°C, as shown in *Figure 5*, a NIF crystal grows first with a fold length of 18.7 nm at $t_c = 1.4$ min. This peak gradually shifts to a relatively wide angle with increasing $t_c$. At $t_c = 320$ min, the fold length decreases to 16.9 nm. However, after $t_c = 2$ min, a new scattering peak at 22.4 nm starts to develop, and increases its intensity with time.

In *Figure 6*, with $T_c = 50$°C, it is of special interest that the synchrotron SAXS data for this fraction show a decrease in the kinetics of the isothermal thickening process compared with that at $T_c = 48$°C (see *Figure 5*). This indicates that the NIF crystal with an initial fold length of 19.5 nm has greater difficulty annealing to the IF($n = 1$) crystal than does the similar NIF crystal at lower $T_c$. Furthermore, this NIF crystal also has a slower thinning process, requiring about 560 min to decrease in fold length from 19.5 nm to 18.8 nm.

Increasing the $T_c$ to 52°C (*Figure 7*) leads to a NIF crystal with a fold length of 22.3 nm. This scattering peak seems more stable than those observed previously. After $t_c = 276$ min, this peak is still largely retained. It is noteworthy that the fold length of IF($n = 1$) crystal in this fraction is 22.4 nm. Therefore, no thickening or thinning process occurs. After a long time period only a slightly asymmetric scattering peak can be seen (*Figure 7*).

*Figure 8* shows synchrotron SAXS data for the PEO(MW = 7100) fraction crystallized at 54°C. It is surprising to find a NIF crystal with an initial fold length of 27.5 nm, which is greater than the fold length of IF($n = 1$) crystal (22.4 nm). Due to limitations of our SAXS experimental set-up, only a thinning process is observable with increasing time. Indeed, at $t_c = 486$ min, a fold length of 25.0 nm exists, caused by a continuous shift from the initial NIF scattering peak towards higher $s$ values. Additionally, the first observance of another scattering peak at 15.0 nm for this prolonged time period is of interest (note that the IF($n = 2$) crystal has a fold length of 15.0 nm).

Finally, at $T_c = 56$°C, a similar isothermal thinning process can be found (*Figure 9*). An initial NIF crystal with a fold length of 33.0 nm shifts to larger scattering angles with increasing $t_c$. At $t_c = 200$ min, the fold length is 30.0 nm. It decreases continuously to 27.5 nm at $t_c = 800$ min. Again, a new fold length of 15.0 nm also grows with time, and it should represent the IF($n = 2$) crystal.

At low to intermediate $T_c$ values ($T_c < 54$°C), one can find another scattering peak with a fold length around 11.0–12.0 nm. This may be associated with the IF($n = 3$) crystal. However, since this peak does not affect the thickening and thinning processes, further discussion will not be pursued.

### *Changes of fold lengths with temperature and time*

If one looks at the initial fold length of NIF crystals grown at different $T_c$ values, it is clear that this fold length increases with temperature. *Figure 10* represents such relationships not only for the change of initial fold length of NIF crystals, but also for the change of IF crystals with isothermal $T_c$. Below $T_c = 52$°C, it seems that the fold length of NIF crystals slightly increases with temperature, and at $T_c = 52$°C, the fold length of this NIF crystal is apparently the same as that of the IF($n = 1$) crystal. It jumps to 27.5 nm at $T_c = 54$°C. Note that this fold length is between the IF($n = 1$) and

