

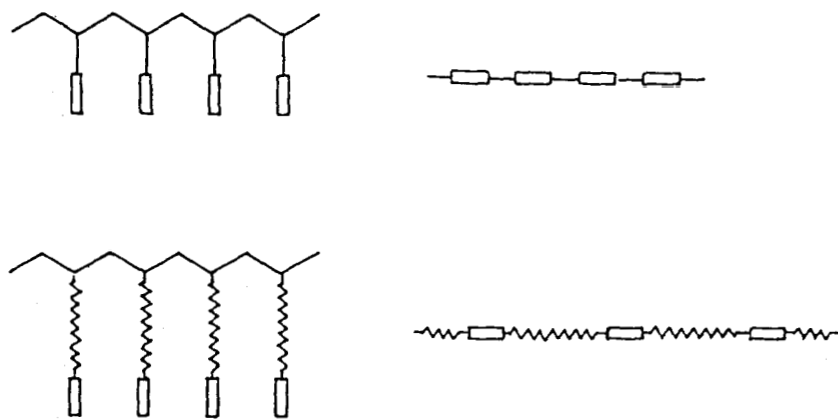
## CHAPTER IX

### PHASE TRANSITIONS OF NEMATIC MAIN-CHAIN POLYMERS UNDER PRESSURE

#### 9.1 INTRODUCTION

Thermotropic mesomorphic polymers' have become a subject of increasing importance in recent years not only from the fundamental point of view, but also because of their technical applications. Through an appropriate combination of mesogen and non-mesomorphic moieties, it is possible to synthesize versatile and novel materials. In this respect, polymers formed by regularly alternating mesogenic groups and flexible spacers in the main chain are among the most actively investigated.<sup>2</sup>

In general, there are two types of thermotropic polymeric liquid crystals<sup>3</sup>: main-chain polymers and side-chain polymers. In the main chain polymers, the mesogenic groups form the backbone of the molecular chains, whereas in the side chain polymers<sup>4</sup> the mesogenic units link to a polymer backbone as pendants in the side chain. The spacer between mesogenic groups in main-chain polymer or between the backbone and the mesogenic units in the side chain polymer, is necessary to form the liquid crystalline phase. Thus the mesophase-forming polymer may either contain one of the two basic structures as shown in Fig. 9.1. Properties of these polymeric liquid crystals are found to depend critically on the length of



Side chain LC polymers      Main chain LC polymers

▭ Mesogenic group      ~ Flexible spacer

Figure 9.1

*Thermotropic polymers with either main-chain or  
side-chain mesogenic units.*

the polymethylene spacer.<sup>5,6</sup> Essentially, three effects can be observed in homologous series of liquid crystalline polyesters:

- 1 On the average, a reduction of the transition temperatures (both melting point and clearing temperatures) with the increased spacer length.
- 2 An odd-even alternation of the mesophase–isotropic transition temperatures in which polymers with an even number of atoms in the spacers generally have higher transition temperatures than those with odd number of atoms.
- 3 In some cases, a smectic mesophase is formed by polymer containing very long spacers.

The synthesis of a homologous series of thermotropic main chain polyesters, based on regularly alternating 2,2'-dimethylazoxybenzene mesogen and alkane dicarboxylic acid spacer was reported recently.<sup>7</sup> The general formula for these polyesters is given in Fig. 9.2. Several interesting features were observed in the thermodynamic behaviour of these polyesters:

- (i) Although the nematic–isotropic transition temperature ( $T_{NI}$ ) showed on the average a downward trend with increasing  $n$ , (where  $n$  is the number of methylene units in the flexible spacer), there was a pronounced alternation with  $n$ , the alternation getting less pronounced with increasing  $n$  (Fig. 9.3)

