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Pressure-Induced Crystal Modification of A Thermotropic Polyester

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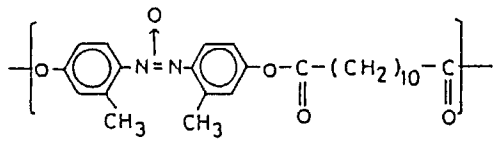
It was found that a crystal polymorph of a thermotropic polyester, poly(4,4′-dioxy-2,2′-dimethylazoxybenzene dodecanedioyl) (labeled as DDA-9), is formed by cooling it from the nematic liquid crystal phase under hydrostatic pressures of 100 MPa. The crystal modification is stable under atmospheric pressure. The sample has a larger density and a higher crystal melting point than those of the DDA-9 polyester formed under normal pressure.

Keywords: thermotropic polyester, nematic phase, crystal modification, high pressures, wide-angle X-ray diffraction

INTRODUCTION

Thermotropic liquid crystalline polymers have been intensively studied from both the theoretical and practical points of view. Blumstein *et al.*[1–4] described the synthesis and thermal properties of main-chain nematic polyesters of poly(4,4′-dioxy-2,2′-dimethylazoxybenzene dodecanedioyl) (commonly labeled as DDA-9).



The polymer consists of a regular sequence of rigid azoxybenzene mesogenic core (mesogen 9) and flexible dodecanedioate "spacer" group (DDA). It has moderately low transition temperatures and a nematic stability range of about 45°C. The polyester shows a remarkable odd-even effect of both the transition temperature and of the entropy of the nematic(N)-isotropic(I) transition.[2] Such polyesters are characterized by a random coil conformation and a high flexibility in the melt well

above the isotropisation temperature. On cooling from the melt, the polymer can transit through a nematic mesophase before crystallizing. In this paper, we present preliminary results of wide-angle X-ray scattering (WAXS) of DDA-9 polyester as a function of temperature and pressure.

EXPERIMENTAL

The synthesis and properties of thermotropic polyesters with a mesogenic moiety of 2,2′-dimethylazoxybenzene and a flexible spacer of dodecanedioyl in the main chain were described elsewhere.[2-4] The unfractionated sample of DDA-9 has a number-average molecular weight $\overline{M}_n$ of 20,000. The phase transition temperatures are K115N160I, where K denotes the crystal, N the nematic and I the isotropic phase, respectively. The compound is perfectly stable within this temperature range.

The high pressure vessel for WAXS scattering used in this study is described elsewhere.[5] The high pressure WAXS system was designed to be operated at hydrostatic pressures up to 600 MPa and at high temperatures up to 300°C. It is equipped with a high-speed X-ray detecting system by a position-sensitive proportional counter (PSPC) so that dynamic measurements such as crystallization, melting and phase transition of polymers can be performed rapidly under high pressures. A sample set in the beryllium spindle was pressurized hydrostatically

