

A STUDY OF LOW-TEMPERATURE CRYSTALLIZATION BEHAVIOR* THE *cis*-1,4 POLYBUTADIENE PREPARED WITH RARE-EARTH CATALYST SYSTEM

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ABSTRACT

The effects of molecular weight and temperature on crystallization processes at low temperature for *cis*-1,4 polybutadiene prepared with rare-earth catalyst (Ln-PB) have been studied by WAXD method. In the range of molecular weight from $\langle M_n \rangle = 2.13 \times 10^5$ to 46.8×10^5 , there are a maximum of crystallization rate at $\langle M_n \rangle \approx 29 \times 10^5$ and a minimum at $\langle M_n \rangle \approx 8 \times 10^5$. The temperature related to maximum crystallization rate, $T_{c, \max}$ is observed to be between -60°C and -70°C . The degree of equilibrium crystallinity of Ln-PB is independent of molecular weight at $\langle M_n \rangle$ greater than 10^6 , also the linearity is shown between the correspondent temperature, degree of equilibrium crystallinity and molecular weight. Values of unit cell parameters of Ln-PB increase with temperature. The main crystallization of Ln-PB belongs to heterogeneous nucleation. The crystallization processes are mixed growth one and two dimensions.

The chain structure of Ln-PB is quite regular. It has better molecular symmetry and flexibility as well as small branches. Its *cis*-1,4 content is more than 98%. The Ln-PB is amorphous at room temperature, but it can rapidly crystallize at low temperature^[1]. Crystallization processes of polymer are rather complicate. At whole crystallization process, it is not only dependent on the regularity of molecular chain and geometrical symmetry, but also on its molecular weight and crystallization temperature. The effects of molecular weight on crystallization process were different described by various authors^[2,3]. Recently, by using dilatometric techniques and TEM method XU et al.^[4] found that crystallization rates of Ln-PB existed a maximum and a minimum when changing molecular weight. In this paper, we have studied the behavior of crystallization at different molecular weight and temperature by means of WAXD method.

EXPERIMENTAL

Samples

In this report, samples of Ln-PB were provided by other laboratory in our institute. Their features are reported in Table 1. Microstructures of samples were determined by infrared spectroscopy. For the methods of determination of $[\eta]$, $\langle M_w \rangle$, $\langle M_n \rangle$ and $\langle M_z \rangle$ see reference [4].

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Table 1 Characteristics of the Ln-PB samples

Samples	Microstructure			$[\eta]$	$\langle M_w \rangle \times 10^{-5}$	$\langle M_n \rangle \times 10^{-5}$	$\langle M_v \rangle \times 10^{-5}$	$\frac{\langle M_w \rangle}{\langle M_n \rangle}$
	<i>cis</i> -1,4	1,2-	<i>trans</i> -1,4					
1	98.8	0.4	0.8	1.74	2.08	1.26	2.13	1.65
2	98.5	0.5	1.0	2.49	3.43	2.79	3.56	1.23
3	98.8	0.4	0.8	3.94	6.24	4.85	6.85	1.29
4	99.1	0.3	0.6	6.37	11.82	9.32	13.60	1.27
5	99.0	0.3	0.7	8.31	18.83	10.50	19.90	1.79
6	98.7	0.5	0.8	11.05			29.90	
7	98.9	0.3	0.8	12.71			36.50	
8	98.7	0.3	1.0	15.31			46.80	

WAXD specimens and experimental conditions

Samples of Ln-PB were heat-molded into sheets at ambient temperature under a pressure of 100kg/cm² for 15 minutes and then put into a mould of low temperature attachment. The surfaces of samples were assured of smoothness and absence of gaseous bubbles, so as to prevent the surfaces of samples from roughness, when low temperature attachment was pumped out.

