Macromolecules **2000,** *33,* 2456−2461

Phase Behavior of Crystal Polymorphs of Thermotropic Poly(hexamethylene 4,4′-biphenyldicarboxylate) under Hydrostatic Pressure

Yoji Maeda,*,[†] Kensuke Osada,[‡] and Junji Watanabe[‡]

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba,
Ibaraki 305-8565, Japan, and Department of Polymer Chemistry, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

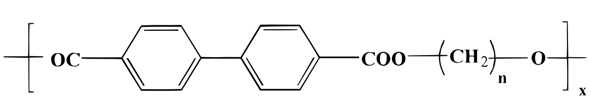
Received August 13, 1999; Revised Manuscript Received December 30, 1999

ABSTRACT: Structural phase behavior of a thermotropic polyester, poly(hexamethylene 4,4′-biphenyldicarboxylate), abbreviated as BB-6, was studied under hydrostatic pressures up to 200 MPa by wide-angle X-ray diffraction apparatus equipped with a high-pressure vessel. The Cα form of BB-6, cooled slowly from the melt under atmospheric pressure, is the most stable in the low-pressure region below 70 MPa, and this sample exhibits the reversible phase transition of $C\alpha \leftrightarrow S_A \leftrightarrow I$. An application of high pressure above about 100 MPa induces another crystal polymorph (Cδ) at high temperature: the $C\alpha \rightarrow C\delta \rightarrow S_A \rightarrow I$ transition process is observed on heating under high pressure. Since the $C\delta \leftrightarrow S_A \leftrightarrow I$ transition occurs reversibly at high pressure, the Cδ form can be regarded as the stable form in the high-pressure region. But this form becomes metastable in the low-pressure region because the $C\delta \rightarrow C\alpha \rightarrow S_A \rightarrow I$ transition is observed at pressures below 50 MPa. The shrinkage of the fiber repeat of the Cδ form by about 2 Å would suggest the conformational change from all-trans to an introduction of gauche (g+ or g−) conformation in the aliphatic sequence. Since the X-ray fiber photograph of the Cδ form shows intense fiber reflections along the direction tilted by 25° from the equatorial line, the molecular chains in the unit cell would be arranged in a herringbone pattern. The phase stability between the crystal modifications of BB-6 was analyzed as s function of temperature and pressure.

Introduction

In the past two decades, the 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[1−8] and their application as high strength materials.[9] The chemical structure of the BB-*n* polyesters is an alternative arrangement of the *p,p*′-bibenzoate as a mesogenic group and the alkanediols as a flexible spacer. These polyesters are slightly different from (4,4′-dihydroxybiphenylyl)alkanedioic acid polyester (PB-*n*) with 4,4′-dihydroxybiphenyl as mesogen and aliphatic dibasic acids as a flexible spacer.[10]

BB-n



Krigbaum et al.[3] found three crystal modifications of BB-6 when the sample is crystallized by cooling and annealing under atmospheric pressure. The α form (Cα) is obtained by slow cooling from the mesophase. The γ form (Cγ) develops on rapid quenching in ice water from the S_A phase, and the β form (Cβ) results when the γ form is annealed at 190 °C for 30 min. Li and Brisse[11] determined the structure of the three modifications of BB-6 polyester as monoclinic systems with different lattice constants and β angle, respectively. Watanabe and Hayashi[6,7] elucidated the smectic structures of the BB-5 and BB-6 polyesters by X-ray diffraction analysis and optical microscope observation. 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, while the BB-5 polyester takes a smectic CA (S_{CA}) phase in which the mesogenic groups are tilted with an angle of about 25° to the layer normal, but the tilt direction is opposite in adjacent layers.

Bae, Watanabe, and Maeda[12] found another crystal polymorph of the BB-6 polyester when the sample was cooled from the isotropic melt at 100 MPa. Study on the phase transition of liquid crystalline polyesters under hydrostatic pressure is very interesting from the scientific and engineering points of view. The knowledge of the structure of the crystal and smectic phases of the BB-5 and BB-6 polyesters gives us the idea to investigate the stability and phase transition behavior of the crystal modifications under high pressure. In this study, the phase changes of the Cα, Cγ, and Cδ forms of the BB-6 polyester were examined structurally under hydrostatic pressure up to 200 MPa. We present the experimental results of the structural phase behavior of the crystalline polymorphs of the BB-6 polyester under high pressure and the *T* vs *P* phase diagrams of these crystal modifications.