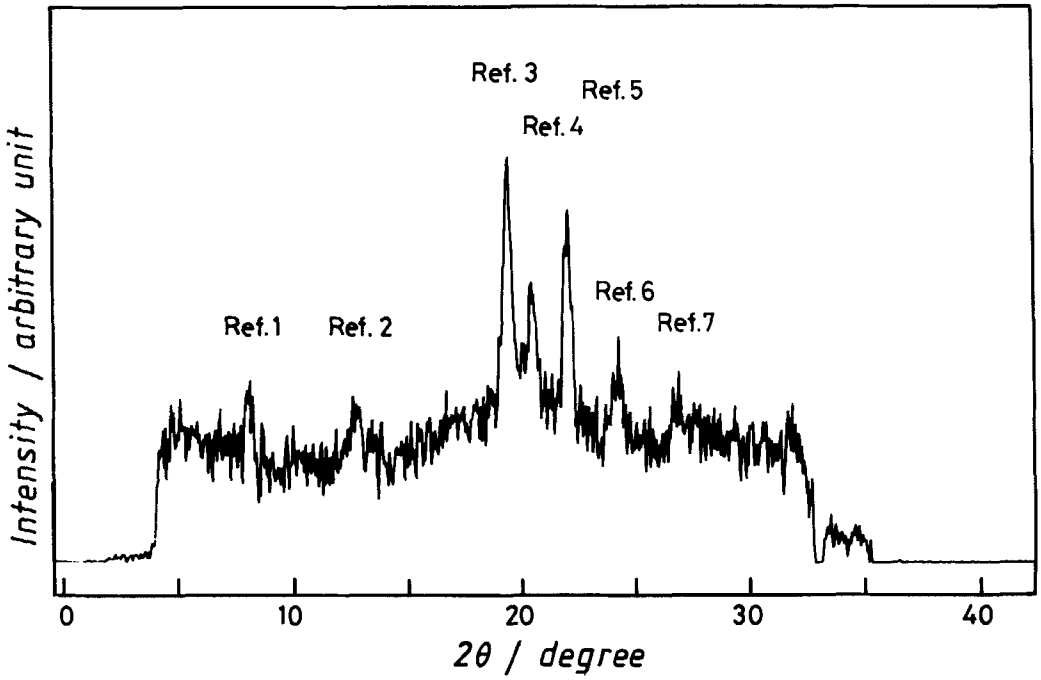


FIGURE 1 A typical WAXS pattern of the normal crystalline form of the DDA-9 polyester under atmospheric pressure.

with dimethyl silicone oil of low viscosity (10 cs, TSF451 Toshiba Silicone Co. Ltd) and the sample was placed in a beam of Ni-filtered CuKα X-rays generated by a rotating anode X-ray generator of 50 kV and 100 mA (Rotaflex RU-200, Rigaku Ltd.). Pressure was read directly within a precision of ±1 MPa by a digital manometer composed of Manganin gauge. The gauge was calibrated against a precision broudon gauge (Heise CM type, Dresser Industries, Inc.) used as a secondary pressure standard.

RESULTS AND DISCUSSION

Figure 1 shows a typical WAXS pattern of the normal DDA-9 crystal at room temperature formed under atmospheric pressure. The crystal reflections are ob-

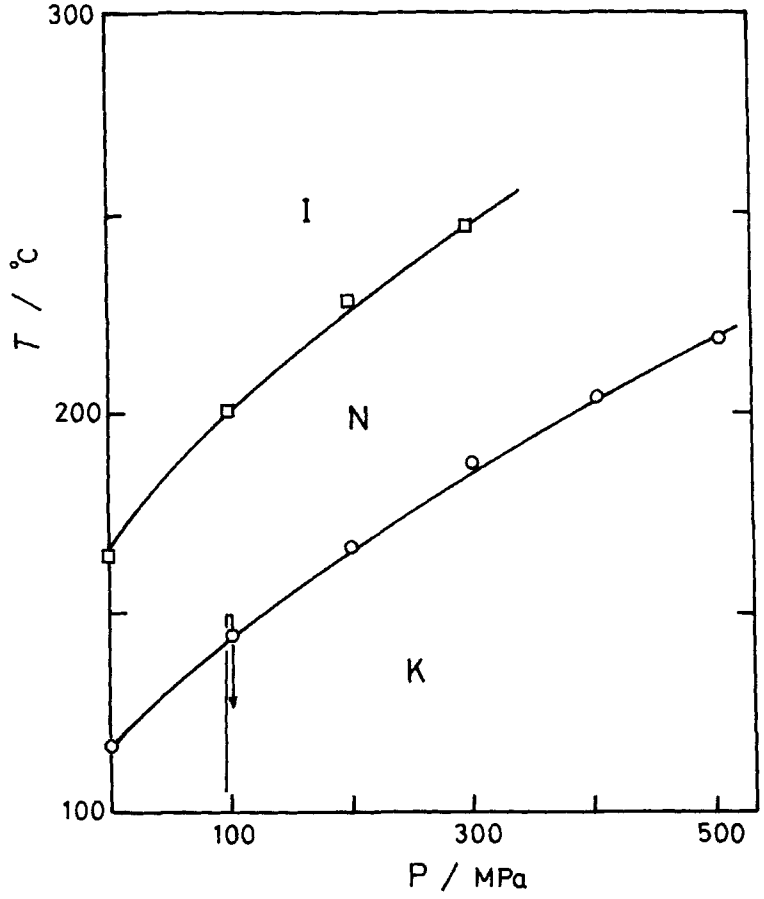


FIGURE 2 A phase diagram of the DDA-9 polyester with the normal crystalline form.

served at $2\theta = 7.8°$ as a low-angle (Reference 1) peak, $2\theta = 12.5°$ as an intermediate-angle (Reference 2) peak, $2\theta = 19.1°$ (Reference 3), 20.4° (Reference 4), 21.8° (Reference 5), 24.0° (Reference 6), and 26.6° (Reference 7) as three strong and two weak peaks in the wide-angle region. Figure 2 shows the phase diagram of the normal sample of DDA-9 polyester measured with a high-pressure DTA appara-