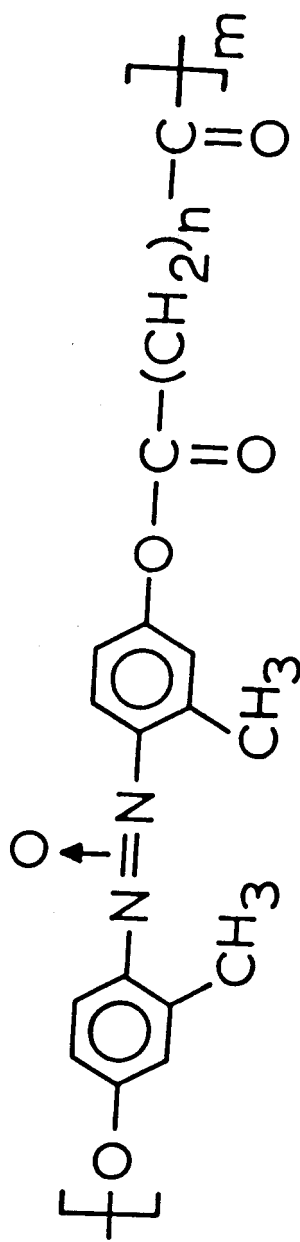
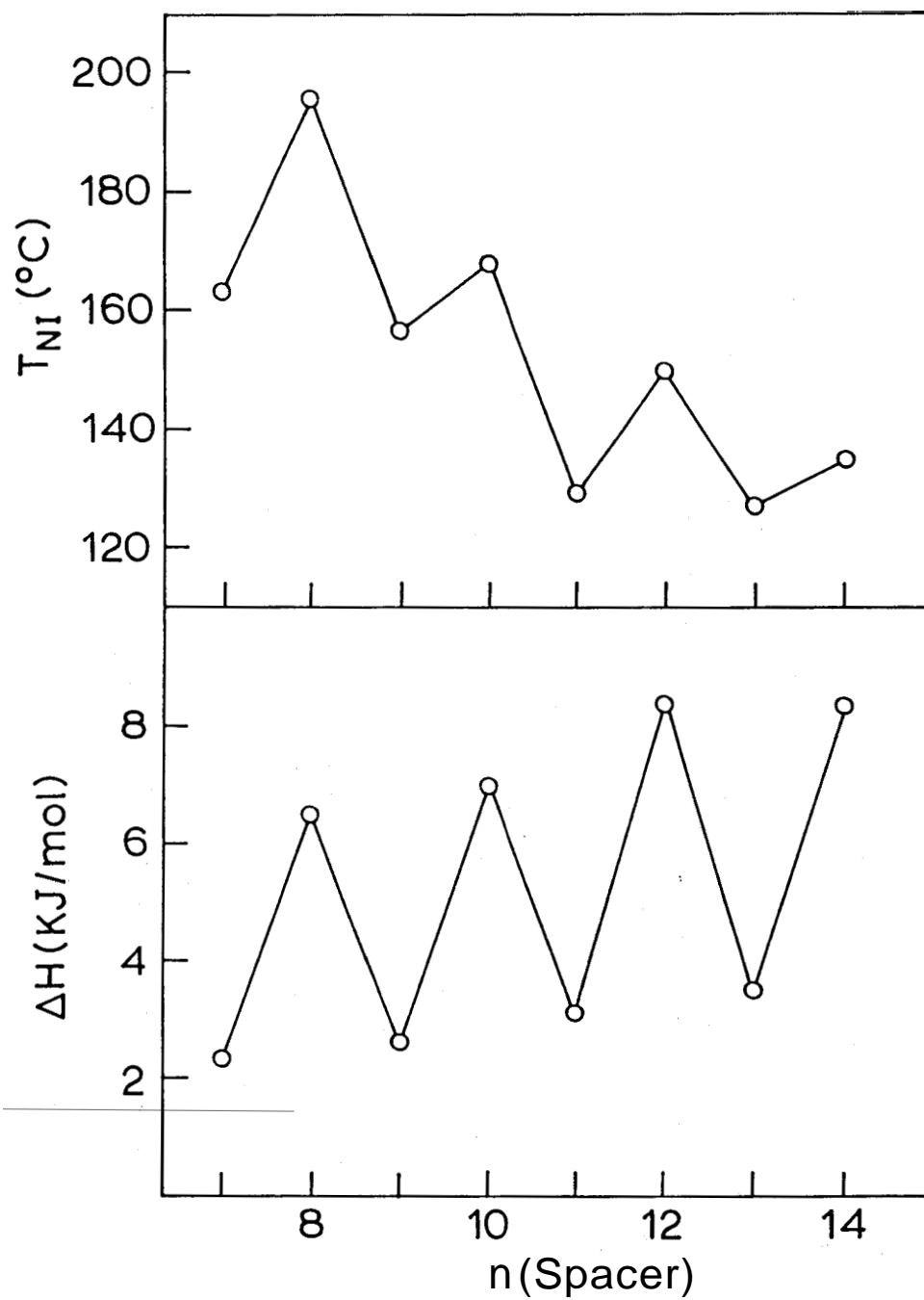