Experimental Section

The BB-6 polyester was synthesized by melt transesterification from diethyl *p,p*′-bibenzoate and hexamethylene glycols with a small amount of titanium(IV) tetraisopropoxide as catalyst. The synthesis, characterization, and thermal properties of the polyester are described elsewhere.[3] The inherent viscosity of the BB-6 polyester was 0.92 dL/g, 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

---

[†] National Institute of Materials and Chemical Research.
[‡] Tokyo Institute of Technology.
* To whom correspondence should be addressed.

10.1021/ma991385c CCC: $19.00

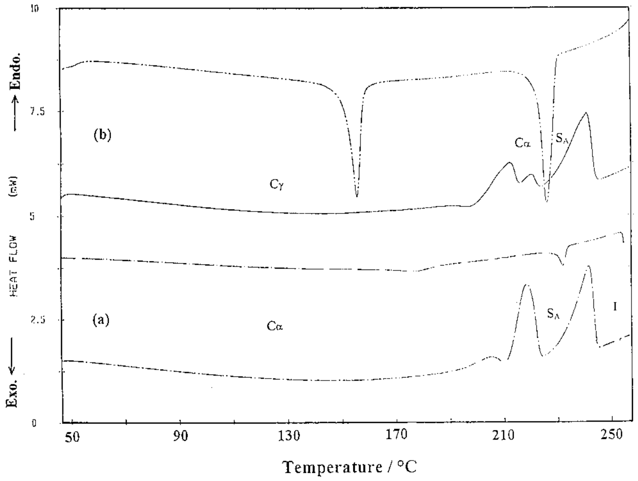


Figure 1. DSC curves of the BB-6 polyester: (a) cooling at 1 °C/min and subsequent heating at 10 °C/min; (b) cooling and subsequent heating at 10 °C/min.

and molecular weight distribution (MWD) of the BB-6 sample were measured by using a size exclusion chromatograh (Polymer Laboratories Mixed-C with a JASCO 830-RI detector) in a 25/75 (v/v) mixture of pentafluorophenol and chloroform at 50 °C on the basis of calibration of standard polystyrene.[13] 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) and 2.30, while the data of the BB-5 sample were not obtained. The Cα and Cγ forms were prepared by cooling at 1 and 10 °C/min from the isotropic melt under atmospheric pressure, respectively. The Cδ form was prepared by cooling slowly the BB-6 sample from the S_A phase at 200 MPa.

The X-ray fiber patterns of the BB-5 and BB-6 polyesters were taken at room temperature under atmospheric pressure by wide-angle X-ray diffraction (Rigaku, RU200 BH) and imaging plate technique. The drawn fibers were prepared by picking up the threads from the molten samples and then were cooled to room temperature.

The wide-angle X-ray diffraction (WAXD) apparatus equipped with a high-pressure sample vessel on the goniometer is described elsewhere.[14,15] The high-pressure vessel is connected through a high-pressure pipe to a Manganin gauge for pressure monitoring, and to a manually operated pump capable of pressurizing up to 500 MPa. The sample is kept in a beryllium spindle with an inner vertical hole of 1 mm in diameter. Hydrostatic pressure of low-viscosity silicone oil (10 cSt) is applied directly to the sample in the beryllium spindle. The incident beam of Ni-filtered Cu Kα X-rays impinges on the sample through the beryllium spindle. The diffracted X-ray beam is detected by a curved position-sensitive proportional counter (Rigaku Corp., PSPC-30) with an equatorial window of $2\theta = 28°$. The camera length, between specimen and PSPC counter, is 200 mm, and the sampling time for each measurement is 200 s. The X-ray measurements were performed on heating or cooling under hydrostatic pressure.

The densities of the Cα, Cγ, and pressure-crystallized Cδ forms of BB-6 were measured in a density-gradient column of water and NaBr saturated aqueous solution at 25 °C. Also, the density of the BB-5 crystal cooled at 5 °C/min under atmospheric pressure was measured for comparison. The density-gradient column covered a density range of 1.24−1.33 g/cm^3.

Results and Discussion

Figure 1a shows the DSC curves of the BB-6 polyester on slow cooling(1 °C/min) and subsequent heating(10 °C/min), indicating the reversible phase transitions of Cα $\leftrightarrow$ S_A $\leftrightarrow$ I. Li and Brisse[11] identified structurally that the slowly cooled fiber is the pure Cα form, while the quenched fiber is mostly composed of the Cγ and Cβ forms. According to their identification, the DSC curves at a constant scanning rate of 10 °C/min in Figure 1b show two exothermic peaks of the I → S_A and S_A → (Cγ + Cβ) transitions on cooling and triple endothermic peaks of the Cα → Cβ, Cβ → Cγ, and Cγ → S_A transitions and finally the S_A → I transition. But in this study the major two peaks of the triple endothermic peaks can be interpreted as the Cγ → Cα and Cα → S_A transitions with no identification of the Cβ transition. The thermal characterization was confirmed by the X-ray experimental results. In this study the Cα form is the most stable at atmospheric pressure, while the Cγ form is metastable. The WAXD measurements in this study detected only the Cα and Cγ forms by cooling slowly and rapidly, respectively. The Cβ form could not be seen clearly on slow heating and cooling modes. Further, the X-ray pattern of the sample prepared by annealing the Cγ form at high temperature was substantially the same as that of the Cα form.