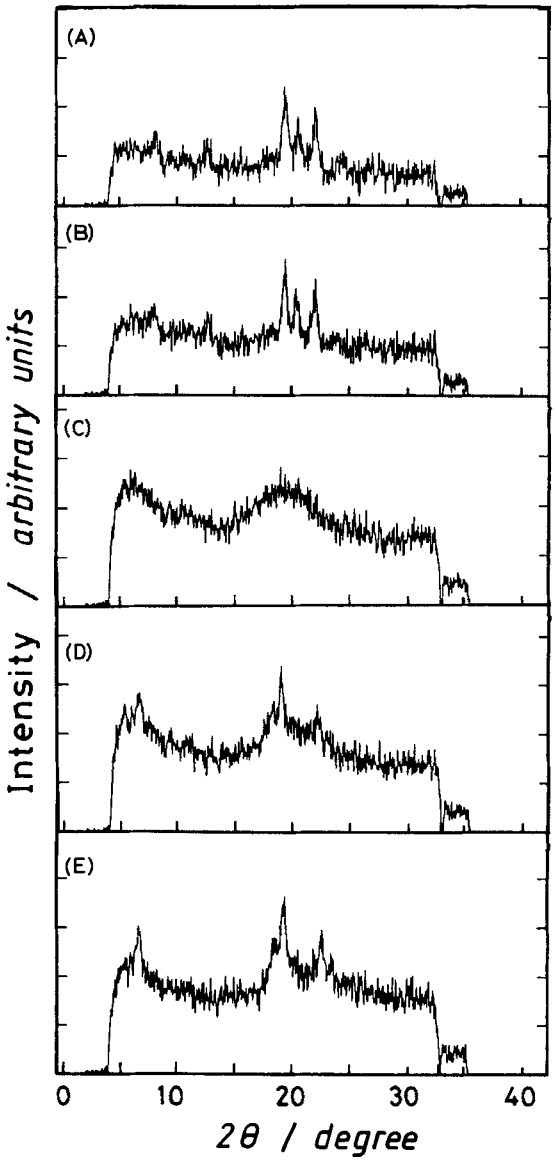


FIGURE 3 WAXS patterns of the DDA-9 polyester at 100 MPa; (A) Normal crystalline form at 24°C (1st heating), (B) Normal form at 100°C (1st heating), (C) Amorphous pattern of the nematic phase at 150°C, (D) High-pressure modification form at 104°C (1st cooling), and (E) High-pressure modification form at 50°C (1st cooling).

tus.[5] The thermal behaviors of the K-N and the N-I transitions at 100 MPa were observed similarly at about 146°C and 195°C, respectively. The thermal behaviors and the phase diagrams of these polyesters are described elsewhere.[6,7]

The structural change in the crystalline pattern of the DDA-9 polyester was investigated as a function of temperature under hydrostatic pressures. Figure 3 shows the change in WAXS pattern of the normal DDA-9 crystal with increasing and then decreasing temperature under pressures of 100 MPa. The WAXS pattern of the normal crystalline phase remains unchanged until the melting of the crystal at the K-N transition point of about 146°C. At 146°C and above, the WAXS pattern changed from that of a crystalline to that of an amorphous compound. After reaching 150°C the sample was cooled and the WAXS pattern was monitored. At 140°C a new WAXS pattern substantially different from the original one appeared. It shows a clear low-angle reflection at about $2\theta = 6.6°$, four wide-angle reflection peaks at about $2\theta = 18.4°$, 19.3°, 22.5°, and 25.8°, and no intermediate-angle reflection. Table I gives the values of d-spacings for both the normal crystal form and the high-pressure crystal form of the DDA-9 polyester at 50°C and 100 MPa. Figures 4 and 5 show the temperature dependence of d-spacings for the normal form in the first run and for the high-pressure form in the second run at 100 MPa. The d-spacing for the low-angle reflection of the normal form tends to increase slightly with increasing temperature, while that of the high-pressure form is almost constant, independent of temperature. The WAXS pattern is stable below the K-N transition and remains also unchanged on decreasing the pressure from 100 MPa to atmospheric pressure at room temperature. Once formed, the crystal mod-

TABLE I

d-Spacings at 50°C and 100 MPa for the normal crystal form and the high-pressure modification of DDA-9 formed by cooling from the nematic state at 150°C and 100 MPa

d-Spacing / Å	
Normal form	High-pressure Modification
11.08	13.39
7.02	----
----	4.81
4.59	4.59
4.34	----
4.03	3.95
3.71	3.45

