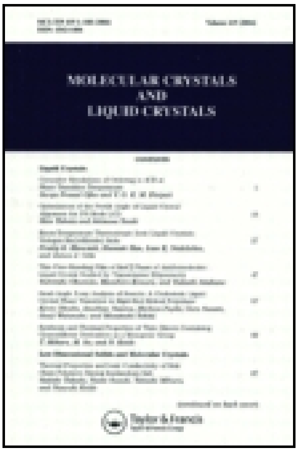

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Effect of Pressure on Formation of Crystal Polymorph of a Liquid Crystalline Polyester

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Effect of Pressure on Formation of Crystal Polymorph of a Liquid Crystalline Polyester

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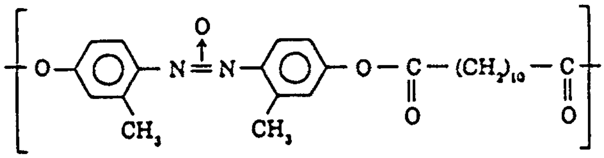
The phase behavior of a liquid crystalline polyester, poly(4,4′-dioxy-2′-dimethylazoxybenzene dodecanedioyl) (labeled as DDA-9), under hydrostatic pressures up to 300 MPa has been studied by using a wide-angle x-ray scattering apparatus equipped with a high-pressure sample vessel. Generally, the normal crystalline form, form I, is predominantly formed, on cooling from the isotropic liquid phase, via the nematic mesophase. An interesting fact is found under hydrostatic pressure: a crystal polymorph, form II, is concurrently formed by cooling slowly from the nematic phase just above the crystal-nematic point T_{k-n} (form I) at pressures ranging from 50 to 200 MPa. Furthermore, the form II polymorph can be seen at very low pressures as 1 MPa when the sample is annealed at temperatures just above T_{k-n} (form I) for 1 ~ 2 hrs under pressure and then cooled slowly. Once formed, the form II polymorph is metastable at room temperature under atmospheric pressure. The polymorph has a melting point T_{k-n} (form II) higher by 4 ~ 5°C than the T_{k-n} (form I). It is concluded that the formation of the crystal polymorph is substantially accelerated by hydrostatic pressure and heat treatment.

Keywords: thermotropic polyester, nematic phase, hydrostatic pressures, crystal modification, heat treatment, wide-angle x-ray diffraction

INTRODUCTION

Main-chain thermotropic polymers have been extensively studied from both the theoretical and practical points of view. The synthesis and thermal properties of thermotropic polyesters of poly(4,4′-dioxy-2,2′-dimethylazoxybenzene dodecanedioyl) (commonly labeled as DDA-9) have been investigated by Blumstein *et al.*[1-6] The polymer consists of a regular sequence of rigid azoxybenzene mesogenic cores (mesogen 9) and flexible dodecanedioate "spacer" group (DDA).



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The polymer is a semicrystalline solid and the wide-angle x-ray scattering (WAXS) pattern shows several strong reflections of the normal crystalline form, form I.[1] It has moderately low transition temperatures and a nematic stability range of about 40°C.

We have been particularly interested in the phase transitions, melting and crystallization, the mesophase glass transition, and the mesophase-isotropic transition of DDA-9 polyester under hydrostatic pressure.[7-10] In the course of this study we found an interesting experimental fact of the formation of the crystalline polymorph of DDA-9 under hydrostatic pressure. A crystal polymorph, form II, of the DDA-9 polyester is formed preferentially when the sample is cooled slowly from the nematic phase at temperatures several degrees above the melting point T_{k-n} (form I) at 100 MPa.[10] Once formed, the form II is metastable under atmospheric pressure.

In this paper the structural change and formation of the crystal polymorph of the DDA-9 polyester under various conditions are further studied by using a WAXS apparatus equipped with a high-pressure sample vessel that was developed in our laboratory.[11]

EXPERIMENTAL SECTION

Materials

The synthesis and thermal properties of DDA-9 polyester are described elsewhere.[1-6] The DDA-9 sample has a number-average molecular weight ($\overline{M}n$) of 20,000 and a polydispersity ($\overline{M}w/\overline{M}n$) of about 2 ~ 3. The phase transition temperatures are K115N160I, where *K* denotes the crystal, *N* the nematic and *I* the isotropic phase, respectively.