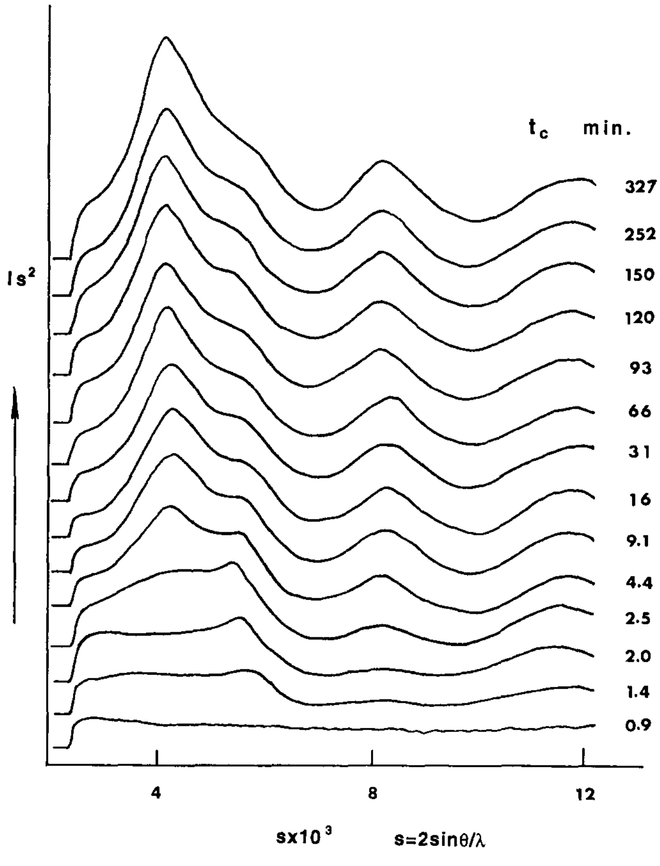

**Figure 5** Time-resolved synchrotron SAXS traces for the PEO(MW = 7100) fraction at $T_c = 48$°C

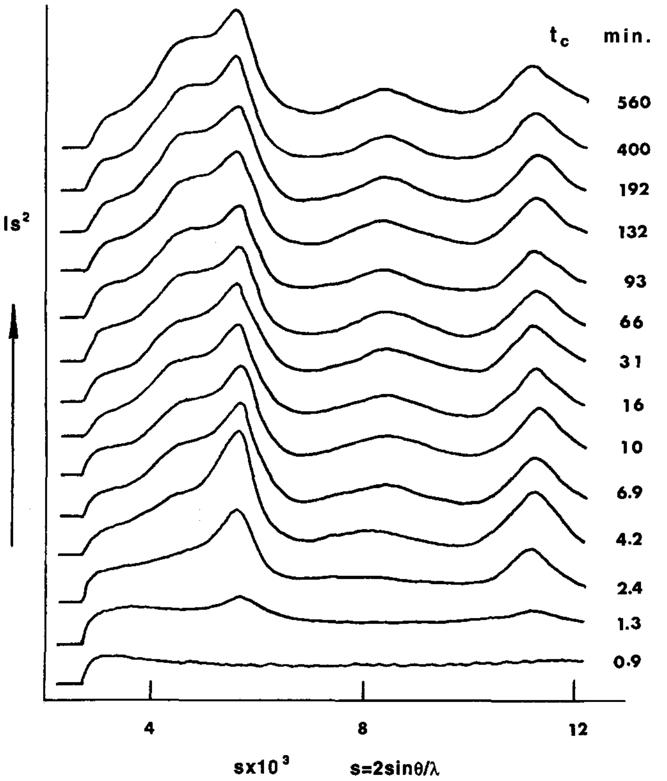

**Figure 6** Time-resolved synchrotron SAXS traces for the PEO(MW = 7100) fraction at $T_c = 50°C$

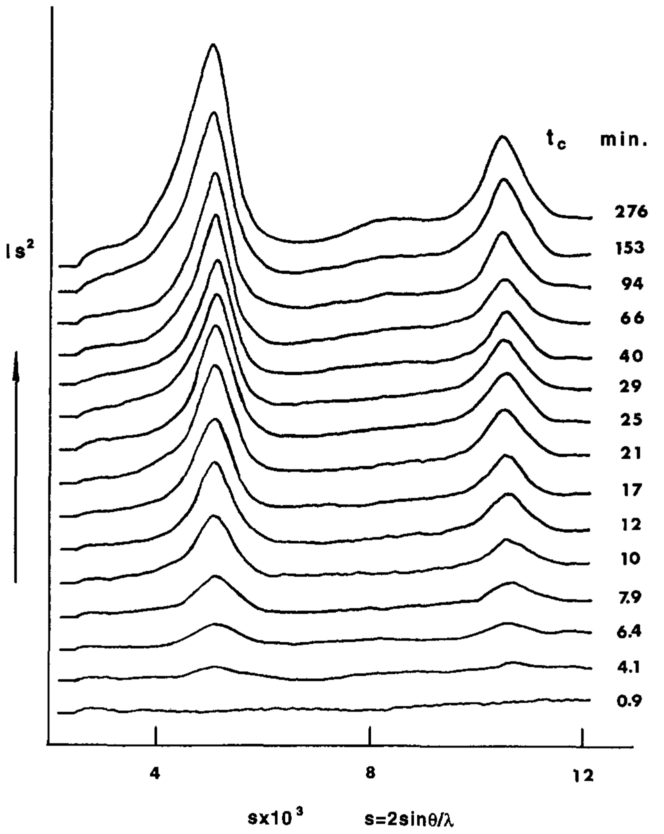

**Figure 7** Time-resolved synchrotron SAXS traces for the PEO(MW = 7100) fraction at $T_c = 52°C$

IF($n = 0$) crystals. At $T_c = 56°C$, the fold length reaches 33.0 nm. By extrapolating to a fold length of 44.9 nm, it is found to correspond to $T_c \approx 61°C$.