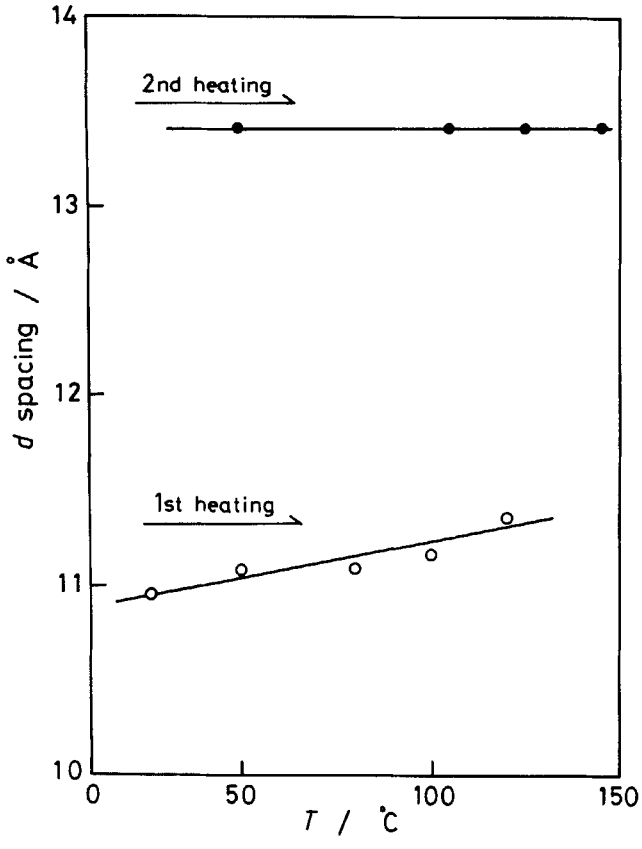


FIGURE 4 Temperature dependence of the d-spacing of the low-angle (Reference 1) reflection of both forms of DDA-9 crystals at 100 MPa.

ification is stable even under atmospheric pressure. The sample of DDA-9 with the high-pressure crystalline modification displayed a density of ca. 1.200 g/cm^3 substantially larger than the density (1.070 g/m^3) of the sample with the normal crystal form, confirming its stability. It is noteworthy that the high-pressure crystalline form of DDA-9 was not observed at 100 MPa by cooling the sample from the isotropic state at 200°C nor was it observed by cooling the sample from the nematic state at low pressures below 50 MPa. Under these circumstances only the normal crystalline form of DDA-9 was observed.

The molecular mass appears also to have a strong influence. The high-pressure form could not be observed for low molecular weight samples of DDA-9 ($\overline{M}_n$ = 4,000). It appears that the crystalline high-pressure form of DDA-9 is related to its supermolecular structure. Figure 6 shows the DSC heating curves of the DDA-9 sample with the high-pressure form cooled from 150°C at 100 MPa and with the normal form crystallized on the subsequent DSC runs. After heating the sample with the high-pressure modification to the isotropic liquid state at 170°C (1st run),

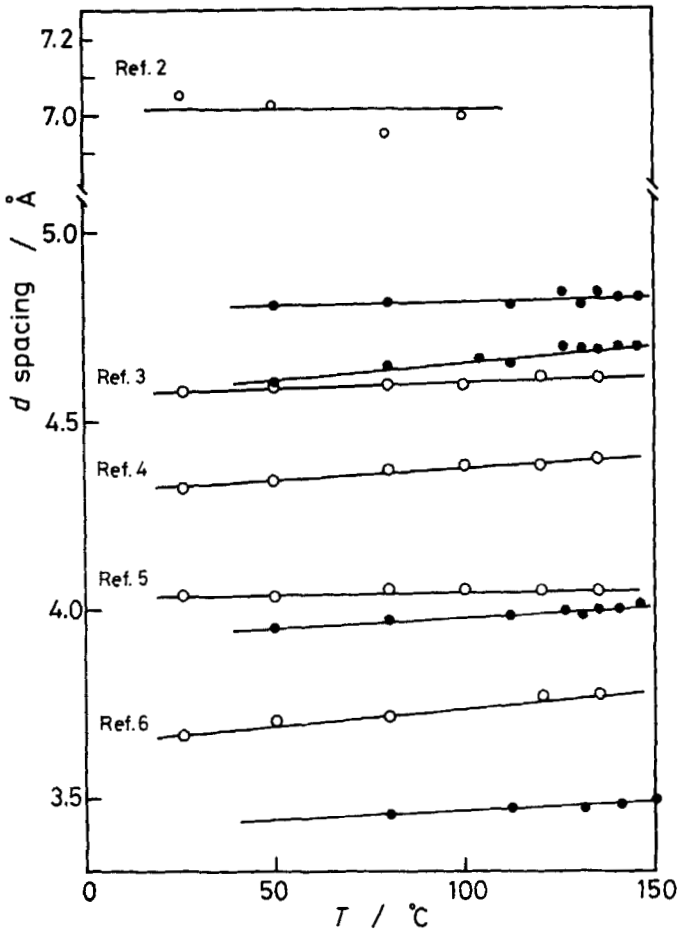


FIGURE 5 Temperature dependence of the d-spacings of the intermediate-angle (Reference 2) reflection and 4 wide-angle (Reference 3–6) reflections observed in the WAXS patterns of both forms of DDA-9 crystals at 100 MPa.

