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Pressure-Induced Crystal Polymorph of Thermotropic Polyesters Composed of *p,p′*-Bibenzoic Acid and Penta- and Hexamethylene Diols

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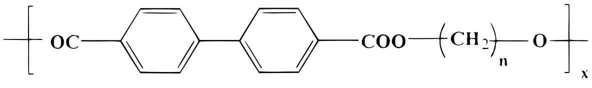
Study on pressure-induced polymorph and liquid crystallinity of main-chain thermotropic polyesters has been performed by several groups since 1970s. Hsiao, Shaw, and Samulski[1,2] reported two interesting pressure effects, a pressure-induced crystal habit and a pressure-induced mesophase, of the aromatic copolyester, HIQ-20, composed of 20% hydroxybenzoic acid, 40% isophthalic acid, and 40% hydroquinone. Maeda and Blumstein[3] reported the pressure-induced crystal polymorph of poly(4,4′-dioxy-2,2′-dimethylazoxybenzene dodecanedioyl), labeled as DDA-9, which was crystallized under hydrostatic pressure above about 50 MPa. Maeda and Watanabe[4,5] reported the pressure-induced mesomorphism of (4,4′-dihydroxybiphenylyl)tetradecane dioic acid polyester, labeled as PB-12. The smectic H phase of the PB-12 polyester at atmospheric pressure is transformed irreversibly to the smectic B(S_B) phase at about 100−120 MPa on a quasi-isothermal process and also the crystal−S_B−isotropic liquid transition process is observed reversibly under pressures above 100−120 MPa.

In the last 20 years, poly(alkylene 4,4′-biphenyldicarboxylate) (BB-*n*, *n* is the number of methylene units in the flexible spacer) and its analogues have been investigated for their scientific interest[6−13] and their application as high strength materials.[14] The BB-*n* polyesters have the chemical structure of an alternative arrangement of the *p,p′*-bibenzoate as a mesogenic group and the alkanediols as a flexible spacer, which they have a slightly different chemical structure from the PB-*n* polyesters.



BB-n

Krigbaum et al.[8] reported that there are three crystal modifications when the BB-6 sample is crystallized by cooling and annealing under atmospheric pressure. The α form is formed by slow cooling from 190 °C. The γ form is formed on rapid quenching in ice water from the S_A phase at 190 °C, and the β form is formed on annealing the γ form at 190 °C for 30 min. Li and Brisse[15] determined these crystal structures of the BB-6 polyester to be monoclinic systems, respectively. Watanabe and Hayashi[11,12] elucidated the smectic structures of the BB-5 and BB-6 polyesters by X-ray diffraction analysis and optical microscope observation. They deduced that the mesogenic groups in the BB-5 polyester are tilted with an angle of about 25 degree to the layer normal, but unlike the normal smectic C(S_C) phase, the tilt direction is opposite in adjacent layers. They called the novel type of smectic C phase as smectic CA(S_{CA}). On the other hand, the BB-6 polyester takes a typical smectic A(S_A) structure in which the mesogenic groups are arranged parallel to the polymer chain and both lie perpendicular to the smectic layers. The knowledge on the structure of the crystal and smectic phases of the BB-*n* polyesters stimulates us to investigate how the crystal and smectic structures are transformed under hydrostatic pressure. The research on the phase transition of liquid crystalline polyesters under high pressure not only is interesting from the scientific point of view but also is very important for the basic technology of polymer processing. In this study we investigated the effect of pressure on the structural behavior of the BB-5 and BB-6 polyesters by wide-angle X-ray diffraction. We present here the preliminary results of the structural behavior of the two polyesters and a new finding of another crystal polymorph of the BB-6 polyester under hydrostatic pressure above about 100 MPa.

