Comparative Study on Quiescent Crystallization Kinetics of Isotactic Polyolefins

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ABSTRACT: Quiescent melt crystallization rates of various polyolefins including high density polyethylene (PE), isotactic form of polypropylene (PP), polybutene-1 (PB1), and poly(4-methyl pentene-1) (P4MP1) were investigated under both isothermal and nonisothermal conditions using differential scanning calorimetry (DSC). The order of overall crystallization rates under quiescent conditions from fast to slow was found to be: PE, P4MP1, PP and PB1. The Avrami equation was used to analyze isothermal and nonisothermal crystallization processes, respectively. In order to compare relative crystallization rates of these polymers, continuous cooling transformation curves for each polymer under nonisothermal condition as well as the plot of crystallization half-time as a function of crystallization temperature under isothermal conditions were constructed. Comparisons were made of the relative rate of crystallization of the different isotactic polyolefins with each other and with reports in the literature. Isotactic polyolefins with linear side groups crystallize increasingly more slowly as the side group lengthens with polypentene-1 (PPT1) and polyhexene-1 (PH1) crystallizing even more slowly than PB1. It is notable that P4MP1, which has isobutyl as a bulky side group, and apparently poly(3-methyl butene-1) (P3MB1) showed fairly high crystallization rates. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 276–282, 2007

Key words: polyolefins; isothermal; nonisothermal; crystallization

INTRODUCTION

Polyolefins are very important thermoplastics that comprise the largest portion of the world's commercial polymers and have attracted many researchers.[1] These include the two major commercial thermoplastics of polyethylene (PE) and isotactic polypropylene (PP) and two lesser commercial thermoplastics isotactic polybutene-1 (PB1) and poly(4-methyl pentene-1) (P4MP1) as well as their copolymers. The chemical structures of these polymers are shown in Figure 1, where asymmetric carbon atoms are indicated with asterisks. They are members of a much larger isotactic polyolefins, most of which have received much less study (Fig. 2).

There have been several crystallization kinetic studies of the four polyolefins of Figure 1, and they are primarily for PE[2–4] and isotactic PP.[5–8] For example, dependence of wide range of molecular weights of PE (from 2900 up to 8×10^6) on its crystallization rate was extensively studied and the Avrami exponents were found to be independent of temperature and have an integral value, depending on molecular weights. An Avrami exponent value of 4 was reported below the molecular weight of 5800 and it became 3 with increasing molecular weight up to 1.2 $\times 10^6$. For molecular weights over 1.2×10^6, a value of 2 was found.[2–4]

The effect of density and comonomer content on the crystallization of PE copolymers has been investigated.[9–11] Increasing comonomer content and reduced densities lower crystallization rate. The effect of isotacticity as well as molecular weight in various grades of PP on the crystallization rate was also investigated by several researchers.[12–15] Unlike these detailed investigations of PE and PP, there have been only a few studies on isotactic PB1[16–18] and P4MP1.[19–21]

Understanding the development of the crystalline phase during solidification of semicrystalline polymers is important not only from the perspective of theoretical interest, but also in setting-up optimum processing conditions as well as predicting properties of final products after industrial fabrication processes. In the present paper, the overall crystallization rates of the various polyolefins mentioned above will be investigated under both isothermal and nonisothermal conditions. These results will be compared with other isotactic polyolefins in the literature.

EXPERIMENTAL

Materials

The four of semicrystalline polyolefins shown in Figure 1 were used in this study. The effect of side group in the repeating unit of semicrystalline polyolefins on
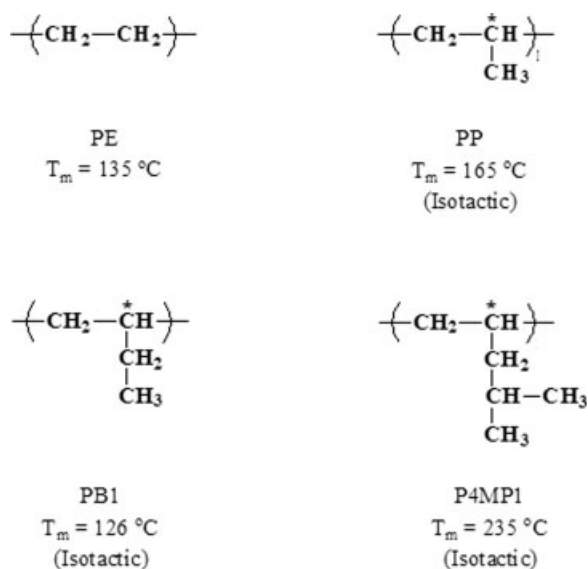
Figure 1 Structural units and melting points of commercial polyolefins.

