sensitive to the details of the particle structure. The cylindrical rigid-rod model obviously needed to be refined if one realized that the particles were aggregated from a bunch of rodlike molecules. A fully straightened P4BCMU molecule would have an average length of 2.2 μm and a thickness of 4 nm,[4] while the narrowly distributed aggregates had an average length of ~0.9 μm with an aggregation number of 14. Thus, it would not be unreasonable to propose a model in which the aggregate particle consisted of a bunch of thin rods parallel to each other. The effective thickness d of each individual rod would be bigger than the 4-nm side length since each individual rod was not fully straightened, but the rod in the same aggregate would be taken as all the same for simplicity. The average length of the aggregates was obtained by using the average translational diffusion coefficient from the CONTIN result, the rotational diffusion coefficient from transient electric birefringence (TEB), and the radius of gyration from static light-scattering measurements [4].

The form factor for such a parallel-rod model could be constructed according to Oster and Riley.[10] By analogy with the scattering from polyatomic gases,[11] the form factor (P) of a bundle of similar molecules, each of the form factor S, would be S times the double summation of the intermolecular interference. In the case of n rods, where the centers of the ith and jth rods are at a distance r_{ij} apart

$$P = \frac{S}{n^2}\sum_i^n\sum_j^n \exp(iqr_{ij}\cos\alpha) \qquad (2)$$

with

$$S = \int_0^{\pi/2} \frac{\pi}{2\nu\cos\beta}\left[J_{1/2}(\nu\cos\beta)\frac{2J_1(\mu\sin\beta)}{\mu\sin\beta}\right]^2 \sin\beta\,d\beta \qquad (3)$$

In eq 3, ν $(=ql/2)$ and μ $(=qd/2)$ are functions of the length l and the diameter d of each rod. If all rotational orientations about an axis parallel to the lengths of the cylinders are equally probable, each term is integrated between the limits of 0 and 2π for α, we then obtain:

$$P = \frac{S}{n^2}\sum_i^n\sum_j^n J_0(qr_{ij}) \qquad (4)$$

In eq 2–4, J_i stands for the ith-order Bessel function. To take into account of the fact that the P4BCMU molecules are not fully straightened and that the molecules are not in close contact owing to interparticle repulsion or hydration, we used $r_{ij} = \gamma d$, with γ being a "swelling" parameter.

In the process of connecting the experimental data with model computations, the scaling constants (A; eq 1) for LS and SAXS were floated in order to yield the best fitting. In a log-scaled plot such an adjustment is related to a vertical shift without changing the shape of the scattering curve. By using different geometrical arrangement of 14 parallel rods, in which the longer cross-section dimension was restricted to ~0.1 μm, (i.e., the D dimension), we found that, in the small q range, all the computed scattered intensity for rod-shaped particles can be made to agree with the experimental data. However, over the entire q range, i.e., by combining LS data with SAXS data, only an arrangement of 1 row × 14 columns could yield the best fitting, i.e., the particle configuration is ribbonlike as shown by the solid line in Figure 1. A further more detailed scattering curve covering a broader q range in order to confirm the ribbonlike structure of P4BCMU is under way. If the 14 parallel rods were arranged in a condensed contact style, the simulated intensity curve would be similar to the one from a single thick rod (Figure 1, dotted line).

In summary, by combining SAXS with LS, the rigid-rod model for P4BCMU aggregates in dilute toluene solution is refined. The P4BCMU molecules in dilute toluene solution form ribbonlike aggregates.

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Registry No. P4BCMU (homopolymer), 68777-93-5; P4BCMU (SRU), 76135-61-0.

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Studies on the Post-Polymerization of a Liquid-Crystal Polymer with X-Shaped Mesogens

Introduction. An interesting phenomenon was observed in our laboratory during the study of liquid-crystal polymers with X-shaped mesogens: if the sample is annealed for some time at a temperature somewhat higher than its isotropization temperature, the isotropic melt of the sample will become birefringent again. In this article we describe the study of this phenomenon.

