Pressure-Induced Mesomorphic Transition of a Liquid Crystalline Polyester at High Temperatures

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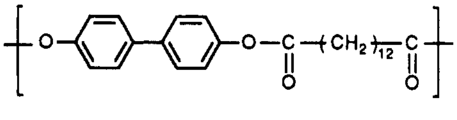
The pioneering work on the study of the pressure-induced liquid crystallinity for low molecular weight samples was performed by Chandrasekhar and his group.[1] Chandrasekhar et al.[2] reviewed extensively the studies of low molar mass liquid crystals at high pressure. One of the important conclusions of their review is that isotropic liquids of anisometric molecules can be transformed into mesophases at elevated pressure. Only a few studies of pressure-induced liquid crystallinity for polymers have been performed until now. Samulski et al.[3,4] reported two interesting pressure effects, a pressure-induced crystal habit and a pressure-induced mesophase, of an aromatic copolyester (HIQ-20) composed of 20% hydroxybenzoic acid, 40% isophthalic acid, and 40% hydroquinone. One of the authors has been studying the effect of pressure on the structure and thermal properties of a main-chain thermotropic polyester in which crystalline polymorphs are found under pressure.[5,6]

This work is in a series of studies of pressure effects on structure and thermal properties of main-chain thermotropic polyesters showing various mesophases. Alternate arrangement of rigid mesogenic core and aliphatic flexible spacer in a repeating unit is an important structural characteristic of main-chain thermotropic polyesters. These polyesters exhibit several types of mesophases, i.e., nematic, cholesteric, and various smectic phases. Among them, smectic liquid crystals are especially interesting for the study of pressure-induced mesomorphic transition since significant pressure effects might be expected because of the segregated structures that may be induced among the rigid mesogenic groups and flexible spacer groups.

Watanabe et al.[7-10] have been studying the synthesis, structure, and thermal properties of several kinds of thermotropic main-chain polyesters showing smectic mesophases under atmospheric pressure. In this study one of these thermotropic polyesters, based on 4,4′-dihydroxybiphenyl as a mesogen and the aliphatic dibasic acid with 12 methylene units as a flexible spacer, is used. Its chemical structure is as follows:



We designate the polymer PB-12. The synthesis, characterization, and thermal properties of PB-12 polyester are described elsewhere.[9] The inherent viscosity of the sample used in this study was 0.75 dL/g, which was determined at 25 °C using a 0.5 g/dL solution in a 60/40 mixture by weight of phenol and tetrachloroethane. The PB-12 polyester exhibits the phase transitions

$$\mathrm{K} \xrightarrow{198\ ^\circ\mathrm{C}} \mathrm{S_H} \xrightarrow{231\ ^\circ\mathrm{C}} \mathrm{I}$$

where K denotes the crystal, S_H the smectic H phase, and I the isotropic molten phase. This polyester is thus characterized by showing a highly ordered S_H phase over a wide temperature range.[10]

The X-ray diffraction patterns of the crystalline and smectic phases of the unoriented PB-12 polyester can be divided into an inner ring and outer rings; the former is due to a layered structure along the molecular chain direction and the latter are due to the lateral packing within the layers.[11] The structural behavior of the PB-12 sample has been measured at various temperatures under hydrostatic pressures of low-viscosity silicone oil (10 centistokes) by using a wide-angle X-ray scattering (WAXS) apparatus equipped with the high-pressure sample vessel that was developed in our laboratory.[12] We present here the experimental facts of pressure-induced mesomorphism in the PB-12 polyester, in which the S_H phase observed at atmospheric pressure is altered to another smectic phase by applying hydrostatic pressure above 90 MPa.