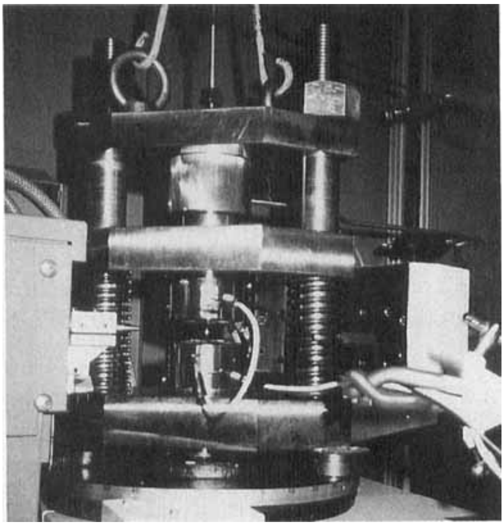

FIGURE 1 Photograph of the high-pressure sample vessel for WAXS.

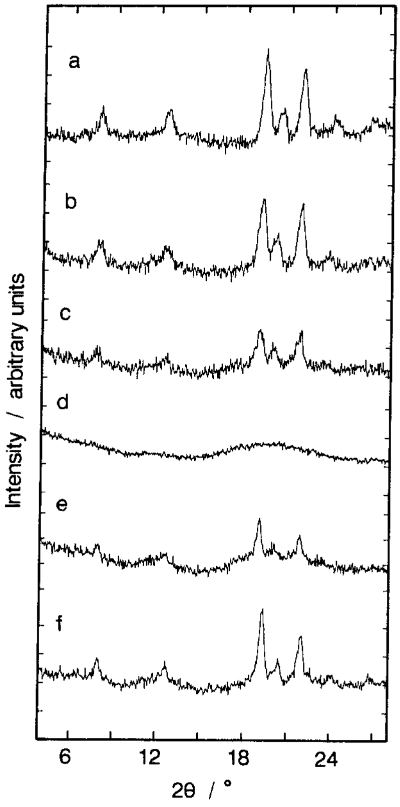

FIGURE 2 WAXS patterns of the DDA-9 polyester on heating and subsequently cooling at 50 MPa: (a) 23°C, (b) 100°C, (c) 130°C, (d) 135°C, (e) 120°C, and (f) 32°C.

WAXS Apparatus

The photograph of the high-pressure sample vessel of the WAXS apparatus is shown in Figure 1. The WAXS system was designed to be operated at hydrostatic pressures up to 600 MPa and at temperatures up to 300°C. Dimethylsilicone oil of low-viscosity (Toshiba Silicone, TSF 451, 10 centiStokes) was used as a pressure transmitting medium. The WAXS apparatus is equipped with a high-speed x-ray detecting system, using a curved position-sensitive proportional counter (PSPC). The PSPC device (PSPC-30, Rigaku Ltd.), having a distance of 200 mm between the sample and itself, is capable of detecting x-ray reflections simultaneously in the region of $2\theta = 28°$. The beryllium (Be) spindle as sample holder having a vertical hole (1.2 mm diameter) is sandwiched between the upper and lower heater blocks, so that it can be perfectly sealed by compressing the Be spindle. The sample in the vertical hole of the Be spindle is pressurized hydrostatically and then is irradiated by a beam of Ni-filtered CuKα x-rays generated by a rotating anode x-ray generator of 60 kV and 200 mA (Rotaflex RU-200, Ragaku Ltd.). Pressure is displayed on a digital manometer within a precision of ±1 MPa, by transferring voltage signals from the gauge of manganin bridges. The manometer was calibrated

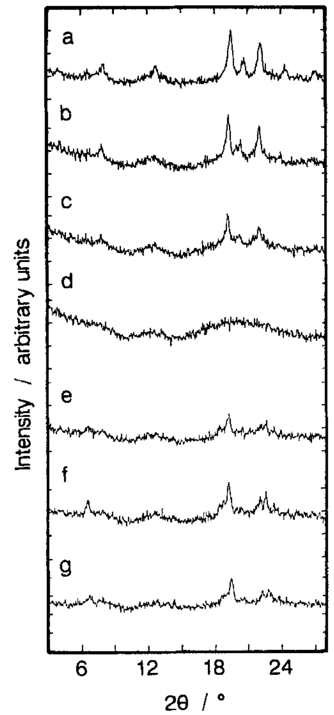

FIGURE 3 WAXS patterns of the DDA-9 polyester on heating and subsequently cooling at 200 MPa: (a) 32°C, (b) 145°C, (c) 160°C, (d) 175°C, (e) 130°C, (f) 90°C, and (g) 45°C.

against a precision Broudon gauge (Heise, type CM, Dresser Industries, Inc.) used as a secondary pressure standard.

