

THE SOLID STATE REACTIONS AND TRANSITIONS IN HIGH POLYMERIC SYSTEMS

III. THE BULK CRYSTALLIZATION OF LANTHANIDE- CATALYTICALLY POLYMERIZED POLYDIENES

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ABSTRACT

For the mechanism of isothermal bulk crystallization of high polymers, beside the nucleation and growth steps, the unimpingement of growing crystal aggregates should be taken into account for the modification of the Avrami equation. Starting from Poisson distribution function of growing crystal aggregates, the probability of the unimpinging ones should be $P(0) + P(1)$, then the Q-modified Avrami equation thus derived can be expressed as

$$Q(V_0) = \ln[1 - \ln(1 - V_0)] + \sum_{i=1}^{\infty} \frac{[1 - \ln(1 - V_0)]^i}{i \cdot i!} - 1.3179 = K_q t^n$$

where V_0 represents the volume fraction of crystal aggregates at crystallization time t at a given temperature, while the exponent n on t relates to the mode of nucleation and growth, and K_q is the corresponding shape factor. This Q-modified one is verified satisfactory by the isothermal bulk crystallization of lanthanide-catalytically polymerized polybutadiene (Ln-PB), polyisoprene (Ln-PIR) and their copolymers (Ln-PB/IR). Furthermore, the proposed mechanism is well identified by the change of morphological state during the course of crystallization of the corresponding cast film of Ln-PB/IR (92/8) at -60° (Fig.1).

Upon examination of the influence of the number of entanglement on crystallization rate, it reveals the existence of two stages of entanglement, the primary and the secondary ones (Fig.19).

The equation for dependence of molecular weight and entanglement on bulk crystallization rate has been derived as Eq.13 or 18 for Ln-PB, and verified by the experimental rate data of well fractionated Ln-PB samples crystallized at -9.1 to -15°C (Fig.20).

A MODIFICATION OF THE AVRAMI KINETIC EQUATION

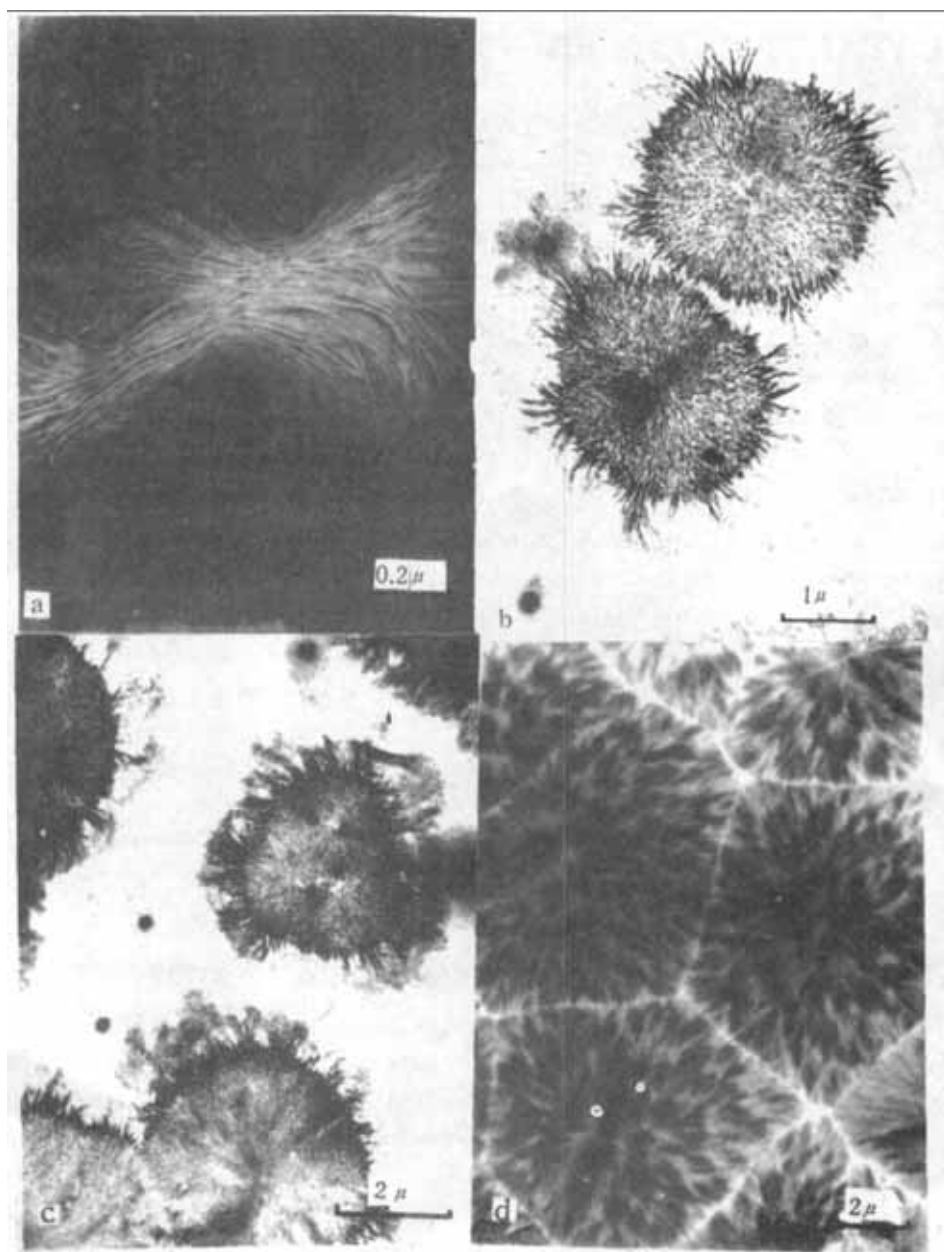
The Avrami kinetic equation has been used for the treatment of isothermal crystallization of bulk polymer for fifty years^[1,2]. As known, the early stage of overall crystallization obeys Avrami equation very well, but in most cases the expected curve from the equation deviates from experimental data in later stage (see Fig.2). There were some modifications for the Avrami equation, such as the one based on the assumption of complex crystallization behavior, e.g. a combination of primary and secondary crystallization processes^[3]. In our opinion, based on the morphological

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change during the course of crystallization, we think that the deviation might originate from the fact that besides the two steps such as nucleation and growth, but with both impingement and unimpingement, were considered in the derivation of the equation, as Evens^[4] and Chien and Tang^[5] did. It is evident that the rate of growth of crystal aggregates will be reduced successively as they impinge on each other during the latter stage of crystallization as shown in morphology Fig. 1.



a) Nucleation, 10min

b) Growth, 10min

c) Impingement, 20min.

d) Perfection of Crystallization, 160min.

Fig.1 Morphological representation of the mechanism of crystallization-Ln-PB/IR (92/8), -60, $n=3.9$

In this paper, Avrami equation for isothermal bulk crystallization of polymer is modified by considering the crystallization process would consist of nucleation and growth, while beside these two steps, the differentiation between impingementation and unimpingementation of growing crystal aggregates should be considered on derivation. The probability P of reaching a randomly chosen point A by m growing crystal aggregates follows the Poisson distribution function

$$P(m) = E^m \exp(-E) / m! \quad (1)$$

while $P(m) = 1$ and $mP(m) = E$ is the expected number of crystal aggregates which have reaches point A at time t . If we assume that some parts of the aggregates will impinge as they meet, and the probability is equal to the one of that when the randomly chosen point A is reached by two or more crystal aggregates,

$$P(2) + P(3) + P(4) + \dots$$

then the probability of the unimpinging crystal aggregates is equal to

$$1 - [P(2) + P(3) + P(4) + \dots] = P(0) + P(1) = \exp(-E) + E \exp(-E) \quad (2)$$

Thus the actual number of the unimpinging growing crystal aggregates per unit area (or volume) N at time t should be

$$N = N_0(E + 1) \exp(-E) \quad (3)$$

where N_0 represents the total number of growing aggregates, including unimpinged and impinged, per unit area (or volume).