The WAXS behavior of the K–S–I phase transitions was measured in an isobaric way under pressures up to 350 MPa. From the X-ray profiles at atmospheric pressure in Figure 1a, the PB-12 crystal shows a low-angle reflection at $2\theta = 3.8°$ (23.2 Å) and two strong wide-angle reflections at ca. 20.3° (4.3_8 Å) and 21.5° (4.1_3 Å). On heating to the S_H phase in the temperature region above 198 °C, the low-angle reflection shifts to a larger angle at $2\theta = 4.2°$ (20.9 Å) and the wide-angle reflection appears at $2\theta = 19.5°$ (4.5_5 Å). These observations correspond well to the data of the intense reflections previously elucidated from X-ray photographs.[11] Increasing hydrostatic pressure up to 90 MPa does not change significantly this trend of the X-ray profiles on the transition from crystal to the smectic phase, although the transition temperatures are increased with an increase of pressure. Further increase of the pressure above about 100–120 MPa, on the other hand, results in a quite different change in the X-ray profiles at the K–S phase transition as shown in Figure 1b. The low-angle reflection at 150 MPa shifts to a smaller angle at $2\theta = 3.3°$ (26.7 Å) at the transition. This trend is obviously opposite to that observed at the lower pressures including atmospheric pressure, indicating that a new smectic phase is formed. The new smectic phase is denoted here as a smectic X (S_X) phase, remarkably different from the S_H phase. The layer spacing for the S_H phase is around 21.0 Å while the spacing is around 26.7 Å for the new S_X phase. The corresponding spacing of the crystal has an intermediate value which varied from 23.3 to 22.4 Å with an increase of pressure. The estimated lattice spacings for the crystal, the S_H phase, and the S_X phase are listed in Table I.

As we are concerned with X-ray profiles, the phases can be distinguished from each other through the *d* spacing of the low-angle reflection, and so the phase transition can be precisely determined from the temperature dependence of this spacing. Figure 2 shows the variation of the *d* spacing of the low-angle reflection with temperature at various pressures. This figure indicates that the transition occurs sharply in all cases and also signifies that the resultant smectic phase is altered from the S_H phase to the S_X phase by changing the applied pressure from 90 to 120 MPa. This latter fact can also be confirmed

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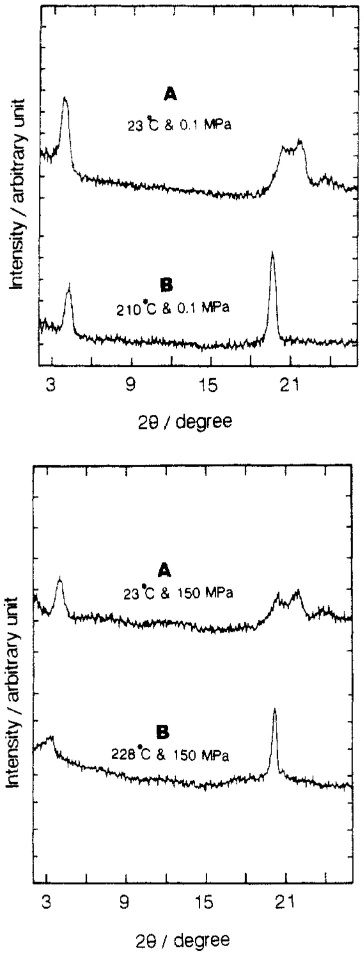

Figure 1. (a, Top) WAXS patterns of PB-12 at atmospheric pressure: (A) crystal at 23 °C; (B) S_H phase at 210 °C. (b, Bottom) WAXS patterns of PB-12 at 150 MPa: (A) crystal at 23 °C; (B) S_X phase at 228 °C.

Table I
***d* Spacings of PB-12 Polyester under Various Pressures**

	d spacing/Å	
press./MPa	cryst phase	smectic phase
0.1 (1 atm)	23.2	20.9 (S_H)
	4.3_8	4.5_5
	4.1_3	
75	23.1	21.1 (S_H)
	4.3_7	4.5_2
	4.0_7	
100	22.7	26.9 (S_E)
	4.3_6	4.4_6
	4.0_8	
200	22.4	26.5 (S_E)
	4.3_8	4.4_2
	4.0_3	

from the experiment in which the pressure is altered from 50 to 200 MPa in the temperature region of the mesophase as shown in Figure 3.

