

MORPHOLOGY OF POLYBUTADIENE "SHISH KEBABS"

XU Yang (徐洋), ZHOU Enle (周恩乐), YU Fusheng (余赋生)

and QIAN Baogong (钱保功)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun.)

ABSTRACT

Shish kebab structure of *cis*-1,4-polybutadiene has been obtained by quiescent solution crystallization at suitable temperature. The morphology and growth mechanism of formation of shish kebab structure have been studied in detail. The higher the molecular weight the faster the sample crystallizes.

INTRODUCTION

Shish kebab is a special crystal morphology of a few polymers only formed by crystallization in solution during stirring. Recently, many researchers have investigated this special structure in detail. But until now the structure and its growing mechanism are still in dispute. This paper presents our investigation on the quiescent solution crystallization behaviour of *cis*-1,4-polybutadiene polymerized with rare-earth catalyst (Ln-PB). In this study it was first found that shish kebab can also be formed in quiescent solution crystallization of polymer. This might provide a new clue to the study of the structure and growth mechanism of shish kebab.

EXPERIMENTAL

1. Samples

Ln-PB was fractionated by precipitation (toluene / methanol) into a number of fractions. Characteristics of some selected fractions are given in Table 1. The *cis*-content was determined by IR (Perkin-Elmer 599B). Weight-average molecular weight $\overline{M}_w$, number-average molecular weight $\overline{M}_n$ and dispersity index $\overline{M}_w / \overline{M}_n$ were determined by GPC. Intrinsic viscosity $[\eta]$ was determined in toluene solution at 30 °C by extrapolating method. Viscosity-average molecular weight $\overline{M}_v$ was calculated by the following equation^[1],

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

Table 1. Characterization parameters for the Ln-PB samples

Sample	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_v \times 10^{-5}$	$\overline{M}_w / \overline{M}_n$	$[\eta]$ (dl/g)	Micro-structure(%)		
						cis	1,2	trans
D-1			36.50		12.71	98.9	0.3	0.8
D-2	18.83	10.50	19.89	1.79	8.31	99.0	0.3	0.7
D-3	11.82	9.23	13.61	1.27	6.37	99.1	0.3	0.6
D-4	6.24	4.85	6.85	1.29	3.94	98.8	0.4	0.8
D-5	3.43	2.79	3.56	1.23	2.49	98.5	0.5	1.0
D-6	2.08	1.26	2.13	1.65	1.74	98.8	0.4	0.8
D-7	0.95	0.52	1.51	1.82	1.36	98.8	0.4	0.8
D-8	0.30	0.17	0.38	1.78	0.52	98.6	0.5	0.9
D-9	5.49	1.68	5.25	3.28	3.27	98.7	0.6	0.7

2. Solution crystallization of Ln-PB

Ln-PB was dissolved in toluene or tetrahydrofuran. Solution concentrations between 0.1 and 30% were used, most commonly 0.5%. The solution was transferred into a glass tube of 0.7 cm diameter immersed in a constant temperature bath. Temperatures ranged from -78°C to -15°C , and were controlled to within $\pm 0.1^\circ\text{C}$.

3. Preparation of specimens for electron microscopy

After crystallization, the solution was diluted. Then a drop of this dilute solution was put on a grid with carbon support film, and then stained with OsO_4 at the same temperature for five hours. Structure observations were made under a Hitachi H-500 electron microscope.

4. DSC study

Differential scanning calorimeter used was PERKIN-ELMER DSC-2C. Procedure reported in (2) was adopted for this study.

RESULTS AND DISCUSSION

During recent years, much attention has been paid to the bulk crystallization of *cis*-1,4-polybutadiene^[1,3-6], but yet no one has studied its quiescent solution crystallization behavior. Ln-PB has good macromolecular linearity, and possesses a *cis*-1,4-content higher than 98%^[1]. This paper presents our study on quiescent solution crystallization behaviour of Ln-PB.

1. Morphology of Ln-PB crystallized in solution

When 0.5% Ln-PB toluene solution was crystallized at different temperatures, the following phenomena were observed:

(1) When the crystallization temperature was higher than -25°C , no crystal was produced and there were only some small black spheres and clusters of these small black spheres which could be seen under electron microscope (see Fig. 1 and 2). The radius of these black spheres were about several hundred angstrom, which was in the same order of the Ln-PB's radius of gyration. The clusters probably consisted of many Ln-PB molecules or were microgels with catalyst as its center.