crystallization rates was investigated. We obtained materials, kindly provided from their manufacturers, including high density polyethylene (PE), isotactic polypropylene (PP), isotactic polybutene-1 (PB1), and isotactic poly(4-methyl pentene-1) (P4MP1). The characteristics of the materials investigated are tabulated as shown in Table I.

Thermal analysis

The isothermal and nonisothermal quiescent crystallization rates were investigated using a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). Isothermal crystallization temperatures for these polymers were in the ranges where it was experimentally feasible. They were from: 122°C to 118°C for PE, 131°C to 117°C for PP, 84°C to 66°C for PB1, and 221°C to 216°C for P4MP1. The compression molded thin samples were placed in aluminum DSC pans with a weight of ca. 5 mg and heated up to 200°C (291°C for P4MP1) for 3 min to erase any thermal history they had. The heated samples, then, were quenched quickly to the specific isothermal crystallization temperatures and stayed at these temperatures until the crystallization process is completed.

For the study of nonisothermal crystallization, the melts were cooled down from 200°C (291°C for P4MP1), after being maintained for 3 min to remove thermal history, to a room temperature at various cooling rates (1–40°C/min). All measurements were carried out in an nitrogen atmosphere with an intercooler connected to make sure of stable thermal control.

RESULTS

With the assumption that the development of crystallinity is proportional to the amount of heat released

during the process of crystallization, the relative degree of crystallinity, $X(t)$ can be described as

$$X(t) = \int_0^t (dH_c/dt)dt / \int_0^\infty (dH_c/dt)dt \qquad (1)$$

where dH_c is the rate of heat evolution during an infinitesimal time interval dt. The time limits, t and ∞, correspond to the elapsed time during the course of crystallization and at the end of crystallization process, respectively. The increases of crystallinity level with time for the four polyolefins investigated are shown in Figure 3(a–d), where we plot the logarithm of $\ln[1/(1 - X(t))]$ versus the logarithm of time.

It can be seen that well-defined straight lines are obtained at several crystallization temperatures for each of polyolefins with deviation from linearity in the region close to the beginning and the end of crystallization, which is attributable to the characteristics from initial nucleation and secondary crystallization processes. The individual isotherms can be brought into together by shifting each curve along the horizontal axis, and as the crystallization temperature is increased, isotherms move to the right along the horizontal axis, indicating that the crystallization rate becomes slower. This suggests that crystallization rate data involves the concurrence of nucleation and growth processes.[22]

The crystallization half-time, $t_{1/2}$ is defined as the time required for relative crystallinity, $X(t)$ to reach 50% of its final crystallinity and obtained directly through eq. (1) and corresponding Figure 3(a–d). In Figure 4, the crystallization half-time is plotted in a logarithmic scale as a function of supercooling, which was calculated from the difference between specific crystallization temperature and equilibrium melting temperature of each polymer.[23–25] The relative crystallization rates among the four polyolefins investigated may be determined through relative positions and slopes with supercooling from Figure 4 and it seems that the ranking of these polymers in terms of crystallization rate would be

$$PE > P4MP1 > PP > PB1 \qquad (2)$$

The validity of supercooling as crystallization rate comparison may be maintained as long as there is no delayed nucleation.[26]
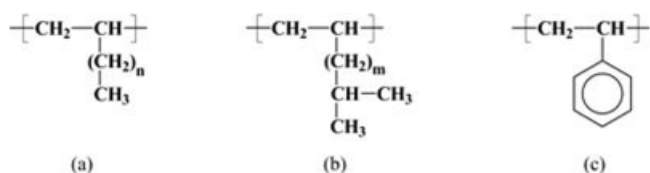

Figure 2 Structural units of isotactic (a) polyolefins with linear alkyl side group, (b) polyolefins with a branched methyl side group, (c) polystyrene.