Figure 9.2

The general formula for the homologous series of thermotropic main-chain polyesters.

(ii) The transition enthalpy ( $\Delta H$ ) associated with nematic-isotropic transition shows a very pronounced alternation with  $n$ , the strength of this alternation remaining unchanged even up to  $n = 14$  (Fig. 9.3). Thus both  $\Delta H_{NI}$  and  $T_{NI}$  showed a strong alternation with  $n$ . It may be mentioned, although an alternation of  $T_{NI}$  and  $\Delta H_{NI}$  has been seen<sup>8,9</sup> in low molecular mass liquid crystals, the extent of this alternation is far greater in the thermotropic polyesters discussed above. It was also observed that no such alternation was seen for the thermodynamic data of the melting or crystal-nematic (K-N) transition. Another interesting feature was observed, viz., the ratio of  $\Delta S_{NI}/\Delta S_{K-N}$  was found to be generally about 0.2 - 0.3 which is 10 times larger than what is usually found in low molecular weight liquid crystals. (For instance in 4,4'-alkoxy azoxybenzenes it is about 0.02 to 0.03.<sup>10</sup>) It was suggested<sup>7</sup> that this is indicative of a considerable degree of order in the nematic phase of these polyesters.

Since it is known that in low molecular weight liquid crystals the  $dT/dP$  alternates<sup>11,12</sup> with respect to the chain length in the same way as  $T_{NI}$ , it is of interest to conduct a pressure study of the main chain polyesters to see if a similar behaviour can be seen here also. With this in view a detailed study of the  $n = 7$  to  $n = 14$  the members of the homologous series of thermotropic polyesters based on alternating 2,2'-dimethylazoxybenzene mesogen



*Figure 9.3*

*Plot of the nematic-isotropic transition temperature ( $T_{NI}$ ) and enthalpy of transition ( $\Delta H$ )<sub>N-I</sub> measured at 1 bar vs. n (From Ref. 7).*

and alkane dicarboxylic acid spacer was undertaken. The results of these studies are described in this chapter.

## 9.2 MATERIALS

The general formula for the homologous series of thermotropic main chain polyesters has already been given in Fig. 9.2. Their transition temperatures are listed in Tables I and II for K-N and N-I respectively.

## 9.3 EXPERIMENTAL

The optical high pressure cell described in Chapter II has been 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). The phase transitions were detected by the optical transmission technique. The onset of the transition was signalled by a sudden change in the transmitted light intensity. The experiments were always conducted along isobars and in the heating mode, i.e., keeping pressure constant at any desired value, the temperature of the sample was increased at a linear rate of  $1^{\circ}\text{C}/\text{min}$ . Typical intensity scans showing the changes of transmitted light intensity near the different phase transitions are shown in Fig. 9.4.