The BB-5 and BB-6 polyesters were synthesized by melt transesterification from diethyl *p,p′*-bibenzoate and penta- or hexamethylene glycols with a small amount of titanium(IV) tetraisopropoxide as catalyst. The synthesis, characterization, and thermal properties of the polyesters are described elsewhere.[8] The inherent viscosities of the BB-5 and BB-6 polyesters were 1.09 and 0.92 dL/g, respectively, which were determined at 25 °C by using 0.50 g/dL solutions in a 60/40 (w/w) mixture of phenol and tetrachloroethane. The average molecular weight and molecular weight distribution (MWD) of the BB-6 polyesters were measured by using a size exclusion chromatograhy (Polymer Laboratories Mixed-C with a JASCO 830-RI detector).[16] The M_n and M_w/M_n ratio of the BB-6 sample used here were 3.23×10^4 (on the M_n scale of standard polystyrenes) and 2.30, while data for the BB-5 sample were not obtained. The wide-angle X-ray diffraction (WAXD) apparatus used here is equipped with a high-pressure sample vessel on a goniometer. The high-pressure vessel is connected to a Manganin gauge for pressure monitoring and manually operated pump capable of pressurizing up to 500 MPa.[17,18] The sample is kept in a beryllium spindle with a vertical hole of 1 mm in diameter. Hydrostatic pressure of low-viscosity silicone oil (10 cSt) is applied directly to the sample in the vertical hole of the beryllium spindle. The camera length between specimen and counter is 200 mm. Diffraction pattern by using a Ni-filtered Cu Kα X-rays is detected successively in a period of 200 s by a curved position sensitive proportional counter (Rigaku, PSPC-30) with an equatorial window of $2\theta = 28°$. The X-ray measurements were performed on heating or cooling at each hydrostatic pressure.

Figure 1 shows the DSC cooling and subsequent heating curves of the BB-5 and BB-6 polyesters measured at a scanning rate of 10 °C/min. Before the DSC measurements, each sample was held in the isotropic liquid state at high temperatures. Then the sample was

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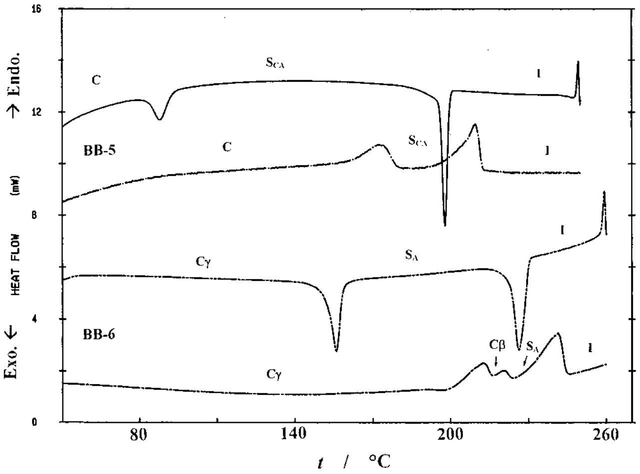

Figure 1. DSC cooling and subsequent heating curves of the BB-5 and BB-6 polyesters. Scanning rate: 10 °C/min.

cooled at 10 °C/min to room temperature and then reheated at 10 °C/min to the isotropic state. These DSC curves are in good correspondence with the data reported by Watanabe et al.[11] It is known that the BB-*n* ($n = 3-9$) polyesters form smectic mesophases whose isotropization temperature, T_i, and isotropization entropies, ΔS_i, exhibit a typical odd–even oscillation[11,13] with the number of intervening methylene units, n, which is generally observed for the nematic mesophase. The BB-5 polyester exhibits the enantiotropic transitions of crystal (C)–S_{CA}– isotropic liquid (I) process, while BB-6 shows the C_γ–C_β–S_A–I transition process on heating of the rapidly cooled sample. As both samples showed the same DSC curves on recycled process, they seem to show no degradation of the samples affecting the lowering of average molecular weight.