TABLE I
List of Materials Used in this Study

Material (identification)	Melting temp. (°C)[a]	Density (g/cm^3)	Melt index (g/10 min)	Resin provider and commercial grade
PE	132	0.953	4.5 (190°C, 2.16 kg)	Equistar chemicals. And Alathon® M5350
PP	161	0.90	5.0 (230°C, 2.16 kg)	Equistar Chemicals and Petrothene® PP8001LK
PB1	110	0.915	1.6 (190°C, 2.16 kg)	Basell and PB0200
P4MP1	224	0.834	26 (260°C, 5.0 kg)	Mitsui Chemical Inc. and TPX® MX004

[a] Measured by second heating rate of 10°C/min for the samples cooled down as fast cooling rate.

We have also studied rates of crystallization following steady rates of cooling and this allows us to obtain continuous cooling transformation (CCT) curves, originally used by metallurgists for steel[27,28] and later applied to polymers.[29,30] These are shown in Figure 5. To compare crystallization rates among different polymers, CCT curves were plotted with the same value of supercooling. It may be seen that the order of crystallization rates is equivalent to that found from isothermal experiments.

INTERPRETATION

Comparison to earlier studies of these polymers

We first sought comparison of our results with the earlier literature. Generally for the polymers studied,

the rates of crystallization observed are very similar to those reported in the literature. Griffith and Ranby[21] made dilatometric measurements on crystallization rate of P4MP1 and compared it with those of PE, PP, and PB1. It was found that the crystallization rate of P4MP1 is slower than that of PE and faster than those of PP and PB1. Silvestre et al.[20] also carried out isothermal crystallization study of P4MP1 and argued that Avrami exponent of 2, which is same as we obtained in our own Avrami analysis, describes the crystallization process of P4MP1 better than $n = 4$ reported by Griffith and Ranby[21] or $n = 3$ by Yadav et al.[31] The data of Silvestre et al.[20] through the plot of the crystallization half-time as a function of isothermal crystallization temperatures seemed to be in
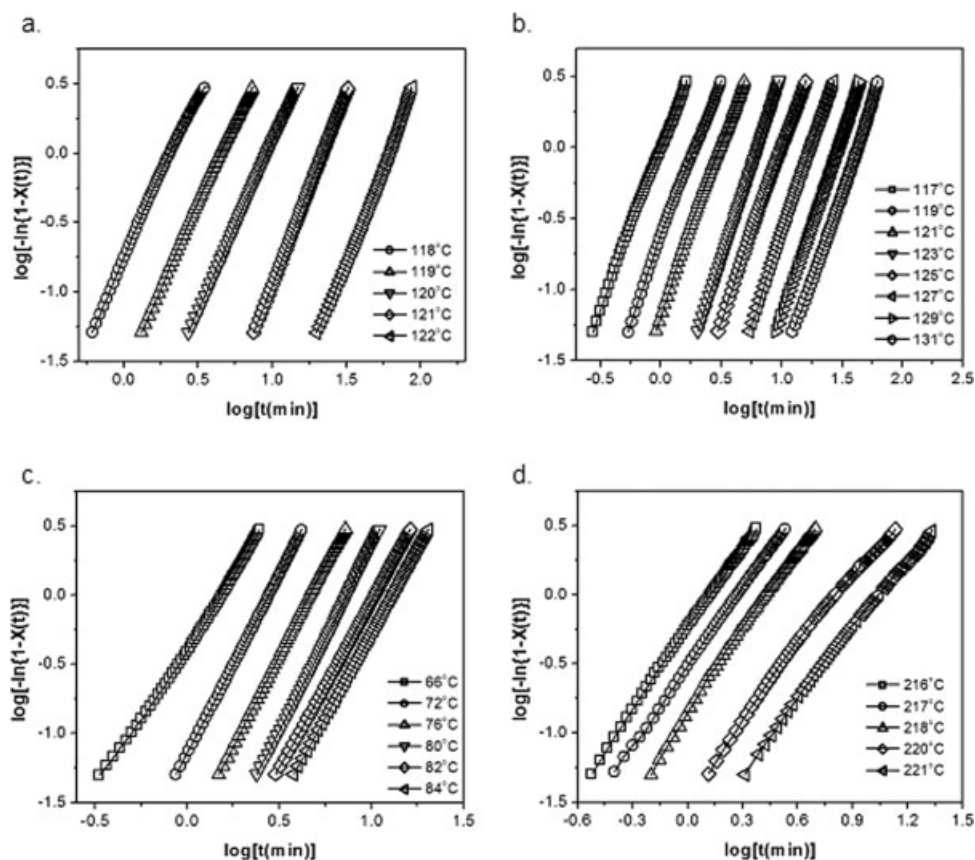