the sample was cooled at 10°C/min to room temperature (2nd run). The cooled sample has the usual WAXS pattern indicating the regeneration of the sample with the normal crystal form. The subsequent heating curve (3rd run) is for a sample with the normal crystal form. The small exothermic peak just below the main peak of the K-N transition (3rd run), suggesting an occurrence of some reorganization of the crystal to a more stable one with the normal crystalline form in the premelting region, is not observed in the 1st run. The temperature corresponding to the melting peak of the high-pressure modification form is 119°C about 4 degrees higher than that of the K-N transition point for the normal crystal form. It is to be noted that a stable melting behavior of the K-N transition is observed in the 1st run for the sample with the high-pressure modification. Figure 7 summarizes our finding.

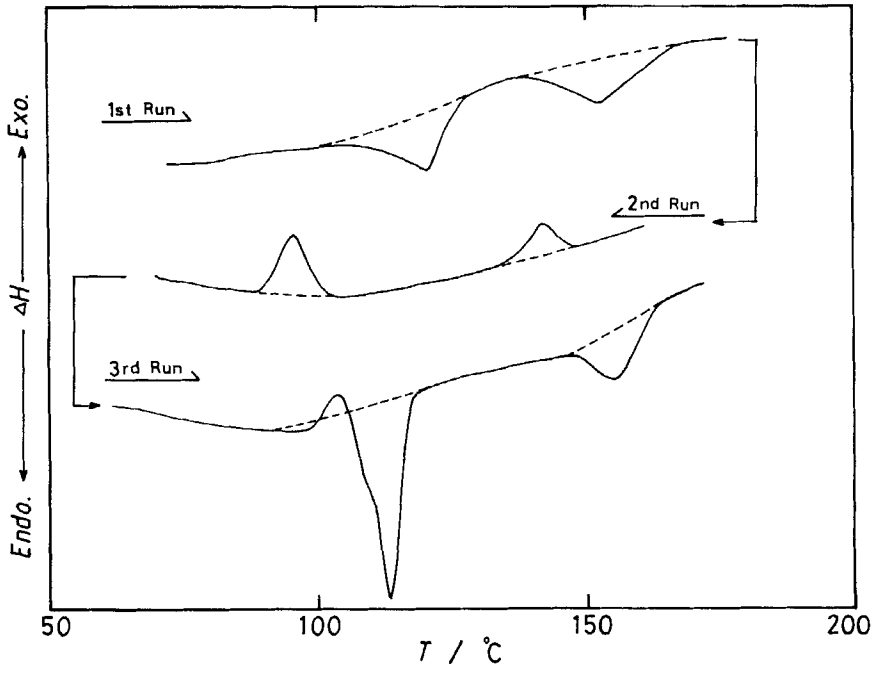


FIGURE 6 Comparative DSC curves of the high-pressure polymorph of DDA-9 and of the normal DDA-9 form.

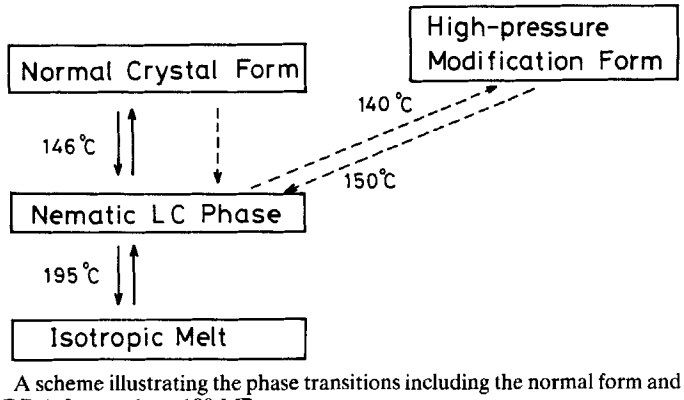


FIGURE 7 A scheme illustrating the phase transitions including the normal form and the high-pressure form of the DDA-9 crystals at 100 MPa.

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