On the other hand, one can trace the change of fold lengths at constant temperature with $t_c$, as shown in *Figure 11* for the isothermal thinning process (below $T_c = 52°C$). It is interesting to find that with increasing temperature the thinning process slows down, as indicated by the increase in slopes ($dL/d \log t_c$) of these relationships (note that slopes are negative). The common feature indicating thinning behaviour is the initial appearance of NIF crystal peaks which continuously shift to wider angle regions. Even in the case of high temperature crystallization, above $T_c = 52°C$, the isothermal thinning processes to the IF($n = 1$) crystal follow the same pattern as found at low $T_c$ (see *Figure 12*). When isothermal thickening occurs as a simultaneous process (to a different NIF crystal population than that undergoing thinning), it is manifest by the development of a new scattering peak in a lower angle region. *Figure 13* illustrates the development of IF($n = 1$) crystals at different temperatures through an isothermal thickening process. This can be characterized by taking the ratio of the integrated IF($n = 1$) crystal intensity to that of total scattering intensity as a function of $t_c$. It is interesting to find that this development slows down with increasing temperature (from $T_c = 46$ to $50°C$). It should be noted that the curves in *Figure 13* initiate at the end time for overall crystallization (*Table 1*).

## DISCUSSION

Although numerous results have been presented here for PEO(MW = 7100) fraction, we only focus on one central issue in this discussion, namely, how does the NIF crystal

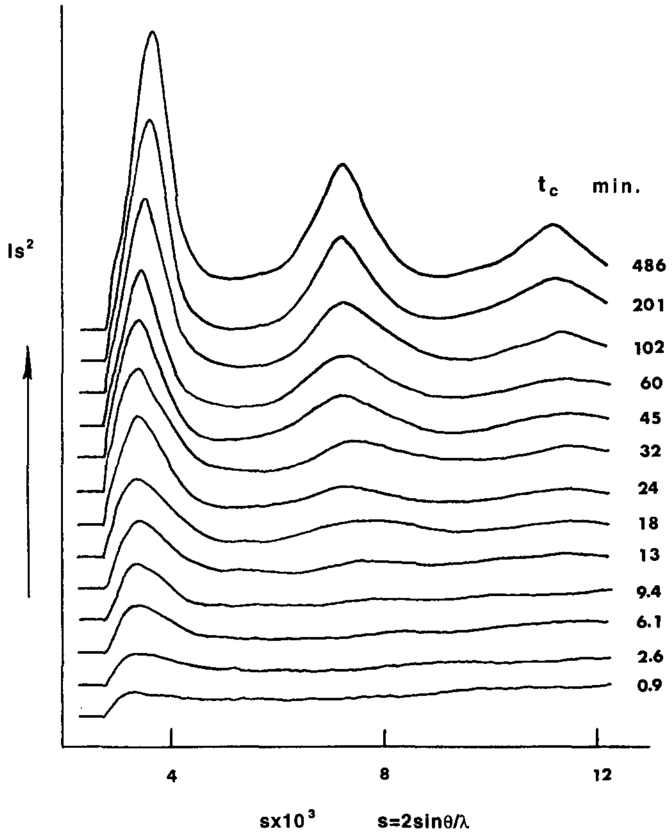

**Figure 8** Time-resolved synchrotron SAXS traces for the PEO(MW = 7100) fraction at $T_c = 54°C$

behave for the case where final IF crystals can be more than once-folded ($n > 1$)?

In principle, these isothermal thickening and thinning processes are guided by thermodynamic driving forces. Therefore, any process that occurs should go from a less stable state to a more stable state, so that the change in Gibbs free energy is smaller than zero. If an isothermal thickening process is carried out by a transition from the NIF to IF($n = i$) crystals, (where $i$ can be 0 or 1 in this case) or an isothermal thinning process occurs by a transition from the NIF to IF($n = i + 1$) crystals, the NIF crystal must be the thermodynamically least stable state compared with both IF($n = i$) and IF($n = i + 1$) crystals. As soon as the Gibbs free energy of NIF crystal is lower than that of IF($n = i + 1$) crystal the isothermal thinning process is not possible: only the thickening process can be carried out.