Take the case of a thermal nucleation and followed by growth in two dimensional disc of area πr^2 (in which growing radius $r = vt$, v is uniform linear growing rate) as an example, in which the expected number of unimpinging growing aggregates is $E = N\pi r^2$, then the increment dE from growing time t to $(t + dt)$ will be

$$dE = N_0(E + 1) \exp(-E) \cdot 2\pi r dr \quad (4)$$

putting $E' = E + 1$ and by integrating,

$$\int_1^{E'=E+1} \frac{\exp(E')}{E'} d(E') = \int_0^{r=vt} N_0 2\pi r dr = e\pi N v^2 t^2 = K_q t^2 \quad (5)$$

in which K_q means Q-modified shape factor, for disk growth $K_q = e\pi N_0 v^2$.

If we use V_c denoting the volume fraction of crystal aggregates transited in the sample at time t , then it should be noted that any where in the sample not reached by any crystal aggregates remains amorphous, i.e.,

$$1 - V_c = P(0) = \exp(-E) \quad (6)$$

or

$$E' = 1 - \ln(1 - V_c)$$

Then Eq.(5) can be written as

$$\ln[1 - \ln(1 - V_c)] + \sum_{i=1}^{\infty} \frac{[1 - \ln(1 - V_c)]^i}{i \cdot i!} - 1.3179 = K_q t^2 \quad (7)$$

The kinetic equation of bulk crystallization by other modes can be treated in the same way, a general equation for all modes, by putting the left part of the above equation as $Q(V_c)$,

$$Q(V_c) = K_q t^n \quad (8)$$

In Table 1 are listed the representation of K_q and n of crystallization by different modes, including the rate of nucleation I^* , which is assumed to be linear, together with that of one-, two- or three-dimensional growth. The calculated value of $\log Q(V_c)$ from various V_c values are listed in Table 2.

Table 1 Mode of bulk crystallization

Nucleation	Growth	K_q	n , $\left(\begin{smallmatrix} \text{derived} \\ \text{exponent on } t \end{smallmatrix} \right)$
athermal	two-dimensional	$\pi n N_0 v^2$	2
thermal	two-dimensional	$\pi I^* v^2 / 3$	3
athermal	three-dimensional	$4\pi I^* N_0 v^3 / 3$	3
thermal	three-dimensional	$\pi I^* v^3 / 3$	4

I^* —Linear nucleation rate; v —Linear growth rate

Original Avrami E_q :: $-\ln(1 - V_c) = Kat^n$

Q-modified Avrami E_q :: $Q(V_c) = K_q t^n$

Table 2 Values of $\log Q(V_c)$ from V_c

$\log Q(V_c)$ V_c	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0		-1.56	-1.26	-1.08	-0.95	-0.85	-0.77	-0.70	-0.64	-0.59
0.1	-0.54	-0.50	-0.46	-0.42	-0.39	-0.35	-0.32	-0.29	-0.27	-0.24
0.2	-0.21	-0.19	-0.17	-0.14	-0.12	-0.10	-0.08	-0.06	-0.04	-0.02
0.3	-0.01	0.01	0.03	0.05	0.06	0.08	0.10	0.11	0.13	0.14
0.4	0.16	0.17	0.19	0.20	0.22	0.23	0.25	0.26	0.27	0.29
0.5	0.30	0.32	0.33	0.34	0.36	0.37	0.38	0.40	0.41	0.43
0.6	0.44	0.45	0.47	0.48	0.50	0.51	0.53	0.54	0.56	0.57
0.7	0.59	0.60	0.62	0.63	0.65	0.67	0.68	0.70	0.72	0.74
0.8	0.76	0.78	0.80	0.82	0.84	0.87	0.89	0.92	0.95	0.98
0.9	1.01	1.05	1.09	1.13	1.19	1.25	1.32	1.42	1.55	1.78

Table 3 Kinetic parameters $t_{A/2}$ and n for PBs and PIRs crystallized at -26°C

Sample	Crystallinity (%)	$t_{A/2}$	n (experimental)	
			Avrami	Q-modified
Ln-PB	40.5	170 sec	2.1~1.7	2.1
U-PB	36.0	158 sec	2.1~1.4	2.0
Co-PB	29.2	427 sec	1.6~2.1	2.4
Ni-PB	27.6	692 sec	3.2~2.7	3.1
NR (A)	17.5	112.7 min	1.2~3.0	1.1~4.1
NR (B)	15.1	160.7 min	3.1	3.2
Ln-PIR (GA)	5.9	1513 min	8.0	8.1
Ln-PIR (GB)	6.9	954 min	1.8~6.9	2.0~10.6
Ti-PIR (C)	13.4	1258 min	0.5~5.7	6.2
Ti-PIR (D)		1738 min	6.4	7.7

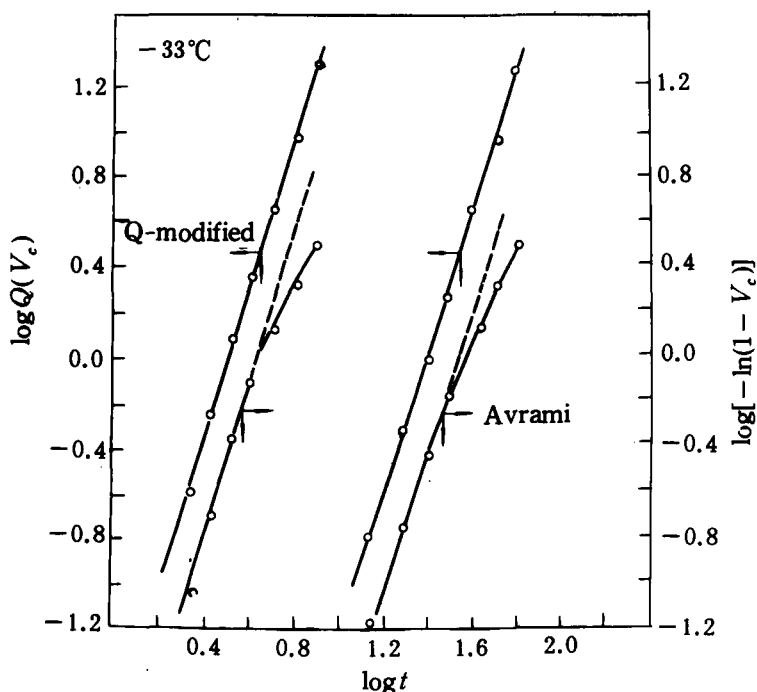


Fig.2. Q-modified and original Avrami plots (left. Ln-PB, -33°C ; right. Ln-PB/IR (90/10), -33°C)

Table 4 Values of n for various Ln-PB/IRs at different temperatures

$\begin{matrix} n \\ \text{mol\% B} \\ \text{temp. } ^{\circ}\text{C} \end{matrix}$	100	97	92	90	88	87	86	84	75
-15	2.9								
-18	3.0								
-21	3.1	3.3							
-25	3.2	3.6							
-30		3.6	2.9	2.9	3.1				
-33	3.3								
-40			4.1	4.1	4.0		2.9	2.9	
-45		3.6	3.9	3.9	3.9	3.8	2.9	3.1	
-52		4.0		4.0	4.2	4.0	3.1	3.0	
-60			3.9 Δ	4.0	3.9	3.6	2.9	3.3	2.8
-65			3.8	3.6		3.8	3.8	3.5	
-70			3.5	2.9	2.9	3.6	3.6	3.4	

Δ the sample used for Fig.1 (-60°C)

* Correlation coefficient (-45°C), take 6 points for calculation

mol% B	97	92	90	88	87	86	84
Q-modified	0.93	0.97	0.96	1.00	1.00	0.99	1.00
Avrami	0.87	0.93	0.91	0.96	0.97	0.97	0.97

While the original Avrami kinetic equation is always expressed as

$$-\ln(1 - V_c) = K_q t^n \quad (9)$$

The same set of experimental data of the homopolymer polybutadiene (Ln-PB) and polyisoprene (Ln-PIR), as well as the copolymer polybutadiene-isoprene (Ln-PB/IR), crystallized at -33°C , were treated by Eq.(8) and (9) respectively, i.e., 'by double logarithmic plotting of $Q(V_c)$ or $[-\ln(1 - V_c)]$ against time t (Fig.2), the linearity of the straight line between $V_c=0.2$ to 0.9 range of our Q-modified plots is much better than that of the original Avrami one, in which the straight lines deviate from $V_c=0.6$ to 0.7, i.e., the Avrami exponential value n is not constant, but decreases down as crystallization proceeds, so that there were some modifications^[4]. Furthermore, the correlation coefficient of the former is usually better than that of the latter as exemplified in Table 4.

