

## *Solution-Grown Crystals of Poly(p-phenylene benzobisthiazole)*

Kaoru Shimamura, Chunxiao Zhang and Tetsuya Uchida

(Received December 5, 1996)

Rigid polymer poly(p-phenylene benzobisthiazole) was crystallized from dilute solution. Electron microscopy showed that upon quenching, flat fibrils with several nm thick were produced. Subsequent heat treatment in solvent changed the fibril into "shish-kebab". On the other hand, by isothermal crystallization, an aggregate of parallel rod-like crystals was obtained. The molecular chains were accommodated normal to the rod. Based on the observation of crystal morphology, the isothermal crystallization mechanism was proposed. Because of rigidity of polymer chains and wide distribution of the molecular length, the chain ends were inevitably included within the crystals resulting in crystal defects such as axial shift, lattice curvature and edge dislocation which were directly observed by lattice imaging.

### INTRODUCTION

Although the natural fibers have been used by human being as clothings since the Neolithic Age, it was not until 19th century when their structural investigation had started as polymeric materials. X-ray diffraction showed conclusively in 1913 that crystalline particles were present in the fibers[1]. Thus, Meyer[2] assumed that the natural fiber was built up of brick-like crystalline units or "micelles" in which extended molecules aligned parallel with each other(Fig. 1). But these micelles were not linked with polymeric chains because there was no idea of macromolecules at that time. After the argument about the length of the molecules of cellulose and other polymers in 1930s, it was recognized that the molecules were about ten times as long as the micelles[3]. This fact introduced an fringed micellar idea that the same molecules must pass through more than one micelle linking the micelles together in a continuous molecular network[4]. This fringed micellar model(Fig. 2) thereafter has been conveniently used to explain the physical properties of polymer solids for a long time. But since the discovery of polyethylene single crystal(Fig. 3)[5], chain folding has been recognized as the general chain conformation in crystalline polymer solids.

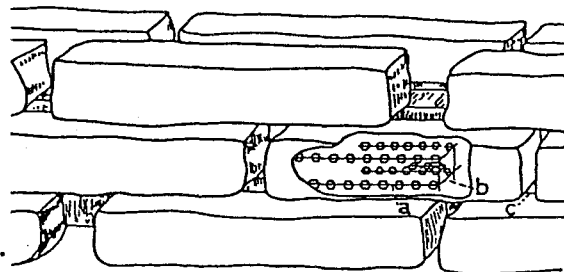


Fig.1 Micellar structure according to Meyer [2]

Department of Applied Chemistry

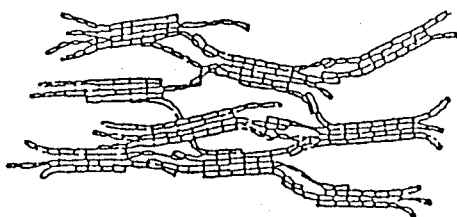


Fig.2 Fringed micellar model[4]

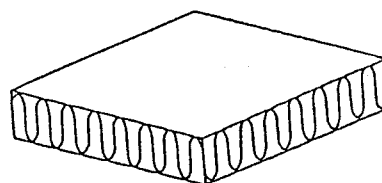


Fig.3 Chain folded lamella[5]

In recent years, rigid polymers have been successfully synthesized and used for achievement of high performance materials. Most of these polymers are crystallizable but can not fold. Wondering what kind of fine structure these rigid polymers can form makes us recall the "out-of-date" models mentioned above. The object of this study is to describe the morphology and structure formed in the crystallization of rigid polymers from dilute solution, an attempt is made to relate this structure to a possible mechanism of crystallization.

## EXPERIMENT

Poly(p-phenylene benzobisthiazole)(PBZT) was synthesized by polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride with terephthalic acid in poly(phosphoric acid) according to Wolfe[6]. The resultant polymer was rinsed with N,N-dimethylformamide(DMF). Intrinsic viscosity of the polymer was determined by extrapolation of  $(\eta_{rel} - 1) / C$  and  $\ln \eta_{rel} / C$  to zero concentration, using freshly distilled methanesulfonic acid. The molecular weight was evaluated by using of Berry's equation[7]:

$$[\eta] = 1.65 \times 10^{-7} M_w^{1.8}$$

PBZT was dissolved in conc.  $H_2SO_4$  at polymer concentration of 0.1wt% at ca.100 °C, then quenched to 0 °C or crystallized isothermally. Precipitates were washed with water until they were acid free.

