

STIRRING INDUCED SOLUTION CRYSTALLIZATION OF *cis*-1, 4-POLYBUTADIENE

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ABSTRACT

In this work, the stirring induced solution crystallization behaviour of *cis*-1, 4-polybutadiene polymerized with rare-earth catalyst (Ln-PB) has been studied by electron microscope, DSC and GPC. It has been found that when 0.5% Ln-PB toluene solution was stirred at a temperature within the range of -15° to -79°C with a speed of 180 rpm, a kind of white swollen thread-like substance wound around the stirrer was formed. It was seen under electron microscope that this swollen thread-like substance consisted of fibrillar crystals of Ln-PB parallel to each other. The amount of Ln-PB wound around the stirrer increased with the decrease in crystallization temperature until a maximum was reached at about -65°C , then it decreased with the decrease in crystallization temperature. However, the higher the crystallization temperature, the higher the average molecular weight and the narrower the molecular weight distribution of Ln-PB which wound around the stirrer. Therefore, Ln-PB sample may be fractionated by stirring its dilute solution at a series of crystallization temperatures.

Ln-PB has good molecular linearity, and possesses a *cis*-1,4-content higher than 98%^[1]. During recent years, much attention has been paid to its bulk crystallization^[1,4-6]. Yet only Chirico et al. have studied its solution crystallization. This paper presents our study of the solution crystallization behaviour of Ln-PB during stirring.

EXPERIMENTAL

1. Samples

The characteristics of the Ln-PB sample used is listed in Table 1. *Cis*-content was determined by IR (Perkin-Elmer 599B). Weight-average molecular weight $\bar{M}_w$, number-average molecular weight $\bar{M}_n$ and polydispersity indexes $\bar{M}_w / \bar{M}_n$ were determined by GPC. Intrinsic viscosity was determined in toluene solution at 30°C by extrapolating method. Viscosity-average molecular

Table 1 Characterization parameters of D-9*

$\bar{M}_w$ $\times 10^5$	$\bar{M}_n$ $\times 10^5$	$\bar{M}_v$ $\times 10^5$	$\bar{M}_w / \bar{M}_n$	$[\eta]$ (dl/g)	<i>cis</i> %	1,2%	<i>trans</i> %
5.49	1.68	5.25	3.28	3.27	98.7	0.6	0.7

* D-9 is one of Ln-PB sample.

weight $\bar{M}_v$ was obtained by the following equation^[1].

$$[\eta] = 3.24 \times 10^{-4} \times \bar{M}_v^{0.7}$$

2. Stirring induced solution crystallization of Ln-PB

AP toluene was used for preparation of 0.5% solution of Ln-PB. The solution was transferred to a glass tube of 2.4 cm diameter immersed in a thermostatically controlled alcohol bath. The temperature range used was from -79° to -15°C and was controlled to within $\pm 0.1^\circ\text{C}$. The solution was then stirred with a glass stirrer usually for about 15 h. at a speed of 180 rpm. The stirrer was 1.0 cm in diameter.

3. Preparation of specimens for electron microscopic observation

After crystallization, the polymer precipitated was in the form of fibrous aggregate wrapping around the stirrer. The sample thus obtained was immediately washed in clean toluene at crystallization temperature. Then some of this dilute solution was dropped on a grid with carbon support film, and then stained with OsO_4 at the same temperature for five hours. Electron microscopic observations were made with a Hitachi H-500 electron microscope.

4. DSC experiment

The differential scanning calorimeter used in this study was Perkin-Elmer DSC-2C. Experimental procedure is described in ref.[2].

5. GPC experiment

GPC was used to analyze the polymer precipitated on the stirrer and dissolved in solution after crystallization using the column system and technique described in [3].

6. Determination of solution concentration

5 ml of the solution which had been kept at 30°C was placed in a weighing bottle and then kept at 100°C for evaporation of the solvent. After complete evaporation of the solvent, the weighing bottle was cooled at room temperature for 30 min. and then weighed. The concentration of the solution could be calculated according to the weight of the polymer and the density of the solvent.

RESULTS AND DISCUSSION

1. The morphology of stirring induced crystal

0.5% toluene solution of D-9 was crystallized at different temperature by stirring. It has been found that when crystallization temperature was lower than -15°C , a kind of white swollen thread-like substances winding around the stirrer formed during the crystallization process. At the