OVERALL KINETIC STUDY OF THE ISOTHERMAL BULK CRYSTALLIZATION OF POLYDIENES

Homopolymers PBs and PIRs

The samples used are polybutadienes(PB) and polyisoprenes(PIR), in which that polymerized with lanthanide coordination catalytic systems, such as Ln-PB and Ln-PIR had been well characterized^[6-9].

The isothermal bulk crystallization of some homopolydienes such as PBs and PIRs were carried out at -60°C , at which the natural rubber (NR, a PIR) crystallized with maximum rate ($T_{c,max}$). As shown in Fig.3, the overall rate of crystallization ($1/t_{A/2}$), in which A represents the maximum degree of crystallinity of PB, increases linearly with the increase of *cis*-1,4-content^[7]. While in Fig.4 both NR and PIR are polyisoprene, the crystallization rate of NR is almost eight to ten times as fast as that of the synthetic PIR, this might be attributed to the existence of some natural viscous resins in crude NR. For PBs and PIRs the -26°C crystallization kinetic data treated by original Avrami equation were reported already^[7,9]. Now we treated by Q-modified one for the same data are plotted in Fig.5 both results are arranged together in Table 3.

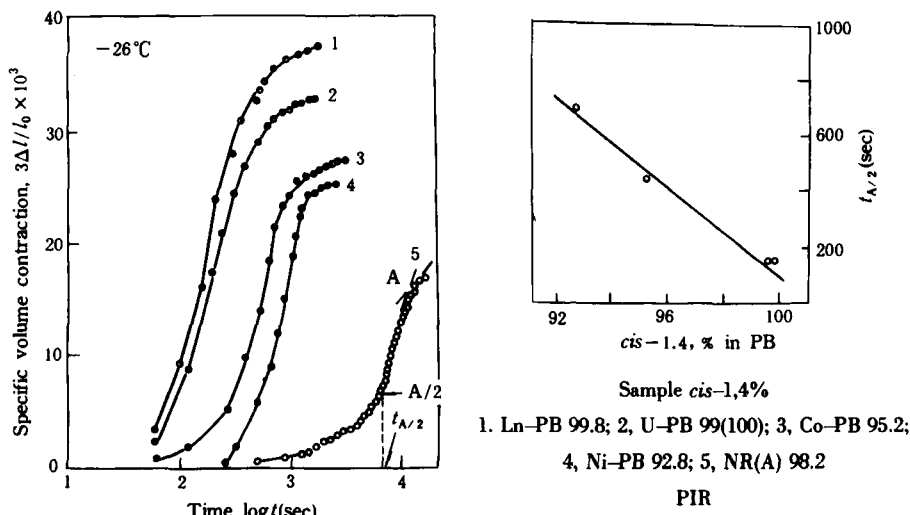


Fig.3 Isothermal bulk crystallization curves of some PBs and NR at -26°C

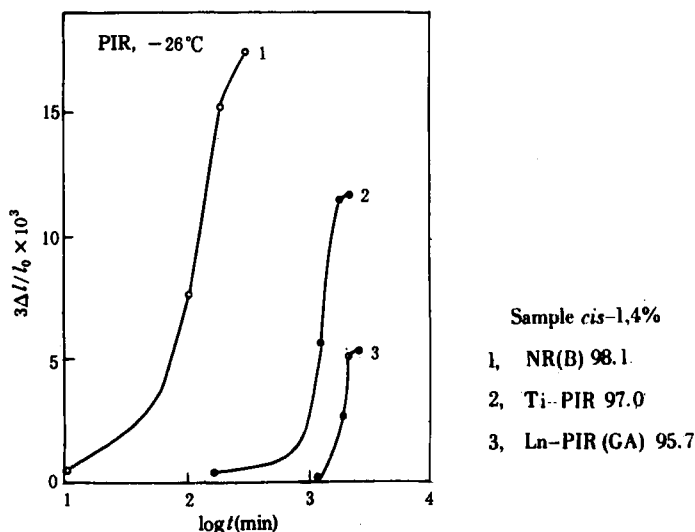


Fig.4 Isothermal bulk crystallization curves of some PIRs at -26°C

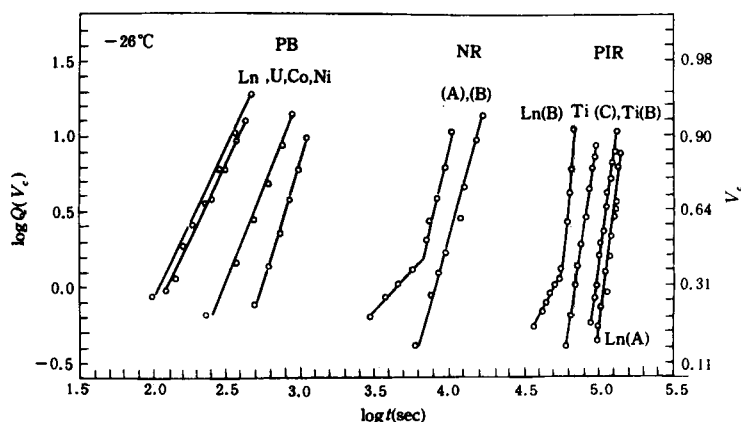
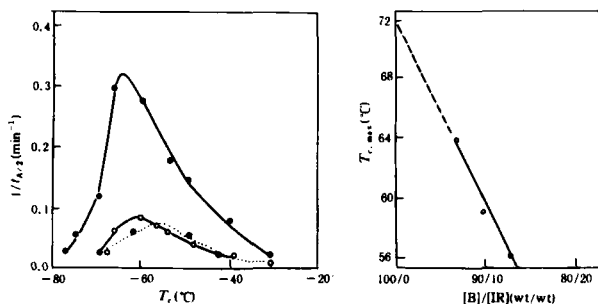


Fig.5 Q-modified Avrami plots for the bulk crystallization of PBs and PIRs at -26°C

From Table 3, it can be seen that the determined value n of PBs are rather normal, from 2 to 3, and that obtained by Q-modified one is better than by original Avrami equation by which n decreases from 2.1 to 1.7/1.4 as the fast crystallization proceeds. Different values of n may mean different mode of crystallization^[2]. The experimental determined values of n are not round numbers, it may be arisen from some possible reasons, such as the rate is not linear, or coexistence of some similar processes, e.g. thermal and athermal nucleation, or experimental errors. The physical meaning for $n=2,3$ and 4 is shown in Table 1. But there exist some special cases, e.g. the value of n for NR(A) changes from 1 to 4 at $V_c \approx 0.4$, while the n for NR(B) from different source is 4. By comparison, it seems that $n=4$ might be the superposition of 1 and 3, originating from the change of mode of nucleation, i.e., from athermal to thermal one, since the two NR samples were obtained from different sources. Beside this case, the value of n for Ln-PIR(GB) varies from 2 to 10 at $V_c \approx 0.4$, while that for Ln-PIR(GA) is 8, it seems that 10 might be the superposition of 2 and 8. The reason for such large value of n may be either one possible reason, (1) according to Morgan's mode^[10], when $n \geq 6$ the mode of crystallization may belong to thermal nucleation and sheaf growth;

or (2) some other secondary crystallization process occurs.