The Polymer. The synthesis of liquid-crystal polymers with X-shaped mesogens was first reported by Ringsdorf and co-workers.[1] In this study the polymer has a structure as shown in Figure 1, which was synthesized by solution polycondensation using the diacid dichloride 1,4-bis[[[4-(chloroformyl)phenyl]oxy]carbonyl]butane (I) and the hydroquinone 2,5-bis[(4-ethoxybenzoyl)oxy]hydroquinone (II) as the monomers. The synthesis of the monomers and the polymers was discussed elsewhere.[2]

The polymer is a white powder but soluble in THF. The molecular weights of the samples were determined by a Waters 201 GPC instrument using THF as the solvent and polystyrene as the calibration standard. The liquid-crystal properties of the polymer samples were measured by a Perkin-Elmer DSC-4 with a heating rate of 20 °C/min and by a polarizing microscope with a Leitz 350 heating stage.

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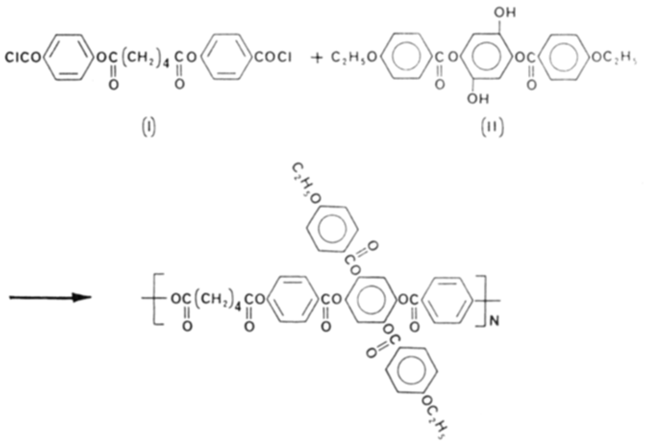

Figure 1. Synthesis of a liquid-crystal polymer with X-shaped mesogens.

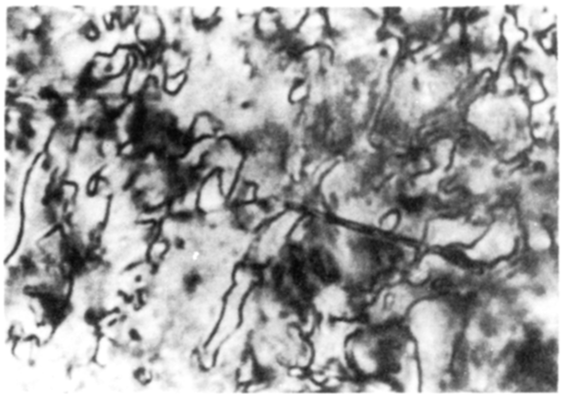

Figure 2. Photomicrograph of the liquid-crystal state of the original sample 2, taken at 215 °C.

Table I[a]

sample	M_n	M_w	M_w/M_n	T_m, °C	T_i, °C
1	4200	5100	1.21	130–165 (156)	218–230 (225)
2	6000	9900	1.65	175–215 (199)	225–245 (235)

[a] Data in parentheses are the peak values.

Figure 2 is a photomicrograph showing a nematic texture of the sample 2 (Table I). The characterization results for the two samples 1 and 2 from two batches of polymerization are shown in Table I.

During the microscopic observation we found the following phenomenon: if the sample is slowly heated to a temperature somewhat above the clearing point determined by DSC, say slowly from room temperature to 245 °C, no clear "clearing" point can be obtained for samples 1 and 2, of which the molecular weights are relatively low. Instead, only local isotropization is observed when the temperature reaches the DSC clearing point; that is, both isotropic and anisotropic phases are observed on the microscope. Moreover, if the sample is kept at the temperature for a few more minutes, the isotropic phase will become birefringent again. This experiment suggests that the local isotropization is a true phase transition of the sample. In another experiment the sample was put on the heating stage, which had already been heated to and kept at, e.g., 245 °C, which is a littler higher than the DSC clearing point of the original sample. The sample melted immediately and became highly birefringent. The birefringence, however, was very short-lived, and a complete isotropization of the sample was soon observed. After a few minutes on the stage the isotropic melt became birefringent again. This and other experiments carried out at varied temperatures suggested that, on the one hand, the liquid-crystal phase of the polymer has a true clearing point as measured by DSC, but, on the other hand, upon annealing on the stage the isotropic melt will become anisotropic again. In order to study the origin of this phenomenon of recurrence of the birefringence, annealing experiments were carried out for sample 2 of the polymer.