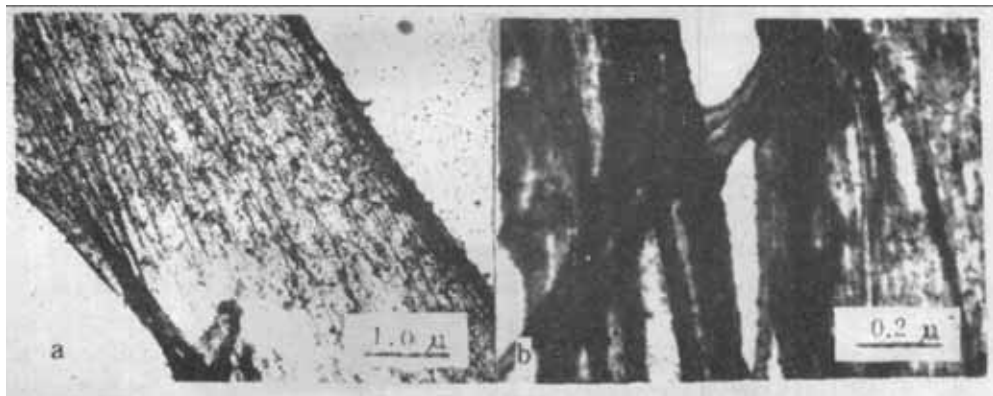


Fig.1 Fibrillar crystals of D-9 grown from stirring induced solution crystallization at -60°C for 900 min.

beginning, the amount of this thread-like substance increased with the increase in crystallization time, but after the crystallization proceeded for a certain length of time it stopped increasing with the further increase in crystallization time. The crystallization temperature and the molecular weight of Ln-PB were the main factors which affected the amount of this thread-like substance precipitated on the stirrer.

As shown in Fig.1(a), the white swollen thread-like substance consisted of fibrillar crystals parallel to each other. From Fig.1(b) it can be seen that some of these fibrillar crystals were perfect and their crystal lamellae could be seen clearly under electron microscope. The widths of these crystal lamellae were about 150 Angstroms. But some of the fibrillar crystals were not perfect, only being a kind of strap-like material as seen under electron microscope.

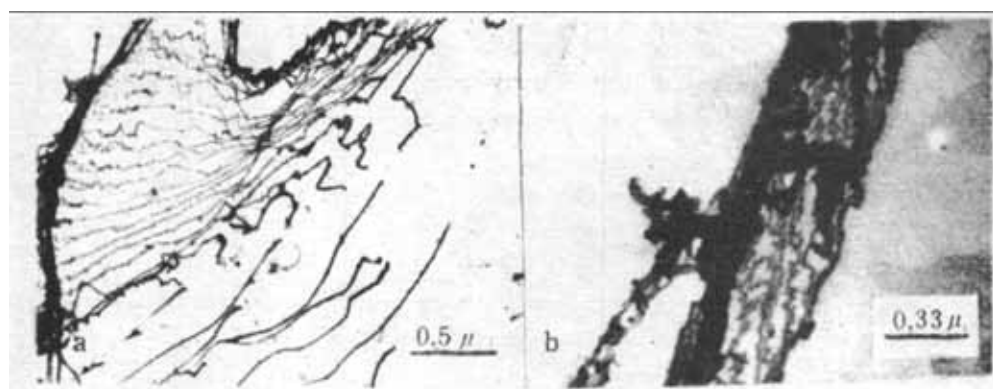


Fig.2 The morphology of D-9's fibrillar crystals after washing and vibrating in toluene for 1 min.

After stirring, if the stirrer with the fibrous aggregate of Ln-PB was washed and vibrated in toluene for 1 min, it could be found that some of the fibrillar crystals were dispersed and some of

Table 2 Characterization parameters of Ln-PB precipitated on the stirrer after stirring induced solution crystallization at different temperatures for 15 hours

Temp. (°C)	$[\eta]$ (dl/g)	$\bar{M}_n$ $\times 10^{-5}$	$\bar{M}_w$ $\times 10^{-5}$	$\bar{M}_v$ $\times 10^{-5}$	$\bar{M}_w / \bar{M}_n$	w %
-21.3	8.84	9.17	18.9	● 21.8	2.06	1.4
-25.6	7.93	8.64	16.2	18.6	1.88	5.3
-28.6	6.12	4.27	11.7	12.8	2.75	8.1
-31.6	6.09	4.18	11.6	12.8	2.78	11.3
-40.0	5.73	3.40	11.0	11.7	3.28	20.9
-45.6	4.58	2.14	8.41	8.49	3.93	30.3
-50.0	3.47	1.55	5.94	5.71	3.83	66.1
-60.0	3.24	1.50	5.37	5.17	3.58	82.8
-64.5	2.75	1.30	4.25	4.10	3.26	86.9
-69.0	2.82	1.30	4.44	4.25	3.42	82.2
-79.0	3.02	1.26	4.92	4.68	3.90	80.6

them began to curled up as shown in Fig.2.