Figure 3 Plots of $\log[-\ln\{1 - X(t)\}]$ as a function of $\log t$ for isothermally crystallized polyolefins (a, PE; b, PP; c, PB1; and d, P4MP1) at various crystallization temperatures.
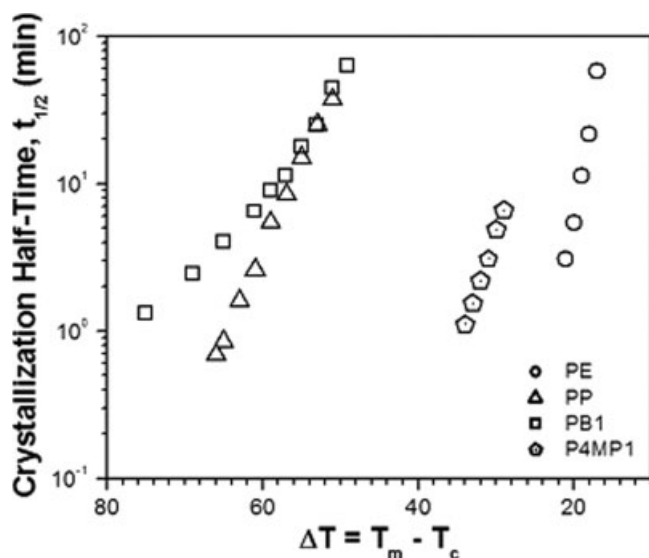
Figure 4 Plots of crystallization half-times as a function of supercooling for the four polyolefins.

good agreement with our results, confirming the order of crystallization rates among those polyolefins.

Comparison to other isotactic polyhydrocarbons

There have been several investigations of crystallization kinetics of other isotactic polyhydrocarbons (compare Fig. 2). These include polypentene-1 (PPT1) ($n = 2$),[32–34] polyhexene-1 (PH1) ($n = 3$),[35] poly (3-methyl butene-1) (P3MB1) ($m = 0$),[34,36] and polystyrene (PS).[37,38] If we first limit ourselves to polyolefins with linear alkyl side groups shown in Figure 2(a), it is clear from our observations and those of Quinn and Powers,[32] Turner-Jones,[35] and Dunham et al.,[34] that crystallization rates order as

$$PP(n = 0) > PB1(n = 1) > PPT1(n = 2) > PH1(n = 3) \tag{3}$$

Crystallization rate of course depends on temperature but it seems clear that the ordering of eq. (3) is valid at the same $T_m - T$ or $T - T_g$.

It may be argued that introduction of linear side groups causes steric hindrance during crystallization. With a longer side group, the chain comes to possess enhanced mobility and flexibility, which is reflected in a decrease of the glass transition temperatures as shown in Table II, where helical conformations and crystalline density with glass transition and crystalline melting temperatures of various polyolefins are summarized from the Polymer Handbook.[39] Up to linear propyl side-chain branching in case of PPT1 ($n = 2$), main chains of a helical conformation are incorporated into crystallites by side-by-side packing of themselves. PP1 crystallizes isothermally with a

maximum rate at 26°C, and although it crystallizes to a fairly high degree, its crystallization rate is much slower than those of PE, PP and PB1.[32,33] As the side chain gets longer, the side-by-side packing of helices becomes more and more open, resulting in difficulties for both main and side chains to form a regular three dimensional network. It is likely, when considering very low density of the monoclinic unit cell of PH1, which was only found to crystallize under stretch at −20°C (by Turner-Jones[35]), that the changeover of crystallization behavior from the main chain crystallization to side-chain crystallization starts to occur in PH1. There seem no studies on isotactic polyolefins with longer side chains (polyheptene-1, etc.).

