

ROLE AND IMPORTANCE OF RADIUS OF GYRATION OF CHAINS IN THE MELT IN THE CRYSTALLIZATION OF POLY(1-BUTENE)*

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Abstract Crystallization in polymer systems actually is a process that transfers the entangled melts into a semi-crystalline layered structure. Whether or not a chain disentangles may result in different crystallization mechanism. When compared to the crystal thickness (d_c), the volume occupied by the chain in the melt, *i.e.*, the radius of gyration (R_g), plays a very important role in polymer crystallization. When $d_c \leq R_g$, crystallization does not necessitate a chain disentangling. The entanglements are just shifted into the amorphous regions. However, as $d_c > R_g$, *i.e.*, as the crystal thickness gets larger than the radius of gyration of the chain in the melt, it becomes necessary for a chain to disentangle. Then a change of crystallization mechanism occurs. Such change has been experimentally observed in the crystallization of poly(1-butene). A change in the crystal morphologies from spherulite to quadrangle, is seen via PLM, as crystallization temperatures increase. Even more, such a change is molecular weight dependent, and shifts to lower temperature as molecular weight decreases. There exists a jump of crystal thickness and crystallinity associated with morphological change, as seen via SAXS. A change of crystallization kinetics and crystallinity is further evidenced via dilatometry. The unique feature of P1b crystallization has been discussed based on the radius of gyration of chain in the melt (R_g), and very good agreement is obtained.

Keywords Poly(1-butene), Crystallization, Radius of gyration

INTRODUCTION

Crystallization in polymer systems is a process of primary importance and has long been studied. How polymers crystallize? This is a long-standing question and has been argued for many years. Much attention has been paid to understanding the molecular processes involved in the transformation from entangled melt to a semi-crystalline structure. Several conceptual models have been proposed and worked out over the years, namely, (1) Nucleation and growth theory developed by Hoffman and Lauritzen^[1, 2]; (2) Surface roughing theory proposed by Sadler^[3]; (3) Spinodal decomposition suggested by Kaji^[4, 5]; and (4) Multisteps model (via mesomorphic layer and granular structure) put forth by Strobl^[6, 7]. Nevertheless, all of the models do not much involve the effect of chain disentangling in the melt state on polymer crystallization. Experimental observations have shown that crystallization from the chain entangled melt and from the less entangled melt results in entirely different crystal morphologies, crystallization kinetics and crystallinities^[8–10]. In this case, the chain mobility plays an important role in the formation of crystallites.

There exists another case in which chain disentangling may also result in totally different crystallization mechanisms in polymer crystallization. We understand that crystallization occurs outside an entangled polymer melt and then results in crystal layers embedded in and coupled by the fluid matrix. Crystallization does not necessitate a chain disentangling. The entanglement of chains is just shifted into the amorphous regions, where

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the chains become accumulated together with the other non-crystallizable chain parts like end-groups, co-units and stereo-defects. This normal situation, however, has a prerequisite: The crystal thickness (d_c) must not be larger than the diameter of the volume occupied by the chains in the melt. This diameter is in the order of the radius of gyration R_g . We therefore have the condition

$$d_c \leq R_g \quad (1)$$

If it is not fulfilled, *i.e.* the crystal thickness is larger than the radius of gyration of the chain in the melt, it becomes necessary for a chain to disentangle. The consequence is a change in the crystallization mechanism (crystallinity, kinetics and morphology).

In this paper, we are going to demonstrate such a change, by using poly-1-butene (P1b) as an example. We observed two crystal morphologies, two crystallinities and two kinetics in P1b crystallization, and the changes of crystal morphology, crystallinity and crystallization kinetics are dependent not only on temperature but on molecular weight as well. As we will see, a comparison between the radius of gyration of a chain in the melt and the crystal thickness, d_c , indicates that our presumption might be right, *i.e.* the radius of gyration of a chain in the melt may play very important role in polymer crystallization.

EXPERIMENTAL

Samples

Three samples of poly-1-butene with different molecular weights were investigated. P1b2 ($M_w = 185000$) was purchased from Acros Organics Company. P1b1 and P1b3 are commercial products from Montell. P1b1 has $M_w = 141000$ and $M_n = 40000$, while P1b3 has $M_w = 380000$ and $M_n = 87000$ respectively. All the molecular weight data were determined by high temperature GPC.

Instrumentation

The small angle X-ray scattering (SAX) experiments were carried out with the aid of a Kratky-camera attached to a conventional Cu-K α X-ray source, employing a temperature controlled sample-holder. Scattering curves were usually recorded with a few minutes counting time, with the help of a position-sensitive metal wire detector. The slit-smear data obtained were deconvoluted by the application of an algorithm developed in our group^[11]. Before starting an isothermal crystallization, samples were kept at 170°C for 20 min to destroy the thermal history completely, and then cooled in the sample holder as fast as possible to the crystallization temperature. By observing the intensity it was made sure that crystallization did not start before reaching the isothermal conditions.

A polarized light microscope (PLM) attached to a camera was used to observe the macroscopic morphology, and microscopy crystal morphology was obtained with an atomic force microscope (AFM, Nanoscope III).

Crystallization kinetics and final crystallinity were recorded with a mercury-filled dilatometer. Weight fraction crystallinities were derived from the change in the specific volume by calculating the ratio to the ideal value. For P1b, Δv is 0.039 cm³/g^[12].

