

CRYSTALLIZATION KINETICS OF HOMOGENEOUS AND HETEROGENEOUS LLDPE*

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Abstract Based on thermal analysis, the isothermal and nonisothermal crystallization kinetics of Ziegler-Natta catalyzed linear low density polyethylene (Z-N LLDPE) and metallocene catalyzed LLDPE (*m*-LLDPE) were studied. Treating the results with the Avrami equation and the Ozawa equation, the crystallization constant $\lg k$ and the Avrami exponent n were obtained. Some other crystallization parameters were also discussed. According to the different characteristics of the chain structures of Z-N LLDPE and metallocene LLDPE, their crystallization behaviors were analyzed. It is indicated that the homogeneity and heterogeneity of the two polymers act in different way during the crystallization process of polymers, including the nucleation and the growth of crystals under various conditions.

Keywords Crystallization kinetics, Homogeneity, Heterogeneity, LLDPE

INTRODUCTION

Since 1980's linear low density polyethylene (LLDPE) has become one of the most widely produced polymers. LLDPE is a copolymer that possesses short chain branching (SCB) due to the incorporation of α -olefins in the polymer chains used as comonomers. In comparison with the common low density polyethylene (LDPE), LLDPE exhibits better thermal and mechanical properties, thus giving an impetus to its fast development.

In its early development stage, LLDPE was synthesized by a conventional Ziegler-Natta catalyst system (Z-N LLDPE)^[1]. It has been shown that Z-N LLDPE often exhibits high heterogeneity both in its molecular weight distribution (MWD) and in the inter- and intramolecular distribution of SCB along the polymer chains due to the diverse active sites and the heterogeneity of the catalyst system^[2, 3, 4]. The need to produce semi-crystalline polymers with chemically tailored molecular architectures, leading to a better control over processing characteristics and improvement of physical properties, has stimulated the chemical industry since the early 1990's to produce a new generation of polyolefins synthesized with metallocene catalysts (*m*-LLDPE)^[5, 6, 7]. The use of metallocene and single site catalyst technology has allowed the very rapid development of new olefin copolymers with a broad spectrum of structure and related physical properties. This technology is making significant inroads in commodity polyolefin markets. The control of molecular architecture afforded by the new catalysts makes it possible to produce homogeneous ethylene copolymers with the crystallinity considerably lower than that of conventional LLDPE or its fractions^[8, 9].

Since the final mechanical and thermal properties of the resulting materials are closely related to the morphology, which is determined by the crystallization process^[10], the crystallization kinetics of polymer materials plays an important role in their processing and application. Though some publications have studied the

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crystallization kinetics of ethylene polymers, they focused only on the effect of branching content^[11, 12, 13, 14]. The effects of the homogeneity and heterogeneity of the polymers, the distribution of SCB in polymer chains varying with the catalyst systems on the crystallization kinetics were investigated in this work.

EXPERIMENTAL

The samples used in this work were all available commercially. Z-N LLDPE, LLDPE-1 and *m*-LLDPE, LLDPE-2 were supplied by Panjin Petroleum Co. and Exxon Co. respectively. The structure parameters of the samples are listed in Table 1. The MW and MWD were measured with a PL-GPC210 instrument operated at 160°C with dichlorobenzene as eluant, using a flow rate of 10 mL/min, and calibrated with polystyrene standards. The branching degree of the samples was calculated from the ¹³C-NMR spectra obtained with a Bruker DMX-300 NMR spectrometer in 10% 1,2,4-trichlorobenzene (TCB) solution at 125°C, the calculation was according to the literature^[15]. DSC was performed on a Mettler-Toledo DSC822 instrument in N₂ atmosphere. Calculation of crystallinity was based on the heat of fusion of 273 J/g for the perfect polyethylene crystals.

Table 1. The fundamental characterization results of the samples used

Samples	$M_n (\times 10^3)$	M_w/M_n	$T_m (^\circ\text{C})$	$X_c (\%)$	SCB/1000C
LLDPE-1	116	4.6	123.7	34.5	18.3
LLDPE-2	145	2.0	119.3	35.0	13.2

The crystallization kinetics experiments of the samples were operated in DSC instrument equipped with an intra-cooler in the following two different ways.