X-ray photographs are also taken by a cylindrical camera having a radius of 2.87 cm. Thermal analysis of the sample at atmospheric pressure was performed at a scanning rate of 10°C/min by using a Perkin-Elmer DSC II apparatus.

RESULTS AND DISCUSSION

Formation of a Crystal Polymorph

Slow cooling from the nematic state under hydrostatic pressure. The typical WAXS pattern of the form I crystals under atmospheric pressure shows reflections at $2\theta = 7.8°$ as a low-angle peak, $2\theta = 12.5°$ as an intermediate peak, two strong reflections at $2\theta = 19.1°$, 21.8°, and three weak reflections at $2\theta = 20.4°$, 24.0°, 26.6° in the wide-angle region up to 30°.[10] The structural changes in the WAXS pattern of the DDA-9 polyester were investigated as a function of temperature and pressure. Figure 2 shows the WAXS patterns of the original form I crystal on heating and successive cooling at 50 MPa. The WAXS pattern of the form I crystal is reversible on thermal cycling. Figure 3 shows the WAXS patterns of the form I crystal on heating and subsequent cooling at 200 MPa. The WAXS pattern of the

TABLE I

Room-temperature *d* spacings for the normal crystal, form I, and the two polymorphs, form II and form III, of the DDA-9 polyester

d Spacing / Å					
form I (normal crystal)		form II (pressure polymorph)		form III (polymorph in fibers)	
11.3	m	13.6	m	....	
7.0_7	m	....		7.3_7	w
....		....		5.3_9	m
5.1_2	w	5.1_0	w	5.0_8	s
....		4.8_7	m	....	
4.6_4	s	4.6_4	s	4.6_3	s
4.3_6	m	....		4.3_7	w
....		....		4.2_1	s
4.0_7	s	4.0_6	s	4.1_2	s
....		3.9_8	s	....	
....		3.8_3	m	....	
3.7_2	m	3.7_1	w	3.7_6	m
....		3.4_6	m	....	
3.3_4	m	....		....	

form I crystal is held on heating until the melting of the crystal at the T_{k-n} (form I) point. The nematic phase at temperatures above 172°C (T_{k-n} (form I) at 200 MPa) shows an x-ray pattern similar to the one of an amorphous compound. After heating at 175°C, the sample was cooled slowly to room temperature at a rate of 0.2 ~ 0.3°C/min. New crystal reflections appeared at 130°C on cooling. The diffraction pattern is substantially different from the one of the original form I, indicating the formation of the crystal polymorph, form II, as reported previously.[10] The low-angle reflection at $2\theta = 6.55°$ (13.5 ± 0.1 Å) of the form II polymorph is held constant on cooling under pressure. The *d* spacing of the form II is longer by about 2.3 ± 0.2 Å than that of the form I crystal. The form II polymorph is held on releasing pressure from 200 MPa to atmospheric pressure. Table I lists the values of *d* spacings for both the form I and the form II crystals under atmospheric pressure. Figures 4(a) and 4(b) shows the typical WAXS patterns and x-ray photographs by cylindrical camera of the form I crystal (A) formed at 10 MPa, and the form II enriched sample (B) obtained at 150 MPa. The former sample was normally cooled (~5°C/min) from the nematic phase at 135°C and 10 MPa, and the latter was obtained by slow cooling from the nematic phase at 165°C and 150 MPa. Figure 4(a) shows clearly the difference of the WAXS patterns between the

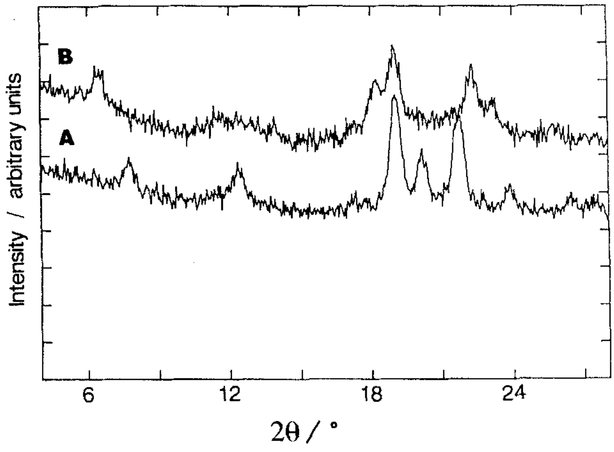

FIGURE 4(a) WAXS patterns at 24°C and atmospheric pressure of the two crystalline forms of the DDA-9 polyester: (A) form I and (B) form II.