The rate of crystallization of Ln-PB is so rapid that it is very difficult to determine the temperature for the maximum rate of crystallization ($T_{c,max}$) directly. Then it was estimated as -72°C by extrapolation of the determined values of ($T_{c,max}$) of the copolymers Ln-PB/IRs with different co-compositions Fig.6^[7]. The glass temperature (T_g) of Ln-PB was determined as -113°C . The ratio of $T_{c,max} (^{\circ}\text{K}) / T_g (^{\circ}\text{K}) = 201 / 160 = 1.26$, while for natural rubber was known as $247 / 201 = 1.23$. On average, the ratio can be taken as 1.25, it means that, when the crystallization temperature $T_0 (^{\circ}\text{K})$ is raised up to 1.25 times than $T_g (^{\circ}\text{K})$, the macromolecular motion will get an optimum condition to take well crystallization, so that the maximum rate thus will be attained.



● 93.5/6.5 Pyro gas chromatography; ○ 90.0/10.0 Pyro gas chromatography; ● 86.9/13.1 Infrared spectroscopy

Fig.6 Temperature for maximum rate of crystallization, $T_{c,max}$ of Ln-PB/IR

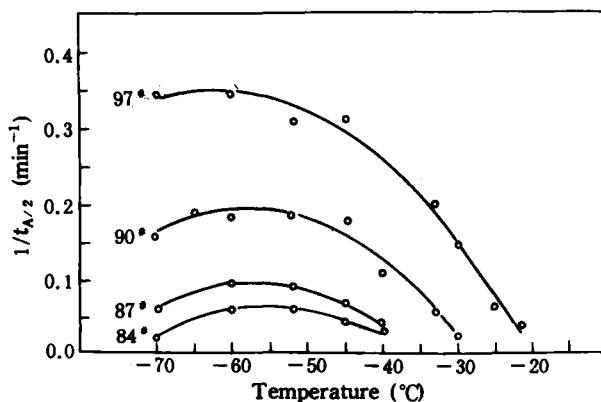


Fig.7 Plots of crystallization rate ($1/t_{A/2}$) versus crystallization temperature (T_c) for Ln-PB/IRs of different compositions

Copolymers: PB/IRs

The crystallization kinetics of the polybutadiene-isoprene copolymers PB/IRs with butadiene content between 97 to 84 mole % has been studied at given low temperature from -15 to -70°C . As shown in Fig.7, the rate of crystallization ($1/t_{A/2}$) decreases as increasing IR content, and each sample shows the highest rate in a certain temperature range between -50 to -65°C .

In these copolymers, such decreasing of crystallization rate as increasing IR content should be attributed to the fact that the IR co-unit had given the influence to the crystalline unit cell. As examined by X-ray diffraction method (Fig.8) the lattice parameters a and b of the unit cell are decreased upon the introduction of IR unit into the copolymer but reached a limiting value, always

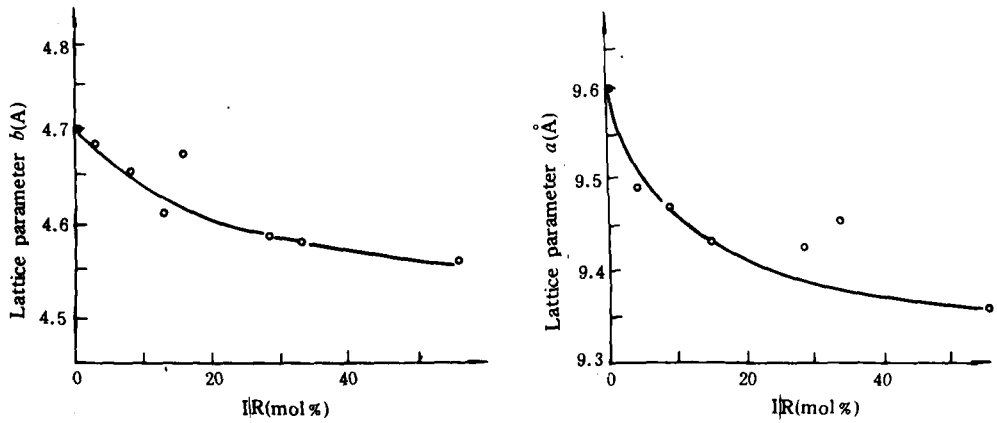


Fig.8 Plots of lattice parameters b and a versus isoprene content (IR) in the Unit Cell of Ln-PB/IR