Isothermal crystallization kinetics: The sample was maintained at 150°C for about 10 min to eliminate its thermal history, then quenched to a selected annealing temperature and the heat flow data were recorded along with the crystallization time (t). The results were normalized to obtain the variation of relative crystallinity $X(t)$ with respect to t . After treating with the Avrami equation (Eqs. 1 and 2)^[16], the crystallization constant $\lg k$ and Avrami exponent n were obtained.

$$1 - X(t) = \exp(-k t^n) \quad (1)$$

$$\lg(-\ln(1 - X(t))) = \lg k + n \lg t \quad (2)$$

Nonisothermal crystallization kinetics: The sample was melted at 150°C for about 10 min and was cooled to room temperature at various cooling rates (*i.e.*, 2.5, 5, 10, 20 and 40 K/min, respectively). The heat flow data were recorded along with the crystallization time (t). Then the results were normalized to obtain the variation of relative crystallinity $X(t)$ with respect to t . Subsequently, the crystallization parameters were obtained after treating the results with the Ozawa equation (Eqs. 3 and 4)^[17] and $\lg D$ - $\lg t$ plots (Eqs. 5 and 6)^[18].

$$1 - X(t) = \exp(-k(T/D)^m) \quad (3)$$

$$\lg(-\ln(1 - X(t))) = \lg k(T) - m \lg D \quad (4)$$

$$t = (T_0 - T)/D \quad (5)$$

$$\lg D = \lg F(T) - a \lg t \quad (6)$$

RESULTS AND DISCUSSION

From Table 1, it is observed that LLDPE-1 and LLDPE-2 have nearly equal T_m and crystallinity, while the branching content of LLDPE-1 is higher than that of LLDPE-2, indicating that the branching efficiency of LLDPE-1 is lower than that of LLDPE-2, *i.e.* the SCB distribution in LLDPE-2 is more homogeneous than that of LLDPE-1. As it is well known, SCB can reduce the crystalline segment length and the crystallinity of ethylene

copolymers, but the tendency of reduction for *m*-LLDPE is more obvious than that of Z-N LLDPE when their SCB levels are the same. The LLDPE-1 macromolecules are different from each other in both MW and SCB content, and longer molecules contain less SCB while shorter molecules contain more SCB. On the other hand, the LLDPE-2 macromolecules are similar to each other in both MW and SCB content, *i.e.* the LLDPE-2 molecules are relatively homogeneous. That is the main difference between the Z-N and the metallocene catalyst systems, which has been discussed extensively in the literature^[2-8].

The typical results of isothermal crystallization kinetics and Avrami treatment of samples are shown in Fig 1. It can be seen that the front part of the curve in the Avrami plot is linear while the hinder part becomes nonlinear due to the impingement of the crystals. From the linear part of the curve the crystallization rate constant, $\lg k$ and Avrami exponent, n are obtained by treating the experimental data with linear simulation. The Avrami parameters together with the peak crystallization time t_p and the half crystallization time $t_{1/2}$ are listed in Table 2 and 3 for the Z-N LLDPE and the metallocene LLDPE, respectively.

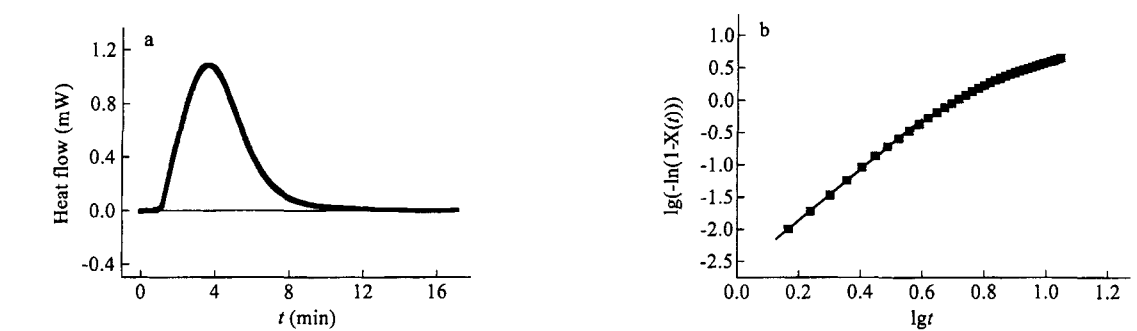


Fig. 1 The isothermal crystallization kinetics result (a) and Avrami plot (b) of the samples

Table 2. The isothermal crystallization kinetics results of Z-N LLDPE-1

T_c (°C)	$\lg k$	n	t_p (min)	$t_{1/2}$ (min)
115.0	-1.69	3.99	2.23	2.45
115.5	-2.07	3.97	2.91	3.22
116.0	-2.65	3.96	3.60	3.96
116.5	-2.82	3.97	4.72	5.21
117.0	-3.45	3.94	6.49	7.01