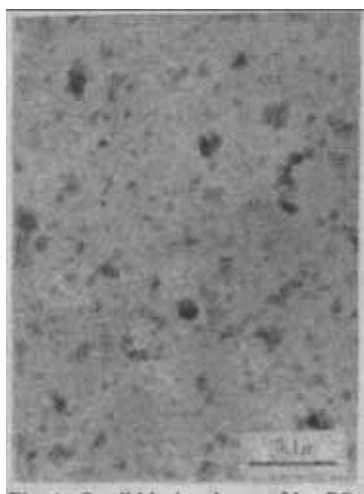


Fig. 1 Small black spheres of Ln-PB grown at -22°C for 10 hours

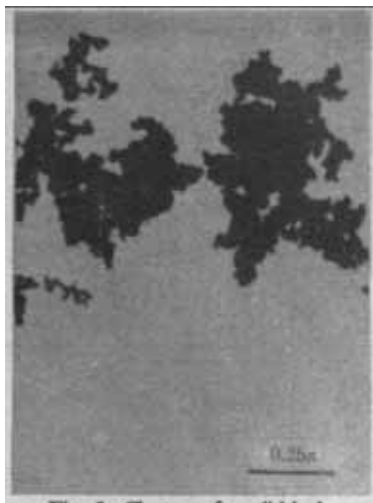


Fig. 2 Clusters of small black spheres of Ln-PB grown at -22°C for 10 hours

(2) When the crystallization temperature was between -40°C and -25°C , beside the small black spheres and their clusters, some straplike structure appeared (see Fig. 3).

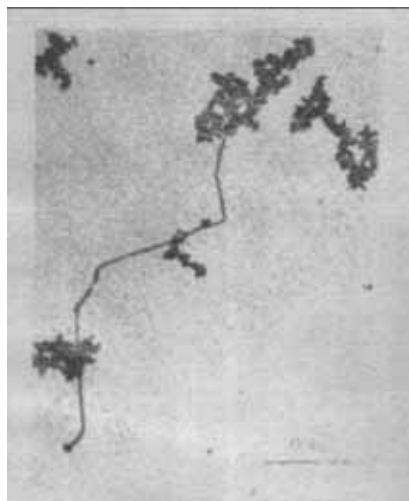


Fig. 3 Strap material of Ln-PB grown at -33°C for 8 hours

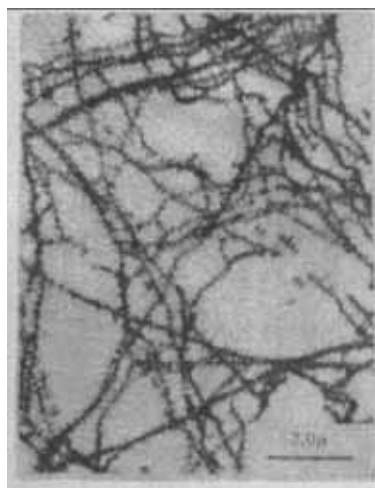


Fig. 4 Shish kebabs of Ln-PB grown at -60°C for 8 hours

(3) When the crystallization temperature was within $-65^{\circ}\text{C} - 40^{\circ}\text{C}$, shish kebabs were formed in specimens of higher molecular weight (see Fig. 4). The width of the shish kebabs increased with the decrease in crystallization temperature. For example, when the crystallization temperature was -60°C , the width of the shish kebabs was about 2000 Angstroms; when the crystallization temperature was -42°C , the width of the shish kebabs was only about 600 Angstroms. Morphology of Ln-PB's shish kebabs grown at different crystallization temperatures were shown in Fig. 5, in which it can be seen that the lamellae in the shish kebab arranged parallel with each other when crystallized at higher temperature, but as the temperature decreased they

were less and less in parallel arrangement, some of their ends connected with each other.