Effect of Pressure on the Behavior of the Cα Form. The density of the slowly cooled sample (Cα form) was 1.264_6 g/cm^3 at 25 °C. The WAXD pattern of the Cα form of BB-6 at room temperature under atmospheric pressure exhibits multiple crystal reflections on the equatorial line. The d values in this study are larger than the published data,[12] which were incorrectly estimated by the wrong conversion coefficient of the channel-2θ equation. The X-ray pattern of the Cα form does not change until the Cα−S_A transition occurs at about 217 °C. The S_A phase shows clearly a low-angle reflection at $2\theta = 4.52°$ (19.52 Å) with a broad peak at wide angles. The d spacing is corresponded well with the fiber repeat (19.45 Å) of the α-form reported by Li and Brisse.[11] This suggests the fully extended conformation of the BB-6 molecule in the repeating unit, which the aliphatic sequence of BB-6 is in the all-trans conformation. Afterward, the low-angle reflection disappears completely at the S_A−I transition. The phase change of the Cα → S_A → I transition was observed at pressures up to 100 MPa. Applying hydrostatic pressure of 150 MPa on the Cα form, however, induced another crystal modification during the heating process. Figure 2 shows the temperature dependence of X-ray pattern of the Cα form on heating at 200 MPa. The X-ray pattern of the Cα form was held at temperature up to 240 °C and then changed to the pattern of the crystal modification (Cδ) reported already by Bae et al.[12] The Cδ form was observed in a temperature region between 246 and 275 °C, and then the Cδ−S_A transition occurred at about 277 °C. The S_A phase at 280 °C shows a small low-angle reflection (d = 19.52 Å), indicating the invariance of the d spacing of the S_A phase with pressure. Figure 3 shows the T vs P diagram of the Cα form of BB-6 as starting material. It is noted that the Cδ form appears as the high-temperature phase of the Cα form in the high-pressure region above about 100 MPa.

Effect of Pressure on the Behavior of the Cγ Form. The density of the rapidly cooled sample (mainly Cγ form) was 1.256_5 g/cm^3 at 25 °C. The Cγ form shows a low-angle reflection of d = 19.52 Å and several broad reflections at wide angles. The Cγ form was held at temperatures up to about 190 °C under atmospheric pressure. Then the wide-angle reflections changed into those of the Cα form in the high-temperature region. Krigbaum et al. reported the X-ray pattern of the Cβ polymorph by annealing the Cγ sample at high temperatures, but in this case the diffraction pattern is

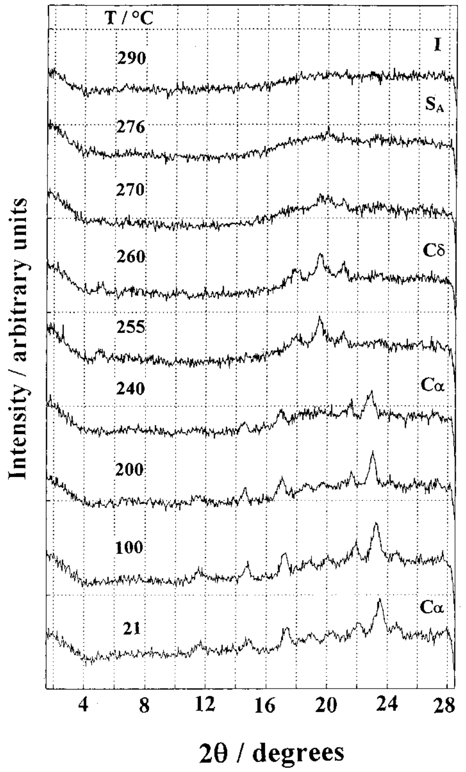


Figure 2. WAXD patterns on heating of the Cα form of the BB-6 polyester at 200 MPa. Heating rate: ca.1 °C/min.