Parts a and b of Figure 2 show the WAXD patterns of the crystal and smectic phases of the BB-5 and BB-6 samples under atmospheric pressure, respectively. The BB-5 crystal at 25 °C shows a low-angle reflection at $2\theta = 6.01°$ ($d = 14.68$ Å), an intermediate reflection at $2\theta = 12.08°$ (7.32 Å), and several strong wide-angle reflections at $2\theta = 18.68°$ (4.74 Å), 21.76° (4.08 Å), 23.13° (3.84 Å), and 26.01° (3.42 Å). The diffraction experiments of the BB-5 polyester at 100 and 200 MPa exhibited the same change in X-ray pattern as those at atmospheric pressure. The BB-5 polyester shows the same C–S_{CA}–I phase transition process, independent of the applied pressure. On the other hand, the BB-6 polyester has a crystal structure of the γ form when it is cooled at 10 °C/min from the isotropic liquid. The γ form at 25 °C shows a sharp low-angle reflection at $2\theta = 4.89°$ ($d = 18.05$ Å), intermediate reflections at $2\theta = 12.08°$ (8.56 Å) and 14.08° (6.28 Å), and several wide-angle reflections at $2\theta = 20.24°$ (4.38 Å), 21.91° (4.05 Å), 22.84° (3.89 Å), 24.16° (3.68 Å), and 27.43° (3.24 Å). The X-ray pattern of the γ form is held at temperatures up to about 195 °C and then changes to a different pattern having more wide-angle reflections at $2\theta = 18.19°$ ($d = 4.87$ Å), 19.12° (4.63 Å), 20.05° (4.42 Å), 23.03° (3.86 Å), and 24.30° (3.66 Å), indicating the existence of a crystal transition. The observation in this study agrees well with the X-ray photographic data of Krigbaum and Watanabe reported previously.[8] They designated the crystal modification as the β form. The β form is stable in a temperature region between 195 and 210 °C until it transforms into the S_A phase. So the rapidly cooled sample shows the phase transition of $C\gamma$–195 °C–C_β–210 °C–S_A–232 °C–I. Since the transition behavior is observed repeatedly on the recycled process, it is a genuine phase transition. The S_A phase shows a sharp reflection at $2\theta = 4.89°$ ($d = 18.05$ Å) and a diffuse halo at wide angles ($2\theta \cong 20°$). The low-angle reflection indicates the layer spacing of the S_A phase in the molecular chain direction, under which the smectic layer spacing is slightly smaller than the fully extended length of the repeating unit.[11] It is interesting to note that the *d* spacing of the low-angle reflection is held constant during the $C\gamma$–$C\beta$–S_A transition process.

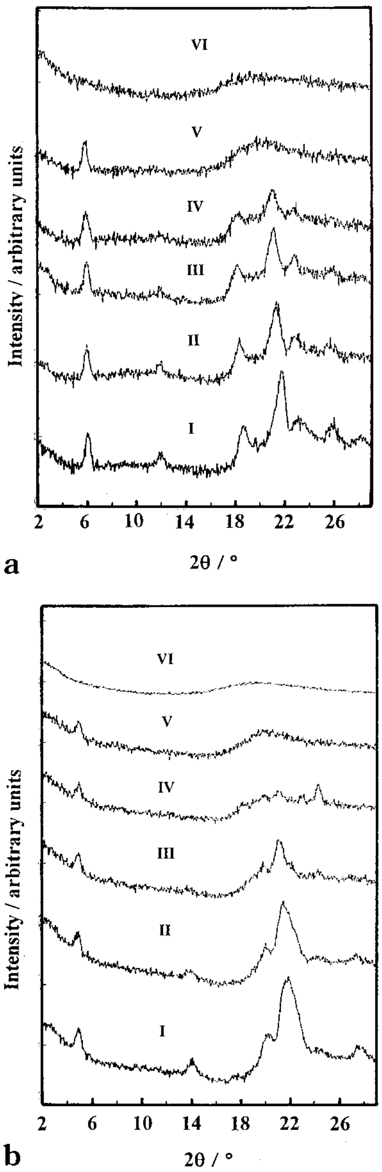

Figure 2. (a) WAXD patterns of the BB-5 polyester observed on heating at atmospheric pressure: I–IV, crystal at 25, 124, 165, and 180 °C; V, S_{CA} phase at 190 °C; VI, isotropic liquid at 208 °C. Heating rate: 1–2 °C/min. (b) WAXD patterns of the BB-6 polyester observed on heating at atmospheric pressure: I–III, γ form at 30, 100, and 186 °C; IV, β form at 202 °C; V, S_A phase at 211 °C; VI, isotropic liquid at 235 °C. Heating rate: 1–2 °C/min.

Figure 3 shows the X-ray patterns of the γ form on heating at 1–2 °C/mn under high pressure of 150 MPa. The sample was formed by cooling at 10 °C/min from the isotropic liquid under atmospheric pressure. One can see in parts IV and V of Figure 3 that the low-angle