SAXS Data Analysis

The evaluation of the SAXS patterns was carried out, assuming that the stack lamellae have an infinite side dimension. In practice, this assumption takes into account a one-dimensional electron density change along the normal direction to the lamellae. Scattering intensity can be related to the one-dimensional electron density correlation function $K(z)$, defined as:

$$K(z) = \langle (\rho_e(z) - \langle \rho_e \rangle) (\rho_e(0) - \langle \rho_e \rangle) \rangle = \langle \rho_e(z) \rho_e(0) \rangle - \langle \rho_e \rangle^2 \quad (2)$$

and its second derivative $K''(z)$, which gives the interface distance distribution function, can be directly calculated by applying the Fourier relation.

$$K''(z) = \frac{O_{ac}}{2} \Delta \rho_c^2 [h_a(z) + h_c(z) - 2h_{ac}(z)] \quad (3)$$

h_a , h_c and h_{ac} give the distribution of the thickness of the amorphous and the crystalline layers, and long spacing, respectively. The linear crystallinity ϕ is defined as:

$$\phi_l = \frac{h_a}{h_{ac}} \quad (4)$$

For two-phase systems, the asymptotic behavior of the scattering pattern can be described by Porod's law:

$$\lim_{q \rightarrow \infty} \Sigma(q) = r_c^2 \frac{P}{(q/2\pi)^4} \quad (5)$$

The Porod coefficient P is directly related to the specific internal surface O_{ac} , *i.e.*, the area per unit volume of the interface separating crystalline and amorphous regions, by:

$$P = \frac{1}{8\pi^3} O_{ac} \Delta \rho_c^2 \quad (6)$$

P shows also up in the slope of the triangular part of $K(z)$ as:

$$P = \frac{1}{4\pi^3} \frac{dK}{dz} \quad (7)$$

Due to the small density difference between the crystal (0.89) and the amorphous (0.86), special care was taken during data smoothing. A Trial and error method was used to minimize the error, which may be caused due to the low contrast between the crystal and the amorphous material. Also the calculated lamella thickness and long spacing were compared with the results obtained from AFM to make sure that the data analysis is all right.

RESULTS AND DISCUSSION

Two Crystal Morphologies

In most cases, the crystal morphology of P1b can be seen under PLM as spherulite. Quadratic crystals were first reported by Alfonso and ourselves only recently. Figure 1 depicts the crystal morphology at three temperatures representing different temperature ranges, as seen via PLM for sample P1b2. In the low temperature range, $T_c = 85^\circ\text{C}$, one observes spherulite crystal morphology. Quadrangular shape, however, is obtained in the high temperature range, $T_c = 104^\circ\text{C}$. Very interestingly, in the transition temperature range $T_c = 100^\circ\text{C}$, one observes the coexistence of two morphologies, both the spherulite and the quadrangle at the same temperature.

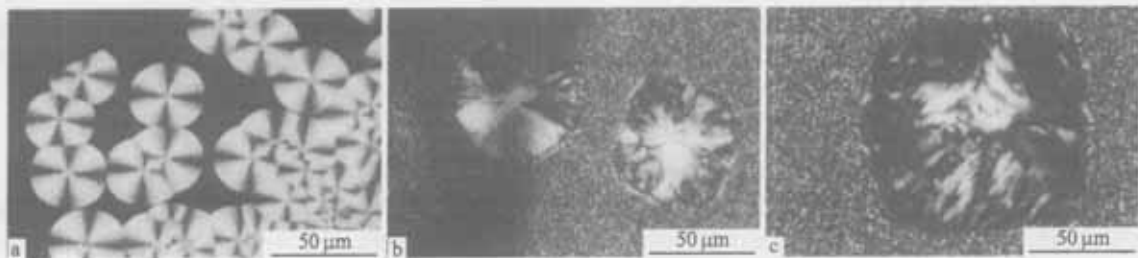


Fig. 1 Macroscopic crystal morphology of P1b2 observed via PLM at different crystallization temperatures
a) $T_c = 85^\circ\text{C}$, b) $T_c = 100^\circ\text{C}$, c) $T_c = 104^\circ\text{C}$

Moreover, the morphology change is not only temperature dependent, but molecular weight dependent as well. As shown in Figs. 2 and 3, for lower molecular weight sample P1b1, a change of spherulite to quadrangle is

seen at 90°C, and for higher molecular weight sample P1b3, up to 104°C, only spherulite shape is seen, a change of morphology shifts to higher temperatures (above 104°C).

