

CHAIN ENTANGLEMENT AND CRYSTALLIZATION OF *cis*-1,4-POLYBUTADIENE

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ABSTRACT

The morphological structure and mechanism of nucleation and growth of Ln-PB and Ni-PB with different molecular weight were investigated by transmission electron microscopy. The crystallization of low molecular weight fraction is primarily from predetermined nuclei, crystallization for the high molecular weight fraction is primarily from sporadic nuclei. Two types morphology of spherulite with different lamellar entanglement have been observed. The entanglement of higher molecular weight fractions are found to be of significance in the morphology and rate of crystallization of polymer.

The effect of molecular weight on morphology and rate of crystallization of polybutadiene (PB), has been reported in part I^[1]. This paper will present the result of detail study about the effect of molecular weight distribution, by fractionating and mixing on crystallization behaviour of PB, and the relationship between crystallization and entanglement.

EXPERIMENTAL

1. Sample

Cis-1,4-polybutadiene synthesized by lanthanide catalyst (Ln-PB) and nickel catalyst (Ni-PB) respectively were used in this study. The microstructure and intrinsic viscosity $[\eta]$ are listed in Table 1. The *cis*-content was determined by IR spectroscopy (Perkin-Elmer 599B). Intrinsic viscosity $[\eta]$ was determined with toluene solution at 30°C by viscometer.

Table 1 The microstructure and intrinsic viscosity of PB

Sample	Intrinsic viscosity $[\eta]$ (dl/g)	Microstructure (%)		
		C _{1,4}	T _{1,4}	V _{1,2}
Ln-PB	3.87	96.98	2.49	0.52
Ni-PB	2.52	92.80	4.21	2.99

2. Fractionation

Ln-PB was fractionated by precipitation (toluene / methanol) into 5 fractions. The distribution index $\bar{M}_w/\bar{M}_n$ were determined by GPC. It is about 2.50. The molecular weight and microstructure of some selected fractions are given in Table 2.

Samples with different molecular weight distribution index were prepared by mixing of different fractions Ln-PB. Their intrinsic viscosity and microstructure were given in Table 3.

Table 2 The molecular weight and microstructure for fractions of Ln-PB

Sample fraction	Viscometric average molecular weight $\bar{M}[\eta]$	Microstructure (%)		
		$C_{1,4}$	$T_{1,4}$	$V_{1,2}$
Ln-1	20.7×10^5	96.10	2.98	0.93
Ln-2	8.44×10^5	96.35	2.86	0.79
Ln-3	6.65×10^5	97.30	2.20	0.48
Ln-4	2.18×10^5	97.14	2.26	0.59
Ln-5	0.58×10^5	95.55	3.87	0.58

Table 3 The structure data for mixture of different fractions Ln-PB

Sample	The composition of mixture	$[\eta]$ (dl/g)	Microstructure (%)		
			$C_{1,4}$	$T_{1,4}$	$V_{1,2}$
Ln-B	(Ln-4) 73% + (Ln-2) 27%	3.757	96.13	3.06	0.80
Ln-C	(Ln-5) 31% + (Ln-2) 69%	4.018	96.93	2.56	0.51
Ln-D	(Ln-5) 40% + (Ln-1) 60%	4.178	95.76	3.60	0.59
Ln-E	(Ln-5) 25% + (Ln-2) 57% + (Ln-1) 18%	3.129	96.83	2.61	0.55

3. Preparation of specimens for electron microscopic observation

Solution-cast films were made for electron microscopy by dissolving the polymer in toluene to form a 0.5 wt % solution. Films were cast onto a glycerine surface at room temperature. When all the solvent had evaporated, the films were floated off on distilled water 3 times, and picked on electron microscope grids.

Film was quickly transferred to a crystallization bath set at predetermined fixed temperature T_c . The isothermal crystallization studies were carried out at -30°C . After crystallization, the films were stained with OsO_4 at the same temperature for 30 min. Specimens

crystallized at -30°C after different time intervals were observed with electron microscope (Hitachi H-500) at room temperature.

RESULTS AND DISCUSSION

Cis-1,4-polybutadiene obtained with lanthanide catalyst has very high degree of molecular regularity and linearity in comparison with Ni-PB. Generally, the *cis*-content of Ln-PB is above 96%. Ln-PB can crystallize in bulk state easily and rapidly at suitably low temperature^[2]. The electron microphotograph of Ln-PB and Ni-PB crystallized at -30°C for 30 min are shown in Fig. 1. It can be seen that in the case of Ln-PB spherulites have met with each other and stopped growth for 30 min, but the spherulites of Ni-PB have not met yet at the same conditions. The rate of crystallization of Ln-PB was more rapid than that of Ni-PB. It depends primarily on the regularity of its macromolecules.