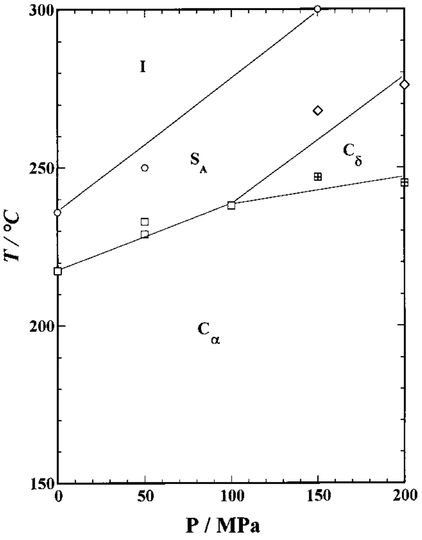


Figure 3. *T* vs *P* phase diagram of the Cα form of the BB-6 polyester as starting material.

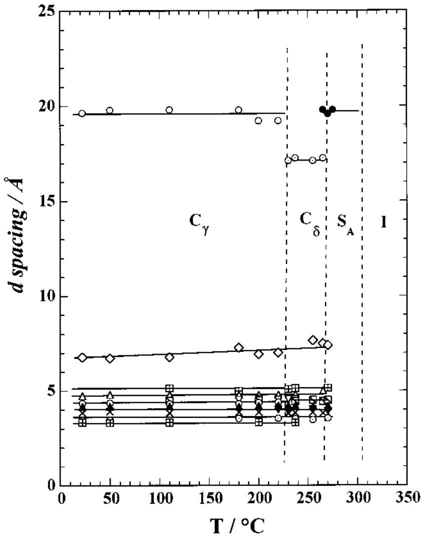


Figure 4. Temperature dependence of the *d* spacing of the Cγ form of the BB-6 polyester at 150 MPa.

substantially the same as one of the Cα form. The transformed phase was stable in a temperature region until the S_A phase appeared at 210 °C. The sample exhibited the phase transitions of Cγ-190 °C−Cα-210 °C−S_A-232 °C−I under atmospheric pressure. The transition behavior was observed at hydrostatic pressure up to 70 MPa. Applying a higher pressure on the rapidly cooled sample (Cγ) induced the Cδ form at 220−230 °C in a manner similar to the Cα−Cδ transition described in the previous section. The transition process at 150 MPa was observed at Cγ-228 °C−Cδ-267 °C−S_A-302 °C−I. Figure 4 shows the change in *d* spacing of each reflection of the Cγ sample on heating at 150 MPa. It is interesting to see that the *d* spacing (ca. 19.5 Å) of the low-angle reflection decreases by about 1.9 Å at the Cγ−Cδ transition and then springs back at the Cδ−S_A transition. From the X-ray measurements in this study, the Cγ form changes to the Cα form at lower pressures below 70 MPa, while the Cγ form transforms into the Cδ form at higher pressures above 80 MPa. Therefore, it can be concluded that the Cγ form is metastable at all pressures.

Structural Behavior of the Pressure-Crystallized Form. As has already been reported, the pressure-crystallized polymorph, i.e., Cδ form, appears preferentially from the S_A phase under high pressure above 100 MPa.[12] The density of the pressure-crystallized sample (Cδ form) was 1.263_0 g/cm^3 at 25 °C, which is comparable to that of the Cα form. The phase change of the Cδ form was studied at various low pressures. Figure 5 shows the temperature dependence of the X-ray patterns of the Cδ form on heating under atmospheric pressure. The Cδ form exists stable at temperatures up to 165 °C, and then the Cδ−Cα transition occurs clearly at temperatures between 165 and 170 °C, while this transition is not observed on the DSC curve. The Cα form is observed in the temperature region between 170 and 205 °C, and then it is transformed to the S_A phase at 210 °C. The Cδ → Cα → S_A → I transition was observed under hydrostatic pressures below 55 MPa. Figure 6 shows the WAXD patterns of the Cδ form on heating at 100 MPa. The Cδ form was maintained at about 235 °C until the Cδ−S_A transition occurred. Since the Cδ−S_A−I transition occurs reversibly at high pressure above about 100 MPa, it is concluded that the Cδ form is the stable in the high-pressure region. Figure 7 shows the *T* vs *P* diagram of the Cδ form crystallized at 200 MPa, in addition to the *T* vs *P* diagrams of the Cα and the Cγ forms mentioned before. One can see clearly that the Cδ form is stable at high pressures above 100 MPa, while the Cδ form is reorganized into the Cα form at high temperature in the low-pressure region. It is noted here that pressure does not enlarge the S_A-phase domain (20−30 °C) in the whole pressure region. This is a special case, apart from the broadening trend in the temperature domain of smectic and nematic phases by pressure. Obviously, it is due to that the crystal modification (Cδ) appears at high pressure and that the d*T*/d*P* coefficient of the Cδ−S_A transition is almost the same as one of the S_A−I transition.

