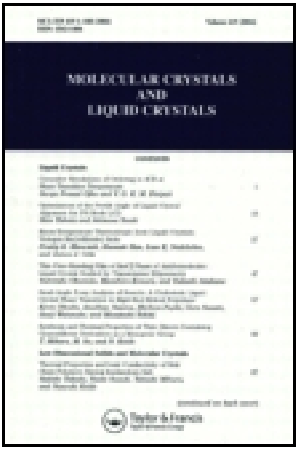

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Phase Transitions of Nematic Main-Chain Polyesters Under High Pressure

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PHASE TRANSITIONS OF NEMATIC MAIN-CHAIN POLYESTERS UNDER HIGH PRESSURE

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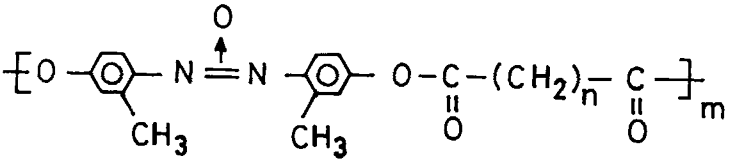
Abstract. The nematic-isotropic (NI) and crystal-nematic (KN) transition temperatures were measured from atmospheric pressure to 1 kbar for a homologous series of thermotropic polyesters based on regularly alternating 2,2'-dimethylazoxybenzene mesogen and alkanedicarboxylic acid spacer. The values of (dP/dT) for the NI transitions show an odd-even alternation with n, consistent with the previously reported alternation of T_{NI} and $(\Delta H)_{NI}$. The characteristic temperature T* calculated for n = odd is approximately 300 K, similar to the values for noncybotactic nematics. On the other hand, for n = even, T* could not be reliably calculated, perhaps due to the existence of cybotactic ordering. At the KN transition there is no such clear alternation in (dP/dT). The specific volume changes $(\Delta V)_{KN}$ at melting are very small and comparable in magnitude with $(\Delta V)_{NI}$. They are much smaller than the corresponding values for low molar mass liquid crystals and conventional polymers. This suggests that the crystals of these polyesters may have a high degree of imperfection.

INTRODUCTION

The synthesis of a homologous series of thermotropic main-chain polyesters, based on regularly alternating 2,2'-dimethylazoxybenzene mesogen and alkanedicarboxylic acid spacer was reported previously.[1] The general formula for the polyesters is given below.



It was found that the nematic-isotropic transition temperature T_{N-I}, as well as the transition enthalpy $(\Delta H)_{N-I}$ show an alternation similar to that observed in low molar mass liquid crystals. In the present paper we investigate the effect of pressure on the crystal-nematic (K - N) and nematic-isotropic (N - I) transitions on these polyesters for the homologues n = 7 to 14.

THE HIGH PRESSURE SET UP

An optical high pressure cell was used for the experiments. The polymer sample was sandwiched between two optically polished sapphire cylinders and enclosed in a fluran tube so that the sample is isolated from the pressure-transmitting fluid (Plexol). Details of the cell are identical to those used in our earlier studies on low molecular mass liquid crystals and lipids.[2-4] The phase transitions were detected by the optical transmission technique. Light from a helium-neon laser was incident normaly on the sample and the intensity of the light transmitted by the sample in the forward direction was measured by a photodetector. The experiments were always conducted along isobars and in the heating mode, i.e., keeping the pressure constant at any desired value, the temperature of the sample was increased at a linear rate of about 1°C/min. The on-set of the transition was signalled by a sudden change in the transmitted light intensity (Fig. 1).

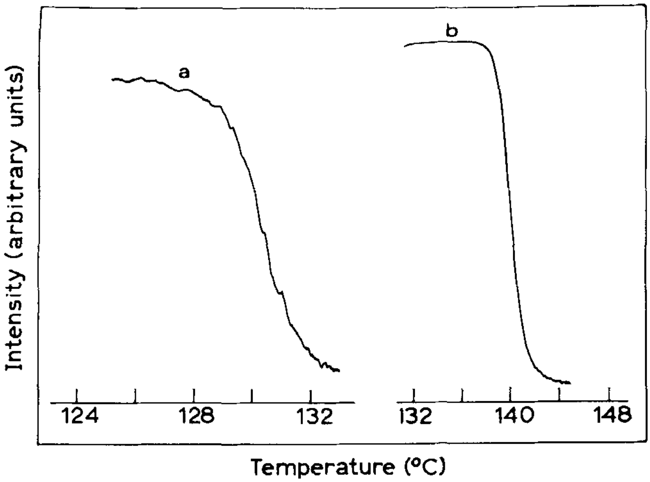


Fig. 1. Raw traces showing the change in the transmitted light intensity at the (a) crystal-nematic and (b) nematic-isotropic transitions for the $n = 14$ polyester. The pressures are (a) 263 bars and (b) 67 bars.