TEM sample were prepared by depositing the precipitates suspension in water onto carbon grids and dried in air at room temperature. The TEM samples were Pt-Pd shadowed prior to investigation. For lattice imaging, specimens were mounted on gold-coated carbon grids. Lattice imaging was performed on a JEOL 2000EX operated at 200KV for axial bright field imaging with no objective aperture. The microscope direct magnification for lattice imaging was  $\times 100000$ .

## RESULT AND DISCUSSION

### Fibrillar Crystals (by Quenching)

On quenching dilute PBZT solution, the precipitates took the form of flat fibrils with several nm thick (Fig.4a). Electron diffraction(ED) showed that the molecular chains oriented parallel to the fibrils. Heat treatment of them in the solvent at a temperature several degrees below their dissolving

temperature changed the fibrils into "shish-kebabs"(Fig. 4b). It was supposed that "shish" was composed of longer chains and "kebab" of shorter chains with the chain ends being excluded onto the kebab surface for more stable state.

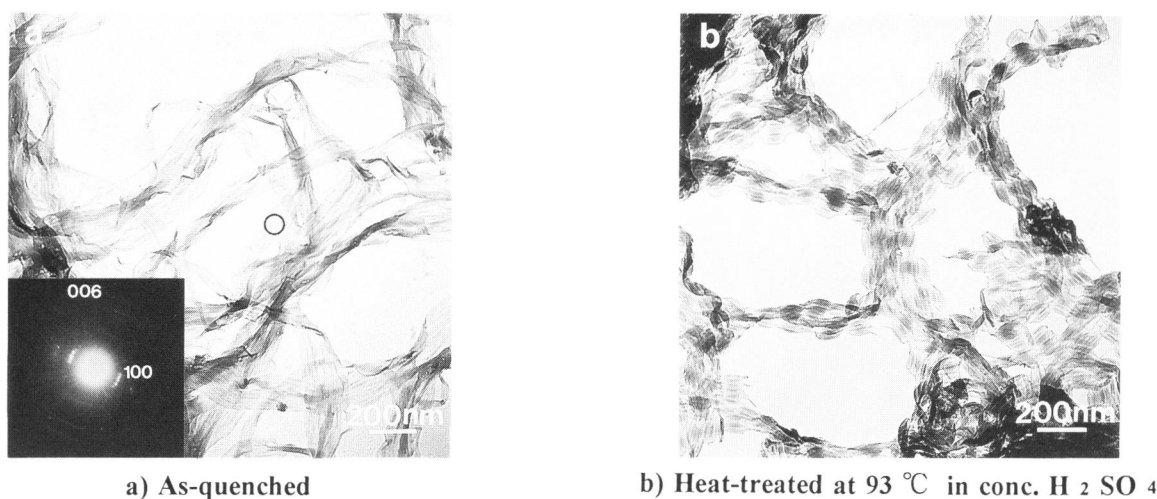


Fig.4 Fibrillar crystals of PBZT

#### Rod-Like Crystals (by Isothermal Crystallization)

Isothermal crystallization gave essentially rod-like crystals, a few to several tens of which got together to make a group. The morphology was dependent on the average molecular length ( $\ell$ ) as follows;

- $\ell < 50\text{nm}$ , a sheaf-like aggregate of the rod crystals,
- $\ell \sim 120\text{nm}$ , an aggregate of parallel rod crystals of same length looking like a log raft on a lake (Fig. 5),
- $\ell > 200\text{nm}$ , the rods became shorter and developed along the molecular chains(Fig.6). This morphology is similar to shish kebabs or the out-of-date structural model proposed earlier for geratine(Fig.2)[4].

ED showed that chains oriented normal to the rod (the crystalline *a*-axis was along the rod).