2. The effects of molecular weight and temperature on stirring induced solution crystallization of *Ln*-PB

0.5% D-9 toluene solution was crystallized at -21.3°C by stirring with a speed of 180 rpm for 15 hours. Then the molecular weight distribution of *Ln*-PB precipitated on the stirrer and that remained in solution were measured by GPC respectively. The result was presented in Fig.3. It may be seen that the fibrous aggregate precipitated on the stirrer contained the longer molecules, while in the solution remained the shorter molecules. The average viscosity molecular weight of *Ln*-PB on the stirrer and that in the solution were 2.18×10^6 and 4.60×10^5 respectively.

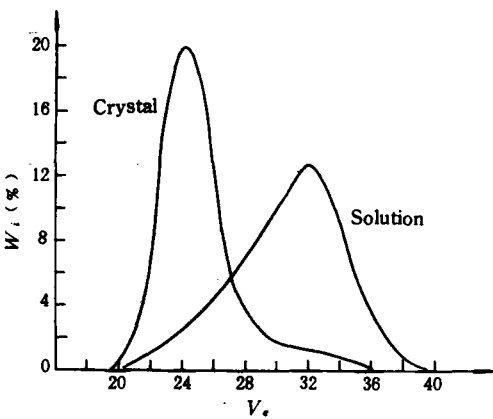


Fig.3 Chromatograms of D-9 precipitated on the stirrer and that remained in solution, after stirring induced solution crystallization at -21.3°C for 15 hours

Table 3 Characterization parameters of *Ln*-PB remained in solution after stirring induced crystallization at different temperature for 15 hours

Temp. ($^{\circ}\text{C}$)	$[\eta]$ (dl/g)	$\bar{M}_n$ $\times 10^{-5}$	$\bar{M}_w$ $\times 10^{-5}$	$\bar{M}_v$ $\times 10^{-5}$	$\bar{M}_w / \bar{M}_n$	Conc. (mg/ml)
-21.3	2.98	1.49	4.72	4.60	3.17	4.26
-25.6	3.00	1.81	4.60	4.64	2.54	4.10
-28.6	2.63	1.83	3.73	3.84	2.04	3.98
-31.6	2.55	1.66	3.58	3.68	2.16	3.84
-40.0	2.42	1.29	3.45	3.41	2.68	3.43
-45.6	2.32	1.16	3.24	3.21	2.79	3.02
-50.0	2.13	1.47	2.71	2.84	1.84	1.47
-60.0	1.94	0.97	2.51	2.49	2.58	0.74
-64.5	1.77	0.96	2.15	2.08	2.24	0.57
-69.0	2.03	0.96	2.73	2.66	2.84	0.77
-79.0	2.06	1.13	2.71	2.77	2.40	0.84

From Table 2 and Fig.4, it can be seen that the higher the crystallization temperature, the higher the average molecular weight and the narrower the molecular weight distribution of *Ln*-PB

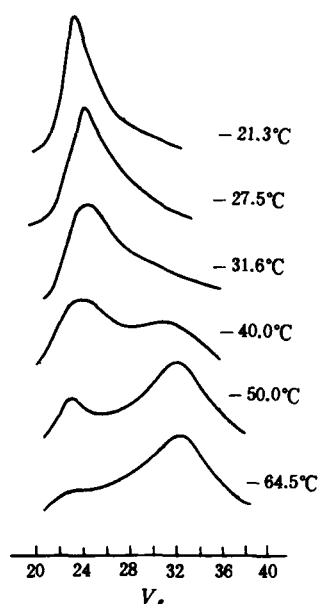


Fig.4 Chromatograms of D-9 precipitated on the stirrer after solution crystallization by stirring at different temperatures for 15 h

which wound around the stirrer. When the crystallization temperature was lower than -40°C , double peaks appeared on the chromatograms, the molecular weight distribution was wider. Perhaps it was due to phase separation. The amount of Ln-PB which wound around the stirrer increased with the decrease in crystallization temperature until it reached a maximum value at about -65°C , then it decreased with the decrease in crystallization temperature.

3. Fractionation of Ln-PB by stirring induced solution crystallization

From the above discussion it can be found that the larger the molecules of the Ln-PB, the

Table 4 Characterization parameters of Ln-PB precipitated on stirrer after repeated stirring induced crystallization at different temperature for 15 hours

Temp. ($^{\circ}\text{C}$)	$[\eta]$ (dl/g)	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-5}$	$\bar{M}_w / \bar{M}_n$	w %
-21.3	8.85	9.17	18.9	21.8	2.06	1.4
-23.5	8.15	9.46	16.7	19.3	1.77	1.8
-25.0	7.34	6.17	14.6	16.7	2.37	2.7
-27.5	6.81	6.43	13.2	15.0	2.06	2.2
-30.0	5.99	3.46	11.6	12.5	3.35	3.4
-35.0	3.07	1.27	4.94	4.80	3.91	4.2
-40.0	2.74	1.29	4.17	4.08	3.22	5.7
-45.0	2.46	1.21	3.55	3.49	2.94	7.6
-50.0	2.39	1.28	3.34	3.35	2.62	17.9
-57.0	2.05	1.11	2.68	2.69	2.41	14.1
-62.0	1.69	0.88	2.03	2.04	2.30	9.3