RESULTS

A typical pressure-temperature (P-T) diagram is shown in Fig. 2. For all the compounds a least square fit of the data to a straight line was carried out for both K-N and N-I transitions and the value of dP/dT was evaluated. It is seen that $(dP/dT)_{N-I}$ shows an odd-even alternation with n (Fig. 3) similar to that exhibited by T_{N-I} and $(\Delta H)_{N-I}$ measured at 1 bar[1] (Fig. 4). Similar instances of odd-even alternation of $(dP/dT)_{N-I}$ has been observed earlier in the case of low molecular mass liquid crystals.[5,6] *On the other hand, the variation in (dP/dT) for* the K-N transition is much less pronounced and, in fact, reverses its trend for high n (Fig. 5).

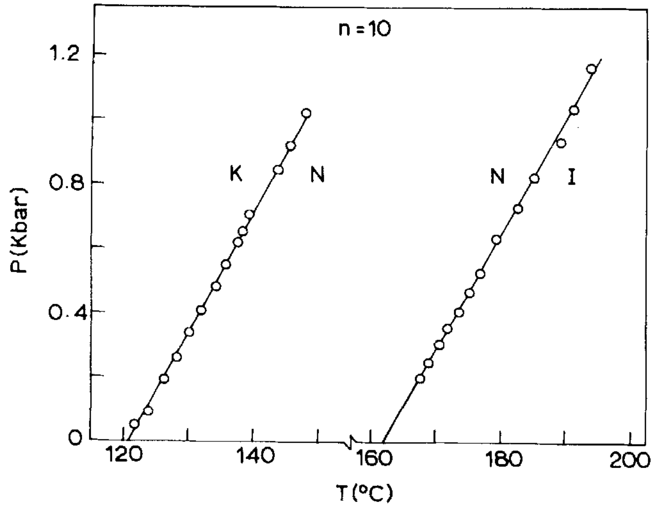


Fig. 2. P-T diagram of the polyester with n = 10

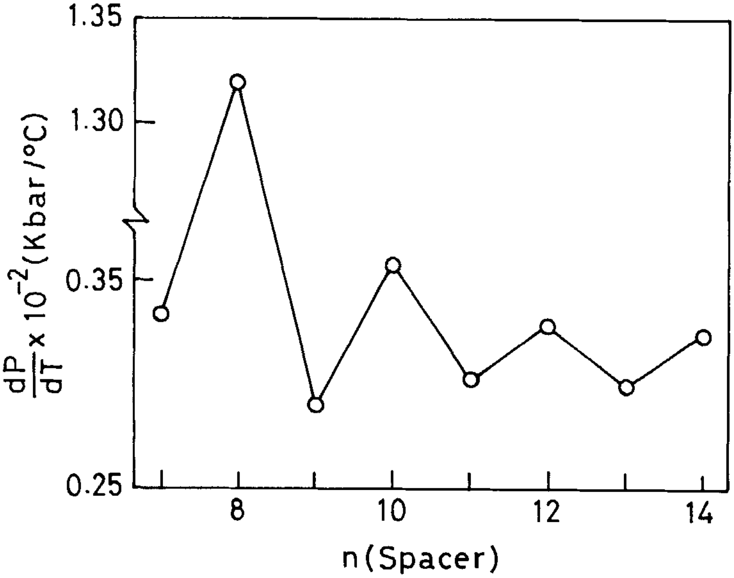


Fig. 3. Variation of dP/dT for the nematic-isotropic transition with n.

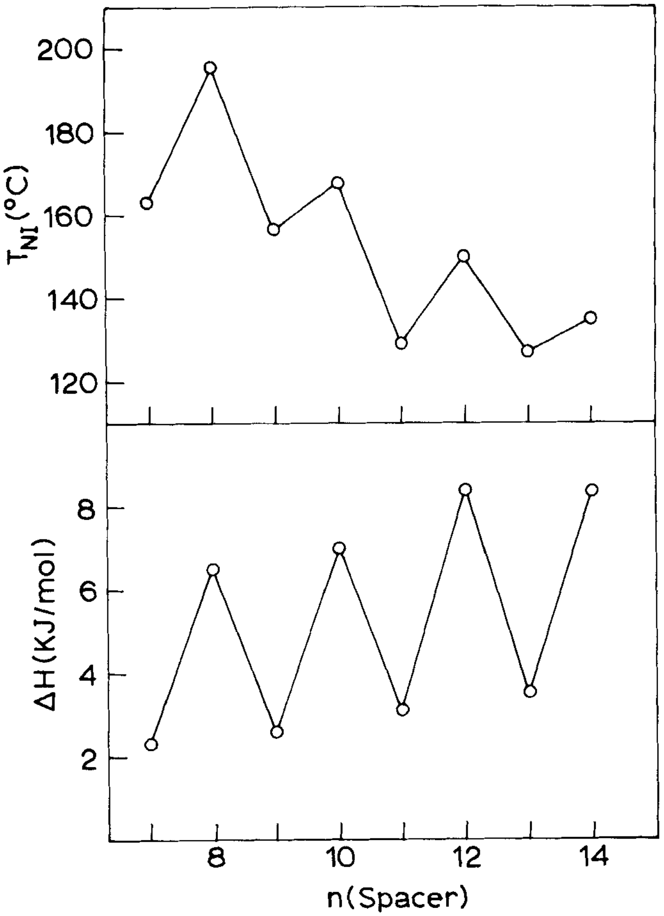


Fig.4. Plot of the nematic-isotropic transition temperature (T_{NI}) and enthalpy of transition $(\Delta H)_{N-I}$ measured at 1 bar vs. n.