Table II[a]

time of anneal, min	M_n	M_w	M_w/M_n	T_m, °C	T_i, °C
0	6 000	9 900	1.65	175–215 (199)	225–245 (235)
30	9 200	16 000	1.74	155–220 (196)	245–275 (256)
90	11 000	20 000	1.82	145–220 (204)	250–275 (262)
150	13 000	25 000	1.92	170–225 (196)	250–288 (273)

[a] Data in parentheses are peak values.

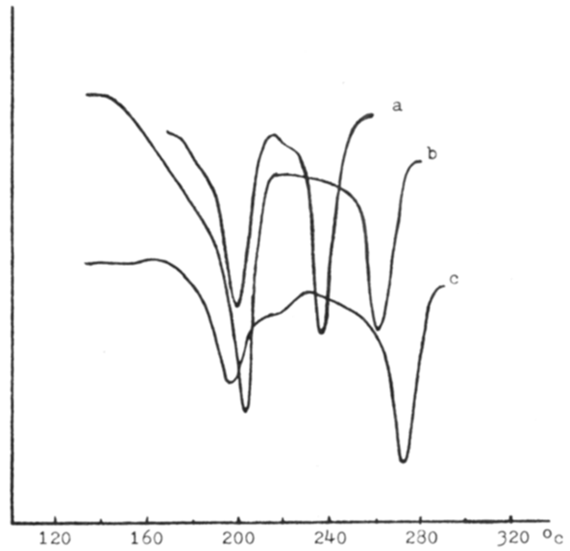

Figure 3. DSC thermograms of the polymer: (a) the original sample 2; (b) sample 2 annealed for 90 min; (c) the sample annealed for 150 min.

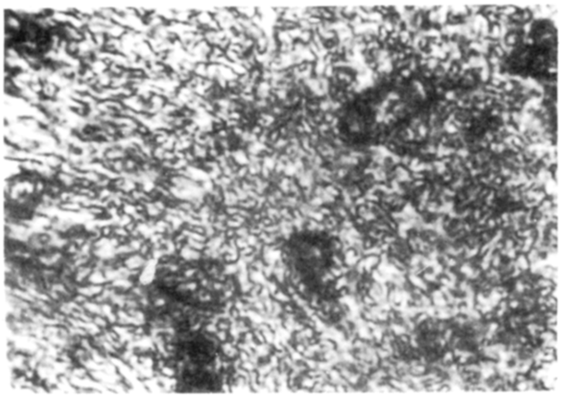

Figure 4. Photomicroscope of sample 2 annealed for 90 min, taken at 220 °C.

Annealing of the Polymer. The sample 2 with a M_n of 6000 and a M_w of 9900 was annealed in vacuo at 200 °C. (This polymer is thermally stable below 300 °C as tested by a TGA.) After a certain period of annealing time, the sample was cooled to room temperature and dissolved in THF. The polymer was then precipitated by methanol. The precipitate was collected by filtration, washed with methanol, and dried in vacuo at 80 °C for 48 h. Samples thus obtained were examined by GPC, DSC, and a polarizing microscope. All of the annealed samples are soluble in THF. The results are shown in Table II and in Figures 3 and 4. Figure 4 is a photomicrograph taken at 220 °C for the sample having been annealed for 90 min.

As shown in Table II, the annealing of the sample in the selected condition is actually a process of further polymerization. The molecular weight of the sample increases continuously during the time, and the molecular weight distribution is approaching the theoretical value $M_w/M_n = 2$ at 100% extent of reaction.

The melting point of this polymer increases with molecular weight only when M_n is very low (Table I). It is 156 °C at $M_n = 4200$ and increases to about 200 °C when M_n is 6000. Further increase in molecular weight has little influence on the melting point of the polymer.

In contrast to the melting point, the clearing temperature of the polymer is affected to a higher extent by molecular weight (Figure 3 and Table II). An increase in the clearing temperature of 50 deg, from 225 °C for sample 1 with an M_n of 4200 to 273 °C for the sample with M_n of 13 000, was observed. It seems to us that the steady value of the clearing temperature of the polymer has not been reached after 150 min of annealing at the experimental condition.