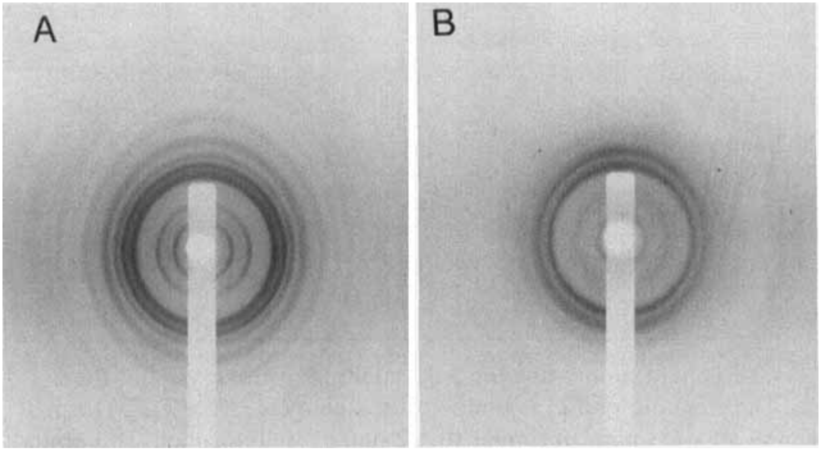

FIGURE 4(b) Cylindrical camera photographs of the two crystalline forms of the DDA-9 polyester: (A) form I sample formed at 10 MPa and (B) form II enriched sample formed at 150 MPa. See Color Plate XIX.

two crystalline forms. The characteristics in the WAXS pattern of the form II is a shift of the low-angle reflection from $2\theta = 8.0°$ to 6.5°, disappearance of the two reflections at $2\theta = 12.6°$ and 20.5° and appearance of a new reflection at $2\theta = 18.4°$ in the 2θ region up to 30°. Figure 4(b) shows the lower crystallinity of the pressure-quenched sample having the form II polymorph, compared with that of the sample having the normal crystal of form I. The form II polymorph is ascertained to be metastable for several months or more under atmospheric pressure.

Figure 5 shows the WAXS patterns at 24°C and 1 atm of the samples cooled slowly from the nematic phase at temperatures several degrees above the T_{k-n} (form I) point under various pressures. Increasing hydrostatic pressure up to 50 MPa does not change significantly the x-ray pattern of the form I crystals formed

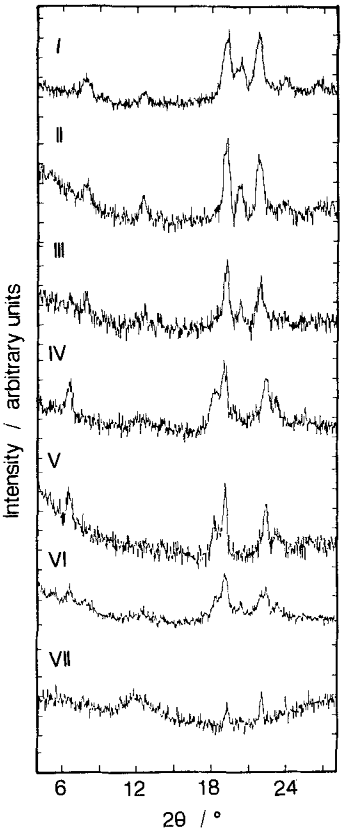

FIGURE 5 WAXS patterns at 24°C and atmospheric pressure of the DDA-9 samples cooled slowly from the nematic state just above the T_{k-n} (I) point under pressures: (I) 0.1 MPa (1 atm), (II) 45 MPa, (III) 60 MPa, (IV) 70 MPa, (V) 100 MPa, (VI) 200 MPa, and (VII) 300 MPa.