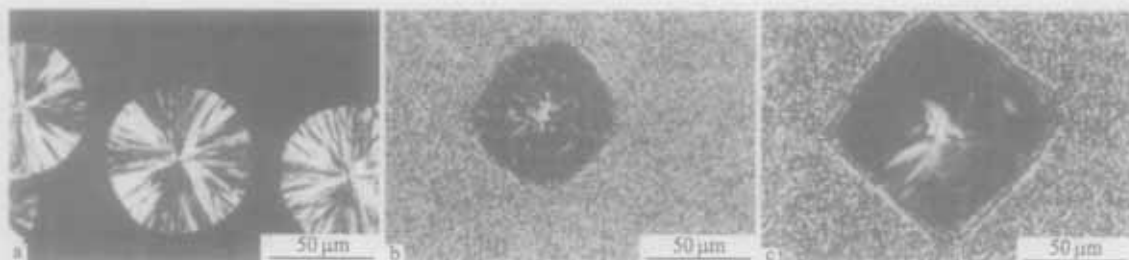


Fig. 2 Macroscopic crystal morphology of P1b observed via PLM at different crystallization temperatures
a) $T_c = 85^\circ\text{C}$, b) $T_c = 90^\circ\text{C}$, c) $T_c = 100^\circ\text{C}$

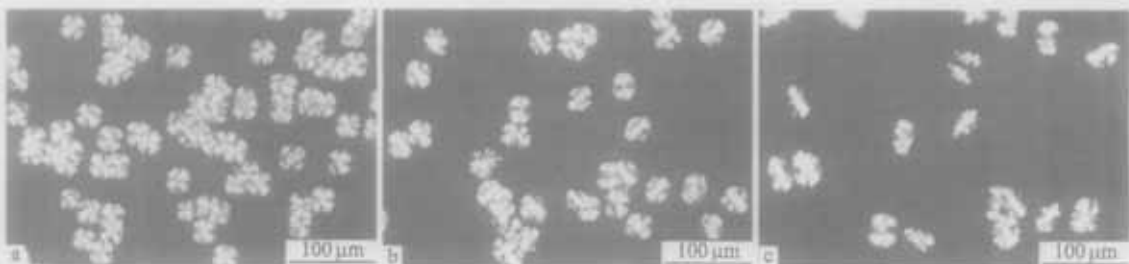


Fig. 3 Macroscopic crystal morphology of P1b3 observed via PLM at different crystallization temperatures
a) $T_c = 85^\circ\text{C}$, b) $T_c = 95^\circ\text{C}$, c) $T_c = 104^\circ\text{C}$

In addition to the unique quadrangular shape in the high temperature range, some of its “dark” appearance can be seen under PLM. This indicates that not only crystal morphology, but also the orientation of lamellae changes with the change of crystal growth mechanism. Edge-on lamella in the spherulite changes to flat-on lamella in the quadratic crystal, *i.e.* the molecular chain is parallel to the beam, which causes the dark appearance to be seen under PLM.

To prove this presumption and to get detailed microscope morphology, we carried out the AFM experiment for sample P1b2, the results of which are shown in Figs. 4, and 5. For comparison, AFM as performed at two temperatures, one in the temperature range $T_c = 85^\circ\text{C}$, and the other in the high temperature range $T_c = 104^\circ\text{C}$. AFM results clearly show the layer-like and edge-on lamella for P1b crystallized at $T_c = 85^\circ\text{C}$, and some layer-like but flat-on lamella for the sample obtained at $T_c = 104^\circ\text{C}$. One can also observe the granular structure, instead of the homogeneous lamella, at both crystallization temperatures, which may represent two initial states of crystallites^[13]. Also from the AFM result, one can calculate roughly the long period as well as the crystal thickness. At $T_c = 85^\circ\text{C}$, the average long period is about 30 nm, and crystal lamella about 15 nm; at $T_c = 104^\circ\text{C}$, the long period is about 40–45 nm, and crystal thickness is about 25–30 nm.

Crystal Thickness and Crystallinity Obtainable from SAXS Data

For SAXS data, we are particularly interested in the interface distance distribution function $K''(z)$, from which the most probable thickness of the crystal and the amorphous material can be obtained. To perceive the temperature dependence of the $K''(z)$ pattern, the SAXS data obtained after the completion of isothermal crystallization of sample P1b2 at the indicated temperatures is shown in Fig. 6. We found that the $K''(z)$ curve systematically changes from one peak to two peaks as the crystallization temperature increases. One prominent peak appears at T_c below 95°C , and two peaks in $K''(z)$ appear at T_c above 100°C . Interestingly, in the transition temperature