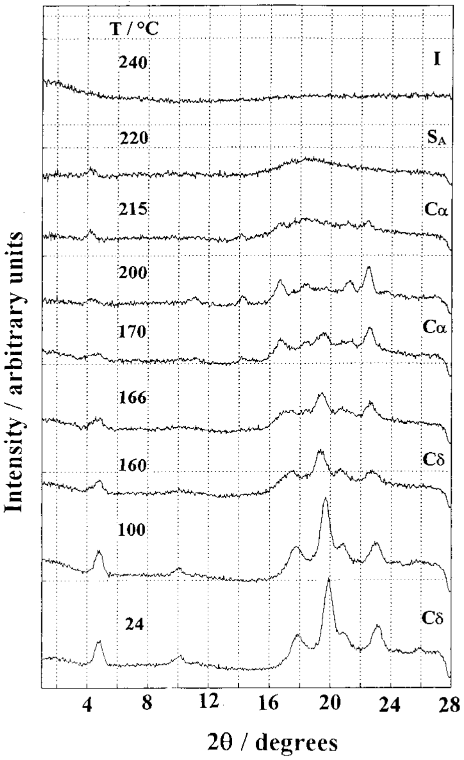


Figure 5. WAXD patterns of the Cδ form taken at different temperatures and atmospheric pressure. The sample was prepared by cooling from the isotropic melt at 200 MPa. Heating rate: ca.1 °C/min.

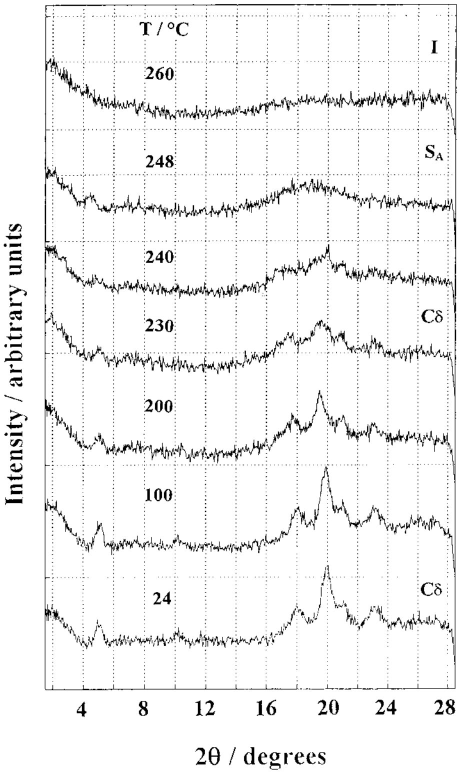


Figure 6. WAXD patterns of the Cδ form on heating at 100 MPa. Heating rate: ca. 1 °C/min.

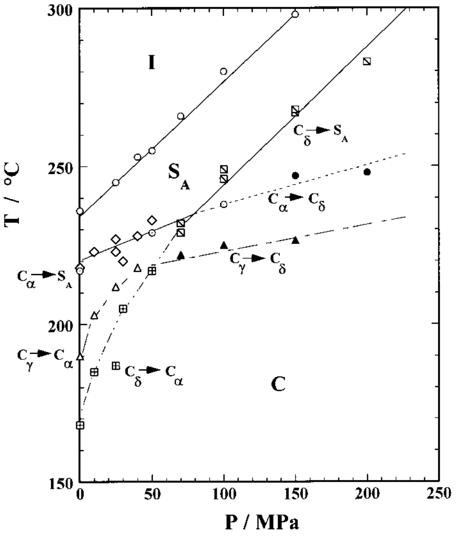
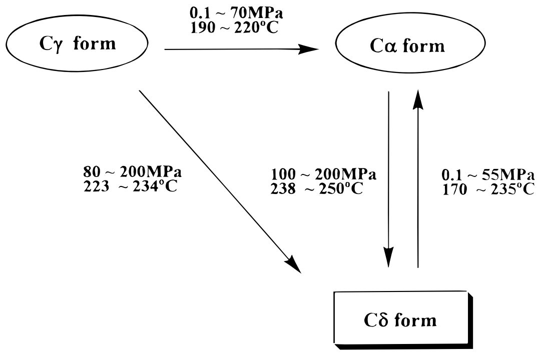


Figure 7. *T* vs *P* phase diagram of the Cα, Cγ, and Cδ forms of the BB-6 polyester.