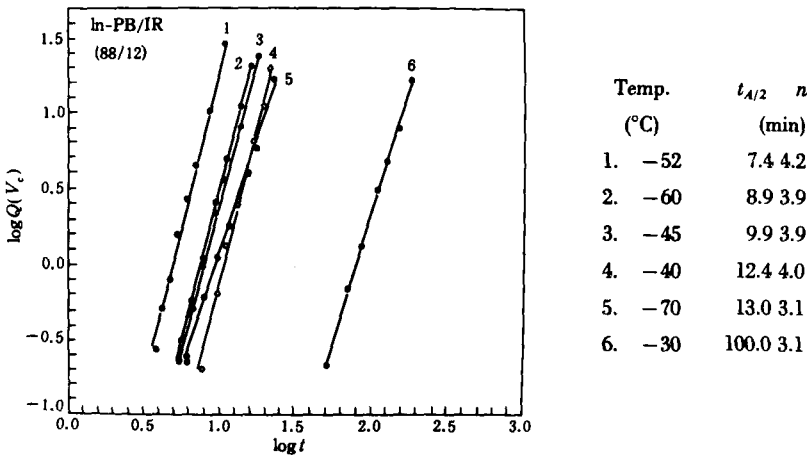


Fig.9 Q-modified Avrami plots for Ln-PB/IR (88/12) at different temperatures

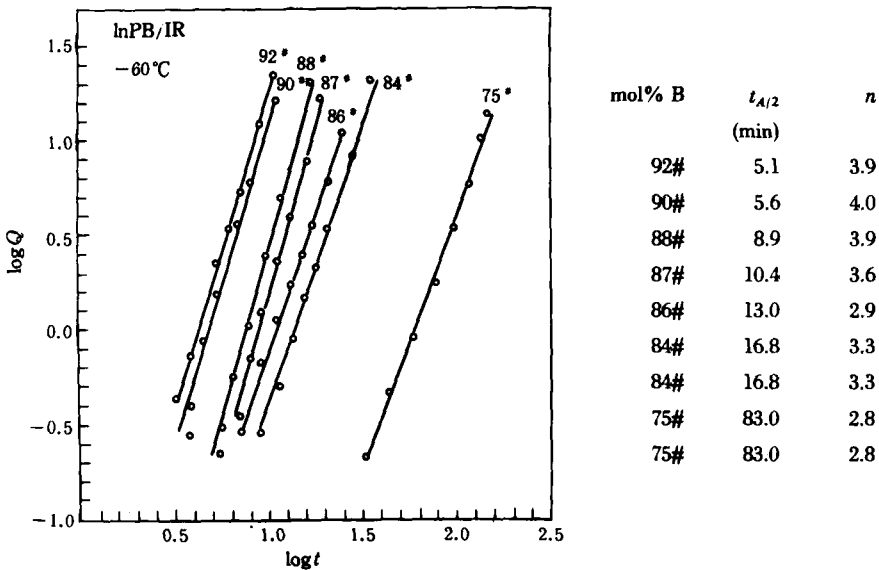


Fig.10 Ln-PB/IRs of different compositions crystallized at -60°C

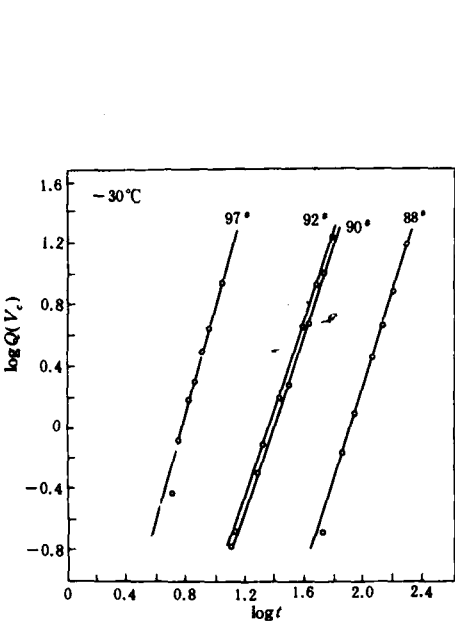


Fig.11 Ln-PB/IRs, -30°C

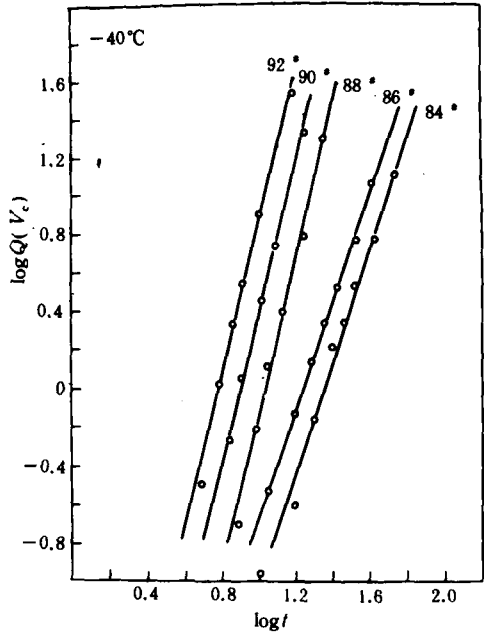


Fig.12 Ln-PB/IRs, -40°C

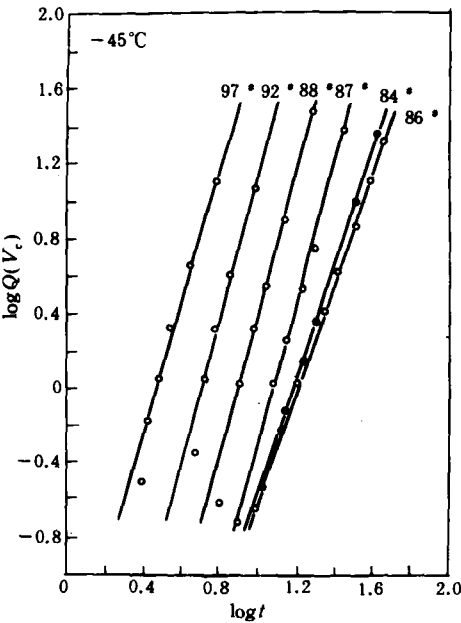


Fig.13 Ln-PB/IRs, -45°C

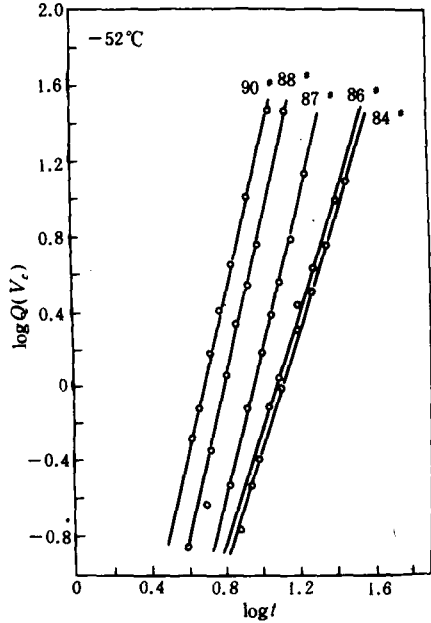
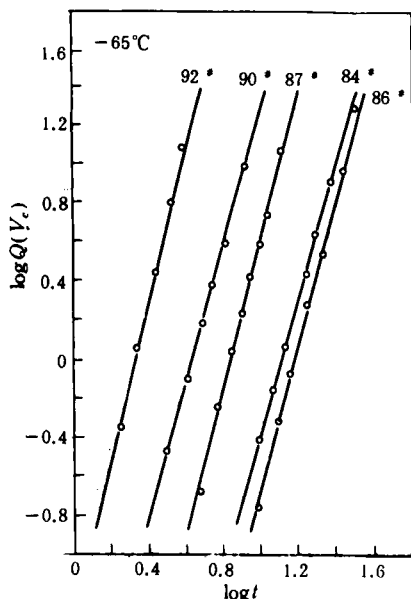
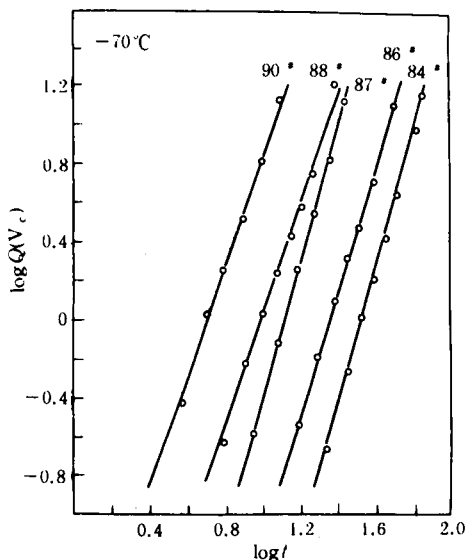


Fig.14 Ln-PB/IRs, -52°C

less than 10%, when the amount of IR is further increased regardless the composition ratio of B/IR in the copolymers.

The isothermal crystallization data of PB/IRs have been treated with the Q-modified Avrami equation. As shown in Fig.9 and 10 for different temperatures and different composition

Fig.15 L_n-PB/IRs, -65°CFig.16 L_n-PB/IRs, -70°C

respectively, as well as Fig.11 to 16, it can be shown that the experimental data fit the Q-modified one very well. And that all values of n are between 3 and 4 as listed in Table 4. It means that the form of crystals is spherulitic, regardless the cocomposition and crystalline temperature, but the mechanism of nucleation is not the same for different co-compositions under different temperatures. For samples of 88 to 100% B, $n=3$ above -30°C , which means the crystallization is nucleated athermally and then followed by three dimensional growth; while $n=4$ at -40 to -65°C belongs to thermal nucleation with three dimensional growth; and for $n=3$ to 4 at -65 to -70°C , the nucleation may be induced athermally mixed with thermally and then growth followed by three dimensional normally.

The above kinetic results are well identified by the change of morphological state of PB/IR (92/8), crystallized at -60°C during the course of the EM cast-film crystallization (Fig.1). The crystallization data of the same specimen undergoing bulk crystallization is 26.2% and $t_{A/2} = 5.1\text{min}$. while $n=3.9$ (Table 4) which means the process should be thermal nucleation with three dimensional growth. As shown in Fig.1 (A) and (B), both the nuclei and growing spherulites coexist in the same cast film at the same time. Thus it can be confirmed that the mechanism of isothermal bulk crystallization of polydienes, either homopolymer or copolymer, should be composed the following three steps: (a) nucleation may be induced athermal or/and thermally, (b) the nuclei are growing in three dimensions to form spherulite, (c) the growing spherulites may impinge on each other as they meet and the overall rate may be thus reduced, and finally (d) after sufficient long time, the impinged spherulites become truncated so that the volume filled state consists of impinged polygonal shaped domains.

THE EFFECTS OF MOLECULAR WEIGHT AND ENTANGLEMENT ON CRYSTALLIZATION RATE

Three sets of well fractionated L_n-PB samples, which were characterized as shown in Table 3,

were used for this study.

Firstly, we consider the dependence of temperature and molecular weight on nuclear density. In Fig.17 the nuclei densities of PB-B3 are given as a function of crystallization temperature, it can be seen that the maximum value of nuclei density occurs in the range of -60 to -50°C . This implies that in this temperature range, the nucleation rate of Ln-PB is the fastest, if homogenous nucleation becomes possible.