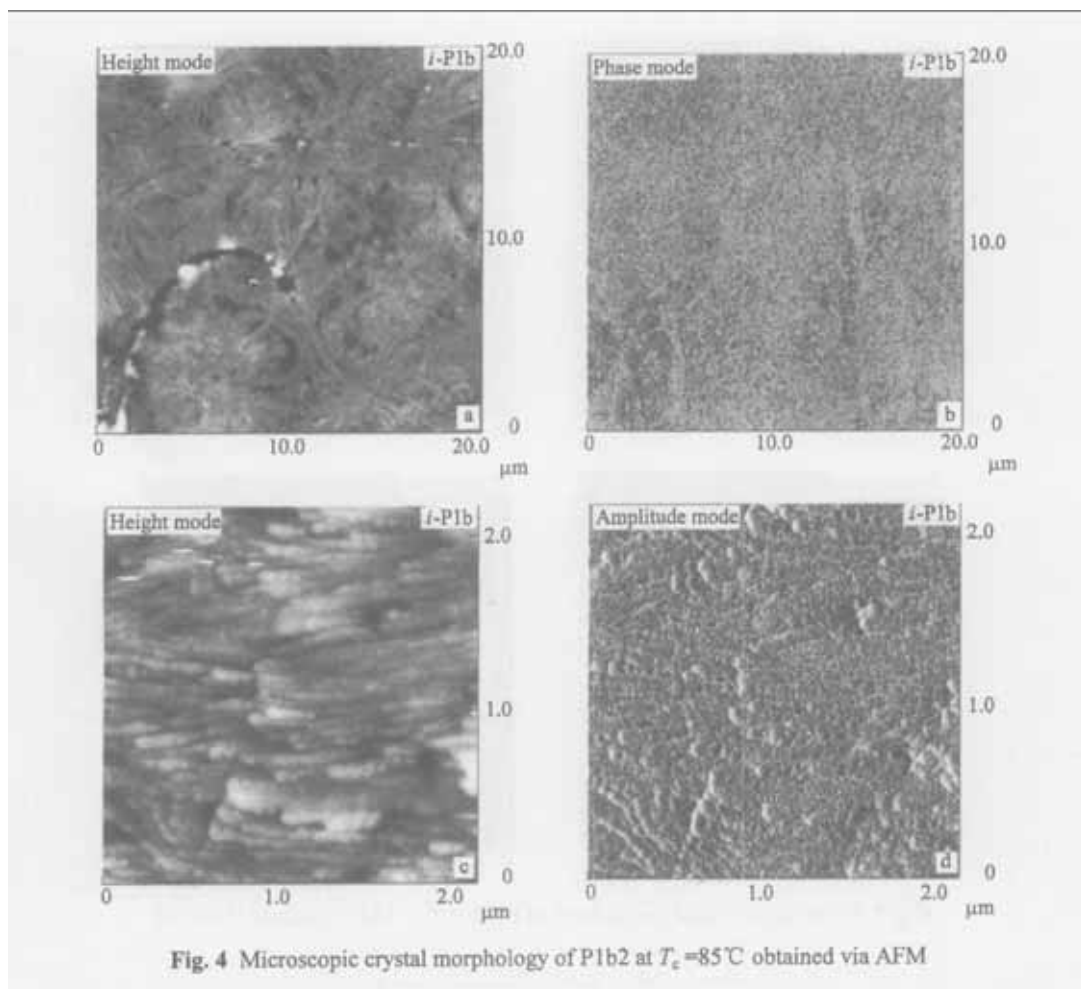


Fig. 4 Microscopic crystal morphology of P1b2 at $T_c = 85^\circ\text{C}$ obtained via AFM

range ($T_c = 95\text{--}100^\circ\text{C}$), one observes three peaks: one amorphous and two crystalline peaks, which may indicate the coexistence of two kinds of lamella at one crystallization temperature. The change of SAXS patterns agrees well with the observed morphology change as shown from PLM. To get more detailed information about structure formation and subsequent heating in the formation of P1b crystallites, Figs. 7 and 8 show, as examples, the evolution of the interface distance distribution function during isothermal crystallization at a high temperature ($T_c = 104^\circ\text{C}$) and a low temperature ($T_c = 85^\circ\text{C}$). The upper part refers to the structure variation during the heating, showing on the left side the change in $K''(z)$ and on the right side the simultaneous changes of the Porod coefficient. It is clearly evident that the crystal thickness remains unchanged during the whole isothermal crystallization process, no matter whether the crystallization occurs at $T_c = 104^\circ\text{C}$ or $T_c = 85^\circ\text{C}$. In fact, this phenomenon holds true for the whole temperature range studied. At $T_c = 104^\circ\text{C}$, two peaks, located at 14 nm and 27 nm, are seen. The minimum corresponding to the long spacing is at 41 nm. As the crystallinity is above 0.5 measured from dilatometry (see below), the assignment is clearly $d_a = 14$ nm, $d_c = 27$ nm. This also gives a linear crystallinity $\phi_l = d_c/h_{ac} = 0.65$, in agreement with the dilatometer value. Only one peak, however, is seen for $T_c = 85^\circ\text{C}$. This peak is located at 14 nm, and the long spacing is 28 nm. So assignment for both d_a and d_c is 14 nm. This gives a linear crystallinity of ϕ_l 0.50, which is also in agreement with the dilatometer data. The crystal thickness and long period obtained by SAXS at both temperatures match well with the above AFM results.