Meanwhile, width of the rod crystal ( $W$ ) increased with  $\ell$  (Fig.7); in the range of shorter molecular length ( $\ell < 70\text{nm}$ ),  $W$  was close to  $\ell$ , while with longer molecular length,  $W$  tended to saturate to a value much smaller than  $\ell$ . This means that longer molecular chains contributed to the formation of a few neighboring rod crystals linking them together.

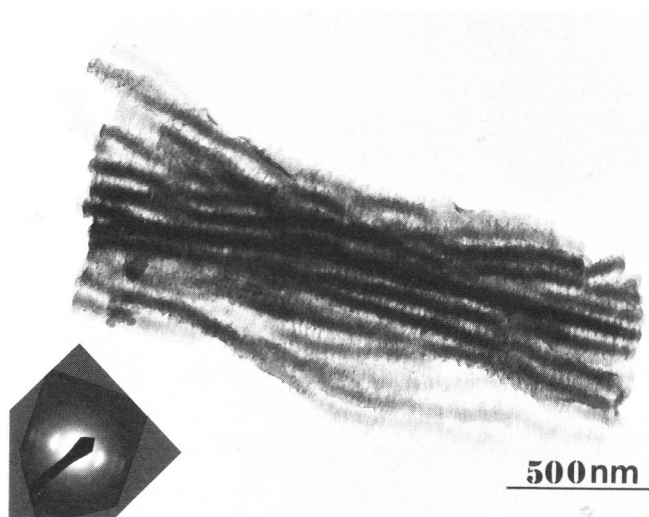


Fig.5 Isothermally crystallized PBZT ( $\ell = 120\text{nm}$ )



Fig.6 Isothermally crystallized PBZT(  $\ell = 200\text{nm}$  )

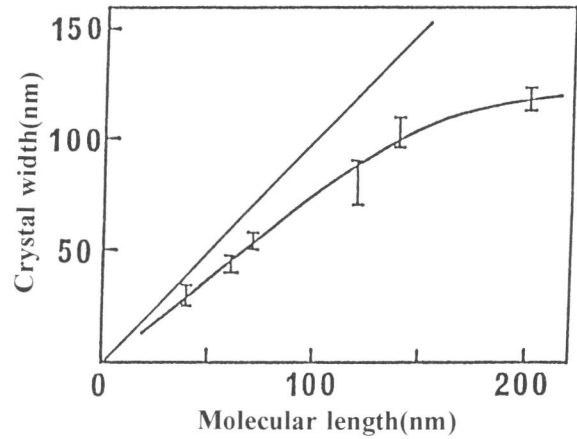


Fig.7 Dependence of rod-like crystal width on molecular length

#### Isothermal Crystallization Mechanism of PBZT ( $\ell \sim 120\text{nm}$ )

Electron microscopy of the isothermal crystallization process revealed the following facts:

- (1) a primary nucleus was composed of longer chains.
- (2) the growing rod crystal (mother crystal) was always accompanied by several fragmental crystallites (daughter crystals) on their sides.
- (3) fibrils started to grow normal to the rod crystal, implying that rigid cilia extended from the rod crystal like a centipede.
- (4) within one aggregate(raft) all rods were of same length and parallel.

Based on these observations, crystallization mechanism is illustrated (Fig. 8). For mother crystal