Five fractions of Ln-PB with different molecular weight has been obtained by fractionating. The microstructure of each fraction is similar, and does not change with different molecular weights (Table 2). Each fraction varies in the crystallization behaviour at low temperature.

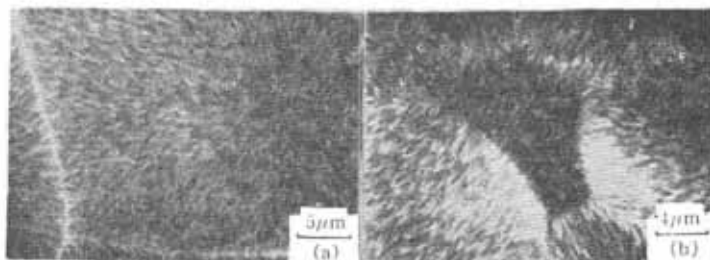


Fig. 1 The spherulitic structure of PB, crystallized at -30°C
(a) Ln-PB; (b) Ni-PB.

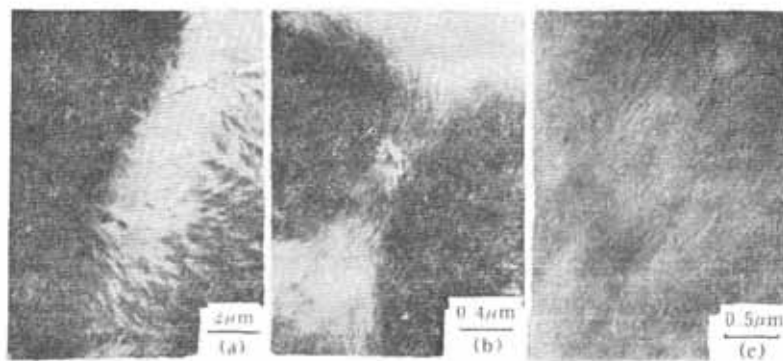


Fig. 2 The morphology of low molecular weight fraction of PB (Ln-5, $M=0.58 \times 10^5$), crystallized at -30°C
(a) nucleus grew from the edges of copper grid;
(b) nucleus grew from the cracks of foreign particle;
(c) lamellar structure.

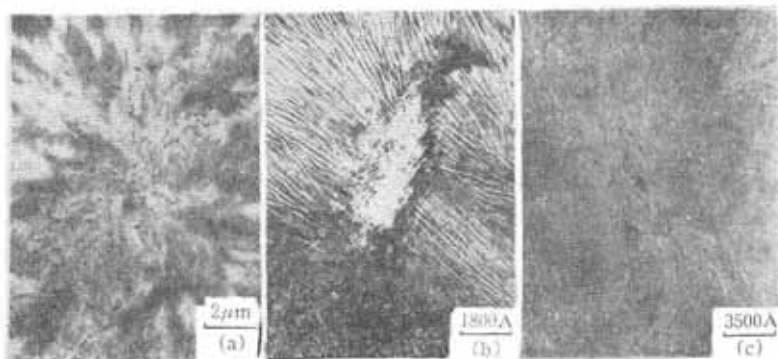


Fig. 3 The morphology of middle molecular weight fraction of PB (Ln-3, $M=6.65 \times 10^5$), crystallized at -30°C
 (a) centre of spherulite;
 (b) nucleus of spherulite grew from the lamellar;
 (c) lamellar structure with entanglement.

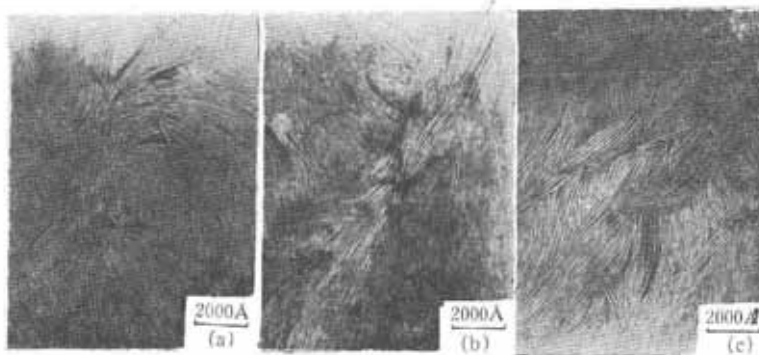


Fig. 4 The morphology of high molecular weight fraction of PB (Ln-2, $M=8.44 \times 10^5$), crystallized at -30°C
 (a) and (b) nuclei grew from the entanglement lamellae;
 (c) the lamellar structure with entanglement.

