Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Pressure-Induced Enantiotropic Transition of a Thermotropic Polyester at Room Temperature

Yoji Maeda [a], Yoshio Tanaka [a], Masatoshi Iguchi [a] & Alexandre Blumstein [b]

[a] Research Institute for Polymers and Textiles, Tsukuba, Ibaraki, 305, Japan

[b] Polymer Science Program, Chemistry Department, University of Lowell, Lowell, MA, 01854, U.S.A.

Version of record first published: 17 Oct 2011.

To cite this article: Yoji Maeda , Yoshio Tanaka , Masatoshi Iguchi & Alexandre Blumstein (1986): Pressure-Induced Enantiotropic Transition of a Thermotropic Polyester at Room Temperature, Molecular Crystals and Liquid Crystals, 138:1, 339-347

To link to this article: http://dx.doi.org/10.1080/00268948608071768

Mol. Cryst. Liq. Cryst., 1986, Vol. 138, pp. 339–347
0026-8941/86/1384–0339/$15.00/0

Printed in the United States of America

Pressure-Induced Enantiotropic Transition of a Thermotropic Polyester at Room Temperature

YOJI MAEDA, YOSHIO TANAKA and MASATOSHI IGUCHI
Research Institute for Polymers and Textiles, Tsukuba, Ibaraki 305, Japan

and

ALEXANDRE BLUMSTEIN
Polymer Science Program, Chemistry Department, University of Lowell, Lowell, MA 01854, U.S.A.

(*Received February 14, 1986; in final form March 3, 1986*)

An enantiotropic transition between crystal and amorphous phases of a thermotropic liquid crystalline polyester, poly(4,4′-dioxy-2,2′-dimethylazoxybenzene dodecanedioyl) (labeled as DDA-9), was found to be induced at room temperature by hydrostatic pressure. The pressure-induced enantiotropic transition is greatly dependent upon the original solid state of DDA-9.

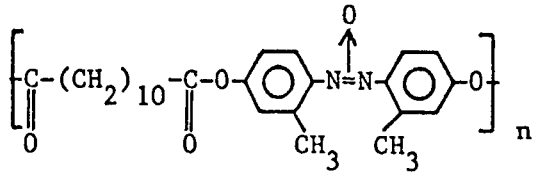
Keywords: pressure-induced, enantiotropic transition, thermotropic polyester, room temperature

During the last ten years several papers have been published concerning the phase behavior of low and high molecular weight liquid crystalline materials under high pressure. Pressure-induced mesomorphism has been found for the first time by Shashidhar and Chandrasekhar[1] in 4-methoxy and 4-ethoxy benzoic acid by using differential thermal analysis (DTA). The mesomorphism is induced by pressure in both compounds which are non-mesomorphic at atmospheric pressure. At atmospheric pressure, there is just a single melting transition, the solid-isotropic liquid transition. As the pressure is raised progressively up to 200 bars, both compounds show mesophases, initially a nematic phase and then, at higher pressures,

a smectic phase as well. These experiments established first the existence of solid-nematic-isotropic and solid-smectic-nematic triple points in single component systems.

The synthesis and properties of thermotropic polyesters with mesogenic moiety of azoxybenzene derivatives and flexible spacers of alkanedioyl in the main chain were recently described.[2,3,4] Such polyesters are characterized by a random coil conformation and a high flexibility in the melt well above the isotropic transition temperature. On cooling from the melt, these polymers may transit through a nematic mesophase before crystallizing. It is known that on a molecular level liquid crystalline flexible polyesters differ substantially from low molecular weight liquid crystals: there is a strong coupling between translational and orientational motions of mesogenic groups in the polymers.[4] Accordingly, high pressure investigations are of value in the understanding of such polymeric liquid crystalline mesophases.

We present, in this paper, the results of a preliminary study of wide-angle X-ray scattering (WAXS) as a function of pressure for the poly(4,4′-dioxy-2,2′-dimethylazoxybenzene dodecanedioyl) (commonly labeled as DDA-9).



The polymer consists of a regular sequence of rigid azoxybenzene mesogenic cores and flexible alkanedioate "spacer" groups. It has moderately low transition temperatures and a nematic stability range of about 45°C. In the fractionated sample of $\overline{M}_n$ = 20,000 used in this study, the phase transitions are K119.6N164.1I. This moderate temperature range insures stability of the compound in the nematic states. The sample used is semicrystalline with a supercooled nematic phase. The glass transition temperature is about 13.5°C.

EXPERIMENTAL

The sample was prepared as described previously.[2,3] Fractionation was carried out by a combination of non-solvent precipitation and chromatographic techniques.