Additionally, one must take the kinetic effect into

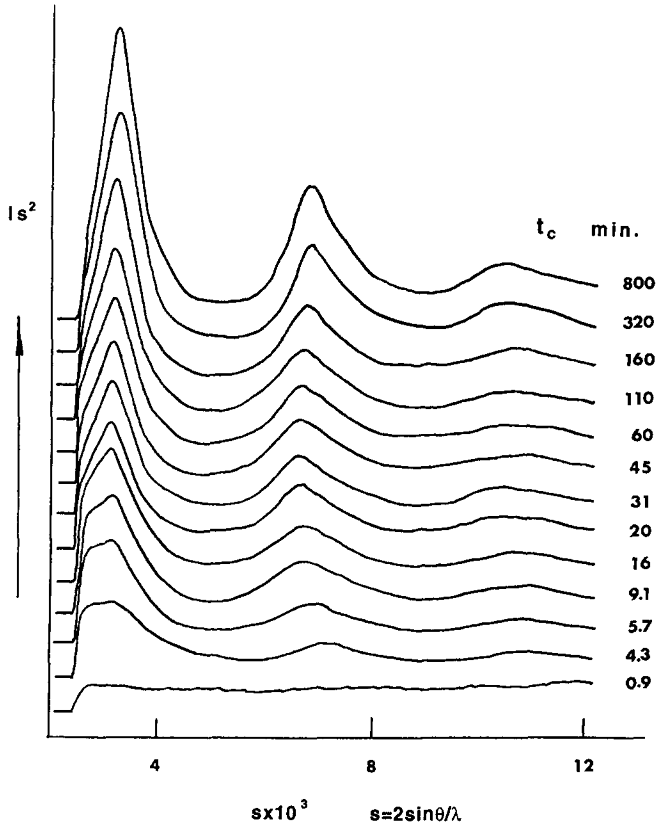

**Figure 9** Time-resolved synchrotron SAXS traces for the PEO(MW = 7100) at $T_c = 56°C$

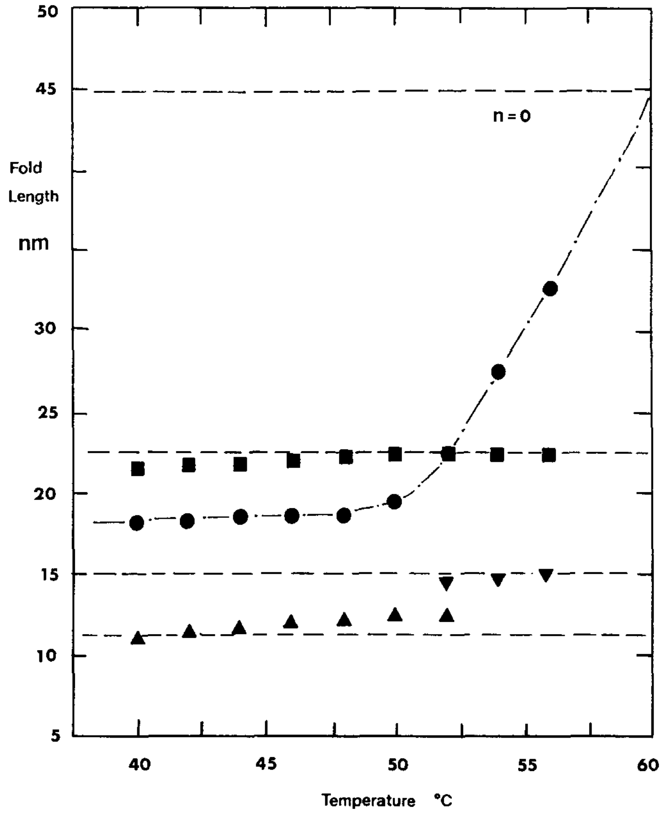

**Figure 10** Relationships between fold lengths of the crystals and crystallization temperatures: ■, IF($n = 1$); ▼, IF($n = 2$); ▲, IF($n = 3$); ●, fold lengths of NIF crystals