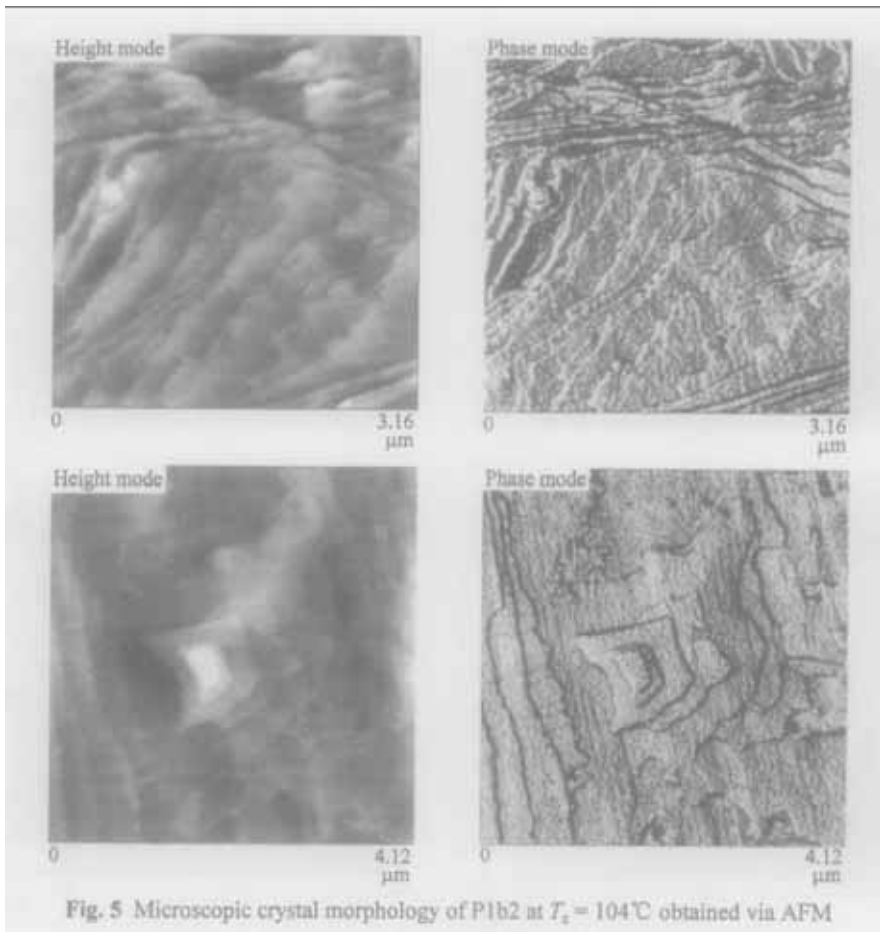


Fig. 5 Microscopic crystal morphology of P1b2 at $T_c = 104^\circ\text{C}$ obtained via AFM

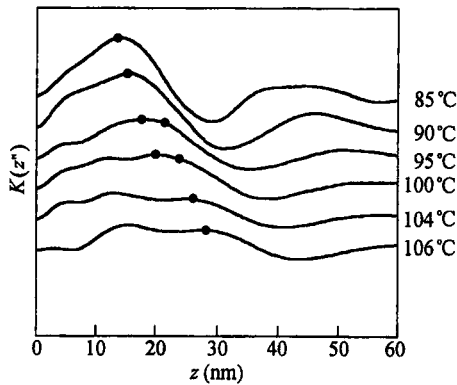


Fig. 6 SAXS-diagram of P1b2 obtained after completion of isothermal crystallization at different temperature T_c

A very similar phenomenon has been observed for a lower molecular weight sample P1b1 and for a higher molecular weight sample P1b3. Again, for P1b1, one observes two peaks from $T_c = 90^\circ\text{C}$ to $T_c = 100^\circ\text{C}$, and another peak at $T_c = 85^\circ\text{C}$. The transition temperature lies between 85°C and 90°C , which also corresponds exactly to the morphology change of P1b1 in this temperature region, as seen via PLM. For P1b3, we always found two peaks in $K''(z)$ at all crystallization temperatures. No change of $K''(z)$ pattern is seen up to $T_c = 104^\circ\text{C}$. We expect that the transition temperature of sample P1b3 will shift to a higher temperature (above 104°C), as

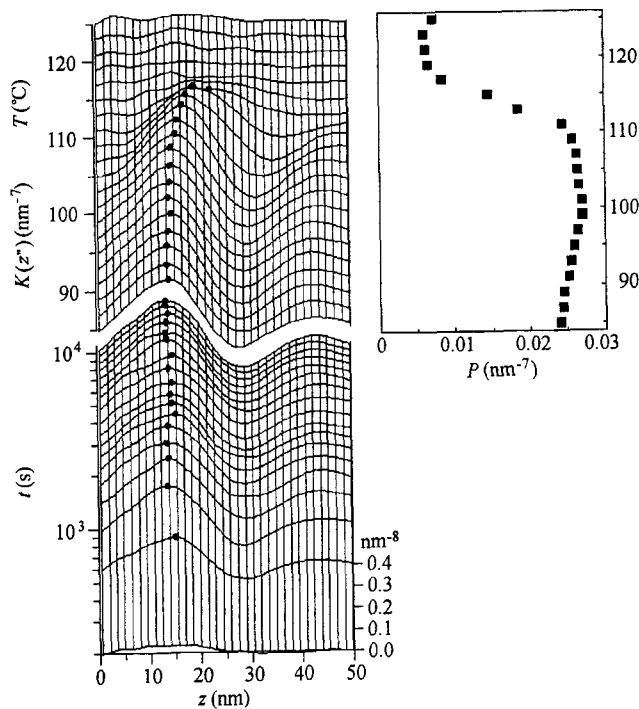


Fig. 7 Evolution of the interface distance distribution function $K''(z)$ of P1b2 during an isothermal crystallization at 85 $^{\circ}\text{C}$ and changes during a subsequent heating to the melt (top left), related changes of the Porod coefficient (top right)