A high pressure and high temperature WAXS apparatus used in this study is described elsewhere.[5] The high pressure WAXS system was designed to be operated at pressures up to 700 MPa and 300°C and was equipped with a high-speed X-ray detecting system by a position-sensitive proportional counter (PSPC) so that dynamic measurements such as phase transitions of melting, crystallization, and crystal transition can be measured rapidly even under high pressures. The sample set in a beryllium cylinder was pressurized hydrostatically with dimethyl silicone oil and was placed in a beam of Ni-filtered Cu Kα X-rays generated by a rotating anode X-ray generator of 60 kV and 200 mA (Rotaflex RU-200, Rigaku-Denki Co.). The pressure was read directly within an accuracy of ±1 MPa by a digital meter (wheatstone bridge manganin gauge). The gauge was calibrated against a precision broudon gauge (Heise, Inc.) used as a secondary pressure standard.

RESULTS AND DISCUSSION

Figure 1 shows a typical WAXS pattern of a DDA-9 crystal at room temperature under atmospheric pressure. The sample was crystallized by cooling at 10°C/min from the melt at 170°C. The crystal reflections are observed at $2\theta \fallingdotseq 8°$ as low-angle peak, $2\theta \fallingdotseq 12°$ as intermediate-angle peak, $2\theta = 19°22'$, $20°27'$, and $22°0'$ as three strong wide-angle peaks, and $2\theta = 24°12'$ as a weak wide-angle peak. The X-ray pattern is almost the same as the X-ray photograph re-

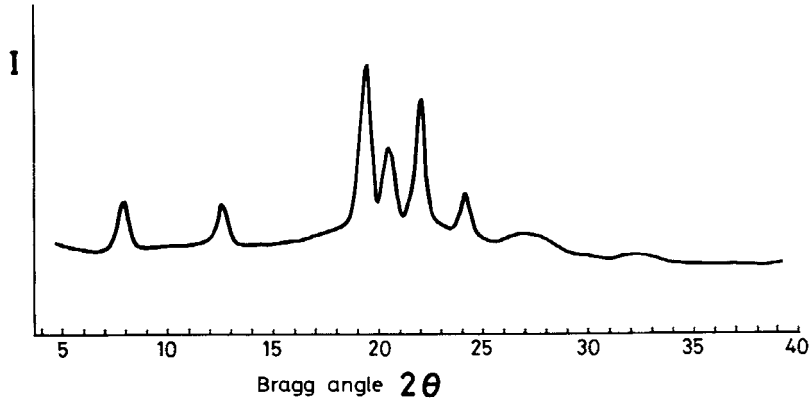


FIGURE 1 Typical WAXS pattern of the DDA-9 crystal at room temperature under atmospheric pressure.

ported previously.[3,6] The effect of pressure on the WAXS pattern of the DDA-9 crystal was investigated at room temperature. Figure 2 shows the change in pattern of the sample at about 30°C with pressure. At elevated pressures of up to 300 MPa, the WAXS pattern of the DDA-9 crystal remains qualitatively unchanged. Quantitatively, however, all the peaks with the exception of the intermediate-angle peak at $2\theta \fallingdotseq 12°$ decreased and shifted slightly with increasing pressure. The intensity and breadth of the intermediate-angle peak are small but sharp at atmospheric pressure, while this peak changed to a broad one under pressures. At 400 MPa, an interesting phenomenon took place. All the sharp peaks of crystal reflection of DDA-9 disappeared completely, suggesting a collapse of the crystalline lattice. Furthermore, the amorphous pattern of DDA-9 remained for a while unchanged on decreasing the pressure down to 100 MPa. Finally at atmospheric pressure the crystal pattern not only fully recovered but the peak intensity was increased and the pattern sharpened with respect to the original sample. Crystallinity is thus recovered and improved on completing the pressure cycle. Figure 2 shows that an enantiotropic transition of the DDA-9 crystal induced by pressure occurs at low temperatures below the temperature of crystal-nematic transition. This type of phase transition is substantially different from the phase transition found by Shashidhar, et al.[1] because it occurs enantiotropically with pressure at constant temperature. It is interesting to study the nature of the collapse of crystal lattice in DDA-9 induced by pressure. We have compared X-ray patterns of the collapsed crystalline phase of DDA-9 under various conditions, Figure 3(b, c, d, e), with the pattern of the nematic structure of DDA-9 at 1 atm, Figure 3(a). It is noted that the X-ray patterns of the collapsed crystalline phase at room temperature, 400 MPa on the 1st run and at room temperature, 100 MPa on the 2nd run are very similar to those of the unidentified phase at 155°C, 100 MPa and at 195°C, 300 MPa. By repeated cycling of pressure, it was found that the phase transition is a reproducible and iterative enantiotropic transition. After the first cycle, however, the transition shifted to a lower pressure of 100 MPa.