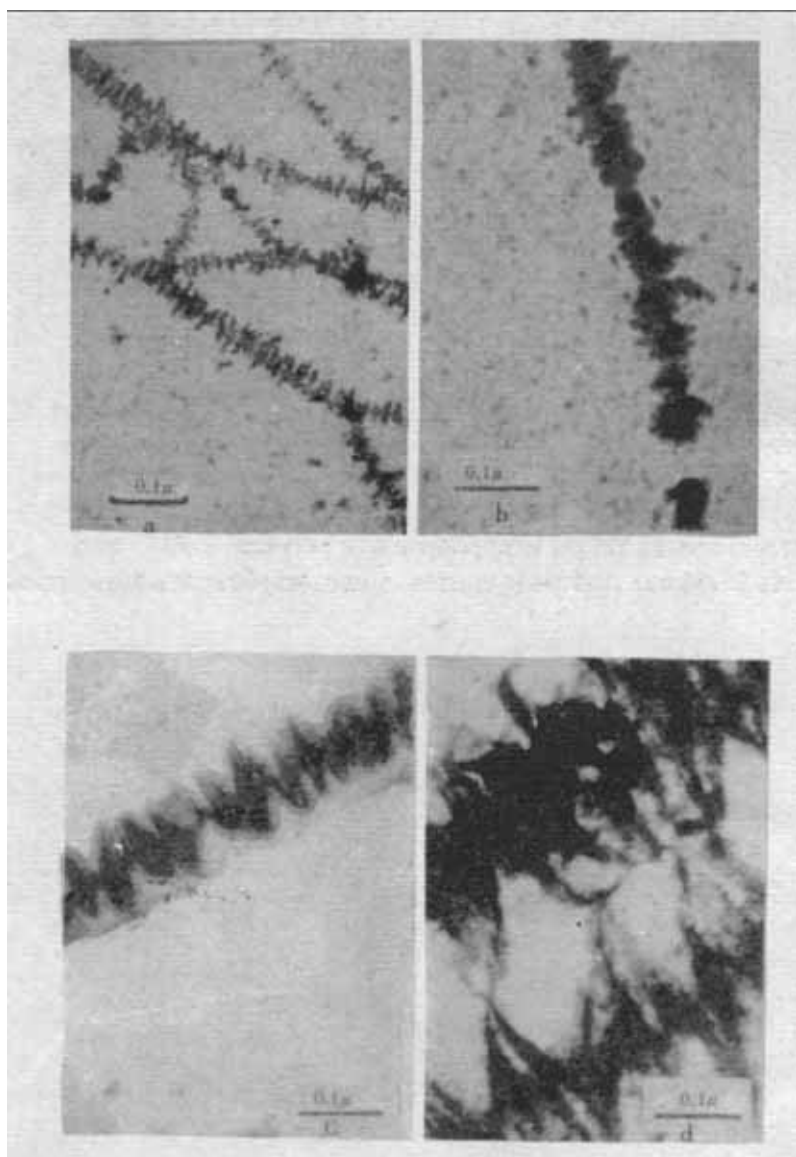


Fig. 5 Shish kebabs of Ln-PB (a) grown at -42°C for 48 hours, (b) grown at -45°C for 48 hours, (c) grown at -53°C for 8 hours, (d) grown at -60°C for 8 hours.

(4) When the crystallization temperature lower than -65°C , with decreasing temperature the growth of Ln-PB's shish kebab became more and more difficult. When the temperature was below -78°C , no shish kebab could be formed.

2. Mechanism of formation of shish kebab structure

Since in 1965 Pennings et al.^[7] first observed that shish kebabs were produced from solution crystallization of polyethylene in xylene during stirring, further investigations have been made on this special structure^[8-12]. It has been found that shish kebab could also be produced from polypropylene or polystyrene solution-on stirring. In 1970 Pennings^[8] proposed a model consisting of a backbone crystal made up of

extended polymer chains from which grew the lamellar crystals containing folded polymer chains. Pennings also proposed a mechanism of formation of this crystal structure. Keller and Machin^[9], Wikjord and Manley^[10] have proposed similar models. However, Krueger and Yeh^[11], according to some of their experimental results, suggested that the kebabs on shish kebab fibers were molecularly integrated with the interkebab material, and the interkebab material did not seem to consist of fully extended chain crystals, but could have a random chain-folded morphology. Nagasawa and Shimonura^[12], based upon their experiments, concluded that the shish kebab structure must be formed by the deformation of spiral crystals.