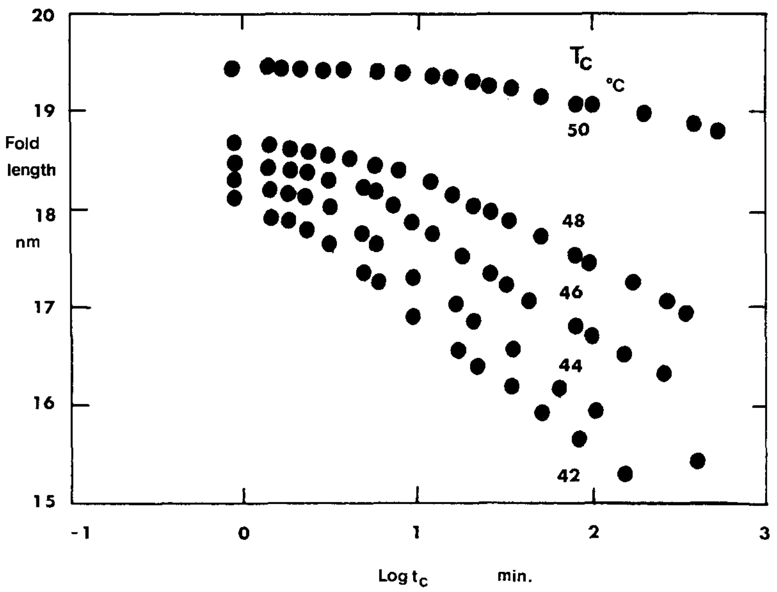

**Figure 11** Changes of fold lengths of the NIF crystal with time ($\log t_c$) at different temperatures ($T_c \leqslant 50°C$) during isothermal thinning. Note that the fold length of IF($n = 2$) crystal is 15 nm

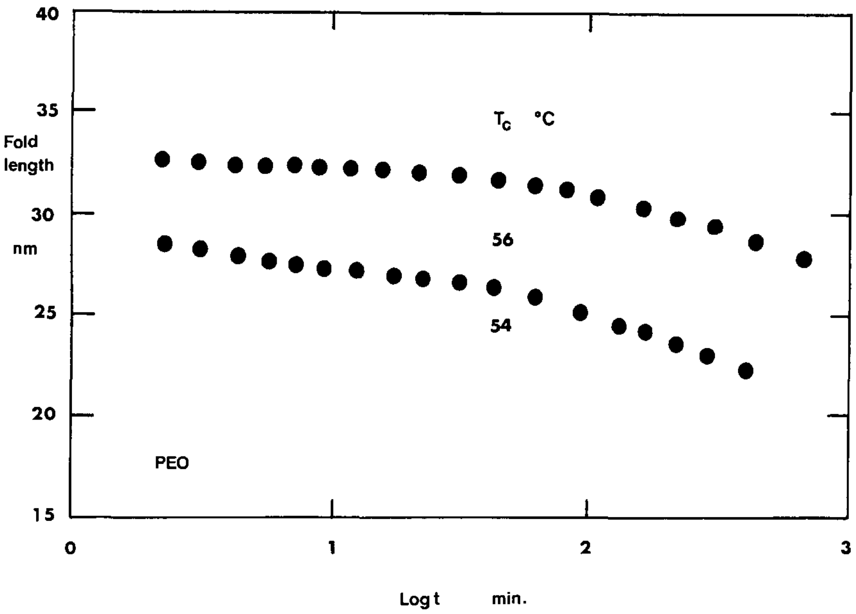

**Figure 12** Changes of fold lengths of the NIF crystal with time at $T_c$ = 54 and 56°C. Note that the fold length of IF($n$ = 2) crystal is 15 nm

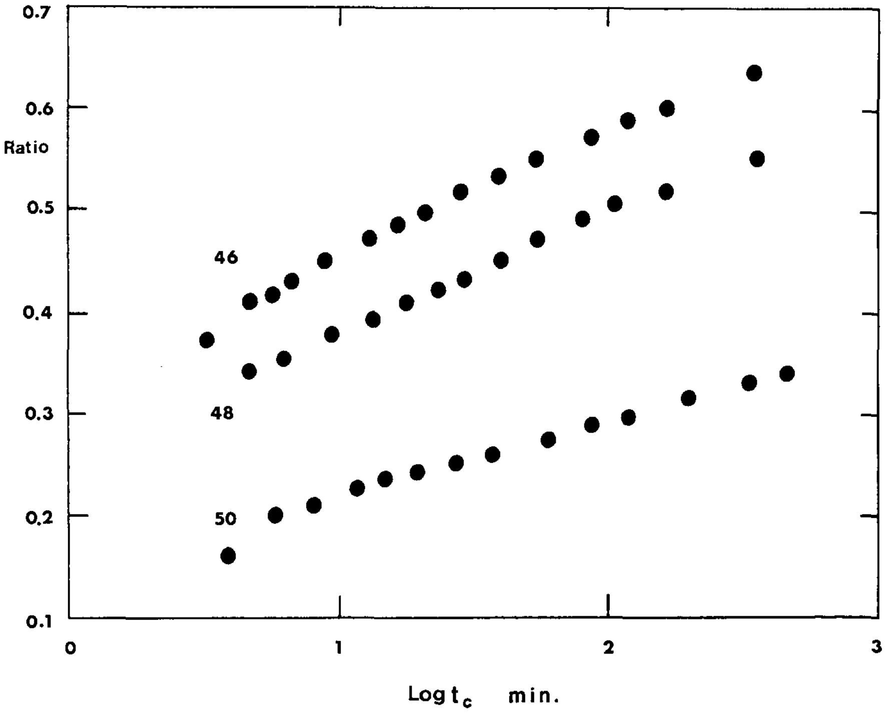

**Figure 13** Relationship between the integration of scattering intensity of the IF($n$ = 1) crystal and time at three different temperatures (46°C, 48°C and 50°C) during isothermal thickening