at atmospheric pressure, although the T_{k-n} (form I) point of the normal crystal is increased with pressure. Further increase of the pressure above about 70 MPa, on the other hand, results in quite different x-ray profiles, as is shown in Figure 5, IV ~ VI. The sample formed at 60 MPa (Figure 5, III) shows a mixed x-ray pattern with reflections from the two crystalline forms. The diffraction patterns of the samples formed at pressures above 70 MPa are identical to those of the form II polymorph at 100 MPa.[10] Unfortunately, the formation of the form II polymorph is ambiguous at high pressures around 300 MPa possibly because of thermal decomposition of the DDA-9 polyester at temperatures above 220°C. Here, it is noted that the polymorph can be obtained preferentially on cooling slowly from the nematic state at high pressures between 70 and 200 MPa. In contrast, the form I crystal is obtained when the sample is cooled rapdily either from the nematic state at higher temperatures or the isotropic melt under all pressures. Consequently it is concluded that the formation of the form II polymorph is dependent strongly upon the thermal history of the sample under high pressure. Figure 6 shows the phase diagram of the K (form I) $- N - I$ phases of the DDA-9 polyester, indicating

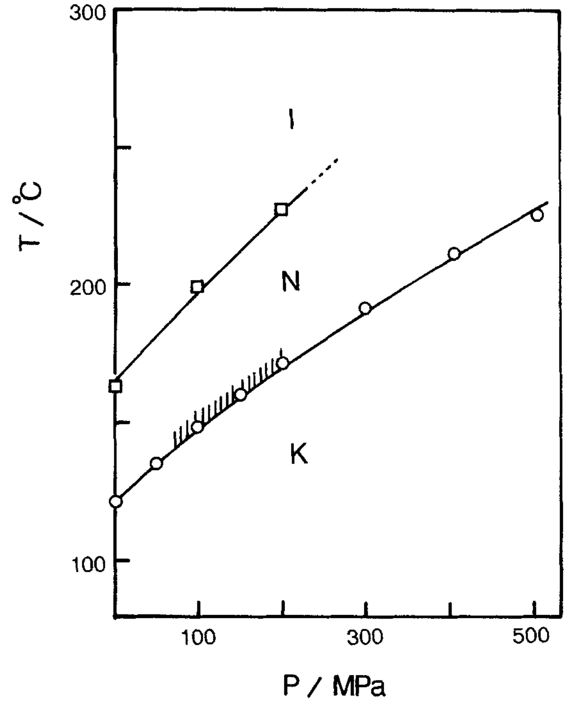

FIGURE 6 Phase diagram of the DDA-9 polyester.

the pressure region of the formation of the form II polymorph as small bars just above the $K - N$ curve.

Effect of Heat Treatment

The annealing effect on the formation of the form II polymorph was studied at various temperatures and pressures. The DDA-9 samples were held at temperatures just 3 ~ 5 degrees above the T_{k-n} (form I) for 1 hr under pressure and then cooled slowly to room temperature. The resulting diffraction patterns are shown in Figure 7. The diffraction peaks of the form II polymorph can be clearly seen with those of the form I crystals in the low pressure region below 50 MPa. The annealing effect on the formation of the polymorph is significant. The experimental fact indicates that pressure is not an essential factor, but it is a major kinetic factor in the formation of the form II polymorph. The polymorphic behavior of the DDA-9 polyester suggests strongly that the form II polymorph could appear probably at 0.1 MPa (atmospheric pressure). Consequently a similar annealing experiment was performed in dimethylsilicone oil without pressurising. The corresponding diffraction pattern of the DDA-9 sample is illustrated in Figure 7, IV. When the sample in silicone oil is annealed at 118–119°C for 2 hrs and then cooled slowly to room temperature, the reflections of the form II crystals appear together with those of the form I crystals. On the other hand, the form I crystal is obtained predominantly when the sample is cooled from both the nematic phase and isotropic melt without annealing.