Table 5 Characterization parameters of Ln-PB remained in solution after repeated stirring induced crystallization at different temperature for 15 hours

Temp. (°C)	$[\eta]$ (dl/g)	$\bar{M}_n$ $\times 10^{-5}$	$\bar{M}_w$ $\times 10^{-5}$	$\bar{M}_v$ $\times 10^{-5}$	$\bar{M}_w / \bar{M}_n$	Conc. (mg/ml)
-21.3	2.99	1.49	4.72	4.62	3.26	4.26
-23.5	2.85	1.40	4.42	4.31	3.16	4.19
-25.0	2.74	1.36	4.17	4.08	3.06	4.07
-27.5	2.59	1.63	3.72	3.76	2.28	4.00
-30.0	2.47	1.32	3.52	3.52	2.60	3.83
-35.0	2.34	1.21	3.29	3.24	2.72	3.65
-40.0	2.13	1.04	2.91	2.84	2.81	3.40
-45.0	2.07	1.02	2.81	2.73	2.77	3.07
-50.0	1.83	1.00	2.28	2.29	2.27	2.30
-57.0	1.74	0.80	2.17	2.13	2.72	1.69
-62.0	1.45	0.76	1.64	1.64	2.15	1.29

higher the temperature at which the Ln-PB could precipitate on stirrer by means of stirring induced solution crystallization. This suggests the possibility of fractionation of Ln-PB samples by stirring induced solution crystallization. For this purpose, 0.5% D-9 toluene solution was crystallized by stirring at -21.3°C for 15 hours. After crystallization the GPC chromatograms of Ln-PB on the stirrer and that in the solution, and the solution concentration were measured. The above crystallization and characterization procedures were repeated at temperatures in decreasing order. The results obtained are listed in Table 4 and 5. From Table 4 it can be seen that narrow distribution fractions could be obtained by repeated stirring induced solution crystallization when the

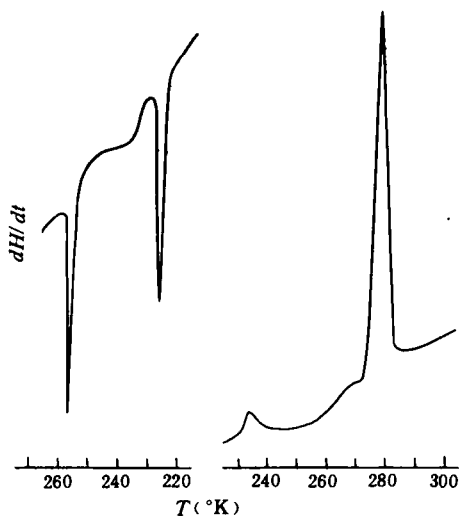


Fig.5 DSC curve of 0.5% D-9 toluene solution which had been crystallized by stirring at -50°C for 8 hours. Heating and cooling rate: $10^\circ\text{C}/\text{min}$

temperature was higher than -30°C . So this method is suitable for separation of longer molecules in Ln-PB sample.

4. The melting temperature of Ln-PB crystal formed during stirring induced solution crystallization

0.5% D-9 toluene solution was crystallized at -50°C for 8 hours by stirring. Then 11 mg. of the fibrous aggregate precipitated on the stirrer was put into a DSC sample holder as quick as possible, cooled to -50°C with a rate of $10^{\circ}\text{C}/\text{min.}$, kept at this temperature for 30 min, and then was heated to room temperature with the same rate. The result was shown in Fig.5, from which it can be seen that during the heating process there appeared a melting peak at about 277°K . It is about 7°K higher than the melting temperature of Ln-PB crystal obtained by bulk crystallization at -50°C .

CONCLUSION

1. When 0.5% toluene solution of Ln-PB was stirred at about -15°C to -79°C with a speed of 180 rpm, a kind of white swollen thread-like substance consisted of fibrillar crystals would be formed.

2. The amount of Ln-PB crystal wound around the stirrer increased with the decrease in crystallization temperature until a maximum was reached at about -65°C , then it decreased with the decrease in crystallization temperature.

3. The longer molecules in Ln-PB sample can be fractionated by stirring its dilute solution at a series of crystallization temperatures.

4. The melting temperature of Ln-PB crystal obtained by stirring induced solution crystallization is about 7°C higher than that of Ln-PB crystal obtained by bulk crystallization.

Keywords:

Cis-1,4-Polybutadiene; Stirring induced crystallization; Morphology of polymers; Electron microscopy.

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