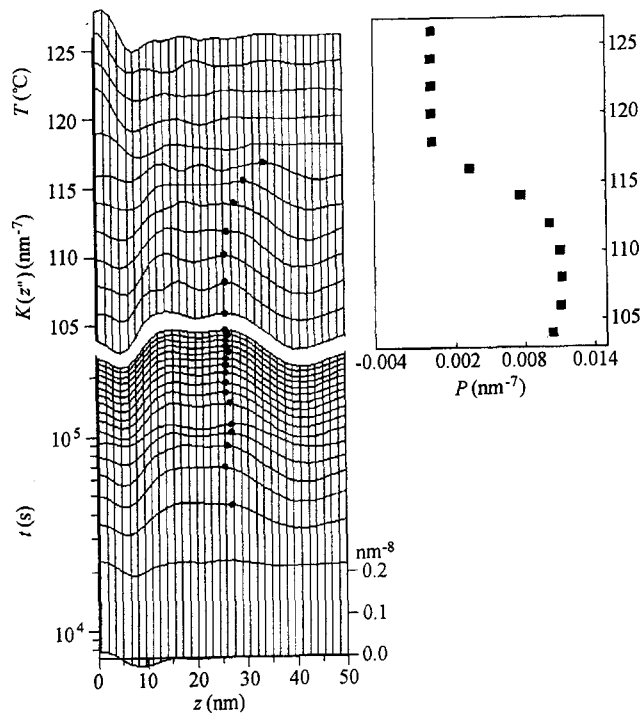


Fig. 8 Evolution of the interface distance distribution function $K''(z)$ of P1b2 during an isothermal crystallization at 104 $^{\circ}\text{C}$ and changes during a subsequent heating to the melt (top left), related changes of the Porod coefficient (top right)

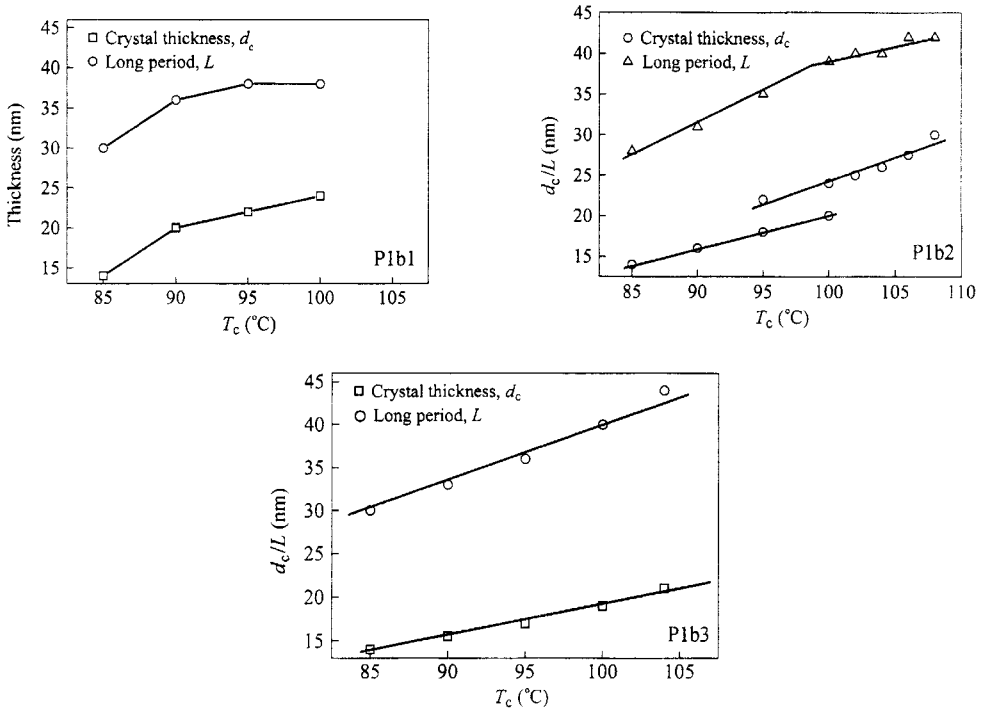


Fig. 9 Crystal thickness as a function of crystallization temperature

a result of its high molecular weight. Having collected a series of data of lamellar thickness (d_c) and long period (L) at different crystallization temperatures, the dependence of d_c and L as a function of T_c is plotted and is shown in Fig. 9. One observes also a jump of crystal thickness at $T_c = 95-100^\circ\text{C}$ for P1b2, and at $T_c = 85-90^\circ\text{C}$ for P1b1, associated with the SAXS pattern change and the morphology change. No such change is observed for P1b3 at all the temperatures studied. It is noticeable that the increase of P1b1 and P1b2 for the long period becomes smaller in the high temperature region.

A jump of crystal thickness and crystallinity as well as the two crystal morphologies, indicate that there may exist two mechanisms in the crystallization of P1b. One mechanism appears at low temperature range (spherulite) and another mechanism appears at high temperature range (quadratic). The transition temperature for such a mechanism change is molecular weight dependent. For a medium molecular weight sample P1b2, one can observe both mechanisms, and the transition occurs at $T_c = 95-100^\circ\text{C}$. For lower molecular weight sample P1b1, the transition shifts to $T_c = 85-90^\circ\text{C}$. For higher molecular weight sample P1b3, the transition temperature is above 104°C , which can not be observed in our study.

