Kinetics of Nonisothermal and Isothermal Crystallization of Metallocene Polyethylene

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Abstract: The kinetics of nonisothermal and isothermal crystallization of metallocene catalyzed and conventional polyethylenes has been studied by differential scanning calorimetry. Using Avrami equation, Ozawa theory and Mo Zhishen method, the experimental data have been analyzed. It is shown that metallocene polyethylene possesses a higher rate of crystallization due to a higher stereoregularity of its molecular chains. Moreover, they have different nonisothermal crystallization mechanisms and identical isothermal crystallization mechanisms.

Keywords: Metallocene polyethylene, nonisothermal crystallization, isothermal crystallization.

The development of metallocene catalysts undoubtedly represents a revolution in the polyolefin business. Metallocene PE (MPE) covers polyethylenes which are produced by metallocene catalyst technology. EXXON Chemical Co. developed a new meta-llocene polyethylene - EXCEED[TM] PE in 1991. Now more and more efforts are spent on this interesting project. Uniform molecular structure and narrow molecular distribution, make MPE better physical properties than those of conventional PE, and also make it low melt strength and bad processability. So the relationship between the structure and properties of MPE is more important. In this paper, the kinetics of isothermal and nonisothermal crystallization of a metallocene catalyzed polyethylene and a conventional one are investigated by differential scanning calorimetry (DSC).

Experimental

Metallocene PE (MPE) was kindly supplied by Research Institute of Petroleum Processing, SINOPEC. Conventional PE was produced by Qilu Petrochemical Industrial Corp. (HDPE DGDA-6098), and denoted as PE6098. The general characteristics of these two polyethylenes are listed in **Table 1**.

Table 1. General characteristics of polyethylenes

Sample	Polymer	Density (g/cm^3)	MFI (g/10min)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$
MPE	Metallocene PE	0.947	1.5	29,600	59,500	2.01
PE6098	Conventional PE	0.949	0.8	15,800	67,300	4.23

Differential Scanning Calorimetry

Isothermal and nonisothermal crystallization was carried out on a PE DSC-7 under a nitrogen purge. Samples were heated to 443 K and kept at this temperature for 5 min to eliminate the influence of their different thermal history.

Nonisothermal: Molten samples were cooled at rates of 2.5, 5, 10, 20 and 40 K/min to the ambient temperature, respectively. The crystallization exotherms recorded were analyzed for the calculation of nonisothermal crystallization kinetics.

Isothermal: Molten samples were quenched (with a cooling rate of ~ 200 K/min) to different temperatures respectively and held at these temperatures until no noticeable exothermic deviation from the baseline was detected.
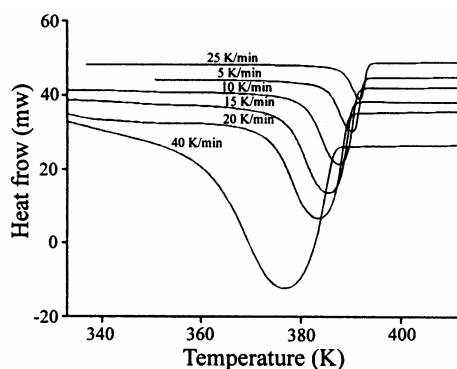
Results and Discussion

DSC curves obtained in the nonisothermal crystallization for polyethylene at different cooling rates are shown in **Figures 1** and **2.**

Figure 1. DSC thermogram of nonisothermal crystallization for MPE
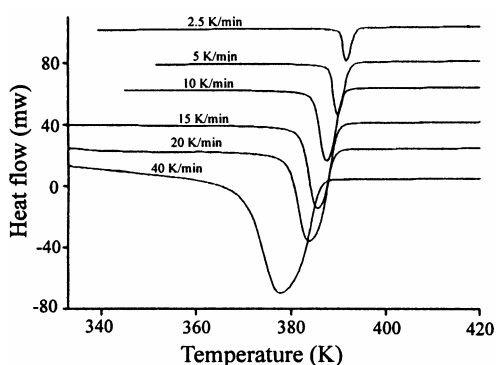
Figure 2. DSC thermogram of nonisothermal crystallization for PE6098

The peak temperature T_p of the exotherm was taken as the maximum crystallization rate temperature. Points corresponding to the initial and final time, t_0 and t_e, of the crystallization process were determined by Jeziorny method[1]. And total crystallization time $t_s = t_e - t_0$. The activation energy ΔE was derived by Kissinger[2] in the following form:

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

where **R** is the universal gas constant, **D** is cooling rate. The value of the crystallization enthalpy ΔH_c was also determined from the thermogram.

It was shown that the peak crystallization temperatures T_p shifted to lower temperatures with increasing cooling rate, and there was no significant difference in T_p between these two polyethylenes **Table 2**. However, shorter t_s's and higher ΔH_c's indicated that MPE had a higher rate of crystallization.

The Ozawa exponent **m** of MPE was 3 and **m** of PE6098 was 1 as showm in **Table 3**. This suggested remarkably different crystallization mechanisms of MPE and PE6098, and a higher growth dimension of the former.