Table 3. The isothermal crystallization kinetics results of *m*-LLDPE-2

T_c (°C)	$\lg k$	n	t_p (min)	$t_{1/2}$ (min)
115.0	-1.42	3.28	1.80	2.77
115.5	-1.71	3.54	2.14	3.28
116.0	-2.20	4.00	2.63	3.96
116.5	-2.45	4.11	3.02	4.58
117.0	-2.75	3.94	3.61	5.29

From Table 2 and 3, it is seen that the $\lg k$ all decrease with rising crystallization temperature T_c , *i.e.* the crystallization rate at lower T_c is faster than that at higher T_c . The reason is that the driving force of crystallization, the degree of supercooling ($T_m^0 - T_c$), decreases with rising T_c in the temperature range studied. The values of $\lg k$ for LLDPE-1 are smaller than that of LLDPE-2 at the same T_c , which proves that the crystallization rate of LLDPE-1 is lower than that of LLDPE-2 at the same T_c . This agreed with the regularity of t_p results, *i.e.* the peak crystallization time of LLDPE-1 is shorter than that of LLDPE-2 at the same T_c . The Avrami exponents of LLDPE-1 and LLDPE-2 are both about 4.0, except that n of LLDPE-2 at lower T_c are somewhat smaller. This

can result from the changes of the nucleation manner or the dimension of crystal growth of LLDPE-2 when T_c decreases. The intrinsic reason may be the fewer long molecular chains containing less SCB in LLDPE-2 compared with LLDPE-1 for the homogeneity of the distribution of branched chains. The molecules containing more homogeneous SCB distribution in LLDPE-2 result in shorter segment length, which may just be able to crystallize in smaller dimensions at lower T_c or the heterogeneous nucleation becomes dominating.

The activation energy of crystal nucleation and growth can be deduced by the Cebe method^[19]:

$$k^{1/n} = k_0 \exp(-\Delta E/RT_c) \tag{7}$$

where k_0 is the nucleation constant, ΔE is the total crystallization activation energy, R is the gas constant (8.31 J/mol). By plotting $(1/n)\lg k$ versus $1/T_c$ (see Fig. 2), the crystallization activation energies of LLDPE-1 ($\Delta E_1 = 275$ kJ/mol) and LLDPE-2 ($\Delta E_2 = 162$ kJ/mol) are obtained from the slope of the lines. The value of ΔE_1 is larger than that of ΔE_2 , which agrees with the results as shown in Table 2 and 3, *i.e.* the variation of crystallization rate of LLDPE-1 with T_c is larger than that of LLDPE-2. The nucleation constants, $\lg k_0$, of LLDPE-1 and LLDPE-2 are -85.7 and -50.6 respectively. The results imply that the nucleation rate of LLDPE-1 is smaller than that of LLDPE-2. That is the main reason for the crystallization rate of LLDPE-1 to be smaller than that of LLDPE-2 at the same T_c . In crystallization thermodynamics, the crystallization rate should be determined by the nucleation rate at the lower degree of supercooling in the T_c range used in the experiment. Of course, both the nucleation rate and the crystal growth rate should be considered when comparing the crystallization rate under general conditions.

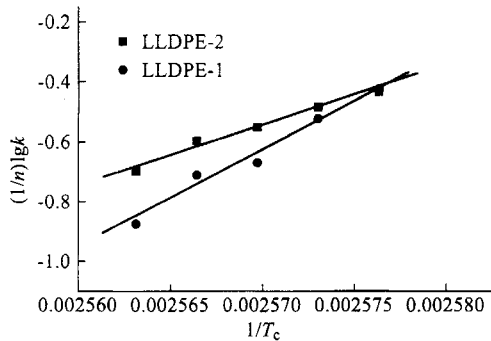


Fig. 2 Plot of isothermal crystallization activation energy for LLDPE-1 and LLDPE-2

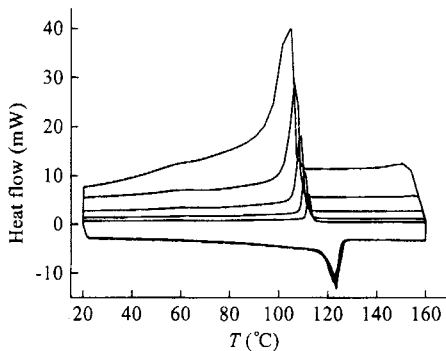


Fig. 3 DSC curves of nonisothermal crystallization kinetics of LLDPE-1 and LLDPE-2