account. This effect is attributed to chain diffusional motion along the direction of the crystallographic $c$-axis (chain direction). In particular, at relatively low $T_c$ values this kind of motion occurs within the crystal state. With increasing temperature, chain motion may also occur near to, as well as at the crystal growth surface. Therefore, one has a compromise between thermodynamic driving force and kinetic effect.

Considering this particular PEO fraction, if the NIF crystal is the thermodynamically least stable crystal, it should display the lowest $T_m$ value. Although $T_m$ is generally dependent on heating rate, it has been found that for the PEO(MW = 7100) fraction this dependence does not change the sequence of the $T_m$ values[15]. For IF($n$ = 0), IF($n$ = 1), IF($n$ = 2) and IF($n$ = 3) crystals, $T_m$ = 64.0, 62.0, 60.5 and 59.3°C, respectively[16,17]. One can thus assign the $T_m$ values shown in *Figure 1*. The lowest $T_m$ is attributed to NIF crystal melting, which is the most $T_c$-dependent. The $T_m$ around 60°C is associated with the IF($n$ = 2) crystal melting. It is surprising to find that at $T_c$ = 56°C, this melting peak can be clearly identified. Below this $T_c$ value, only a shoulder on the main melting peak (around 60–60.5°C) is seen. The $T_m$ in the vicinity of 61–62°C is basically related to the IF($n$ = 1) crystal melting. Nevertheless, it is clear that at about $T_c$ = 50°C there is a minor minimum; by further

**Table 1** End times of isothermal crystallization for the PEO(MW = 7100) fraction observed through d.s.c. experiments

| Crystallization temperature (°C) | End time of crystallization (min) |
|---|---|
| 42 | 0.6 |
| 43 | 0.8 |
| 44 | 1.2 |
| 45 | 1.8 |
| 46 | 2.5 |
| 47 | 3.6 |
| 48 | 6.0 |
| 49 | 9.0 |
| 50 | 11.0 |
| 51 | 21.0 |
| 52 | 40.0 |
| 53 | 82.0 |
| 54 | 150 |
| 55 | 290 |
| 56 | 450 |
| 57 | 800 |
| 58 | 1200 |

increasing the temperature, this crystal is slightly perfected and shows an increased $T_m$ of up to 62.0°C. The highest $T_m$ is associated with the IF($n = 0$) crystal melting. A continuous, slight increase of $T_m$ with $T_c$ indicates a perfection process. It is of special interest that at $T_c = 52$°C, no IF($n = 0$) crystal melting peak can be seen at all, similar to the abnormal crystal melting behaviour in the case of the PEO(MW = 4250) fraction[5]. This is because below $T_c = 52$°C, the IF($n = 0$) crystal appears only during a thickening process after crystallization (see *Table 1*). At and above this temperature, the IF crystal can grow as soon as its nucleus forms through the initial NIF crystal. Furthermore, at this temperature the fold length of NIF crystal is the same as that of the IF($n = 1$) crystal. However, the effects responsible for the absence of IF($n = 0$) crystals are unclear. Above $T_c = 54$°C, two melting peaks are clearly identified at about 62°C, revealing the existence of two different crystal populations. One expects the higher melting temperature to represent the IF($n = 0$) crystal with $T_m = 64.0$°C, and the lower temperature to represent a mixture of the IF($n = 0$) and IF($n = 1$) crystals. This assignment is being further investigated through morphological observations with a transmission electron microscope.