Table 2. Values of the t_s, T_p, and $\triangle H_c$ at various cooling rates for PE samples

Sample	D (K/min)	t_s (s)	T_p (K)	$\triangle H_c$ (J/g)	$\triangle E$ (KJ.mol^{-1})
MPE	-2.5	526.4	391.6	183.9	713
	-5	215.6	389.7	170.8	
	-10	175.2	387.4	179.1	
	-15	116.8	385.6	179.0	
	-20	94.4	383.7	180.4	
	-40	44.2	377.6	174.7	
PE6098	-2.5	688.8	391.7	156.3	773
	-5	334.6	390.1	159.5	
	-10	241.6	387.6	166.2	
	-15	150.8	385.5	162.4	
	-20	120.0	383.5	162.6	
	-40	75.4	376.6	165.4	

Table 3. The parameter m for nonisothermal crystallization of PEs
obtained from the Ozawa theory

Sample	T_c range (K)	m
MPE	383-393	3.1
PE6098	377-397	1.4

Considering the relation between crystallization time **t** and temperature **T**, Mo et al[3] combined the Avrami equation with the Ozawa equation. **Table 4.** shows the results calculated by Mo method. The parameter **F(T)** refers to the value of cooling rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity. A lower value of **F(T)** means a higher rate of crystallization. At the same degree of crystallinity, MPE had a lower value of **F(T)** than PE6098, which demonstrated MPE had a higher rate of crystallization than PE6098.

Table 4. F(T) of nonisothermally crystallized PE samples at different
degrees of crystallinities obtained from Mo Zhishen method

Sample	X (t)						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
MPE	15.1	21.4	26.3	38.0	42.7	51.3	87.1
PE6098	64.6	97.7	162.2	199.5	251.1	239.9	173.8

Isothermal crystallization kinetic data were analyzed using Avrami theory. **Figures 3** and **4** show experimental data for isothermal crystallization of polyethylene in Avrami coordinates. It is clear that straight lines may be drawn through the data points. The crystallization parameters **n** and $t_{1/2}$ of MPE and PE6098 are listed in **Table 5**, where **n** is Avrami exponent, $t_{1/2}$ is the crystallization half time. The activation energy **ΔE** was obtained by[4]:

$$K^{1/n} = K_0 \exp(-\Delta E / RT)$$

where K_0 is constant, **R** is the universal gas constant.

The approximately same Avrami exponents **n** meant MPE and PE6098 had the same isothermal crystallization mechanism. But MPE had smaller values of $t_{1/2}$, *i.e.* it had a higher rate of crystallization. This is the same results as that revealed by nonisothermal crystallization.

Figure 3. Avrami plots for isothermal crystallization of MPE
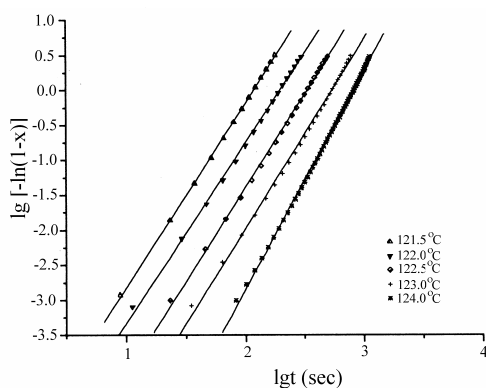
Figure 4. Avrami plots for isothermal crystallization of PE6098
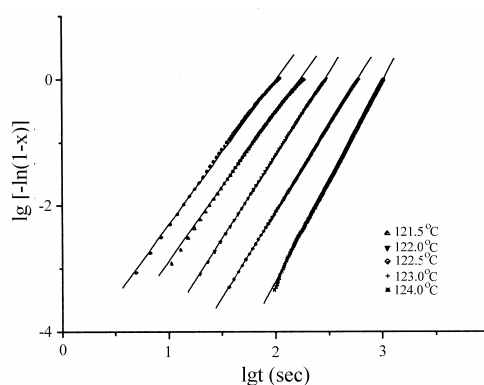
Table 5. Kinetic parameters of isothermally crystallization of PEs at different temperatures

Sample	T_c (°C)	n	$t_{1/2}$ (sec)	$\triangle E$ (KJ.mol$^{-1)}$)
MPE	121.5	2.63	64.99	710
	122.0	2.53	86.05	
	122.5	2.64	116.65	
	123.0	2.63	151.83	
	124.0	2.93	390.37	
PE6098	121.5	2.29	86.92	777
	122.0	2.35	115.87	
	122.5	2.62	126.64	
	123.0	2.68	236.69	
	124.0	3.13	729.04	

The crystallization of polymers is affected by their molecular structures. A high tacticity could result in a higher rate of crystallization and a higher degree of crystallinity. Being a single-site catalytic agent, the metallocene catalyst makes the microstructure and molecular weight of polyethylene different from the conventional ones[5]. Although MPE used in this study had a larger molecular weight, it had a higher rate of crystallization and reached a higher degree of crystallinity.

References

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