Turning to the few studies of the crystallization of polyolefins with linear alkyl side group with methyl branches shown in Figure 2(b), we find that theses polymers seem to crystallize quite rapidly. This is the conclusion we must reach from Dunham et al.[34] and Kirshenbaum et al.[36] for the case of $m = 0$ (P3MB1) and our own work and that of Lopez et al.[19] and Silvestre et al.[20] for $m = 1$ (P4MP1). Crystallization in long chains of helical conformation has been known to take place when adjacent isotactic helices approach each other with opposite rotations, allowing two chains to be locked to each other through van der Waals forces between side chains. Introduction of additional methyl group decreases the degree of flexibility of side chain, which can be related with the increase in melting temperatures from decrease in the entropy of fusion, and favors its positioning for van der Waals bonding. It seems that a better balance between flexibility and bulkiness of side chain for crystallization would be achieved in P3MB1 or P4MP1 than in PP. As the bulky portion of side chain moves away from the vicinity of side chain, melting
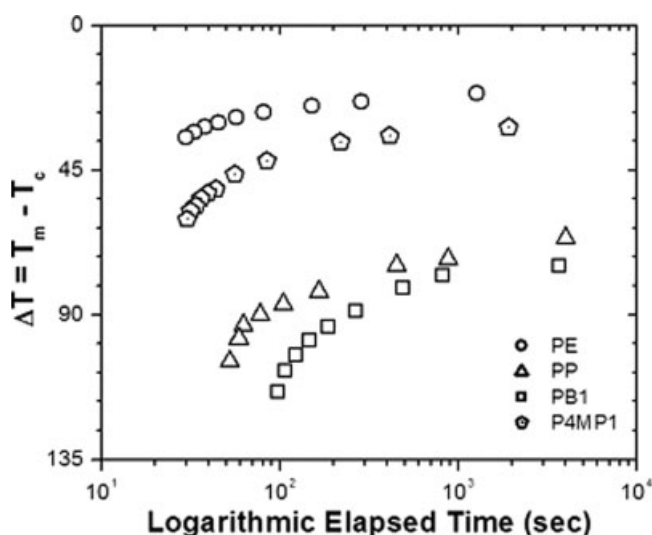

Figure 5 CCT curves of various polyolefins.

TABLE II
Physical Properties of Various Isotactic Polyolefins with Linear Polyethylene

Samples	Conformation	Density[a] (g/cm^3)	Crystallization rates	T_g/T_m (°C)
PE	Planar zigzag	1.00	Very fast	−83/135
PP	3_1	0.94	Fast	−10/165
PB1	11_3	0.90	Medium	−35/126
PPT1	3_1	0.87	Slow	−40/75
PH1	7_2	0.73	Difficultly crystallizable[b]	−55/−
P3MB1	4_1	0.93	Fast	94/300
P4MP1	7_2	0.83	Fast	29/235
P5MH1	3_1	0.84	Slow	−14/130
PS	3_1	1.13	Very slow	100/240

[a] Density from crystalline phase.
[b] Crystallizable to a few degree only under stretch.

temperature and crystallization rate decrease because of increased flexibility of the side chain as observed in the case of $m = 2$, poly(5-methyl hexane-1) (P5MH1).[40,41]

There have also been studies of the crystallization of isotactic polystyrene,[37,38] of which chemical structure is shown in Figure 2(c). These studies indicate that isotactic polystyrene crystallizes very slowly compared to those of the isotactic polymers described above. Improvement in crystallization from PB1 to P3MB1 and PPT1 to P4MP1 seems to become possible with limited chain flexibility from the introduction of methyl group. In case of isotactic polystyrene, however, the substituent phenyl group must create too much crowding and consequently ends up with very slow crystallization.

Avrami interpretation

Isothermal crystallization kinetics is generally interpreted in terms of the kinetic model of Johnson and Mehl[42] and Avrami[43] which has the form

$$dX/dt = N(t)(1 − X) \qquad (4)$$

where N is the crystallization rate constant. Equation (4) may be solved to give

$$X(t) = 1 − \exp(−kt^n) \qquad (5)$$

Of particular interest is the exponent, n, often called the Avrami exponent, which has been related to the dimensionality of the growth and the type of nucleation. The value of n can be determined by slope of the double logarithm plot of eq. (5) as

$$\log[−\ln(1 − X(t))] = \log k + n \log t \qquad (6)$$

For homogeneous nucleation, the Avrami exponent equals 4 for three-dimensional linear crystal growth, $n = 3$ and $n = 2$ for two- and one-dimensional

growth, respectively. For heterogeneous nucleation, n represents the dimensionality of the crystal growth. The overall crystallization rate analysis from Figure 3 shows good adherence to the Avrami equation.