According to the Clausius-Clapeyron equation

$$dT/dP \ \square \ T(\Delta V/\Delta H) \quad ,$$

where ΔV is the volume change at the transition. Using our values of dP/dT and the ΔH data reported earlier,[1] ΔV has been evaluated for both K-N and N-I transitions. These are given in Tables I and II respectively.

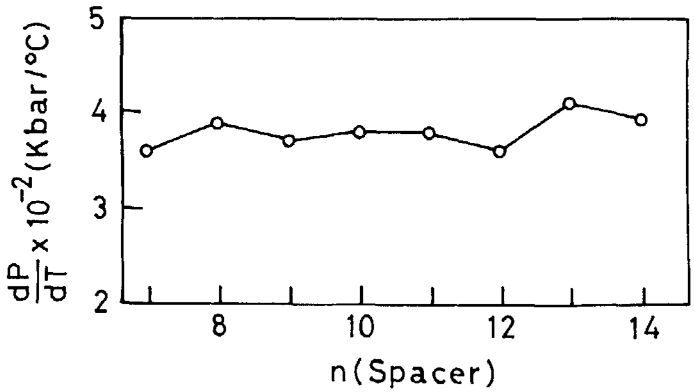


Fig.5. Plot of dP/dT for the crystal-nematic (K-N) transitions vs. n.

Table I. Thermodynamic data for the K-N transitions

n	$(dP/dT)_{K-N}$ J/°K cm^3	ΔS_{K-N} x 10^3 J/g°K	ΔV_{K-N} x 10^3 cm^3/g	T_{K-N} § °K
7	3.64	17.87	4.92	371.3
8	3.93	18.76	4.73	409.8
9	3.70	47.69	12.88	394
10	3.77	49.65	13.15	391.2
11	3.77	55.17	14.63	373.8
12	3.58	41.74	11.65	383.8
13	4.15	53.82	12.97	379.8
14	3.92	45.96	11.72	394
p-azoxyanisole (PAA)	3.13[7]	256.3(8)	95.29(9)	390

§From reference 1.

Table II. Thermodynamic data for the N-I transition

n	T_{N-I} °K	$(dP/dT)_{N-I}$ J/cm^3 °K	ΔS_{N-I} x10^3 J/g°K	$\overline{\Delta V}_{N-I}$ x10^3 cm^3/g	T*
7	437.6	3.35	12.82	3.82	305
8	461.3	13.2	30.11	2.28	-
9	417.0	2.92	13.74	4.70	391
10	436.5	3.57	31.78	8.90	-
11	405.8	2.78	16.61	5.97	329
12	416.8	3.27	33.44	10.23	-
13	395.8	2.99	17.94	6.00	-
14	407.0	3.23	34.40	10.65	-
PAA	408.0	2.1[7]	5.6[8]	3.79[9]	280
Pentamer p-oxy-benzoate[10]	-	-	8.8	-	306

In the case of low molar mass liquid crystals it is seen that the volume change associated with the N-I transition is only a small fraction of that of the K-N transition. For instance, for p-azoxyanisole (PAA) the volume change at the N-I transition is only 0.35% while that for the melting transition is about 11%.[9] In contrast, our results (Tables I and II) show that for the main-chain polyesters studied ΔV for the K-N transition is very small and comparable in magnitude to ΔV for the N-I transition. This suggests that the crystals of these polyesters have a high degree of imperfection. It may also be recalled that recent studies[11] on the polyester with n = 10 (also generally referred to as DDA-9) indicate a collapse of crystallinity in this material for pressures greater than 4 kbar.

Finally, according to the Flory-Ronca theory[12] T*, a characteristic temperature which is a measure of orientation-dependent interactions in a system of rigid rod-like molecules, can be expressed as

$$T^* = \frac{\Delta H^\circ}{RS(1 - \frac{S}{2})} ,$$

where S is the order parameter, ΔH° is the N-I transition enthalpy of the homologues ΔH_{N-I} extrapolated to $n \rightarrow 0$. For homologues with n odd, ΔH° ◘ $\frac{0.94\ \mathrm{kJ}}{\mathrm{mru}}$ or 3.01 J/g (see Ref. 13). ΔH° was corrected for the change in specific volume (ΔV) at the N-I transition. The mesogen order parameter S was obtained from PMR spectra.[13] The value of T* calculated for n = odd polyesters comes out to be approximately 300 K, similar to the values reported for non-cybotactic nematics (see Table II). On the other hand, for the n = even systems ΔV(n) vs. n is not linear and T* could not be reliably calculated. This is presumably because of the strong 'cybotactic' (or smectic-like) ordering in the n even nematics.[14]

In view of the above results, a detailed high pressure xray study of main-chain polyesters would be of considerable interest.

ACKNOWLEDGEMENT

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