The typical DSC curves of nonisothermal crystallization kinetics of sample are shown in Fig. 3. The parameters obtained are listed in Tables 4 and 5, where T_0 , T_{onset} and T_p are the initiative crystallization temperature, the prolonged initiative crystallization temperature and the peak temperature on the crystallization curves, respectively. The crystallization times, t_{onset} and t_p corresponding to T_{onset} and T_p , are obtained from Eq. (5). It can be seen from the data of T_{onset} and t_{onset} at the slow cooling rate that T_{onset} of LLDPE-1 is lower than that of LLDPE-2 and t_{onset} of LLDPE-1 is longer than that of LLDPE-2. It can be seen that the crystal nucleation rate of LLDPE-1 is slower than that of LLDPE-2, which agrees with the result of the isothermal kinetics experiment. The peak crystallization temperature of LLDPE-1 is higher than that of LLDPE-2, and its peak crystallization time is shorter than that of LLDPE-2. It is found that the crystal growth rate of LLDPE-1 is larger than that of LLDPE-2 at the same cooling rate, which agrees with the regularity of the $t_p - t_{onset}$ value. The decrease of the $t_p - t_{onset}$ value with rising cooling rate reflects that the faster the cooling rate, the larger is the crystallization rate. This corresponds to the general rule of nonisothermal crystallization kinetics.

Table 4. The nonisothermal crystallization kinetics results of LLDPE-1

Cooling rate (K/min)	T_0 (°C)	T_{onset} (°C)	t_{onset} (min)	T_p (°C)	t_p (min)	$t_p - t_{\text{onset}}$ (min)
-2.5	116.5	113.7	1.10	112.1	1.80	0.70
-5.0	116.0	112.4	0.70	110.6	1.10	0.40
-10	115.0	110.8	0.42	108.7	0.63	0.21
-20	113.0	109.2	0.19	105.8	0.36	0.17
-40	110.0	107.2	0.07	103.7	0.16	0.09

Table 5. The nonisothermal crystallization kinetics results of LLDPE-2

Cooling rate (K/min)	T_0 (°C)	T_{onset} (°C)	t_{onset} (min)	T_p (°C)	t_p (min)	$t_p - t_{\text{onset}}$ (min)
-2.5	117.5	115.4	0.80	111.4	2.40	1.60
-5.0	116.0	113.6	0.50	109.2	1.40	0.90
-10	113.5	111.3	0.22	107.0	0.65	0.43
-20	112.0	108.9	0.16	104.4	0.38	0.22
-40	110.0	106.3	0.09	101.1	0.22	0.13

The Ozawa treatment results of the nonisothermal crystallization kinetics of LLDPE-1 and LLDPE-2 are plotted in Fig. 4. It can be seen that the Ozawa results of both samples do not obey a linear relation as usual, but reflect that both the crystallization rate and the crystallization dimension change with the cooling rate. While the tangent of the obtained curves is considered as the basis of the Ozawa treatment, some useful conclusions can still be drawn. It is seen that the crystallization rate, *i.e.* the intercept of Ozawa plots, rises with increasing the cooling rate. The crystallization dimension, *i.e.* the slope of the Ozawa plots, also increases with the cooling rate. The variations of the crystallization rate and dimension are more obvious at lower crystallization temperature, which is related to the more complex crystallization mechanism.

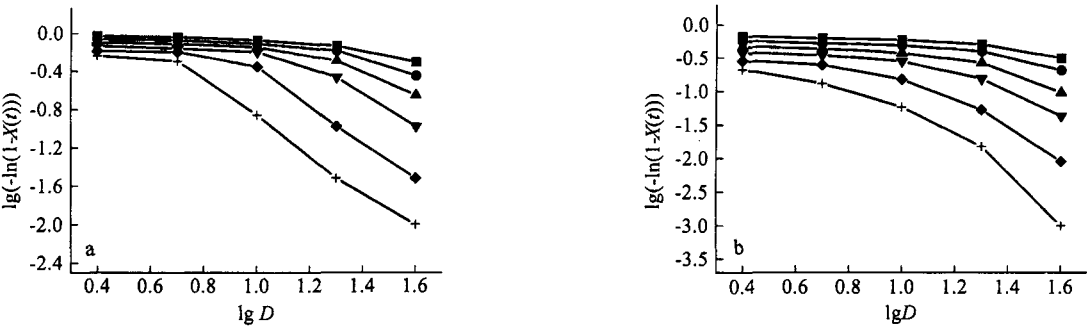


Fig.4 The Ozawa results of nonisothermal crystallization kinetics of sample 1 (a) and 2 (b)