According to these results, a phase diagram can be constructed as illustrated in Figure 4. From this figure, one can see the distinct trend in which the stable region of the smectic phase becomes broad with increasing pressure since the temperature of the S–I transition increases more steeply with pressure than that of the K–S transition. This trend has been similarly observed in many other polymeric systems. The phase boundary distinguishing between the S_H and S_X phases is not determined unambiguously, although the above results show that it lies between 90 and 120 MPa. For convenience, the phase boundary between the S_H and S_X phases is illustrated by the dashed line in Figure 4 (refer to the comments given below).

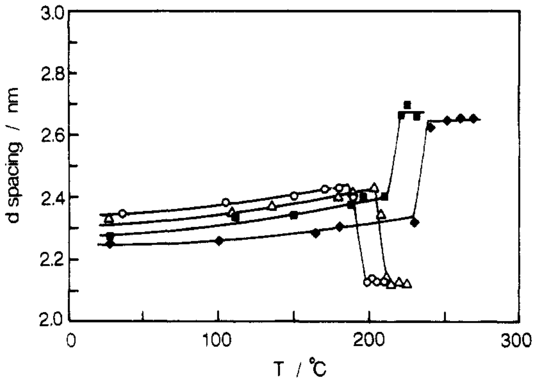

Figure 2. Temperature dependence of the *d* spacing of the low-angle reflection in the WAXS patterns of PB-12 at various pressures: (○) 0.1 MPa (1 atm); (△) 75 MPa; (■) 100 MPa; (◆) 200 MPa.

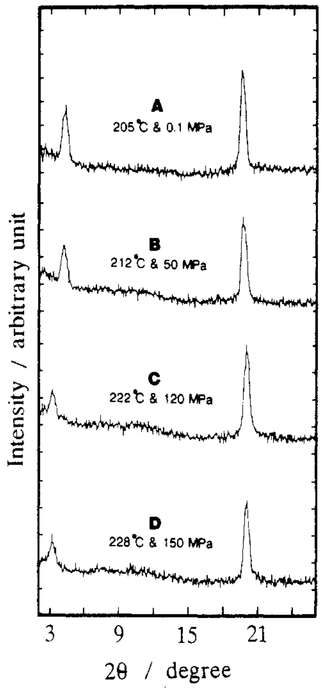

Figure 3. Effect of pressure on the WAXS pattern of PB-12 in the smectic phase region: (A) S_H phase at 205 °C and 0.1 MPa (1 atm); (B) S_H phase at 212 °C and 50 MPa; (C) S_X phase at 222 °C and 120 MPa; (D) S_X phase at 228 °C and 150 MPa.

It is very important to identify the S_X phase of PB-12 polyester. In this limited observation, the S_X phase can be differentiated from the S_H phase only by having the larger layer spacing, ca. 26.7 Å for the S_X phase and ca. 21.0 Å for the S_H phase (refer to Table I and Figure 2). Considering that the repeating length of a molecule in the extended chain conformation is around 27 Å, it is very reasonable that in the S_X phase the molecules lie perpendicular to the layer while the S_H phase is a tilted phase. Since a similar spacing for the wide-angle reflection can be attained for both phases, the lateral packing of molecules within a S_X layer may not be significantly different from that of the S_H phase. These experimental facts suggest strongly that the S_X phase would be either a S_E phase or a S_B phase.[13] The relation of its lamellar spacing close to its molecular length can be seen both in the S_B phase (hexagonal packing) and S_E phase (orthorhombic). One great difference between the S_B and S_E phases is the axiality of the phase, in which the S_B phase is uniaxial and the S_E phase is biaxial.[14] In the future, the S_X phase should