The recurrence of birefringence of the isotropic melt of the polymer thus can be explained as a result of the increased clearing temperature, which is in turn a result of the increased molecular weight. A slower heating on the microscope means a longer annealing time. As a consequence portions of the polymer sample may have already reached a clearing point higher than the DSC value of the original sample before the latter is reached. The increasing clearing temperature during the slow observation will interfere with the observation of a clear clearing point. On the other hand, if the heating stage has been preheated to the clearing temperature before the sample is put on the stage, a complete isotropization of the melt could be observed because there would not be enough time for the polymer to grow to that of higher clearing temperature.

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Registry No. (I)(II) (copolymer), 122313-85-3; (I)(II) (SRU), 122313-86-4.

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Copolymerization of Styrene with Indene by the Ti(O^{i}Pr)$_4$–Methylaluminoxane Catalyst

Introduction. Since the discovery of Ishihara et al.[1] that syndiotactic polymerization of styrene takes place by using some titanium compounds combined with methylaluminoxane (MAO), much attention has been paid to developing more efficient catalysts as well as to clarifying the polymerization mechanism. Similar zirconium compounds were also found to catalyze the polymerization by Zambelli et al.[2,3] More recently, Ishihara et al.[4] found that the polymerization activity is markedly improved by using (η^5-C_5H_5)$TiCl_3$ as a transition-metal compound. Zambelli et al.[2,5] investigated the insertion mechanism of styrene into the living zirconium–carbon bonds by ^{13}C NMR and found that 2,1-addition proceeds in this polymerization.

On the other hand, we estimated the monomer reactivity ratios of substituted styrenes from the copolymerization between styrene and substituted styrenes with the Ti(OMen)$_4$–MAO catalyst and obtained a negative value (−1.17) of ρ in the Hammett equation.[6] Besides, the copolymerization of styrene and α-olefins with the same catalyst did not give any corresponding copolymers.[6] These results might suggest that syndiotactic polymerization of styrene does not proceed via a coordinated-anionic mechanism but via a coordinated-cationic mechanism.

From such a viewpoint, we have carried out the copolymerization of styrene and indene, which is known to polymerize via a cationic mechanism,[7–12] with the catalyst system of Ti(O^{i}Pr)$_4$–MAO.

Experimental Section. Materials. Styrene (Kanto Chemical Co., Inc.) and indene (Wako Pure Chemical Industries, Ltd.) were washed with aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. Toluene used as solvent was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. Ti(O^{i}Pr)$_4$ (Tokyo Kasei Kogyo Co., Ltd.) was purified by distillation under reduced pressure. $AlMe_3$(TMA) and $CuSO_4 \cdot 5H_2O$ were commercially obtained and used without further purification. Methylaluminoxane (MAO) was prepared from TMA and $CuSO_4 \cdot 5H_2O$ according to the literature[13] and reserved as stock solution in toluene, 0.40 mmol/dm^3. Nitrogen of 99.9989% purity was used after passing through the column of 3A molecular sieve.

Polymerization and Analytical Procedures. Polymerizations were carried out in a 100-cm^3 glass reactor equipped with a magnetic stirrer. Polymereization was stopped by adding a mixture of hydrochloric acid and methanol, filtered, and dried under a reduced pressure at 60 °C. The structure and composition of the polymer were determined by ^{13}C NMR. The ^{13}C NMR spectrum of the polymer was measured at 25.1 MHz in chloroform-*d* at 60 °C with a JEOL FX-100 spectrometer. The chemical shifts were referred to HMDS added as an internal standard for $\delta = 2.0$. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Model DSC 7 at a heating rate of 10 °C/min. Gel permeation chromatograms of the polymers were obtained by Waters Model 150 GPC using standard polystyrene as reference and 1,2,4-trichlorobenzene as eluent at 140 °C.

Results and Discussion. Homopolymerizations of indene and styrene were first carried out at 60 °C with the Ti(O^{i}Pr)$_4$–MAO catalyst, the results of which are shown in Table I together with T_g's of the polymers.

Copolymerization of styrene and indene was then conducted under similar conditions. In Figure 1 are illustrated the ^{13}C NMR spectra of syndiotactic polystyrene (a), polyindene (b), and the copolymer (c). The spectrum of (c) shows a peak attributed to the methine carbon of the styrene unit near 40.8 ppm. In addition, broadening of the peak is observed in the methine and methylene region, indicating that the polymer is not a mixture of polystyrene and polyindene but a copolymer between them. The

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