WAXD spectra were taken on a Rigaku X-ray diffractometer and its low temperature attachment using Cu-K α radiation with Ni filter. Liquid nitrogen were used for lowering temperature. Manual temperature controller was used for temperature control. Temperatures were measured with thermopile, and temperature errors are less than $\pm 1^\circ\text{C}$. Continual scanning (8°/min) at isothermal crystallization were adopted throughout the experiment.

RESULTS AND DISCUSSION

WAXD spectra of Ln-PB are shown in Fig. 1. Using computational multipeak resolution method, the degree of crystallinity X_c of Ln-PB can be obtained. The change of degree of crystallinity X_c of Ln-PB with time for samples 2 and 7 are shown in Fig. 2 at different temperatures.

Since the chain structure of Ln-PB is quite regular and its *cis*-1,4 content is rather high, so its nucleation and crystal growth are very quick and induced crystallization time is short. Time for reaching equilibrium crystallinity $X_{c,eq}$ decreases with decreasing temperature and is longer for the sample 7 with high molecular weight than the sample 2 with low molecular weight. The plot with crystallization rate $G_{1/2}$, taken half time of arriving $X_{c,eq}$ against molecular weight $\langle M_n \rangle$ is shown in Fig. 3. Figure 3 shows the nonlinear relationship

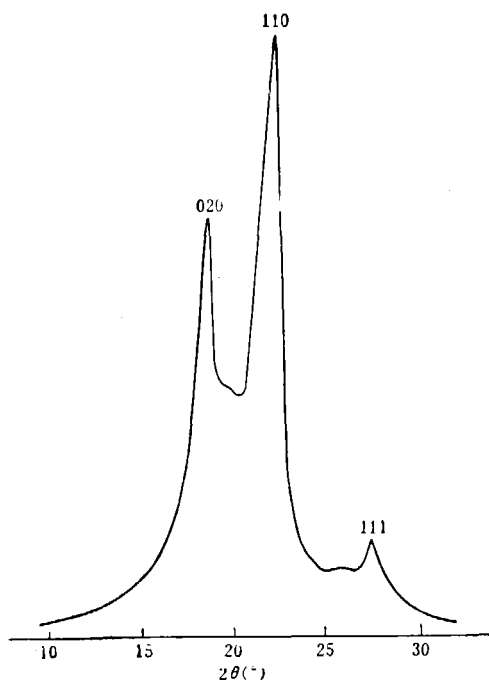


Fig. 1 WAXD spectra of Ln-BP
($T = -10^\circ\text{C}$)

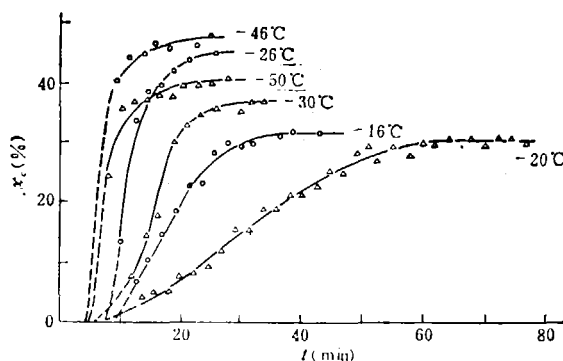


Fig. 2 Plot of X_c vs. t at isothermal condition
○ Sample 2; △ Sample 7

between $G_{1/2}$ and $\langle M_n \rangle$. $G_{1/2}$ has a minimum around $\langle M_n \rangle \approx 8 \times 10^5$, then increases with increasing $\langle M_n \rangle$ until reaches a maximum around $\langle M_n \rangle \approx 29 \times 10^5$, then decreases again.