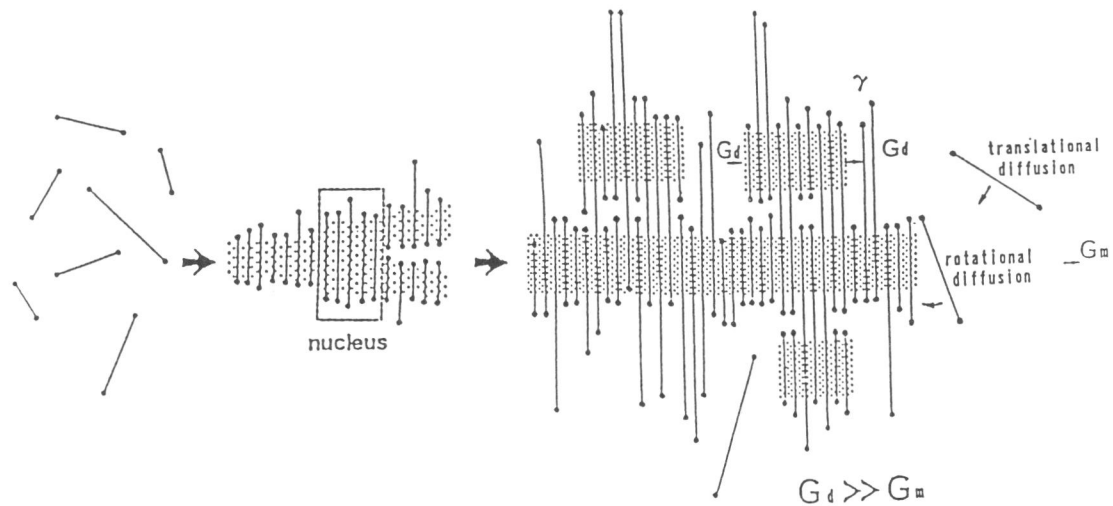


Fig.8 Isothermal crystallization mechanism of rigid polymer from dilute solution

growth, all necessary molecular chains must be transported and oriented suitably to the growing front from solution by translational and rotational diffusions respectively. But for daughter crystals, required molecular chains have already partially supplied with the cilia which came out of the margin of mother crystals satisfying their orientation. Therefore, daughter crystals grew much faster than their mothers and finally caught up with the mothers resulting in same length of all rod crystals in one group.

Length of growing rod crystals ( $L$ ) increased linearly with time ( $t$ ) at early stage of crystallization. From the gradient of the  $L - t$  lines, their growth rate ( $G_m$ ) was obtained.  $G_m$  decreased by increasing  $l$ . Logarithmic  $G_m$  vs. inverse of degree of super cooling gave a straight line (Fig. 9), suggesting that this growth was mainly controlled by nucleation process of the two dimensional nucleus[8]. From Fig.7, it is found that the ratio of the two growth rates of two polymers with different molecular lengths ( $G_{39nm} / G_{61nm}$ ) is about 3.5 at  $\Delta T^{-1} = 0.037K^{-1}$ . Doi showed that translational and rotational diffusion constants of a rigid chain are approximately inversely proportional to  $l^1$  and  $l^3$  respectively[9]. As  $(l_{61nm} / l_{39nm})^3$  is close to 3.5, it was concluded that this crystallization process is mainly controlled by rotational diffusion.

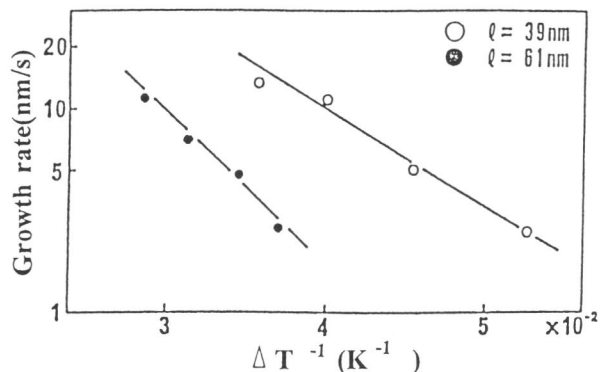
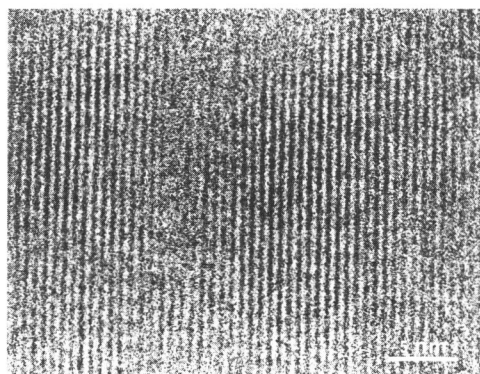


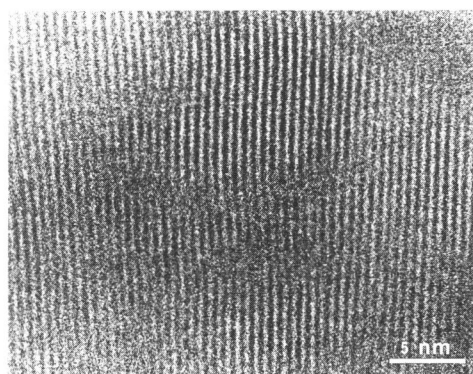
Fig.9 Dependence of growth rate ( $G_m$ ) on degree of supercooling