Particular attention should be paid to the melting temperature of the NIF crystal in *Figure 1* (dashed line). It is interesting to observe that below $T_c = 54$°C, the $T_m$ value is lower than that for all three IF crystals (IF($n = 0$), IF($n = 1$), and IF($n = 2$)). Thermodynamically, it is possible for such NIF crystals to transform to any of these IF crystals. For $T_c$ values between 54 and 58°C, the $T_m$ of the NIF crystal is higher than that of the IF($n = 2$) crystal, but still lower than those for IF($n = 0$) and IF($n = 1$) crystals. Therefore, a thickening process to the IF($n = 0$) crystal or a thinning process to the IF($n = 1$) crystal from the NIF crystal is still conceivable. Above $T_c = 58$°C, however, this NIF crystal becomes more stable than the IF($n = 1$) crystal, and therefore only the transition of the NIF to IF($n = 0$) crystals is observed. Since the NIF crystal fold length is around 18.0–19.5 nm below $T_c = 52$°C (*Figures 3–6*), the isothermal thickening transitions are from the NIF to IF($n = 1$) (22.4 nm) crystals or from the NIF to IF($n = 0$) (44.9 nm) crystals. The former process occurs almost exclusively compared with the latter. In fact, at $T_c < 50$°C the IF($n = 0$) crystal portion is less than one-tenth of the total heat of fusion, even at a heating rate of 0.5°C min$^{-1}$. This indicates that the transition from NIF to IF($n = 0$) crystals is very minor. In addition, the transition from IF($n = 1$) to IF($n = 0$) crystals is also possible. On the other hand, the isothermal thinning process means the transition from the NIF to IF($n = 2$) (15.0 nm) crystals. For $T_c > 54$°C, the fold length of this NIF crystal increases to over 22.4 nm (which is the fold length of the IF($n = 1$) crystal). Nevertheless, the $T_m$ of this NIF crystal is still lower than that of the IF($n = 1$) crystal until $T_c$ reaches 58°C. As a result, the isothermal thinning process can still occur in this crystallization temperature region (*Figures 8* and *9*). With increasing $T_c$, the dashed line in *Figure 1* merges with the $T_m$ of IF($n = 0$) crystal at $T_c = 60.0$°C. This indicates that above that temperature the IF crystals, and in particular the extended chain crystal of the PEO(MW = 7100), may grow from the melt. On the other hand, the $T_m$ value for mixed growth of the IF($n = 0$) and IF($n = 1$) crystals merges with those of the IF($n = 0$) crystal at around $T_c = 61.0$°C. Therefore, above this crystallization temperature, only the extended chain crystal can grow.

From our synchrotron SAXS results, shown in *Figures 3–9*, kinetics of the isothermal thickening and thinning processes for the PEO(MW = 7100) fraction can be traced. For the isothermal thinning process (see *Figure 11*), the decrease in rate of this process with increasing temperature (the slope $\mathrm{d}L/\mathrm{d}\log t_c$ increases) is mainly due to the reduction of thermodynamic driving force ($\Delta G$) with increasing $T_c$ (as indicated in *Figure 1*). This is due to a difference in the initial fold length of NIF crystals ranging up to 1.5 nm in this temperature region. The two-step thinning process (note the change of slopes occurring at each $T_c$ value) is caused by thinning during crystallization and subsequently after crystallization[5]. Indeed, the time corresponding to the change from first to second thinning steps corresponds well to the completion of overall crystallization observed in d.s.c. measurements (*Table 1*) at each temperature. However, the difference between these two slopes is smaller than that observed[5] in the case of the PEO(MW = 4250) fraction irrespective of $T_c$. This indicates that an increase of fold number may seriously hamper the thinning process. Note that in this fraction the greatest occurrence of NIF crystals occurs between once-folded and twice-folded chain conformations below $T_c = 52$°C, as opposed to the cases of PEO(MW = 3000) and PEO(MW = 4250) fractions where NIF crystals show a fold length between extended and once-folded chain conformations[1,2,5]. It is expected that above $T_c = 52$°C, the NIF crystal in the PEO(MW = 7100) has a fold length between extended and once-folded chain conformation, as indicated in *Figures 10* and *12*. Again, the thinning process at $T_c = 56$°C is slower than that at $T_c = 54$°C. Nevertheless, it should be remembered that initial fold lengths of the NIF crystal at these two $T_c$ values are about 6 nm apart. Therefore, not only a decrease in thermodynamic driving forces, but also an increase of molecular diffusional distance along the crystallographic $c$-axis may serve as factors to slow down the isothermal thinning process with increasing $T_c$.

It is evident that for the isothermal thickening phenomenon, as shown in *Figure 13*, the development of

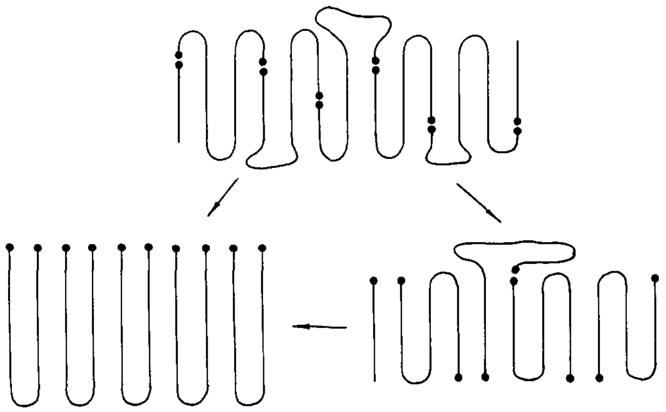

**Figure 14** Molecular mechanism of the isothermal thickening and thinning processes when the fold length of NIF crystal is between those of IF($n = 1$) and IF($n = 2$) crystals