Crystallinity and Crystallization Kinetics from Dilatometry

As a complementary method, dilatometry is very useful to investigate the crystallization kinetics and crystallinity, especially for a slow (long time) crystallization process. In fact, the early work on polymer crystallization was mainly done via this method. From our previous work, we did see the change of crystal thickness as a function of crystallization temperature, but we always got constant crystallinity within the whole temperature range studied. From SAXS data, we have seen two crystallinities at high temperature and also at low temperature for P1b1 and P1b2, respectively. So it will be very important to observe also the two crystallinities via dilatometry. We carried out such dilatometric experiment for sample P1b2. Figure 10 depicts a record of the crystallization kinetics of sample P1b2 measured by dilatometry at indicated crystallization temperatures. It is evident that the final volume change (ΔV) keeps constant when crystallization takes place within the low temperature range (from 85°C to 95°C). ΔV is equal to $0.020\text{ cm}^3/\text{g}$, so the weight crystallinity ϕ_w is $0.02/0.04 = 0.5$, which agrees well with the

SAXS data. ΔV jumps to a higher value (0.025–0.026 cm³/g) when the crystallization temperatures go above 100 °C. So the calculated weight crystallinity $\phi_w = (0.025-0.026)/0.04 = 0.62-0.65$, which is also in good agreement with the SAXS data.

It is interesting to observe that the increase of crystallinity is accompanied by a decrease of the crystallization kinetics. As shown in Fig. 10, there exist a long delay time when the crystallization temperature changes from 95 °C to 100 °C. However, for sample P1b1, there exists a continuous increase of crystallinity, as shown in Fig. 11. The ΔV increases from 0.018 to 0.022 cm³/g, as the crystallization temperature changes from $T_c = 75$ °C to 100 °C. The delay time between two T_c s also systematically increases with increasing T_c . If we refer back to the SAXS Porod coefficient during isothermal crystallization, the same continuous increase of the delay time can be observed, as shown in Fig. 12. Also from the SAXS and dilatometry experiments, the half crystallization time can be obtained as a function of crystallization temperature. This is shown in Figs. 13 and 14 for P1b1 and P1b2, respectively. The curves plotted show an abrupt slope change at $T_c = 100$ °C for P1b2, and a relatively smooth slope change for P1b1. There is a slight difference between the SAXS data and the dilatometry data, it may be due to the small difference in temperature chosen for SAXS and dilatometry experiments. But qualitatively this small difference between the two experiments can be neglected. Now, we are convinced that a change of mechanism is accompanied also by a change of crystallinity and crystallization kinetics.

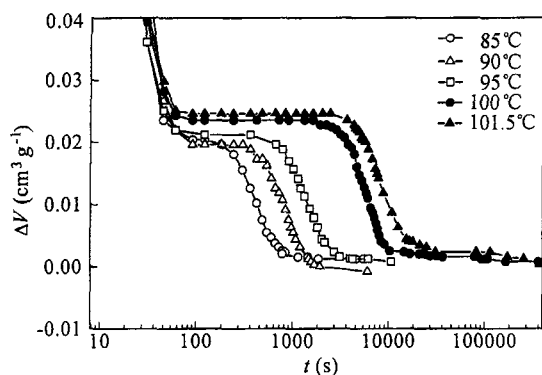


Fig. 10 Kinetics of isothermal crystallization of P1b2 at different T_c s followed by dilatometry

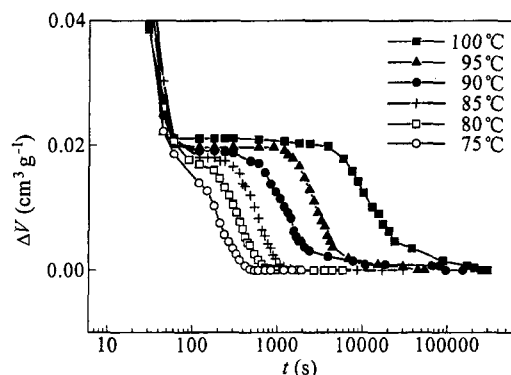


Fig. 11 Kinetics of isothermal crystallization of P1b1 at different T_c s followed by dilatometry

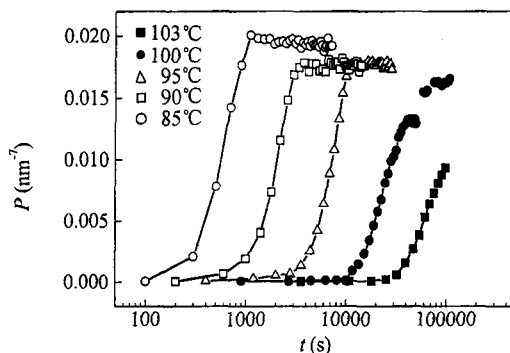


Fig. 12 Kinetics of isothermal crystallization of P1b1 at different T_c s followed by the time dependence of the Porod coefficient

Crystal Thickness and Radius of Gyration of Chain in the Melt

Why have we observed two mechanisms only for P1b so far, not for others in our previous work? One may naturally relate the change of morphology and kinetics to the Hoffman's regime transition theory. The temperature dependence of the crystal growth rate is well documented. And a break in growth rate has been

observed for many polymers, such as, polyethylene, polyethylene oxide. In the case of P1b crystallization, the regime transition theory may explain to certain degree the change of kinetics and morphology, but it cannot be used to satisfactorily explain the dramatic change of morphology from three-dimensional edge-on spherulite to the two-dimensional flat-on quadratic crystal. Also the regime transition theory cannot explain the two forms of crystallinity when crystallization take place in the low temperature region and in the high temperature region. However, by comparing the radius of gyration of chain in the melt with d_c , we can put forward another explanation for this unique feature in the crystallization of P1b.