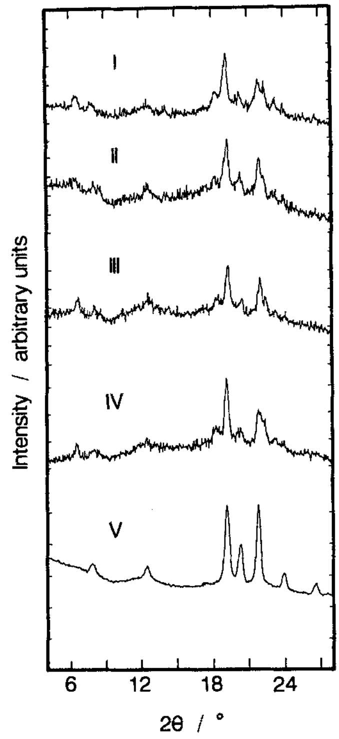

FIGURE 7 WAXS patterns at 24°C and atmospheric pressure of the DDA-9 samples annealed at just above T_{k-n} (I) for 1 hr under pressures: (I) 50 MPa, (II) 20 MPa, and (III) 1 MPa. (IV) shows the WAXS pattern of the sample annealed at 118°C for 2 hr in the DSC sample holder under N_2 gas flow. (V) shows the typical WAXS pattern of the normal form I crystal.

Thermal stability of the normal crystal and of the polymorph. Melting experiments of the sample consisting of the form I and the form II crystals were performed to compare their thermal stability at 0.1 MPa and 50 MPa. The WAXS patterns on heating at 50 MPa showed that the reflections of the form I crystal disappeared first at about 128°C, while those of the form II polymorph remained up to 132 ~ 133°C. Figure 8 shows the DSC heating curve (Run 1) of the mixed crystals formed at 100 MPa. The low- and high-temperature peaks at the *K*-*N* transition belong to the meltings of the form I and form II polymorph.[10] In fact, the form I crystals are formed completely by cooling from the isotropic state (Run 2). Run 3 shows the typical melting behavior of the form I crystals on reheating. Figure 9 shows the DSC heating curves of the crystals formed at various pressures. Both the samples formed at 20 and 60 MPa shows double endothermic peaks at the *K*-*N* transition, while the samples formed at 70 and 200 MPa show another small peak at higher temperatures in the *K*-*N* transition. Comparing with the data in Figure 8, the low- and intermediate-temperature peaks at the *K*-*N* transition correspond to the melting of the form I, while the new peak formed at 70 and 200 MPa corresponds to the melting of the form II polymorph. These results are illustrated in Table II. It is interesting to note that the heat of fusion of the form II crystals is remarkably

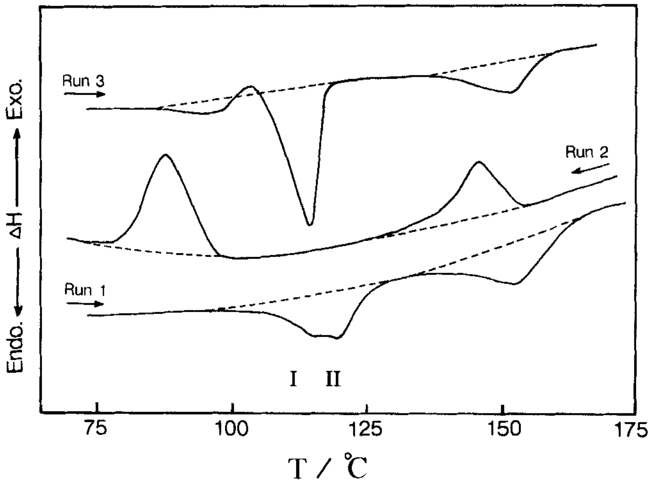

FIGURE 8 DSC curves of the pressure-quenched sample (Run 1) formed by cooling from the nematic state at 100 MPa and the successive cooling (Run 2) and reheating (Run 3) of the normal form I crystals. Scanning rate: 10°C/min.

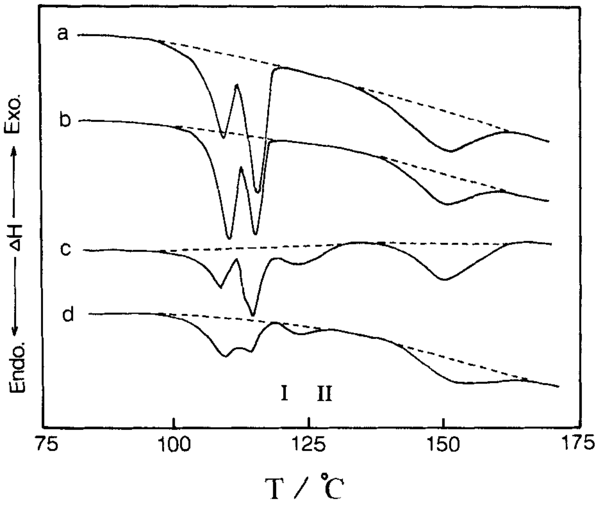

FIGURE 9 DSC heating curves of the DDA-9 samples crystallized under pressures: (a) 20 MPa, (b) 60 MPa, (c) 70 MPa, and (d) 200 MPa. Heating rate: 10°C/min.