Beyond expectation Ln-PB's shish kebabs were produced in the process of quiescent solution crystallization. The fact suggests that shish kebab can also be formed without stress-induction. This should provide a new clue to the study of the structure and growing mechanism of shish kebab.

Since there are double bonds in the chains of *cis*-1, 4- polybutadiene, OsO_4 can be used to stain and to stop the crystallization at any time, so the crystallization process of Ln-PB's shish kebab can be observed under electron microscope. For this purpose, 0.5% D-9 toluene solution was crystallized at -50°C . It was found that when the solution was crystallized for 15 min., there were only some small black spheres and clusters of these small black spheres (see Figs. 1 and 2); when the solution was crystallized for 30 min., beside the small black spheres and their clusters, some strap-like material occurred (See Fig. 6) and the number of these strap-like material increased with the crystallization time; when the solution was crystallized for 60 min., some imperfect lamellae had grown from the straplike material (see Fig. 7); then as the crystallization time increased, the lamellae grew more and more perfect, and the number of lamellae on the strap-like material increased; finally shish kebabs were produced.

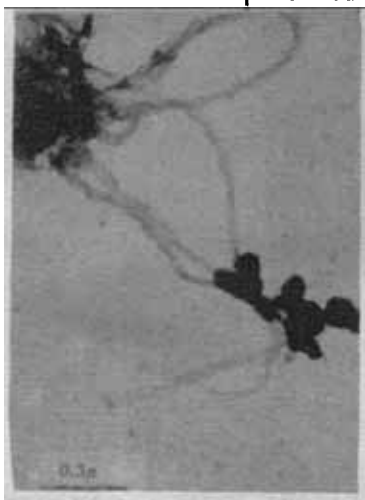


Fig. 6 Strap material of Ln-PB grown at -50°C for 30 min.

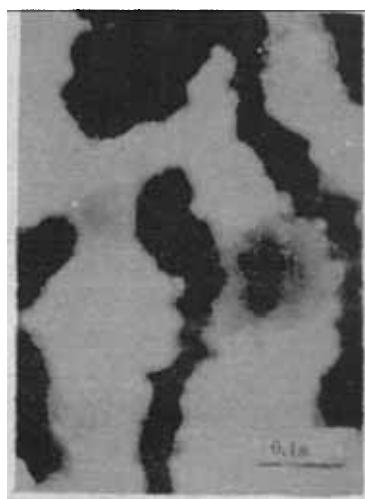


Fig. 7 Growing shish kebabs of Ln-PB grown at -50°C for 60 min.

In order to investigate the crystallization mechanism of Ln-PB's shish kebab, we put 12 mg 0.5% D-9 toluene solution into a DSC sample holder, which was cooled to -50°C at a rate of $10^\circ\text{C}/\text{min}$, kept at this temperature for 30 min. Then it was heated to room temperature with the same rate. The result was shown in

Fig. 8 (a), from which it could be seen that during the cooling process there were not any crystallization peak. In the heating process there was only a small melting peak at about -6°C . Therefore only a few of Ln-PB's molecules had crystallized in the strap-like material. But if we crystallized the 0.5% D-9 toluene solution at -50°C for 8 hours first, and then put 11mg of the crystallized solution into a DSC sample holder as quickly as possible and operated as discussed above. The result was shown in Fig. 8 (b). It could be seen that during the cooling process there was a crystallization peak at about -25°C , and in the heating process there was a melting peak at about 2°C . This showed that after crystallization for 8 hours, a part of Ln-PB's molecules in 0.5% toluene solution had crystallized and its melting temperature was about 2°C . This suggested that in the shish kebabs a part of Ln-PB's molecules had crystallized and its melting point was close to that of the bulk crystal. It may be concluded that the cores of Ln-PB's shish kebabs do not seem to consist of fully extended chains, probably the shish and the kebabs are formed simultaneously. Evidence supporting this concept includes: (1) The Ln-PB's shish kebabs are produced in quiescent solution crystallization process. Under this condition it is impossible to form the crystals made up of extended polymer chains. (2) No fibrillar crystals in the Ln-PB's shish kebabs or in solution could be observed. (3) The kebabs are grown on a strap-like material. (4) If the kebabs grew epitaxially on the backbone crystals to form shish kebabs, as suggested by Pennings, one would expect the size of these kebabs to be more irregular and to increase with crystallization time. But the width of Ln-PB's shish kebabs is about the same width of the strap-like material, as shown in Fig. 6, and does not increase with time.