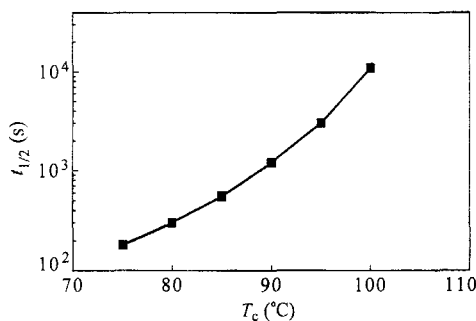


Fig. 13 Half crystallization time of P1b1 as a function of T_c determined by time dependent SAXS experiment and by dilatometry

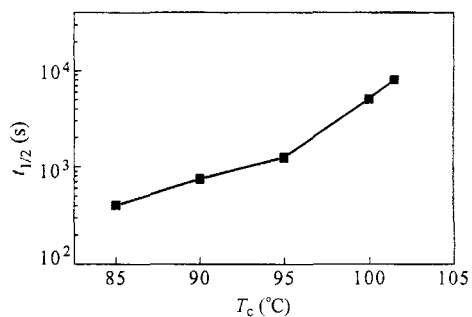


Fig. 14 Half crystallization time of P1b2 as a function of T_c determined by time dependent SAXS experiment and by dilatometry

We understand that the occurrence of crystallization in an entangled polymer melt will result in the formation of homogeneous or granular crystal layers embedded in and coupled by the fluid matrix. It is necessary for a chain to disentangle if the crystal thickness gets larger than the radius of gyration of the chain in the melt. From the theory of polymer dynamics, the radius of gyration, R_g is defined as:

$$R_g^2 = \frac{1}{2N^2} \sum_{n,m=1}^N \langle (R_n - R_m)^2 \rangle \quad (7)$$

Which represents the mean square length between all the pairs of the segment in the chain. For an ideal chain, we have:

$$R_{g,0}^2 = \frac{R_0^2}{6} \quad (8)$$

R_0 , is the size of a polymer, which can be calculated by so called the “characteristic ratio”, C with the aid of a “scaling law”:

$$R_0^2 = \langle R^2 \rangle = C_\infty a_b^2 N \quad (9)$$

a_b^2 stands for the sum of the squares of the lengths of the backbone bonds of one monomer unit, and N is the degree of polymerization.

We take C_∞ as 18 for P1b from a polymer handbook^[12], and a_b is taken as 0.154 nm in this case. The calculated radius of gyration is shown in Table 1, together with the radius of gyration for sPP and PE.

Experimental data of d_c for PE copolymer and sPP copolymer are taken from Ref. [6].

Even though we treat here macromolecule as ideal chain, and it may be more complicated in reality, still the comparison between R_g and d_c really makes sense! For P1b1, R_g is about 13.3 nm. At the transition temperature of 85°C, the crystal thickness is 14 nm, just close to R_g , we get spherulite and probably chain-folded crystallites. Starting from 90°C, d_c jumps to 19 nm, which is much larger than R_g , resulting in a change of mechanism, and we get quadrangle and probably chain-extended crystallites. For sample P1b2, R_g is 15.4 nm, and below 95°C, d_c is below 16 nm, which is less than or just in the range of R_g . However, d_c jumps to 22 nm at a temperature above

100°C, resulting in a change of crystallization mechanism. For P1b3, R_g is 22 nm and the crystal thicknesses obtained at all temperatures are smaller than R_g . So a mechanism change will not happen for this sample. We also calculated the radius of gyration of the samples we investigated before, and are also illustrated in Table 1. For the sPP copolymer, and PE copolymer, their weight percentage is taken into account in the calculation of the degree of polymerization N . It was found that all the crystal thicknesses of PE copolymer and sPP copolymer are below the corresponding R_g . This is in agreement with the observed uniform crystallization mechanism^[6, 14, 15]. Therefore it could well be that for P1b crystallization the spherulite and quadratic crystals are due to two crystallization mechanisms. Whether or not a change of mechanism occurs depends on the crystal thickness, d_c , when compared to the radius of gyration R_g . One would expect a change in crystallinity, crystal morphology and crystallization kinetics when d_c is over R_g , as it is observed. We did not consider this as important and did not draw any attention in our previous studies.

Table 1. The radius of gyration R_g of polymers under study

Sample	M_w	C_∞	a_b	Radius of gyration R_g (nm)	d_c Range (nm)
P1b 1	141000	18	0.154	13.3	14–24
P1b 2	185000			15.4	14–30
P1b 3	380000			22	14–21
P(E-co-O)7	87360	6.8	0.154	8.4	5.5–7
P(E-co-O)14	90600			7.9	4.5–6.6
s-PP	176800	6.2	0.154	10	6.6–10
s-PP(P-co-O)4	153300			9	5.8–8.3
s-PP(P-co-O)15	159800			8.5	3.7–5
s-PP(P-co-O)20	99200			6.5	3–4.2

CONCLUSION

In summary, there exist two crystal morphologies, two crystallinities and two kinetics in the crystallization of P1b, which may represent the growth of chain-folded crystallites and the growth of chain extended crystallites, respectively. A change of crystal morphology, crystallinity and crystallization kinetics is not only temperature dependent but molecular weight dependent as well. It seems that radius of gyration plays an important role in the mechanism change. Whether or not such a change occurs depends on the crystal thickness when compared with the radius of gyration of chains in the melt.

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