small, compared with the value of the form I crystal. The small heat of fusion is due to the low crystallinity of the polymorph formed under pressures. In any way, it is pointed out that the T_{k-n} (form II) point of the polymorph is higher by 4 ~ 5°C than the T_{k-n} (form I) point of the normal crystal at 0.1 MPa and 50 MPa.

In the aging at room temperature of the pressure-crystallized sample containing only the form II polymorph, the reflections of the form I crystals appeared after aging for several days and then became gradually strong with aging up to several months, while those intensities of the form II polymorph seem almost unchanged.

TABLE II

Thermodynamic data of the crystal-nematic and the nematic-isotropic phase transitions of the DDA-9 polyester

P	K - N transition				N - I transition	
P MPa	T_{k-n}(I) °C		T_{k-n}(II) °C	ΔH cal/g	T_{n-i} °C	ΔH cal/g
1atm(P_c/MPa)	DSC method					
(20)	109	116			153	
(60)	110	114			150	
(70)	108	115	119		150	
(80)	107	115	119		149	
(200)	107	111	117		147	
(100)			119	2.3_2	152	2.2_9
2nd-run		115		4.5-6.7	154	2.3-2.4
P/MPa	X-ray method					
1 atm		112	117			
50		128-9	133-4			
100		146-7	150			

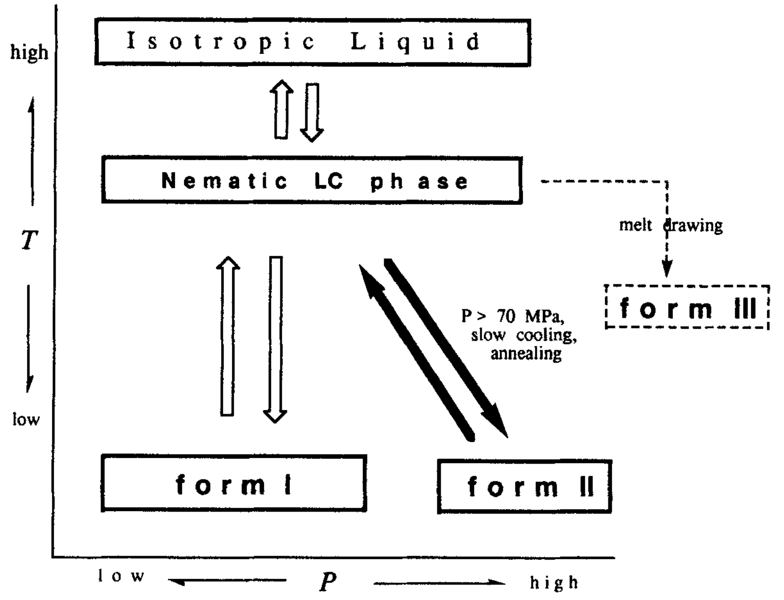

FIGURE 10 Relation of phases between the crystal polymorphs of the DDA-9 polyester.

This behavior suggests that the form I crystal is a stable low-temperature crystal phase that can be easily formed at room temperatures, while the form II polymorph might be a high-temperature phase because of the higher T_{k-n} (form II) point. The phase relation between the form I and form II crystals is illustrated in Figure 10. Application of hydrostatic pressure and annealing at temperatures around the T_{k-n} (form I) point enhances the formation of the form II crystals compared to that of the form I crystals. The experimental results in this study imply that the crystallization rate, presumably the nucleation rate, of the form II crystals under hydrostatic pressures is extremely small, compared with the value of the form I crystals.

Recently a third polymorph has been found in the DDA-9 fibrous samples drawn from the melt. The x-ray pattern and its photograph are quite different from both previous forms. This polymorph is designated as form III. The data of the *d* spacing of the form III polymorph are listed also in Table I. This polymorph corresponds to the crystal modification of a fiber extruded from the nematic melt.[2] The structural analysis of these polymorphs is in progress.

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