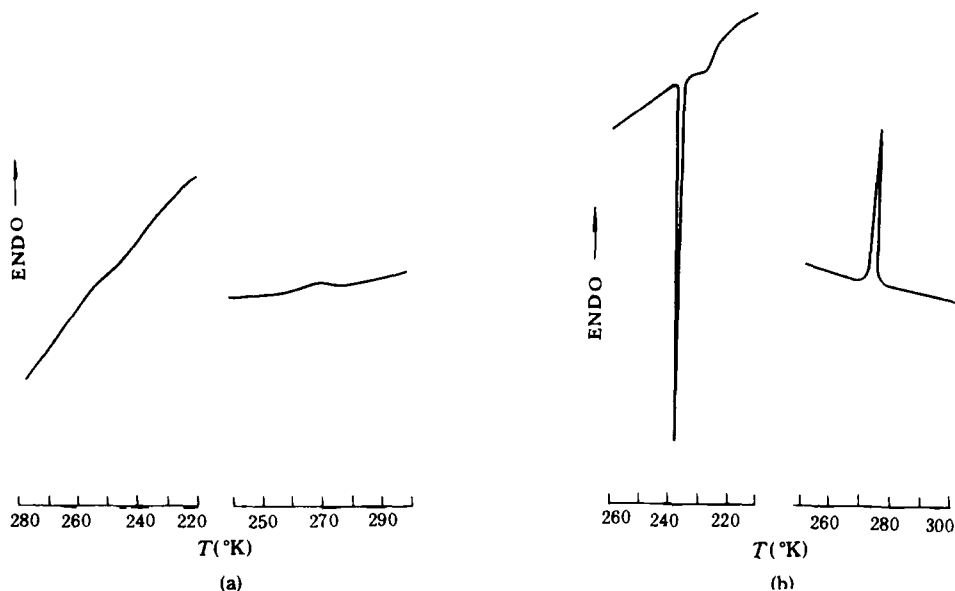


Fig. 8 DSC curves. (a): for 0.5% D-9 toluene solution; (b): for 0.5% D-9 — toluene solution which had been crystallized for 8 hours. Heating and cooling rate: $10^{\circ}/\text{min}$.

The above facts suggest that the Ln-PB's shish kebab structure may be produced by the following process: (1) At the beginning of crystallization, some Ln-PB's molecules impinge and entangle with each other, and some clusters of black spheres, as shown in Fig. 1, are formed. (2) As crystallization time increases the chains of

molecules in the clusters start to arrange more or less in order and some of them begin to nucleate, so a kind of strap-like material, as shown in Fig. 6, are formed. (3) On the strap-like material, the crystal growth takes place following nucleation, and some imperfect crystal lamellae are formed. (4) After a long period of crystallization the lamellae on the strap-like material increase and grow more and more perfect. (5) Finally shish kebabs are produced.

3. The effect of molecular weight on quiescent solution crystallization of Ln-PB

The 0.5% toluene solutions of samples listed in Table 1 were crystallized at -50°C . It was found that the higher the molecular weight of the sample, the faster the sample crystallized. For example, when the solutions were crystallized for 90 min., some shish kebabs occurred in D-1, D-2, D-3; when the solutions were crystallized for 180 min., some shish kebabs also occurred in D-4, D-5; but there was still no shish kebab could be seen in D-6, D-7, D-8 after crystallization for 15 hours. The only crystals which could be seen were some small spherulites as shown in Fig. 9.

After crystallization, sometimes a few extremely long shish kebabs were formed. But when we filtered the solution through 0.6 — 1.4 μm membrane filter first, then crystallized the filtrate under the same conditions, these extremely long shish kebabs no longer could be found in the solution. This result revealed that these extremely long shish kebabs were formed from some molecular entanglements or from gels.