Scheme 1. Transitions between the Polymorphs of BB-6



The phase transition between the crystal polymorphs of BB-6 is summarized in Scheme 1. The phase behavior of the polymorphs of BB-6 can be explained qualitatively by Gibbs energy curve. The temperature dependence of the Gibbs energies of the Cα, Cγ, and Cδ forms and S_A phase is illustrated schematically in Figure 8. The Gibbs energy of the polymorphs is on the order of Cα < Cγ < Cδ under atmospheric pressure, while the order changes to Cδ < Cα < Cγ under high pressures above 100 MPa. The Gibbs energy of the Cδ form is the lowest among the polymorphs at high pressure, but it becomes higher than those of the Cα and Cγ forms at atmospheric pressure. The reason such a drastic change of the Gibbs energy occurs in the Cδ form is not clear at present. Probably it is due to the stability of the crystal structure of the Cδ form which is strongly influenced by applied pressure.

Table 1 lists the data of *d* spacing calculated from the observed reflections of the crystalline α, γ, and δ forms and the S_A phase of the BB-6 polyester. The data of the crystal and smectic CA (S_{CA}) phase of the BB-5 polyester are shown for comparison. It is noted that the *d* spacing (17.6 Å) of the low-angle reflection of the Cδ form is shorter by 1.9 Å than that (19.5 Å) of the Cγ form. Table 1 also exhibits that the *d* spacings of the Cδ form are corresponded fairly well with those of the BB-5 crystal. The BB-5 sample shows the density of 1.264_1 g/cm^3, comparable to those of the Cα and Cδ forms. Figure 9 shows the X-ray fiber photographs of the S_A phase (a) and the Cα form (b) of BB-6 prepared at atmospheric pressure and the Cδ form (c) crystallized slowly at 100 MPa. The fiber diffraction pattern of the Cα form agreed well with that of the α-form of P6BP reported by Li and Brisse.[11] Figure 10 shows the S_{CA} phase (a) and the BB-5 crystal (b) annealed at 140 °C under atmospheric

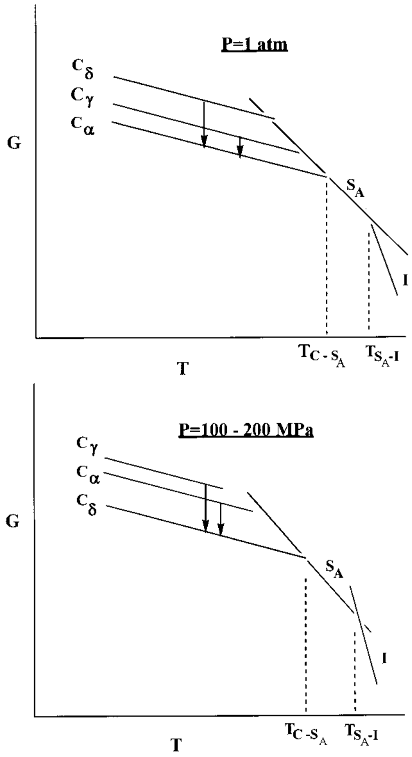


Figure 8. Schematic diagrams of the Gibbs free energies for the polymorphs of BB-6 at atmospheric pressure and 100−200 MPa.

Table 1. Bragg Spacing (Å) of the X-ray Reflection of the Crystal and the Smectic Phases of the BB-5 and BB-6 Polyesters under Atmospheric Pressure

BB-5		BB-6			
C	S_{CA} phase[a]	Cα form	Cγ form	Cδ form[b]	S_A phase[c]
17.0 s	17.3		19.5 m	17.6 m	19.5 m
8.00 w		7.61 m		8.52 w	
			6.98 w		
		5.96 m			
5.06 m		5.06 m		4.84 m	
		4.65 w	4.68 m		
4.32 s		4.39 w	4.40 s	4.38 s	
4.06 m		4.00 s		4.13 w	
		3.76 s	3.79 m	3.79 m	
3.61 m		3.60 w			
3.32 w				3.38 w	
		3.18 w			

[a] S_{CA} phase was measured at 210 °C. [b] Cδ form was prepared by cooling the sample slowly from the S_A phase at 200 MPa. [c] S_A phase was measured at 222 °C.