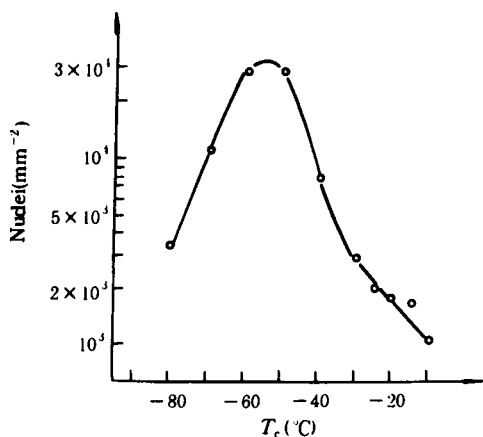


Fig.17 Number density of nuclei of PB-B3 as a function of crystallization temperature T_c

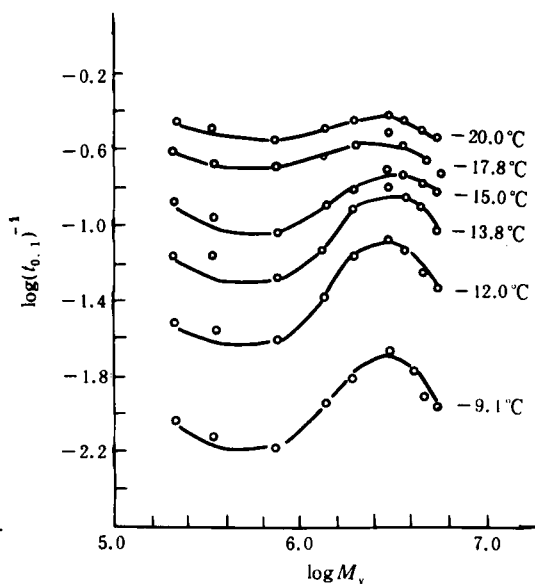


Fig.18 Plots of $\text{Ln}(1/t_{A/10})$ vs. $\text{Log} M_v$
Experimental curves

In Table 5,6 the nuclear density and induction time of Ln-PB samples crystallized at different temperatures are listed separately. They show that at the same crystallization temperature, the higher the molecular weight of the sample, the shorter the induction time and the higher the nuclear density are. And show that when samples with different molecular weight are crystallized at the same temperature, the higher the molecular weight of the sample, the easier the nucleation is.

Effect of molecular weight

The effects of molecular weight on polymer crystallization rate are very complex, and the results reported in literatures are different, for example crystallization rate of polymer decreases with the increase of molecular weight^[11,13] the crystallization rate increases with the increase of molecular weight^[14,16] there is a minimum value of crystallization rate at a definite molecular weight^[17]; and there is a maximum value of crystallization rate at definite molecular weight^[18,19].

The crystallization rates of 10% transition ($1/t_{A/10}$) of some Ln-PB samples crystallized at different temperatures are shown in Fig.18. It can be seen that as molecular weight increases, the crystallization rate decreases at first, reaching a minimum value in the range of $M_v = 4.6$ to 6.7×10^5 ; then it increases with the increase of molecular weight until a maximum value occurs in the range of $M_v = 3.0$ to 3.8×10^6 ; finally it decreases with the increase of molecular weight again. It seems that this curve has put altogether the controversy results reported in literatures^[11-19] about the changes of crystallization rate of a polymer with its molecular weight of wide range. In the temperature range investigated, the crystallization rates of all samples increase with the decrease of temperature.

Table 5 Number density of nuclei capable of Ln-PBs crystallized at different temperatures (mm.^{-2})

Sample Ln-PB	M_v $\times 10^{-5}$	Crystallization temperature ($^{\circ}\text{C}$)					
		-10	-15	-20	-25	-30	-40
B-2	19.89	8—20	12—30	14—34	22—40	26—56	72—122
B-3	13.61	6—16	12—22	12—24	16—34	16—42	62—106
B-4	6.85	6—14	8—20	10—20	12—26	18—34	25—37

Table 6 Crystallization induction time of Ln-PBs crystallized at different temperatures (min.)

Sample Ln-PB	M_v $\times 10^{-5}$	Crystallization temperature ($^{\circ}\text{C}$)					
		-23.2	-22.0	-18.7	-17.2	-15.4	-12.7
B-2	19.89	1.3	2.0	3.1	5.6	12.3	25.7
B-3	13.61	1.4	2.2	4.9	8.1	15.4	31.5
B-4	6.85	2.0	4.2	7.3	10.1	19.0	42.0

Effect of entanglement

The effect of entanglement on crystallization rate of polymer gained interest during recent years. However a more detailed look at this effect reveals a much more complicated picture. From Fig. 18, it can be seen that when M_v is within the range of 5×10^5 to 3×10^6 , the crystallization rate of Ln-PB increases with the increase of M_v . Chirico et al.^[17] found the same phenomena in the study about the crystallization of U-PB. Because the critical molecular weight of entanglement of Ln-PB is 1.27×10^5 ^[20], when M_v is higher than this critical value, the higher the molecular weight, the higher the density of chain entanglemental networks is. The function of entanglementation may be two sides, at first it will be favorable to the arrangement between macromolecules, and then the crystallization rate might be enhanced; while on the other side, it will give more restrictions to the molecular motion of the macromolecule itself, and thus might cause the reduction of crystallization rate.

Zhang and Qian^[20] have investigated the chain entanglement of Ln-PB and found the relationship describing the average number of entanglement segments, ε , and the entanglemental molecular weight M_e could be expressed as:

$$\varepsilon = 1.96 \times 10^{-12} \cdot M_v^{2.29} \quad (10)$$

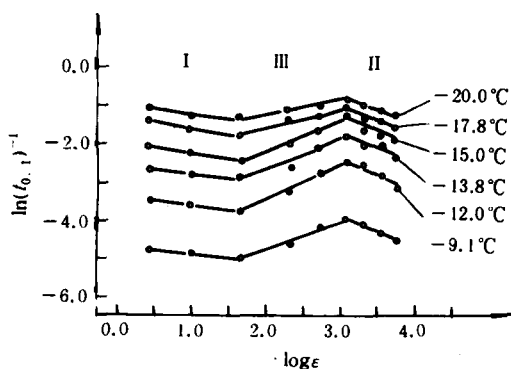
and

$$M_e = M_v / \varepsilon = 5.1 \times 10^{11} \cdot M_v^{-1.19}$$

If $\text{Ln}(1/t_{A/10})$ of Ln-PB is plotted against $\log(\varepsilon)$, a three section zigzag line can be obtained as shown in Fig. 19. From such zigzag lines, it can be suggested that there may exist two types of entanglement, the primary one occurs in the range of $\varepsilon = 1$ to 50 and secondary one at M_v greater than 1300. Thus the line can be separated into three regions: In both the primary region I and secondary region II the crystallization rate $1/t_{A/10}$ is decreased as the number of entanglement ε is increased, this may be attributed to the restriction of macromolecular motion by the type of entanglementation. In either region I or II, the slopes ($\alpha = \text{Ln}(1/t_{A/10})/\text{Ln}\varepsilon$) are parallel approximately, and their ratio $\alpha_{11}/\alpha_1 = -0.27/-0.11 \approx 2.5$. Then it can be proposed that the secondary entanglement may be formed

inside the primary one, gives more restriction on macromolecular motion, and thus reduces the effect by 2.5 times on crystallization rate. The intermediate region III is addible one between the two neighbour separation points, $\varepsilon \approx 50$ and 1300 respectively, it means that there may be co-existence of primary and secondary entanglements.

$$\text{slope} \quad a = \frac{\text{Ln}[1/t_{A/10}]}{\text{Ln}\varepsilon = 2.303 \log \varepsilon}$$



$T_c(^{\circ}\text{C})$	a_1	a_{11}	a_{11}/a_1	a_{111}
-20.0	-0.10	-0.27	2.67	0.16
-17.8	-0.13	-0.27	2.07	0.16
-15.0	-0.12	-0.27	2.26	0.30
-13.8	-0.10	-0.27	2.73	0.30
-12.0	-0.10	-0.27	2.77	0.31
-9.1	-0.10	-0.27	2.77	0.31
Av.	-0.11	-0.27	≈ 2.5	

Av. no. of entanglemental segments, $\text{Log } \varepsilon = 2.3 \text{ Ln } \varepsilon$.