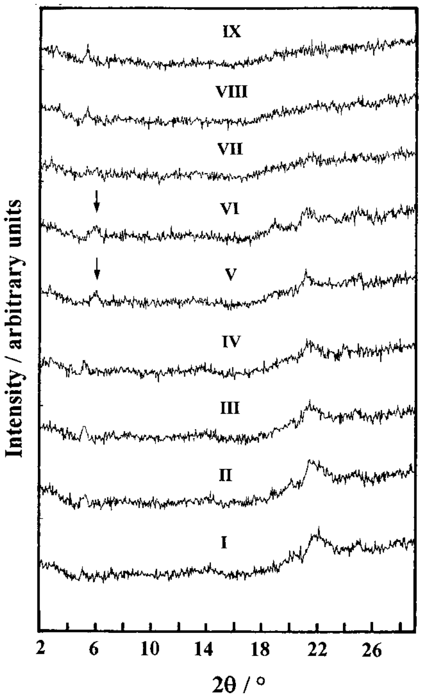

Figure 3. WAXD patterns of the BB-6 polyester on heating at 150 MPa: I−IV, γ form at 22, 110, 200, and 220 °C; V−VII, δ form at 230, 240, and 265 °C; VIII−IX, S_A phase at 270 and 275 °C. Heating rate: 1−2 °C/min. An arrow shows the low-angle reflection of the δ form which was transformed from the γ form on heating at 150 MPa.

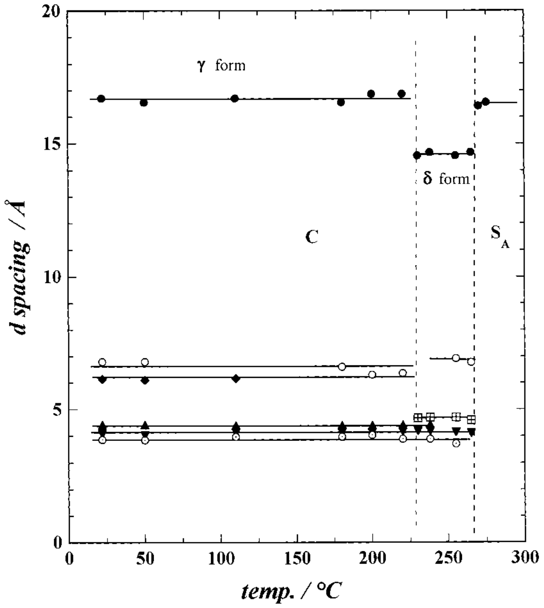

Figure 4. Temperature dependence of the d spacing of the reflections of the γ and δ forms, and the S_A phase of the rapidly cooled sample (C_γ) of the BB-6 polyester at 150 MPa.

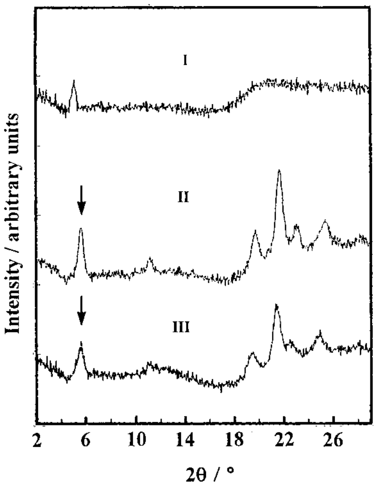

Figure 5. WAXD patterns of the BB-6 polyester on cooling from the S_A phase at 300 °C under pressure of 200 MPa. Cooling rate: 2−3 °C/min. Key: I, S_A phase at 300 °C; II, δ form at 80 °C; III, δ form at 60 °C and 0.1 MPa.