The same experiment has been performed on another sample of DDA-9 annealed at 100°C for overnight under atmospheric pressure. In this case, the collapsed pattern could not be observed up to 500 MPa but the individual peaks became very weak with increasing pressure, and could extrapolate to zero above 500 MPa. Figure 4 shows the recovering of diffraction peaks of the annealed DDA-9 sample with

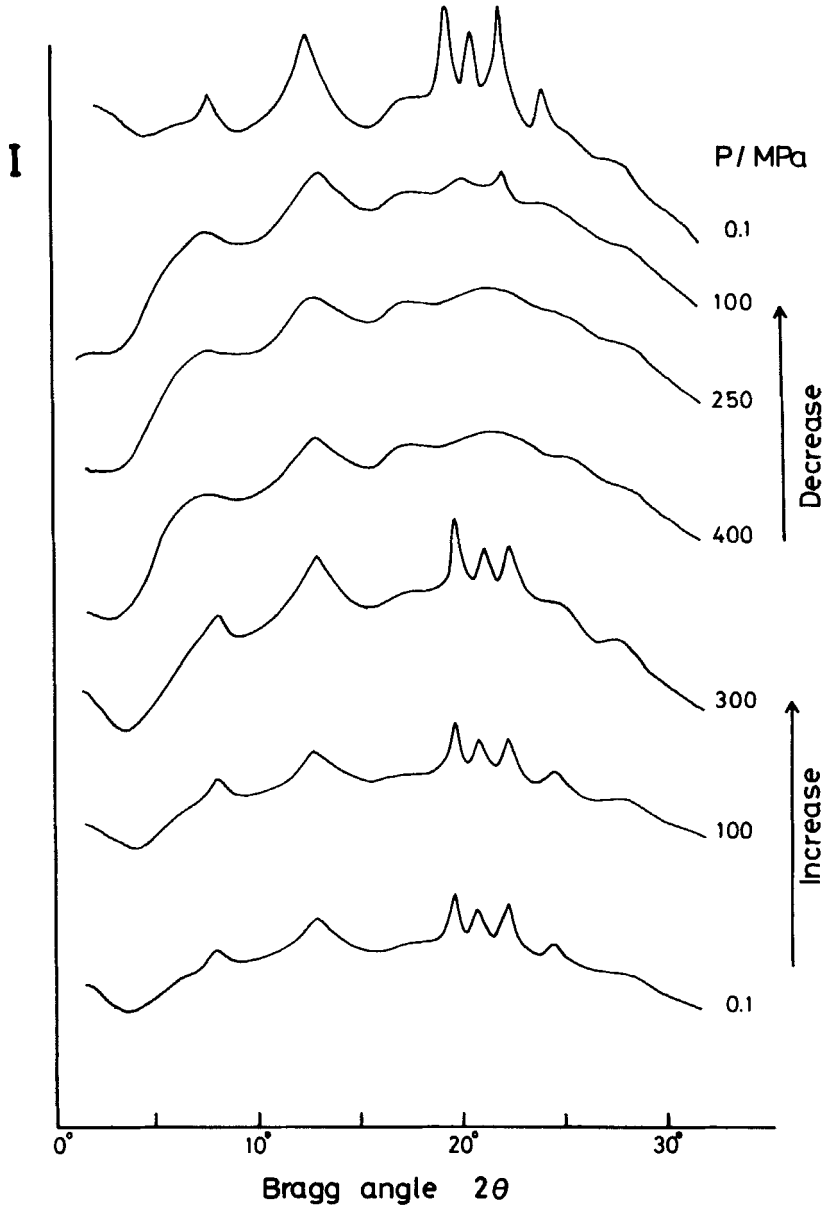


FIGURE 2 Effect of pressure on the WAXS pattern of the DDA-9 crystal at about 30°C.