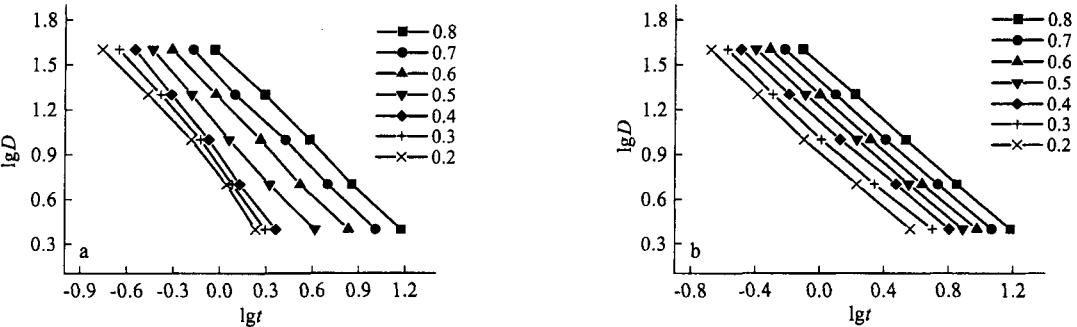


Fig. 5 The lgD - lg t plots of nonisothermal crystallization kinetics of sample 1 (a) and 2 (b)

The $\lg D$ – $\lg t$ plots of nonisothermal crystallization kinetics of LLDPE-1 and LLDPE-2 correspond basically to a linear relation as shown in Fig. 5. The intercept of each line, *i.e.* the value of $F(t)$ is listed in Table 6. $F(t)$ represents the cooling rate needed to obtain a certain crystallinity in a unit time. It can be seen from Table 6 that the larger the value of $X(t)$, the larger is the value of $F(t)$. When $X(t)$ are the same at lower value, $F(t)$ of LLDPE-1 is smaller than that of LLDPE-2, which indicates that the crystallization rate of LLDPE-1 is larger than that of LLDPE-2 similar to the results obtained before.

Table 6. The $F(t)$ value of LLDPE-1 and LLDPE-2 at different $X(t)$

$X(t)$	0.2	0.3	0.4	0.5	0.6	0.7	0.8
LLDPE-1	0.75	0.82	0.88	1.07	1.27	1.41	1.57
LLDPE-2	0.90	1.01	1.12	1.21	1.31	1.39	1.50

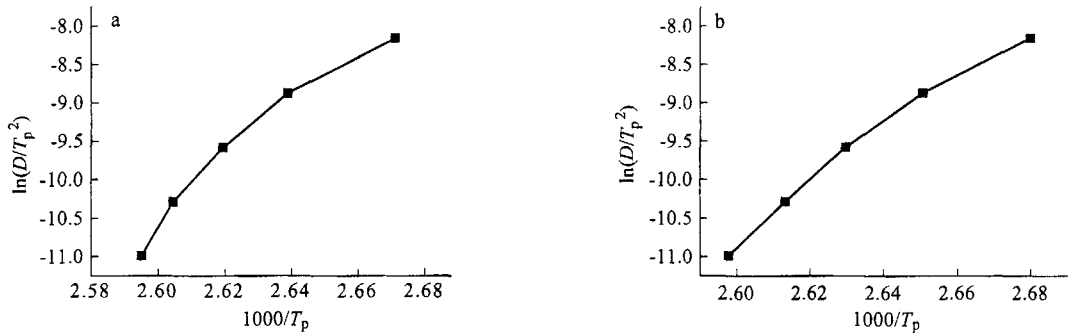


Fig. 6 Plot of $\ln(D/T_p^2)$ versus $1/T_p$ for LLDPE-1 (a) and LLDPE-2 (b)

The crystallization activation energy of nonisothermal crystallization can be calculated by the method of Kissinger *et al.*^[20]:

$$d(\ln(D/T_p^2))/d(1/T_p) = -\Delta E/R \tag{8}$$

where D is the cooling rate, T_p is the peak crystallization temperature during the nonisothermal crystallization process, ΔE is the crystallization activation energy and R is the gas constant. The results of nonisothermal crystallization activation energy of LLDPE-1 and LLDPE-2 obtained from Eq. (8) are plotted in Fig. 6. The nonlinear relations clarify that the crystallization activation energy during nonisothermal crystallization varies with the cooling rate. Then the activation energy could be obtained from the slope of the tangent of the curves. The higher the T_p value, the larger the slope is. It indicates that the activation energy becomes larger when the cooling rate is small and decreases with the rising of cooling rate. At the same time, the variation of the slope of the LLDPE-1 curve is more obvious than that of LLDPE-2, which reflects that LLDPE-1 is more sensitive to cooling rate. The precise values of the activation energy during nonisothermal crystallization are needed to study in more detail.

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