reflection shifts from $2\theta = 4.89°$ ($d = 18.05$ Å) to $2\theta = 5.67°$ ($d = 15.56$ Å) in the temperature region between 220 and 230 °C. The low-angle reflection at 230 and 240 °C is apparently due to another crystal polymorph, which is temporarily designated as the δ form. The crystal polymorph (C_δ) was held until the C_δ−S_A transition occurred at about 267 °C. So the transition behavior at 150 MPa can be described as C_γ−228 °C−C_δ−267 °C−S_A−302 °C−I. It was found that the C_γ−C_δ transition occurs at about 230 °C under hydrostatic pressures between 100 and 200 MPa. Figure 4 shows the temperature dependence of the d spacing of the reflections of the γ-form crystal of the BB-6 polyester on heating at 150 MPa. One can recognize clearly the existence of the δ form in a temperature region between 228 and 267 °C at 150 MPa. We performed the X-ray measurements on cooling from the S_A or I phases at 200 MPa, to observe the crystallization behavior from the S_A or I phases under high pressure. Figure 5 illustrates the X-ray patterns of the BB-6 sample on cooling from the S_A phase at 300 °C and 200 MPa. The S_A phase at 300 °C shows the low-angle reflection at $2\theta = 5.08°$ ($d = 17.36$ Å) and a diffuse halo at wide angles. The d spacing of the S_A phase at 200 MPa is slightly shorter than the value at atmospheric pressure, suggesting the deformation of the S_A structure at such high pressure. The S_A phase is entirely transformed to the crystal of the δ form on cooling. The X-ray pattern (II in Figure 5) of the δ form at 80 °C consists of a low-angle reflection at $2\theta = 5.62°$ ($d = 15.70$ Å), an intermediate reflection at $2\theta = 11.15°$ ($d = 7.93$ Å), and several wide-angle reflections at $2\theta = 19.71°$ ($d = 4.50$ Å), 21.61° (4.11 Å), 23.03° (3.86 Å), and 25.33° (3.51 Å). The sample was cooled at 200 MPa, and then pressure was released to atmospheric pressure. The X-ray pattern (III in Figure 5) at 60 °C and atmospheric pressure shows the same pattern as one (II) at 200 MPa, indicating that the δ form exists as a metastable phase at atmospheric pressure. The X-ray pattern consists of a low-angle reflection at $2\theta = 5.62°$ ($d = 15.70$ Å), an intermediate-angle reflection at 11.15° ($d = 7.93$ Å), and four wide-angle reflections at 19.36° ($d = 4.58$ Å), 21.42° (4.14 Å), 22.79° (3.90 Å), and 24.98° (3.56 Å). It is noteworthy that the d spacing of the low-angle reflection of the δ form is shorter by about 2.3 Å than those of the γ and β forms formed at atmospheric pressure. This suggests that the δ form has a tilted structure such as the S_C and S_{CA} structures. In fact, the X-ray pattern of the δ form is closely similar to one of the BB-5 crystals in Figure 2a. Table 1 lists the data of d spacing calculated from the observed reflections of the crystalline β, γ, and δ forms and S_A phase as well as the crystal and S_{CA} phase of the BB-5 polyester. In conclusion, the BB-5 polyester shows the C−S_{CA}−I transition process under all pressures and the crystal structure is independent upon pressure. On the other hand, the rapidly cooled sample (C_γ) of the BB-6 polyester shows the C_γ−C_β−

Table 1. Bragg Spacing (Å) of the Crystals at 25 °C and Mesophase at High Temperatures of BB-5 and BB-6 Polyesters under Atmospheric Pressure

BB-5		BB-6			
C	S_{CA} phase	C_γ form[a]	C_β form[b]	C_δ form[c]	S_A phase
14.68 m	15.30 m	18.05 m	18.05 m	**15.70** m	18.05 m
7.32 w		8.56 w		**7.93** w	
		6.28 m	5.71 w		
			4.87 m		
4.74 s			4.63 m	**4.58** m	
		4.38 s	4.45 m		
			4.22 m	**4.14** s	
4.08 s		4.05 s			
3.84 m		3.89 s	3.86 m	**3.95** m	
		3.68 w	3.66 s	**3.57** m	
3.42 m			3.47 w		
3.16 w		3.24 m		**3.20** m	

[a] C_γ form was formed by cooling the sample from the isotropic state at 10 °C/min. [b] C_β form was formed by heating the sample of the $C\gamma$ form at high temperatures just below the $C-S_A$ transition point under atmospheric pressure. [c] C_δ form was formed by cooling slowly the sample from the S_A phase at 200 MPa.

S_A-I transition process under pressures up to 80−100 MPa. This means that the C_β form is thermodynamically stable under lower pressures including atmospheric pressure. Further increase of pressure on the rapidly cooled sample (C_γ) induces the predominant formation of another crystal modification (δ form) at high temperatures and the $C_\gamma-C\delta-S_A-I$ transition process is observed on heating under high pressures between 100 and 200 MPa. When the sample is cooled from the S_A or I phases at such high pressure, the δ form is formed predominantly. Since the $C_\delta-S_A-I$ transition process is observed reversibly under high pressure above about 100 MPa, it is concluded that the δ form of BB-6 polyester is a thermodynamically stable phase under high pressure. The δ form has a crystal structure with a fairly small axial length in the molecular chain direction, suggesting the tilted structure such as the S_C and S_{CA} phases. Further investigations on the structural and phase behavior between these crystals of the BB-6 polyester are under progress in our laboratory.

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