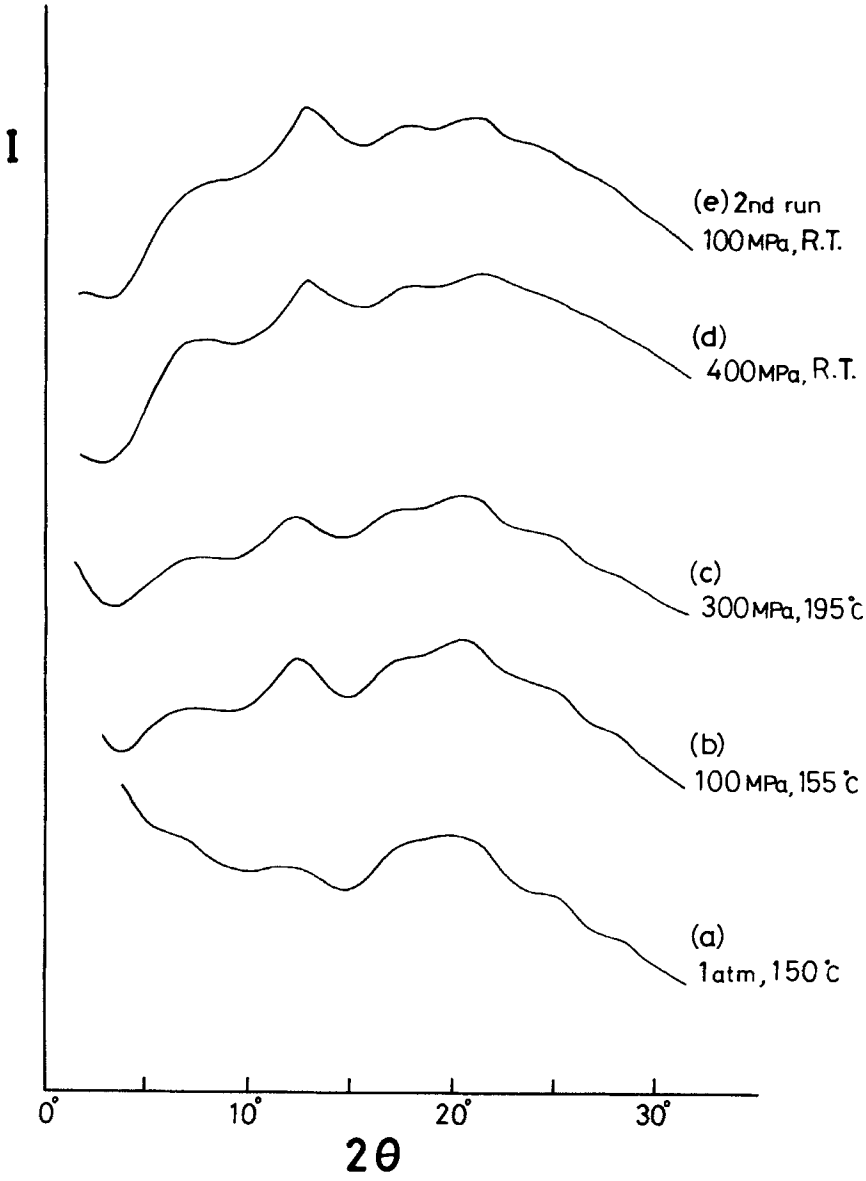


FIGURE 3 WAXS patterns of the collapsed crystalline phase of DDA-9 under various conditions.