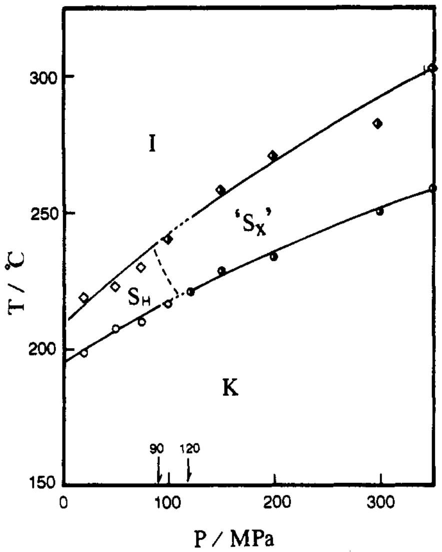

Figure 4. Phase diagram of PB-12 polyester. The phase boundary distinguishing between the S_H and S_X phases is tentatively illustrated by the dashed line in the pressure region between 90 and 120 MPa (see text).

be determined precisely with definite evidence by using WAXS and optical microscopy.

As far as we know, the S_E phase is always located at higher temperatures than its tilted S_H phase.[13] This means that the S_E phase is less ordered than the S_H phase. In other words, the S_E phase has a higher enthalpy and entropy than those of the S_H phase. If this is the case at any pressure, the slope of the boundary line between both phases, dT/dP, which is located in the pressure region between 90 and 120 MPa, should be negative. According to the Clapeyron equation ($dT/dP = \Delta V/\Delta S$), a negative slope in dT/dP suggests that the molar volume of the less ordered S_X phase would be smaller than that of the S_H phase. This may not be irrational in this class of liquid crystalline polymers since aromatic mesogen and aliphatic spacers could be more distinctly segregated in the S_X phase than the tilted S_H phase and therefore more efficient packing of molecules may be possible. This interesting point needs further investigation by using the homologous series of PB-*n* polyesters with alkylene spacers of different length.

References and Notes

(1) Chandrasekhar, S.; Ramaseshar, S.; Reshamwala, A. S.; Sadashiva, B. K.; Shashidhar, R.; Surendranath, V. *Liq. Cryst., Proc. Int. Conf.* **1975**, *1*, 117.
(2) Chandrasekhar, S.; Shashidhar, R. *Advances in Liquid Crystals*; Brown, G. H., Ed.; Academic Press: New York, 1979; Vol. 4, Chapter 2.
(3) Hsiao, B. S.; Shaw, M. T.; Samulski, E. T. *Macromolecules* **1988**, *21*, 543.
(4) Hsiao, B. S.; Shaw, M. T.; Samulski, E. T. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 189.
(5) Maeda, Y.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 169.
(6) Maeda, Y.; Tanigaki, N.; Blumstein, A. *Mol. Cryst. Liq. Cryst.*, to be published.
(7) Watanabe, J.; Hayashi, M. *Macromolecules* **1988**, *21*, 278.
(8) Watanabe, J.; Hayashi, M. *Macromolecules* **1989**, *22*, 4083.
(9) Asrar, J.; Toriumi, H.; Watanabe, J.; Krigbaum, W. R.; Ciferri, A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1119.
(10) Watanabe, J.; Krigbaum, W. R. *Macromolecules* **1984**, *17*, 2288.
(11) Krigbaum, W. R.; Watanabe, J.; Ishikawa, T. *Macromolecules* **1983**, *16*, 1271.
(12) Maeda, Y.; Kanetsuna, H. *Bull. Res. Inst. Polym. Text.* **1985**, *149*, 119.
(13) Gray, G. W.; Goodby, J. W. F. In *Smectic Liquid Crystals*; Leonard Hill: Glasgow and London, 1984.
(14) Luckhurst, G. R.; Gray, G. W. *The Molecular Physics of Liquid Crystals*; Academic Press: New York, 1979; pp 263–284, 317–341.