### Reorganization of Rigid Polymer Crystals (by Annealing)

Fig. 10a shows the lattice image of isothermally as-crystallized rod-like crystal. The 100 fringes (0.59nm) approximately  $33 \times 25 \text{ nm}$  in size are seen over the image but no 001 fringes (fiber period of 1.2nm) can be observed, i.e., the crystalline defect of "axial shift"[10] could not be removed even by such slow crystallization. The 100 fringes observed in a wide range are relatively well orientated within an angle of  $2-3^\circ$ . From chain rigidity and wide distribution of molecular length, it is plausible that the molecular ends are included in the crystal lattice as defects.



a) As-crystallized



b) Heat treated at  $450^\circ \text{C}$

Fig.10 Lattice images of PBZT rod-like crystal

Heat treatment at 450 °C in vacuum made the lattice fringes and non-lattice fringes more distinct (Fig.10b). It also gave rise to local lattice curvature and concomitant broadening of its orientation distribution. Close observation around some non-fringes revealed that either upper or lower crystalline part has an additional fringe, exhibiting existence of an edge dislocation. Around both sides of the edge dislocation, the lattice fringes changed their orientation. These phenomena can be understood by inclusion modes of chain ends as shown in Fig. 11. These inherent properties correspond to the fact that high modulus and high strength fiber is achieved only when as-spun fiber is heat treated under tension[11].

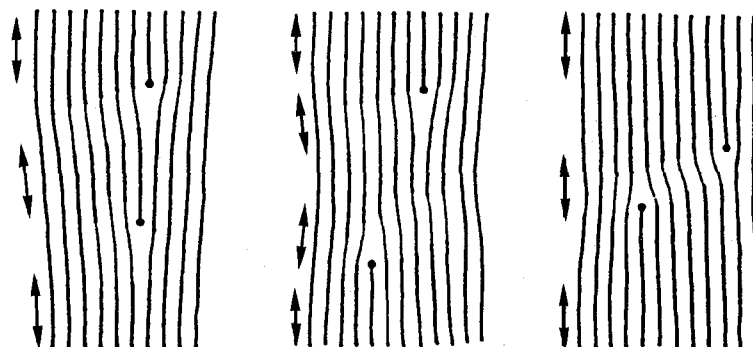


Fig.11 Disorientation of molecular chains within a rigid polymer crystallite due to inclusion of chain ends

## REFERENCES

- (1) S.Nishikawa, S.Ono: *Phys. Math. Soc. Japan*, **20**, Sept. (1913)
- (2) K.H.Meyer and H.Mark: *Ber. Deutsch. Chem. Ges.*, **61B** (1928), 593.
- (3) H.Staudinger: *Trans.Faraday Soc.*, **29** (1933), 18, 43, 234.
- (4) O.Gerngross, K.Herrmann, W.Abitz: *Biochem.Z.*, **228** (1930), 409.
- (5) A.Keller: *Phil.Mag.* **2** (1957), 1171.
- (6) J.F.Wolfe, B.H.Loo and F.E.Arnold: *Macromolecules*, **14** (1981), 915.
- (7) G.C.Berry, P.C.Metzger, S.Venkatraman and D.B.Cotts: *Polym. Prepr.*, **20**(1979), 42.
- (8) V.S.Papkov, V.S.Svistunov, Yu.K.Godovsky, A.A.Zhdanov: *J. Polym. Sci.*, **25**(1987), 1859.
- (9) M.Doï, S.F.Edwards: "The theory of Polymer Dynamics", Oxford University Press Inc., New York, (1986), Chap.8
- (10) K.Shimamura, J.Minter, E.L.Thomas: *J. Matr. Sci., Lett.*, **2**(1983), 54.
- (11) S.R.Allen, A.G.Filippov, R.J.Farris, E.L.Thomas: *J. Appl. Polym. Sci.*, **26**(1978), 291.