Fig.19 Plots of $\text{Ln}(1/t_{A/10})$ vs. $\text{Log } \varepsilon$

Influence of molecular weight and entanglement both on crystallization rate

For the discussion of molecular weight, it is convenient to separate the linear crystal growth rate v expression into its three terms at crystalline temperature T_c based on nucleation theory^[22-27],

$$\text{Ln}v = \text{Ln}v_0 + \frac{-c_1}{C_2 + (T_c - T_g)} + \frac{-4b_0\sigma\sigma_c T_m^0}{\Delta h_f \rho_c T_c K(T_m^0 - T_c)} \quad (11)$$

In the right side of the equation, the first term of growth rate v_0 will be discussed latter; while the second and third two terms are deduced from the nucleation theory, in which C_1 and C_2 represent constants for given sample, K the Boltzman constant, ρ_c the density of crystal; and for Ln-PB, heat of fusion $\Delta h_f = 1.58 \times 10^9 \text{ erg/cm}^2$ and surface energy of side crystal surface $\sigma = 7.17 \text{ erg/cm}^2$. For Ln-PB, the molecular weight M_v dependence upon some defined temperatures such as equilibrium melting temperature T_m^0 and glass transition temperature T_g can be expressed experimentally as^[21]

$$\begin{aligned} T_m^0 &= 278.4 - 1.4 \times 10^5 / M_v \\ T_g &= 173 - 8.7 \times 10^4 / M_v \end{aligned} \quad (12)$$

and upon surface free energy of folded crystal surface,

$$\sigma_e = 20.37 - 3.122 \times 10^{-7} M_v + 2.172 \times 10^{-12} M_v^2$$

It can be seen that the value of last two terms in Eq.11 will decrease with the increase of M_v . In the first term, several approaches have been taken to point the major factor for the molecular weight dependence of v_0 . Several authors suggested that v_0 is largely determined by the mobility and decreases with the increase of molecular weight^[12,22,23]. While someothers found that the crystallization rate of some polymers increases with the increase of molecular weight in some crystallization temperature and molecular weight range^[14-16]. Therefore it is necessary not only to consider the effect of mobility, but also to consider the effect of entanglement on v_0 , since the crystallization rate of Ln-PB increases with the increase of the number of entanglement segments

linearly for $M_v = 5 \times 10^5$ to 3×10^6 , as is pointed out in Fig. 19. If we assumed that the rate of crystal growth v is proportional to the number of entanglement segments ε , then we get

$$V = V_o \cdot \exp \left[\frac{-C_1}{C_2 + (T_c - T_g)} + \frac{-4b_o \sigma \sigma_1 T_m^o}{\Delta h_f \rho_c K T_c (T_m^o - T_c)} \right] \cdot X \varepsilon \quad (13)$$

where X is a constant, $\varepsilon = 1.96 \times 10^{-12} M_v^{2.29}$ (Eq. 10). For the molecular weight dependence upon v_o term of the above equation, we use the empirical equation [24]

$$\ln(v_o) = B \cdot M_v^{-1/2} \quad (14)$$

The numerical values used for the other parameters in Eq. (13) are $C_1 = 750$ cal/mol and $C_2 = 130^\circ\text{K}$ when M_v is greater than 1.27×10^5 , then the rate of crystal growth can be rewritten as

$$\text{Ln} v = C + B M_v^{-1/2} + 2.29 \text{Ln} M_v + \frac{-C_1}{C_2 + (T_c - T_g)} + \frac{-4b_o \sigma \sigma_1 T_m^o}{\Delta h_f \rho_c K T_c (T_m^o - T_c)} \quad (15)$$

where B is constant and $C = \ln X + \ln(1.96 \times 10^{-12})$.

It is expected that at low supercooling, the secondary nucleation is not only the crystal growth rate determining step, but also the overall crystallization rate determining step, so that

$$\ln(1/t_{A/10}) = \ln(v) + d \quad (16)$$

Where d is a constant for the same sample, therefore, the overall crystallization rate can be represented as

$$\text{Ln}(1/t_{A/10}) = D + B M_v^{-1/2} + 2.29 \text{Ln} M_v + \frac{-C_1}{C_2 + (T_c - T_g)} + \frac{-4b_o \sigma \sigma_e T_m^o}{\Delta h_f \rho_c K T_c (T_m^o - T_c)} \quad (17)$$

where $D = C + d$.

By using curve-fitting calculation of the experimental data, the molecular weight, including entanglement dependence upon overall rate, it can be found that $D = -27.09$ and $B = 3214$, so the derived crystallization rate equation of Ln-PB can be expressed as [21]

$$\text{Ln}(1/t_{A/10}) = -27.09 + 3214 M_v^{-1/2} + 2.29 \text{Ln} M_v + \frac{-750}{130(T_c - T_g)} + \frac{-5.972 \sigma_e T_m^o}{T_c (T_m^o - T_c)} \quad (18)$$

In Fig. 20, the curves are computed by means of Eq. (18), the circles represent the values of experimental data, so it can be seen that the calculated curves fit to the experimental data very well.

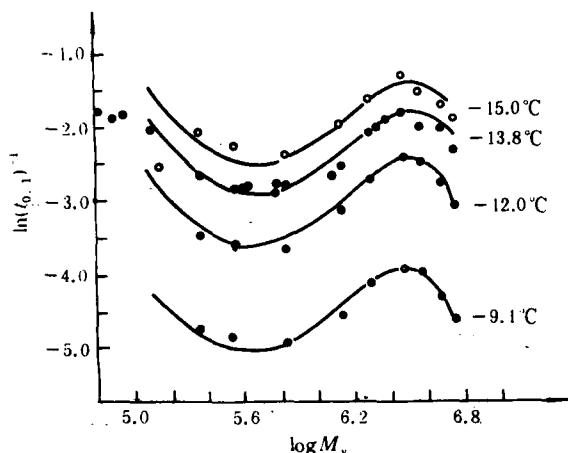


Fig. 20 Plots of $\text{Ln}(1/t_{A/10})$ vs. $\text{Log} M_v$

EXPERIMENTAL

Samples

The samples used for the crystallization rate study were provided by polymerization laboratory in our Institute including the lanthanide coordination polymerized polybutadiene Ln-PB and polyisoprene Ln-PIR, characteristic of high *cis*-1,4 content and good linearity of macromolecular chain^[6-9]. Some commercial PB and PIR polymerized with other catalytic systems, such as U-PB, Co-PB, Ni-PB and Ti-PIR and natural rubber NR (a PIR) were taken for comparison.

Ln-PB/IRs with various co-compositions were prepared, but no commercial PB/IR with both high *cis*-content in PB and PIR units is available, and characterized as shown in Table 7.

Ln-PB was fractionated by precipitation (toluene/methanol) into a number of fractions. Characteristics of some selected fractions are given in Table 8.

Characterization

Weight-average molecular weight M_w , number-average molecular weight M_n and distribution index M_w/M_n were determined by GPC. Intrinsic viscosity $[\eta]$ was determined with toluene solution at 30°C by extrapolating method. Average viscosity molecular weight M_v was got by the following equation^[7].

$$[\eta] = 3.24 \times 10^{-4} \cdot M_v^{0.7}$$

The *cis/trans* content was determined by IR spectra (Perkin-Elmer-559B) at room temperature.

Crystalline parameter was determined on a Rigaku X-ray diffractometer.