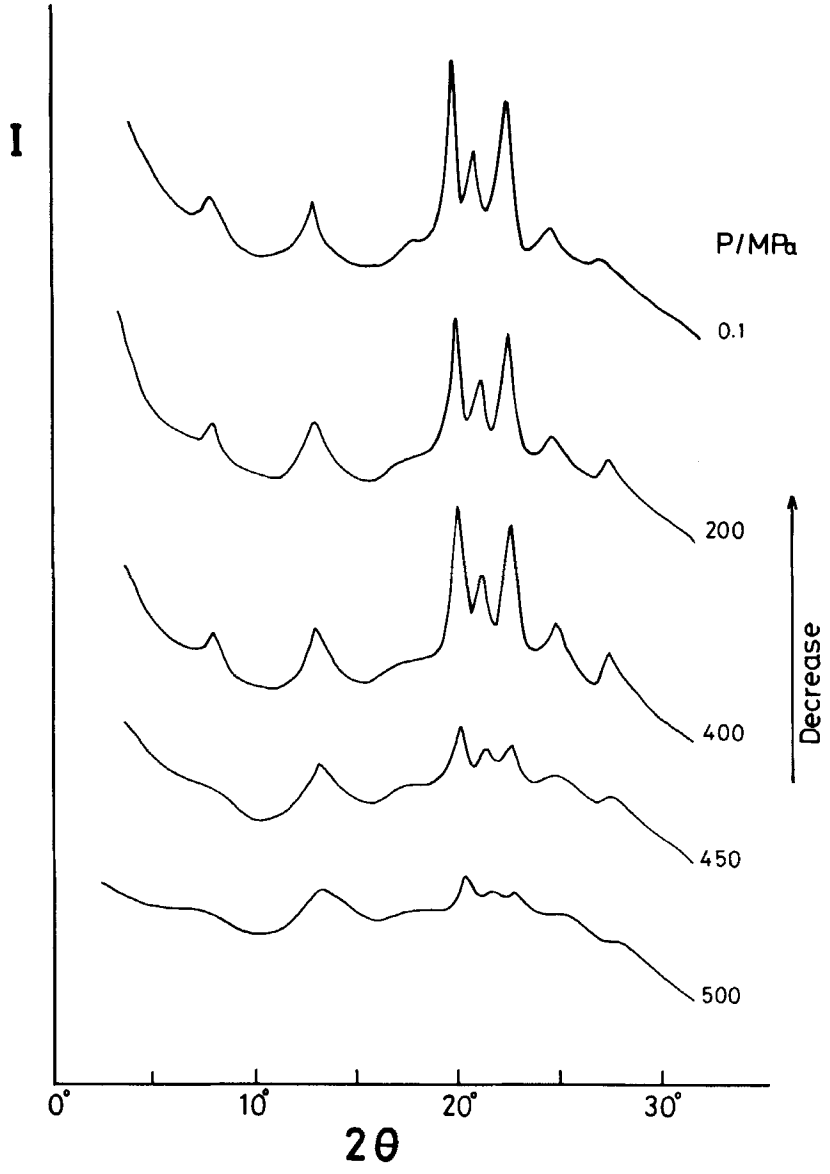


FIGURE 4 Change in WAXS pattern of the annealed DDA-9 crystal on the pressure-decreasing process.

TABLE I

Room-temperature *d* spacings of the annealed DDA-9 crystal at atmospheric pressure and 500 MPa

1 atm		500 MPa	
2θ	d/ Å	2θ	d/ Å
7°54'	11.1_9		
12°30'	7.0_8	13° 0'	6.8_1
19°22'	4.5_8	19°52'	4.4_7
20°27'	4.3_4	20°57'	4.2_4
22° 0'	4.0_4	22°30'	3.9_5
24°12'	3.6_8		

decreasing pressure. On the pressure decreasing process, the wide-, intermediate-, and low-angle peaks recovered rapidly. All the peaks, including the intermediate-angle peak, changed reversibly by about 30' with pressure in the range from 1 atm to 500 MPa. Table I illustrates the Bragg angle and *d* constant of the crystal reflections of DDA-9 both at atmospheric pressure and 500 MPa. Here one can observe that the recovered WAXS pattern of DDA-9 at atmospheric pressure is sharper than that of the original sample. Thus one can conclude that this enantiotropic phase transition is greatly dependent upon the original solid state of DDA-9.

It is clear that pressure generates a large distortion in the crystallites of DDA-9 even at temperatures far below the crystal-nematic transition point. It suggests that crystallites of DDA-9 may carry more free volume than the amorphous phase,[7] a rather unusual phenomenon possibly due to the distorted shape of the substituted mesogen.[8] The distorted configuration of the mesogen may also be related to a strong coupling between translational and orientational motions of mesogenic groups in the polymer. A more detailed phase behavior of DDA-9 and other polyesters with azoxybenzene moieties will be given elsewhere in the near future.

Acknowledgment

We wish to acknowledge the support of the National Science Foundation's Polymer Program under Grant DMR-8303989. Thanks are expressed to Mr. S. Kumar for the preparation of the DDA-9 sample.

References

1. R. Shashidhar and S. Chandrasekhar, *J. de Phys. Coloque C1*, 49 (1975).
2. A. Blumstein and S. Vilasagar, *Mol. Cryst. Liq. Cryst.* (*Letters*), **72**, 1 (1981).
3. A. Blumstein, S. Vilasagar, S. Ponrathnam, S. B. Clough, G. Maret and R. B. Blumstein, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 877 (1982).
4. A. Blumstein, *Polymer Journal* (*Japan*), **17**, 277 (1985).
5. Y. Maeda, H. Kanetsuna and M. Iguchi (to be published).
6. G. Maret and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **88**, 295 (1982).
7. O. Thomas, "*Order in Thermotropic Polyesters*," Ph.D. Thesis, University of Lowell, September 1984.
8. J. Bergés and H. Perrin, *Mol. Cryst. Liq. Cryst.*, **113**, 269 (1984).