IF($n = 1$) crystal through the thickening process is faster at $T_c = 46$°C compared with those at $T_c = 48$ and 50°C. The formation of IF($n = 1$) crystals may occur through two pathways. The first involves the transition from the NIF to IF($n = 1$) crystals, and the second, the transition from the IF($n = 2$) to IF($n = 1$) crystals. For the former case the decrease of these transition rates is mainly due to a decrease of thermodynamic driving force with increasing $T_c$. On the other hand, the driving force between two IF crystals in the latter case is almost constant, and it is smaller than for the former case (*Figure 1*). From a kinetic point of view, molecular diffusional motion in the NIF to IF($n = 1$) case (from around 18.0–19.5 nm to 22.4 nm) is easier than in the IF($n = 2$) to IF($n = 1$) case (from 15.0 nm to 22.4 nm). Therefore, one can conclude that in this temperature region most of the IF($n = 1$) crystal is formed directly through the thickening transition from the NIF to IF($n = 1$) crystals.

Of particular interest is how to relate this finding with the onset temperatures of the IF crystals observed by Kovacs *et al.*[6–10]. Note that the IF crystal region[8] begins at about 53°C. This corresponds to the temperature where the fold length of the NIF crystal is almost equal to that of the IF($n = 1$) crystal (*Figure 10*). Also, at this temperature no extended chain crystal can form, as shown through d.s.c. measurements in *Figures 1* and *2*. Nevertheless, a detailed correlation is not evident. Further research must be conducted to establish this correspondence. Another point which should be emphasized is that the fold length of the NIF crystal observed in *Figure 10* was in fact predicted several years ago by Hoffman[18], Sadler[19] and Buckley[20]. They proposed that IF crystals may result from a NIF crystal with a continuous increase in fold length. Very recently, Hoffman has further developed his nucleation theory to illustrate the crystal growth of short chain oligomers such as pure $n$-alkanes[21] and PEO fractions[22].

The molecular mechanism of these isothermal thickening and thinning processes was first suggested by Ungar and Keller[12,13] for pure $n$-alkane crystallization. We have also adopted their model to illustrate these processes in the case of low molecular weight PEO fractions[1–5]. The model up to now is a description of transitions from the NIF to IF($n = 0$) crystals through thickening, and from the NIF to IF($n = 1$) crystals through thinning. *Figure 14* shows a model which represents transitions from the NIF to either IF($n = 1$) or IF($n = 2$) crystals. The feature of this model is that the NIF crystal usually contains more than one fold. As a result, a cyclic composition of two chain molecules formed by connections of two chain ends through hydrogen bonding is very improbable in this case. During thinning, therefore, it may create some new cilia since the lateral lamellar size must remain constant in the solid state. On the other hand, during thickening, it is also possible to pull in other new chain molecules from the melt or other lamellar layers to fill in the space. Furthermore, under conditions allowing chain diffusional motion on the crystal growth surface, an IF($n = 1$) crystal thickened from the NIF crystal will possess all the chain ends at one side of the lamellar crystal. Note that double-lamellar crystals can form only when chain ends of two adjacent layers lie at the same interface[23]. Therefore, formation of double-lamellar crystals may be associated with an IF($n = 1$) crystal previously formed through isothermal thickening from either the NIF or the IF($n = 2$) crystals as shown in *Figure 14*. However, if the chain diffusional motion is carried out in the solid state, no drastic change of the crystal morphology should be expected. This is, in fact, a guiding molecular mechanism to be examined through morphological observations in these PEO fractions.

## CONCLUSIONS

This is the first experimental report involving the situation in which the NIF crystal exists in a region where transitions to IF crystals of more than one fold can form. This NIF crystal is a transient, initial state. It grows the fastest, but with the least thermodynamic stability. The fold length of this NIF crystal follows similar trends to those of polymer lamellar crystals, namely, it increases with crystallization temperature. When the fold length of NIF crystal is between IF($n = i$) and IF($n = i + 1$) crystals, both isothermal thickening and thinning processes may proceed, depending upon the thermodynamic driving force and molecular diffusional motion along the crystallographic $c$-axis. The final IF crystal is formed through either a thickening or thinning process. Nevertheless, the kinetics of these processes are increasingly hampered by increasing chain length and/or number of folds.

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