Table 7 Microstructure of Ln-PB/IRs

Sample	B(mol%)	[η]	B			IR	
			<i>cis</i> -1,4-B	1,2-B	<i>trans</i> -1,4-B	1,4-IR	3,4-IR
100#	100	6.9	97.9	1.0	1.1	0	0
97#	97	7.1	96.5	0.5	3.0	~100	~0
95#	95	5.6	97.0	1.9	1.1	~100	~0
92#	92	6.9	96.9	0.8	2.3	~100	~0
90#	90	6.8	96.2	0.6	3.2	~100	~0
88#	88	6.7	97.9	0.5	1.6	99.9	0.1
87#	87	7.2	98.2	0.3	1.5	~100	~0
86#	86	6.5	96.7	0.4	2.9	~100	~0
84#	84	7.2	96.5	2.2	1.3	99.1	0.9
80#	80	6.3	96.0	0.5	3.5	99.7	0.3
75#	75	6.4	97.8	0.8	1.4	99.7	0.3
67#	67	5.8	98.0	0.6	1.4	99.0	1.0
54#	54	5.6	98.8	0.7	0.5	98.6	1.4
44#	44	5.6	97.6	0.9	1.5	97.7	2.3
33#	33	5.8	97.9	0.7	1.4	97.8	2.2
20#	20	4.9	97.0	0.6	1.7	97.0	3.0
0#	0	—	0	0	0	97.0	3.0

For electron microscopy, films of Ln-PBs casted from 0.1% toluene solution were quickly transferred to a crystallization bath set at predetermined temperature, controlled to $\pm 0.1^\circ\text{C}$. After crystallization the films were stained with OsO_4 at the same temperature for two hours. The electron microscopy observations were carried out with a Hitachi H-500 electron microscope.

A home made linear dilatometer was used to analyze the isothermal crystallization rate and crystallinity of Ln-PB. By means of a sensitive differential transformer, the accuracy of the measurement was better than $0.5\mu\text{m}$. The size of specimen was $40 \times 4 \times 1$ mm. For volumetric dilatometry, 0.10 to 0.11 g sample was put into a dilatometer with a capillary of 0.4 mm diameter. Alcohol was introduced to the dilatometer after it had been evacuated for half an hour. Then the dilatometer was quickly transferred to a crystallization bath set at a predetermined temperature and controlled to $\pm 0.01^\circ\text{C}$. The height of the alcohol column in the capillary was measured at regular intervals during the whole crystallization process.

Table 8 Characterization parameters of fractionated Ln-PBs

Sample Ln-PB	$\bar{M}_w$ $\times 10^{-5}$	$\bar{M}_n$ $\times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	$[\eta]$ (dl/g)	$\bar{M}_v$ $\times 10^{-5}$	structure		(%)
						<i>cis</i> -1,4	1,2	<i>trans</i> -1,4
A-1				17.02	55.39	98.9	0.2	0.9
A-2				15.13	46.82	98.7	0.3	1.0
A-3				12.71	36.50	98.9	0.3	0.8
A-4				9.56	24.30	98.8	0.4	0.8
A-5				8.89	21.90	98.6	0.6	0.8
A-6	10.62	9.83	1.08	5.89	12.15	98.4	0.5	1.1
A-7	6.16	4.53	1.36	3.88	6.70	98.7	0.6	0.7
A-8	5.50	5.16	2.24	3.64	6.12	98.5	0.6	0.9
A-9	3.81	2.58	1.48	2.69	3.97	98.9	0.5	0.6
B-1				11.05	29.88	98.7	0.5	0.8
B-2	18.83	10.50	1.79	8.31	19.89	99.0	0.3	0.7
B-3	11.82	9.23	1.27	6.37	13.61	99.1	0.3	0.6
B-4	6.24	4.85	1.29	3.94	6.85	98.8	0.4	0.8
B-5	3.43	2.79	1.23	2.49	3.56	98.5	0.5	1.0
B-6	2.08	1.26	1.65	1.74	2.13	98.8	0.4	0.8
B-7	1.35	0.83	1.62	1.24	1.31	98.7	0.4	0.9
B-8	0.90	0.57	1.56	0.95	0.89	99.0	0.3	0.7
B-9	0.59	0.53	1.11	0.78	0.68	98.9	0.4	0.7
C-1	5.56	4.77	1.17	3.65	6.14	99.0	0.4	0.6
C-2	3.64	2.65	1.38	2.64	3.87	98.7	0.5	0.8
C-3	1.46	0.86	1.70	1.32	1.44	99.0	0.4	0.6
C-4	0.84	0.45	1.89	0.86	0.78	98.9	0.5	0.6
C-5	0.30	0.17	1.78	0.52	0.38	98.6	0.5	0.9

The experiments were carried out from room temperature down to -70°C . The volume fraction V_c of crystal aggregates detected at time t on the linear dilatometer is calculated by V_c

$= 3\Delta l / l_0 A$, where $\Delta l / l_0 = (l_0 - l) / l_0$ is the specific length contraction in which l_0 is the original length and l the length at t . A represents the maximum value of primary crystallization, obtained from the plots of specific contraction $3\Delta l / l_0$ against $\log t$. The time attaining $A/2$ is defined as the half-time of crystallization, $t_{A/2}$, and that attaining $A/10$ as 10%-time $t_{A/10}$.

CONCLUSIONS

1. For the mechanism of bulk crystallization of high polymers, in addition to the nucleation and growth steps, the unimpingement of growing crystal aggregates should be taken into consideration for the modification of the Avrami equation.
2. The proposed mechanism is well supported by the change of morphological state during the course of the corresponding cast film crystallization of Ln-PB/IR (92/8) at -60°C (Fig.1).
3. The Q-modified Avrami equation thus derived (Eq.7 and 8) is verified satisfactorily by the isothermal bulk crystallization of the lanthanide catalytically polymerized polybutadiene Ln-PB, polyisoprene Ln-PIR and their copolymers Ln-PB/IR.
4. Based on the examination of the influence of the number of entanglement ε on 10% crystallization rate of Ln-PB (Fig.19), it is revealed that there is existence of two stages of entanglementation, the primary one occurs in the range of $\varepsilon = 1$ to ~ 50 , while the secondary one at $\varepsilon \geq 1300$.
5. The equation for dependence of molecular weight and entanglement on bulk crystallization rate has been derived as Eq.13 or 18 for Ln-PB, and verified by the experimental rate data of well fractionated Ln-PB samples crystallized at -9.1 to -15°C (Fig.20).

Keywords:

Avrami Equation modified; Entanglement influence of; Lanthanide coordination polymerization; Molecular weight influence of; Polybutadiene

SYMBOLS

A —maximum degree of crystallinity

$b_0, B, C(C_1, C_2), d, D$ —constants

$E, (E' = E + 1)$ —expected number of growing crystals reaching a point

Δh_f —heat of fusion

I^* —nucleation rate

K —Boltzman constant (Eq.11)

K_a —shape factor in Avrami Equation

K_q —shape factor in Q-modified Avrami Equation

m —probability number of growing crystals

M —molecular weight(MW)

M_n —number average MW

M_w —weight average MW

M_v —viscosity average MW

M_e —entanglemental segment M_e

n —Avrami exponent, dimensional

N —number of unimpinging growing crystals

N_0 —total number of growing crystals

P —probability

PB—polybutadiene

Co-PB—Cobalt catalytically polymerized PB

Ln-PB—lanthanide catalytically polymerized PB

Ni-PB—nickel catalytically polymerized PB

U-PB—uranium catalytically polymerized PB

PB/IR—copolymer of butadiene and isoprene

PIR—polyisoprene

Q—Q-modified

t —crystallization time

$t_{A/2}$ —time required to attain half A

$t_{A/10}$ —time required to attain tenth 10%A

T_c —crystallization temperature

$T_{c,max}$ —crystallization temperature for maximum rate

T_g —glassy temperature

T_M^0 —equilibrium melting point

V_c —volume fraction of crystal transited

$v(=rt)$ —linear growth rate; r =radius

v_c —constant growth rate

a —slope(Fig.19)

ε —average number of entanglemental segment

$[\eta]$ —intrinsic viscosity

σ —specific surface energy of side crystal surface

σ_c —specific surface energy of folded crystal surface

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