pressure. The X-ray fiber photographs of the S_{CA} phase and the BB-5 crystal show clearly intense fiber reflections along the direction tilted by about 25° to the equatorial line.[6] Here one can notice that the diffraction pattern of the Cδ form of BB-6 closely resembles one of the BB-5 crystal. These experimental facts suggest that the Cδ form may have a tilted layer structure like the BB-5. Li and Brisse[11] determined the crystal structures of the Cα, Cβ, and Cγ forms of the BB-6 polyester as monoclinic systems in which the polymer chains are composed of the aliphatic sequences in the all-trans conformation. According to their results, the unit cell of the Cα form contains six chains that are packed in the "face-to-face" pattern with respect to the aromatic groups, while the four chains of the Cγ form are packed in the herringbone pattern. What kind of crystal structure does one think for the Cδ form crystallized at high pressure? Since the X-ray pattern of the Cδ form shows intense fiber reflections along the direction tilted from the equatorial line, there is one possibility that the molecular chains in the unit cell would be arranged in

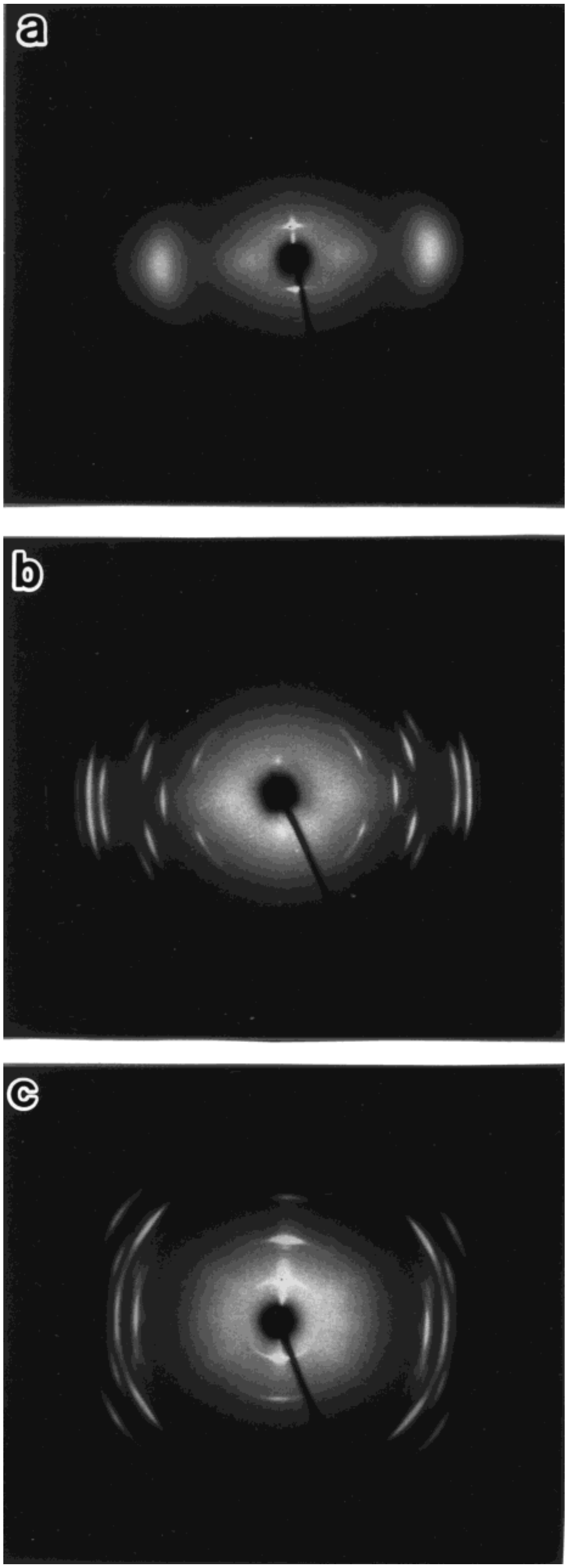


Figure 9. X-ray fiber patterns of the (a) the S_A phase, (b) the Cα form crystallized at atmospheric pressure, and (c) the Cδ form of BB-6 prepared by cooling the BB-6 sample from the melt at 100 MPa.