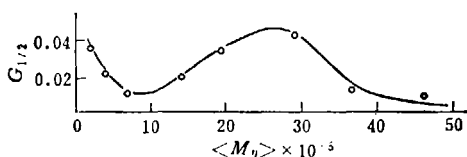
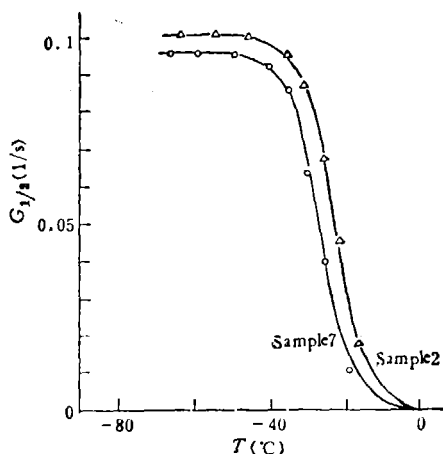
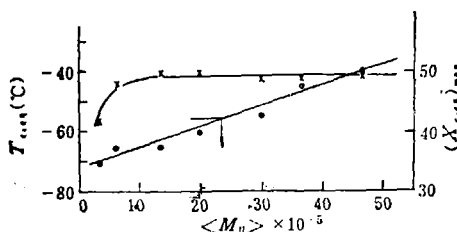


Fig. 3 Plot of $G_{1/2}$ vs. $\langle M_n \rangle$ at $T = -10^\circ\text{C}$

This relationship between $G_{1/2}$ and $\langle M_n \rangle$ drawn from WAXD spectra is in accordance with the result by dilatometric techniques^[4]. Figure 4 shows the relationship between $G_{1/2}$ and T for samples 2 and 7. Above -30°C $G_{1/2}$ increases rapidly, at lower temperature the change of $G_{1/2}$ becomes smaller. Between -60°C and -70°C , the crystallization rate reaches its maximum value. This result is consistent with the report^[5]. Because crystallization process of Ln-PB is rather rapid at low temperature, after T was below -70°C , the rate of reducing temperature by liquid nitrogen in our experiment is slower than the crystallization rates of Ln-PB. Therefore we are not able to perform the experiment below -70°C . The relationship between maximum values of the degree of equilibrium crystallinity $(X_{c,eq})_{\max}$ and its correspondent temperature $T_{c,eq}$ and molecular weight are shown in Fig. 5. When

Fig. 4 Plot of $G_{1/2}$ vs. T

$\langle M_n \rangle$ are larger than 10^6 , $(X_{c,eq})_{max}$ are independent of $\langle M_n \rangle$, but $T_{c,eq}$ increases linearly with increasing $\langle M_n \rangle$. For high molecular weight, the forces of entanglement among molecules in the bulk are greater, so nucleation grows quickly. In the meantime,

Fig. 5 The curve of $(X_{c,eq})_{max}$ and $T_{c,eq}$ vs. $\langle M_n \rangle$

decreasing temperature reduces the kinetic energy of the molecules, the diffusion from amorphous zone into crystalline zone becomes slower, therefore the $T_{c,eq}$ of high molecular weight samples are higher than that of low molecular weight samples at the equilibrium crystallinity maximum $(X_{c,eq})_{max}$. From Fig. 6, it is apparent that the unit cell parameters of Ln-PB increase with temperature.

According to reference [6], Ln-PB may form spherulites. Thus for crystal nucleation the relationship between G and T can be expressed by the following formula:

$$G = G_0 \exp \left[-\frac{\Delta F_D}{RT} \right] \exp \left[-\frac{\Delta F}{RT} \right] \quad (1)$$

where G_0 is a constant, ΔF_D is the activation energy for transport across crystal-phase interface, ΔF is the free energy for nucleation. The term at the extreme right of expression (1) can be substituted by $\exp [-B/(\Delta T \cdot T)]^{[7]}$. Here $B = 4b_0 \delta \delta_e T_m / (\Delta H \cdot K)$, T_m is the equilibrium melting temperature, $\Delta T = T_m - T$, b_0 the interface crystal spacing, ΔH the heat of fusion of the polymer crystal, K the Boltzman's constant, δ_e the end-fold surface free