Spherulites of low molecular weight fraction (Ln-5) grew from the edges of copper grid and the cracks of foreign particles (Fig. 2 a and b). The spherulites of Ln-3 and Ln-4 grew from the entanglement point of its macromolecules (Fig. 3 a, b and Fig. 4 a, b). The crystallization of low molecular weight fraction is primarily from predetermined nuclei, crystallization for the high molecular weight fraction is primarily from sporadic nuclei. Lamellar entanglement developed during crystallization of Ln-3 and Ln-2, while lamellae of Ln-5 was not entangled, as shown in the electron microscopic photos (Fig. 2 c, Fig. 3 c and Fig. 4 c).

The results of study on chain entanglement of Ln-PB using stress relaxation method^[3] indicated that, the number of entanglement segments of entanglement network of macromolecules (m) increases with increasing molecular weight, the average molecular weight of entanglement segments ($\bar{M}_e$) decreases with increasing molecular weight of raw rubber. The critical molecular weight of entanglement networks M_e of the Ln-PB is $M_{m-1}=1.27 \times 10^5$.

The molecular weight of Ln-5 ($M=0.58 \times 10^5$) is lower than M_e , the molecular entanglement is absent, its lamellae of spherulite were not entanglement (Fig. 2 c), nucleation of which grew from foreign particles, lamellar growth was very fast. The molecular weight of Ln-3 and Ln-2 are much higher than M_e . The molecular weight distribution of Ln-PB determined by GPC are shown in Fig. 5. The data of molecular weight distribution and structure parameters of entanglement network from experimental relaxation spectrum calculation are listed in Table 4.

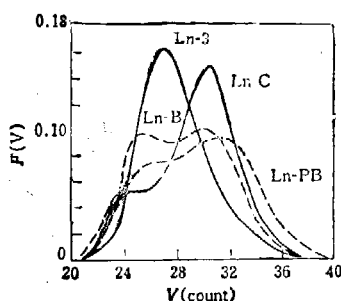


Fig. 5 The molecular weight distribution of PB

Table 4 Molecular weight distribution and parameters of entanglement of various PB

Sample	$\bar{M}_{[\eta]}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{0.9}/\bar{M}_{0.1}$	m	$\bar{M}_e$
Ln-3	6.65×10^4	2.50	22.95	253	2648
Ln-B	6.40×10^4	4.90	51.50	155	4129
Ln-C	7.05×10^4	5.03	48.05	152	4635
Ln-PB	6.70×10^4	8.70	82.86	77	8687
Ni-PB	2.40×10^5	7.61	60.04	24	10832

Sample Ln-3 has a larger number of entanglement segments ($m=253$) and lower average molecular weight of entanglement segments $\bar{M}_e$ ($\bar{M}_e=2684$) comparing with the other samples (Table 4). It must exist the entanglement point and entanglement lamellae. Fig. 6 is the schematic lamellar entanglement of Ln-3 spherulite. Fig. 7 is the schematic model of lamellar entanglement around the point of chain entanglement.

It is also found that the number of entanglement segments of Ni-PB is much lower than that of Ln-PB, due to less molecular weight and intrinsic viscosity $[\eta]$ of Ni-PB. Owing to the variant molecular weight distribution, the number of entanglement of the sample with the same molecular weight may be different (Table 4). The number of effective chain entanglement segment for unfractionated Ln-PB with broader molecular weight distribution decreases because the fractions of lower molecular weight do not get any chain entanglement. For the fractionated Ln-PB with narrower molecular weight distribution the number of effective chain entanglement segment is higher than that of unfractionated Ln-PB, because the molecular

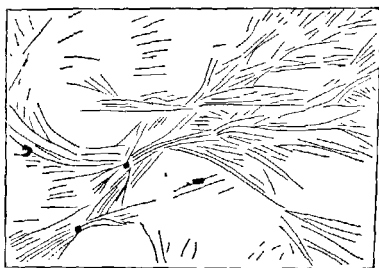


Fig. 6 The schematic lamellar entanglement of PB

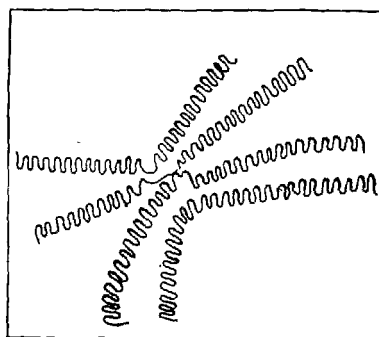


Fig. 7 The schematic model of lamellar entanglement around the point of chain entanglement

weight of almost all of molecules are larger than $\bar{M}_c$. So the m value of Ln-3 is higher than that of Ln-PB and Ln-B as well as Ln-C.