We compare the results of the Avrami analysis in the present study with those values from early investigations. We observed fractional Avrami exponents for the various polyolefins investigated in this study as shown in Table III. Fractional values of Avrami exponents and deviation of experimental data especially at long crystallization times have been known as major problems of analyzing experimental data.[44] The experimentally derived kinetic parameters based on the Avrami equation, however, can represent experimental data conveniently as long as there is a good agreement between theory and experimental

TABLE III
Values of Crystallization Half-time, $t_{1/2}$, Avrami Exponent and Crystallization Rate Parameter, n and k at Different Crystallization Temperatures, T_c for Various Polyolefins

Samples	T_c (°C)	$t_{1/2}$ (min)	n	k $(\min^{-n})$
PE	118	1.79	2.33	1.79×10^{-1}
	119	3.87	2.36	2.85×10^{-2}
	120	8.00	2.39	4.79×10^{-3}
	121	19.17	2.79	1.84×10^{-4}
	122	53.90	2.76	1.14×10^{-5}
PP	121	2.63	2.34	7.19×10^{-2}
	123	5.51	2.60	8.22×10^{-3}
	127	15.13	2.49	8.06×10^{-4}
	129	25.07	2.53	1.98×10^{-4}
	131	36.56	2.51	8.31×10^{-5}
PB1	72	2.41	2.59	7.11×10^{-2}
	76	4.04	2.60	1.83×10^{-2}
	80	6.42	2.69	4.64×10^{-3}
	82	8.94	2.44	3.29×10^{-3}
	84	11.19	2.43	1.98×10^{-3}
P4MP1	216	1.11	1.92	5.70×10^{-1}
	217	1.55	1.89	3.04×10^{-1}
	218	2.24	1.92	1.47×10^{-1}
	220	5.33	1.65	4.37×10^{-2}
	221	8.95	1.64	1.90×10^{-2}

TABLE IV
Avrami Exponents of Polyolefins of this Study
Reported in the Literature

Samples	n	Ref.
PE	2–4	38,39
PP	3–4, 1.8–3.2	40,41
PB1	2–3, 3, 4	9,42–44
P4MP1	2, 3, 4	13,14,24

data, such as well-defined Avrami plots and kinetic parameters shown in Figure 3 and Table III, respectively. We found the Avrami exponents between 2 and 3 for all polyolefins except P4MP1, which showed a lower value close to 2. The range of values for Avrami exponents of the materials of this study are reported in Table IV. For the most part, the values are in the same range as our data.[16,20,21,31,45–51]

CONCLUSIONS

We investigated comparative crystallization rates of various polyolefins under isothermal and nonisothermal crystallization conditions. It is particularly interesting to observe under both conditions the order of relative crystallization rates from fast to slow one as: PE > P4MP1 > PP > PB1. It is notable that the crystallization rate of P4MP1 is faster than that of PP, even though P4MP1 possesses a bulkier side group, which may create larger steric hindrance effect for longer and bulkier molecular chains to be incorporated into crystalline region. This unusual fast crystallization rate of isotactic P4MP1 is probably due to the loose packing nature of the 7/2 helical chain conformation, combined with unique density feature of this polymer, which shows a bit lower density from crystalline phase (0.83 g/cm^3) than from amorphous phase (0.84 g/cm^3) at ambient temperature.[21,52] It has been well known that polyolefins present isotropic melts above its melting temperature. There, however, have been some studies suggesting the possibility of long-range order in the P4MP1 melt,[53,54] which may promote crystallization and could be another explanation for faster crystallization. Except for P4MP1 and earlier studies of P3MB1, the comparative rates of crystallization seem to be in agreement with bulkiness of side groups in a sense that the bulkier side group would provide larger steric hindrance to chain folding, resulting in slower crystallization rate.

Avrami analysis of these polyolefins was carried out successfully, showing good agreement with theory and earlier results. An Avrami equation with exponent a bit less than the value of 2 was found for P4MP1 in our study, which seems to be caused by introduction of around 3 mol % linear alpha-olefin (C_{10}–C_{16}) comonomers. Although it is worthwhile to rank different polymers in their bulk crystallization rates and investigate the dimensionality of crystal growth, attention should be paid since other variables such as molecular weight, its distribution, viscosity of the melt as well as topology of the polymer chain, glass and melting temperatures have great influences on the crystallization process.

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