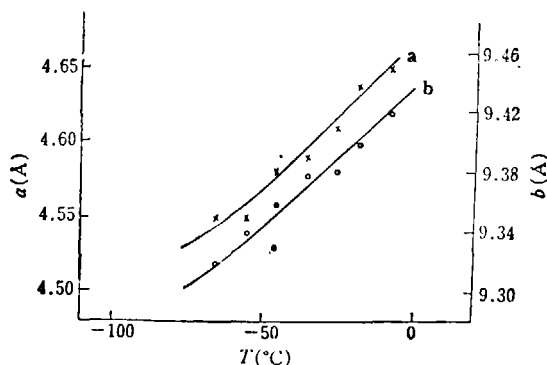


Fig. 6 Effects of temperature on unit cell parameters

energy, and δ the lateral surface free energy. So expression (1) can be represented:

$$\ln G + \frac{\Delta F_D}{RT} = A - \frac{B}{\Delta T \cdot T} \quad (2)$$

According to formula (2), we can draw Fig. 7. Thus slope B can be obtained from Fig. 7. On the basis of reference [8], we can know b_0 , ΔH , also $\delta = 0.1 b_0 \Delta H$. Therefore we can calculate δ_e (see Table 2). δ_e 's values in Table 2 represent that δ_e increases with

Table 2 The values of δ_e of samples 2 and 7

Samples		$B \times 10^{-4}$	δ_e (erg/cm ²)
2		2.18	17.9
7	$T (\leq -33.8^\circ\text{C})$	3.10	25.5
	$T (> -33.8^\circ\text{C})$	2.37	19.5
	Average	2.74	22.5

increasing molecular weight. The molecular chain of sample 7 must overcome greater inter-phase energy barrier than that of sample 2, when diffusing from amorphous phase into crystalline phase. For reaching the same X_c , the time required for sample 7 is longer than that for sample 2. From Fig. 7 we can also calculate G_0 , which is the longitudinal intercept in Fig. 7. $\ln G_0 = 4.29$, $G_0 = 1 \text{ mm/sec}$. Types for the crystal growth and the rule of the nucleation of Ln-PB are shown in Fig. 8. By Fig. 8, we can estimate Avrami's exponents at isothermal crystallization. The second crystallization forms the knee. It is not consistent with crystallization processes for Avrami's equation. Avrami's exponents of Ln-PB for main crystallization at isothermal crystallization were estimated (see Table 3). From Table 3, it is shown that the crystal growth of low molecular weight Ln-PB belongs to one and two dimensions mixed crystallization, but for high molecular weight samples the Avrami's exponents are lower, their crystallization may belong to one dimension. Besides, the Avrami's exponents estimate have nonintegral values. Therefore the crystal growth of Ln-PB belongs to heterogeneous nucleation.

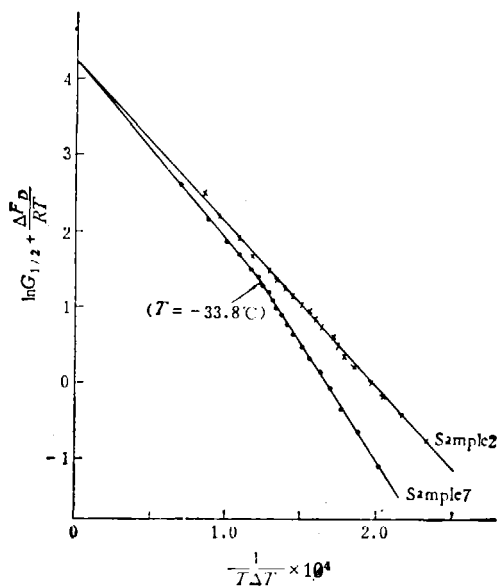


Fig. 7 Plot of $\ln G_{1/2} + \frac{\Delta F_D}{RT}$ vs. $\frac{1}{\Delta T \cdot T}$