The results of electron microscopic observations on the samples of mixture indicated that there are two types of spherulite (Fig. 8 b). The electron microphotograph of Ln-D crystallized at -30°C is shown in Fig. 9 a. It can be seen that the small radiating growth spherulite is lined in the large spherulite with ring spacings growth. The growth rate of ring spherulite

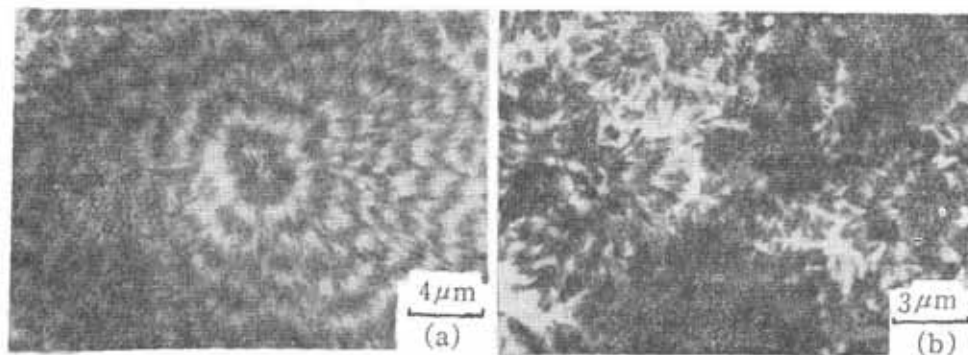


Fig. 8 The morphology of Ln-PB with different molecular weight distribution, crystallized at -30°C
(a) Ln-B; (b) Ln-E.

is $0.12 \mu\text{m}/\text{min}$, but it is $0.04 \mu\text{m}/\text{min}$ for radial spherulite. Crystallization of ring spherulite is 3 times faster than that of radial spherulite. Fig. 9 c is the photograph of local enlargement of a, it is the boundary of two types spherulites. Lamellae of ring spherulite without entanglement is shown in Fig. 9 d. The entanglement lamellar of radial spherulite with helix growth have been found in Fig. 9 e. These data indicate that specimens made by mixing of fractions in dilute solution, is heterogeneous in its dilute solution. Owing to the intermolecular entanglement, the molecules with high molecular weight can not be homogeneously distributed among

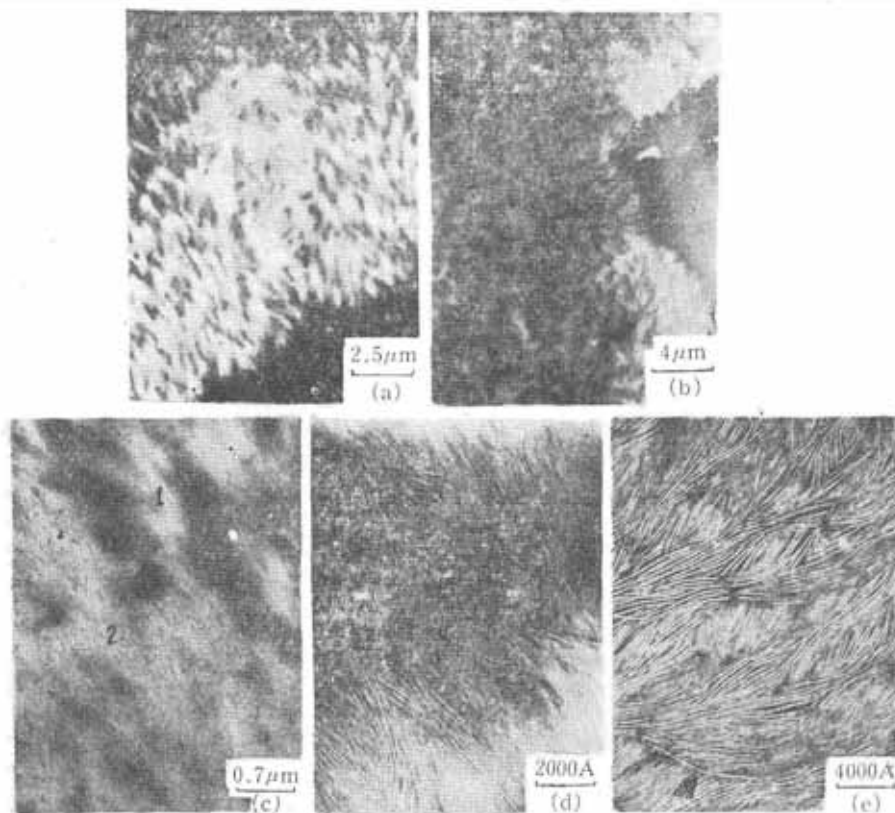


Fig. 9 Two types of spherulites crystallized at -30°C , for mixtures of different fraction Ln-PB
 (a) Ln-D;
 (b) Ln-E;
 (c) the local enlargement of (a);
 (d) the local enlargement of region 1 in (c);
 (e) the local enlargement of region 2 in (c).

low molecular weight fractions and formed a few region of aggregation entanglement lamellae. The crystallization rate of this region is very slow.

In summary, the entanglement of higher molecular weight fractions are found to be of significance in the morphology and rate of crystallization of the polymer.

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