4. The effect of solution concentration on quiescent solution crystallization of Ln-PB.

From experimental results it was found that within the proper range of molecular weight and crystallization temperature shish kebabs could be produced from Ln-PB toluene solutions with concentrations ranging from 0.1% to 12%, while solution concentration of 0.2 — 4% was more favourable for the growth of Ln-PB's shish kebab. When the

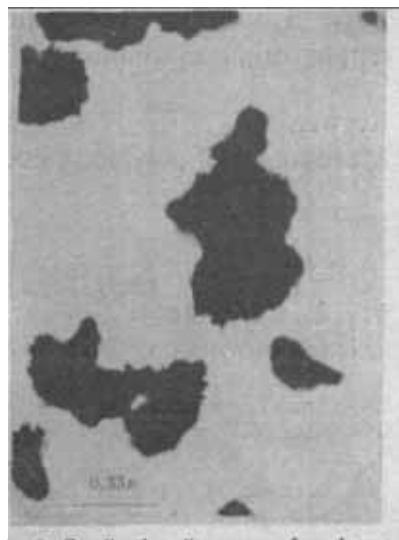


Fig. 9 Small spherulites grown from lower molecular weight samples at -50°C for 15 hours

solution concentration was higher than 2%, some small spherulites occurred, as shown in Fig. 9, the numbers of the spherulites increased with the increase in solution concentration. When the solution concentration was higher than 20%, no shish kebabs would form.

5. The effect of solvent on quiescent solution crystallization of Ln-PB

Under proper condition, shish kebabs of Ln-PB can also be produced from tetrahydrofuran solution. However, under the same condition Ln-PB crystallizes faster in toluene solution than in tetrahydrofuran solution. For example, after 120 min.

crystallization at -50°C , some shish kebabs appeared in the 0.5% D-9 toluene solution, but only some black spheres and their clusters could be seen in the 0.5% tetrahydrofuran solution of the same sample.

CONCLUSIONS

1. When the crystallization temperature is about -75°C — -40°C , shish kebab can be formed in specimens of Ln-PB with higher molecular weight.

2. The Ln-PB's shish kebab may be produced by the following process: (1) At the beginning of crystallization, some Ln-PB molecules impinge and entangle with each other, and some clusters of black spheres are formed. (2) As crystallization time increases the chains of molecules in the clusters start to arrange more or less in order, and some of them begin to nucleate, so a kind of strap-like material is formed. (3) On the strap-like materials the crystal growth takes place following nucleation, and some imperfect crystal lamellae are formed. (4) After a long period of crystallization, the lamellae on the strap-like material increase and grow more and more perfect. (5) Finally shish kebabs are produced.

3. The higher the molecular weight, the faster the sample crystallizes.

4. Under the same condition Ln-PB crystallizes faster in toluene solution than in tetrahydrofuran solution.

Keywords:

Morphology of polymers; Polybutadiene; Shish kebab; Solution crystallization.

REFERENCES

- [1] 钱保功、余赋生、程络时、周恩来, 秦汶, 中国科学 (*Scientia Sinica*), 1982, 5, 297.
- [2] 陈东霖, 化学通报 (*Chemistry*), 1975, 2, 26.
- [3] Chirico, A. De., Lanzani, P. C., Raggi, E., Bruzzone, M., *Makromol. Chem.*, 1974, 175, 2029.
- [4] Trick, G. S., *J. Polym. Sci.*, 1959, 41, 213.
- [5] Natta, G., Crespi, G., Guzzeta, G., Leghissa, S., Sabbioni, F., *Rubb. Plast. Age*, 1961, 42, 402.
- [6] Bruzzone, M., et al., *Rubber Chem. Technol.*, 1974, 47, 1175.
- [7] Pennings, A. J., Kiel, A. M., *Kolloid-Z. u. Z. Polymere*, 1965, 20, 160.
- [8] Pennings, A. J., van der Mark, J. M. A. A., Kiel, A. M., *Kolloid-Z. u. Z. Polymere*, 1970, 237, 336.
- [9] Keller, A., Machin, M. T., *J. Macromol. Sci.*, 1967, B1, 41.
- [10] Wikjord, A. G., John Manley, R. St., *J. Macromol. Sci.*, B2, 1968, 501.
- [11] Krueger, D., Yeh, G. S. Y., *J. Macromol. Sci.* 1972, B6, 413.
- [12] Nagasawa, T., Shimonura, Y., *J. Polym. Sci., Polymer Physics Ed.* 1974, 12, 2291.