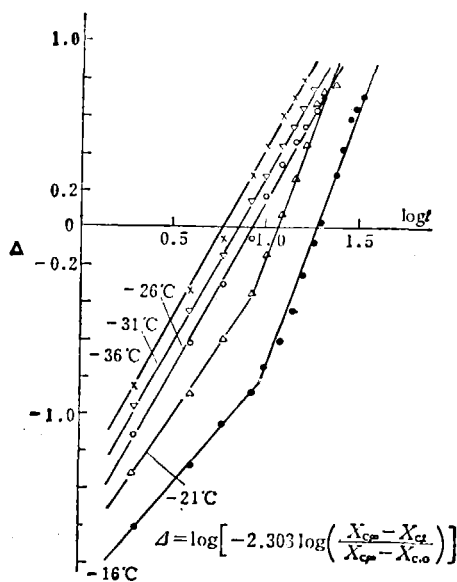


Fig. 8 Plot for estimating the Avrami's exponents

Table 3 Values of Avrami's exponents

Sample 2	$T(^{\circ}\text{C})$	-16	-21	-26	-31	-36
	n	1.13	1.53	1.85	1.85	1.85
Sample 7	$T(^{\circ}\text{C})$	-20	-25	-30	-40	-50
	n	1.18	1.2	1.3	1.3	1.6

CONCLUSION

1. As molecular chain of Ln-PB is rather regular, small branches, it can quickly crystallize. $G_{1/2}$ changes with changing of molecular weight, a maximum $G_{1/2}$ existed at $\langle M_n \rangle \approx 29 \times 10^5$ and a minimum at $\langle M_n \rangle \approx 8 \times 10^5$. Between -60°C and -70°C , $G_{1/2}$ reaches the maximum.

2. $(X_{c,eq})_{\max}$ of Ln-PB are independent of $\langle M_n \rangle$, when $\langle M_n \rangle$ greater than 10^6 , $T_{c,eq}$ increases linearly with increasing $\langle M_n \rangle$.

3. Values of unit cell parameters increase a little with increasing temperature.

4. When increasing molecular weight of Ln-PB, surface free energy δ_e increases. The crystal growth of Ln-PB belongs to heterogeneous nucleation. Its Avrami's exponents are from 1 to 2. The crystallization process of Ln-PB is mixed crystallization of one and two dimensions.

REFERENCES

- [1] 钱保功、余赋生、程铭时、秦 汶、周恩乐、阮梅娜、张延寿, 中国科学B辑, (*Scientia Sinica, Series B*) **1982**, 5, 297.
- [2] Alamo, R.; Fatou, J.G. and Guzman, J., *Polymer*, **1982**, 23, 374.
- [3] Turska, E. and Gogolewski, S., *Polymer*, **1971**, 12, 629.
- [4] 徐 洋、余赋生、周恩乐、钱保功, 应用化学 (*Journal of Applied Chemistry*), **1984**, 1(4), 51.
- [5] 余赋生、徐桂英、张世村、宋襄玉, 应用化学 (*Journal of Applied Chemistry*), **1983**, 1(1), 58.
- [6] 张宏放、莫志深、魏学军、徐 洋, 应用化学 (*Journal of Applied Chemistry*), **1984**, 1(3), 19.
周恩乐、金桂萍、廖玉珍、魏金桂, 中国科学院长春应用化学研究所集刊 (Collected Papers of the Changchun Institute of Applied Chemistry, Academia Sinica), **1982**, 19, 81.
- [7] Magill, J.H., *J. Polymer Sci.*, **1967**, A-2, 5, 89; Magill, J.H., *J. Polymer Sci.*, **1969**, A-2, 7, 1187.
Hoffman, J.D. and Weeks, J.I., *J. Chem. Phys.*, **1962**, 37, 1723.
- [8] Wunderlich, B., "Macromolecular Physics", Vol. 2, Academic Press, New York, **1976**.