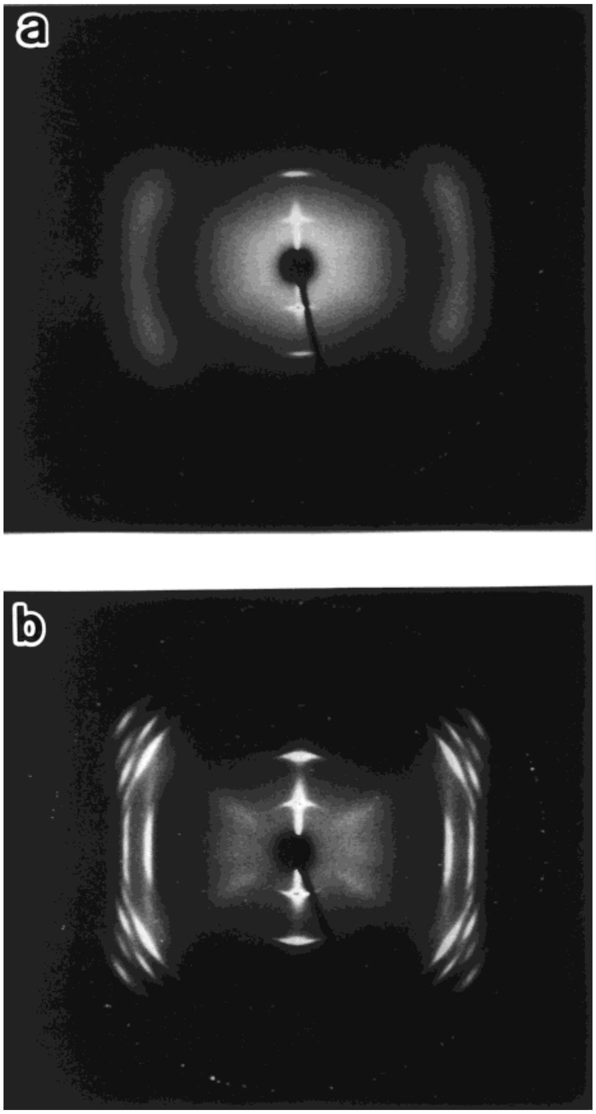


Figure 10. X-ray fiber patterns of (a) the S_{CA} phase and (b) the crystal of BB-5 annealed at 140 °C under atmospheric pressure.

a herringbone pattern and that the experimental fact of the shrinkage of fiber repeat (19.5 → 17.6 Å) would suggest the change of conformation from all-trans to an inclusion of gauche (g+ or g−) conformation in the aliphatic sequence.

In conclusion, the slowly cooled sample of BB-6 takes the Cα form and the Cα−S_A−I transition occurring reversibly at pressures below 70 MPa. The Cα form is the most stable in the low-pressure region. On the other hand, the rapidly cooled sample takes mainly the Cγ form under atmospheric pressure. The Cγ form is always metastable, independent of the applied pressure. When the sample is cooled from the S_A or I phase at high pressures above 100 MPa, the Cδ form is formed predominantly. Since the Cδ−S_A−I transition is observed reversibly at pressures above 100 MPa, it is concluded that the Cδ form is the stable one in the high-pressure region. The determination of the crystal structure of the Cδ form will be an intriguing study for the understanding why and how the Cα−Cδ crystal transition occurs under high pressure.

Acknowledgment. Y. Maeda acknowledges Dr. K. Nakayama for help of the density measurements of the BB-5 and BB-6 polyesters.

References and Notes

(1) Meurisse, P.; Noel, C.; Monnerie, L.; Fayolle, B. *Br. Polym. J.* **1981**, *13*, 55.
(2) Krigbaum, W. R.; Asrar, J.; Toriumi, H.; Ciferri, A.; Preston, J. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 109.
(3) Krigbaum, W. R.; Watanabe, J. *Polymer* **1983**, *24*, 1299.
(4) Krigbaum, W. R. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1985**, *41*, 105.
(5) Jackson, W. J., Jr.; Morris, J. C. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1985**, *41*, 307.
(6) Watanabe, J.; Hayashi, M. *Macromolecules* **1988**, *21*, 278.
(7) Watanabe, J.; Hayashi, M. *Macromolecules* **1989**, *22*, 4083.
(8) Jackson, W. J., Jr.; Morris, J. C. *Polym Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 489.
(9) Jackson, W. J., Jr.; Morris, J. C. *ACS Symp. Ser.* **1990**, *435*, 16.
(10) Maeda, Y.; Watanabe, J. *Macromolecules* **1997**, *30*, 4042.
(11) Li, X.; Brisse, F. *Macromolecules* **1994**, *27*, 7725.
(12) Bae, H.-G.; Watanabe, J.; Maeda, Y. *Macromolecules* **1998**, *31*, 5947.
(13) Tokita, M.; Takahashi, T.; Hayashi, M.; Inomata, K.; Watanabe, J. *Macromolecules* **1996**, *29*, 1345.
(14) Maeda, Y.; Kanetsuna, H. *Bull. Res. Inst. Polym. Text.* **1985**, *149*, 119.
(15) Maeda, Y.; Tanigaki, N.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1993**, *237*, 407.

MA991385C