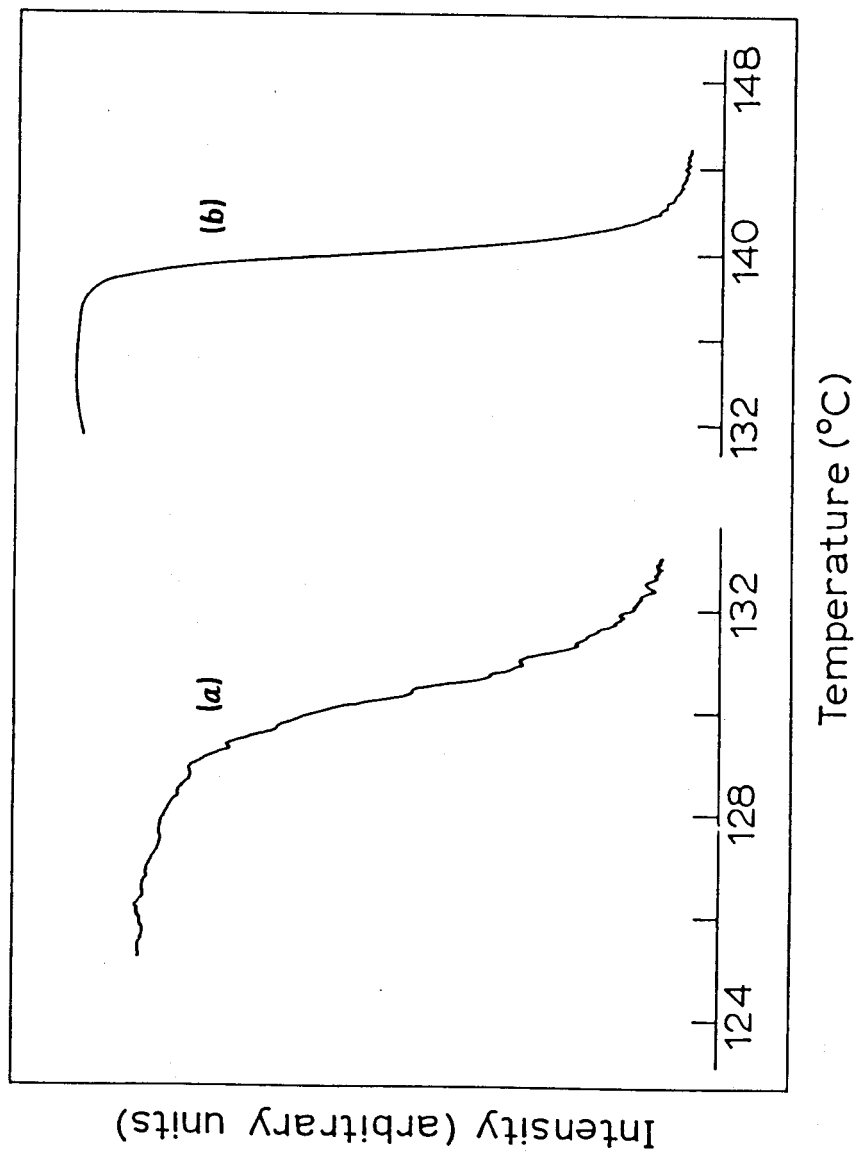


Figure 9.4

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



#### 9.4 RESULTS AND DISCUSSION

We have carried out high pressure studies of the polyesters with  $n = 7$  to  $n = 14$ . The pressure-temperature diagrams are given in Figs. 9.5-9.12. It is evident from the diagrams that both the K-N and N-I phase boundaries are linear in all the cases. In the case of  $n = 13$ , the nematic phase was hardly stable at atmospheric pressure, but the range of the nematic increases rapidly with increasing pressure. 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 then evaluated. Fig. 9.13 shows the plot of  $dP/dT$  vs.  $n$ . It is seen that  $(dP/dT)_{N-I}$  shows an odd-even alternation with  $n$  a behaviour which is similar to that exhibited by  $T_{N-I}$  and  $\Delta H_{N-I}$  measured at 1 bar<sup>17,13</sup> (see Fig. 9.3). As remarked earlier similar instances of odd-even alternation of  $(dP/dT)_{N-I}$  has been observed earlier in the case of low molecular weight liquid crystals.<sup>11,12</sup> 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 value of  $n$  as shown in Fig. 9.14. As mentioned earlier, Blumstein et al.<sup>14</sup> have investigated for the same homologous series of nematic polyesters, the odd-even alternation of  $\Delta H_{N-I}$  in the interval of  $n = 3$  to 15. They found that

$$\Delta H_{NI}^{\text{even}} = 4.7 + 0.16n \text{ kJ/mru} \quad (1)$$

and

$$\Delta H_{NI}^{\text{odd}} = 0.94 + 0.19n \text{ kJ/mru} \quad (2)$$

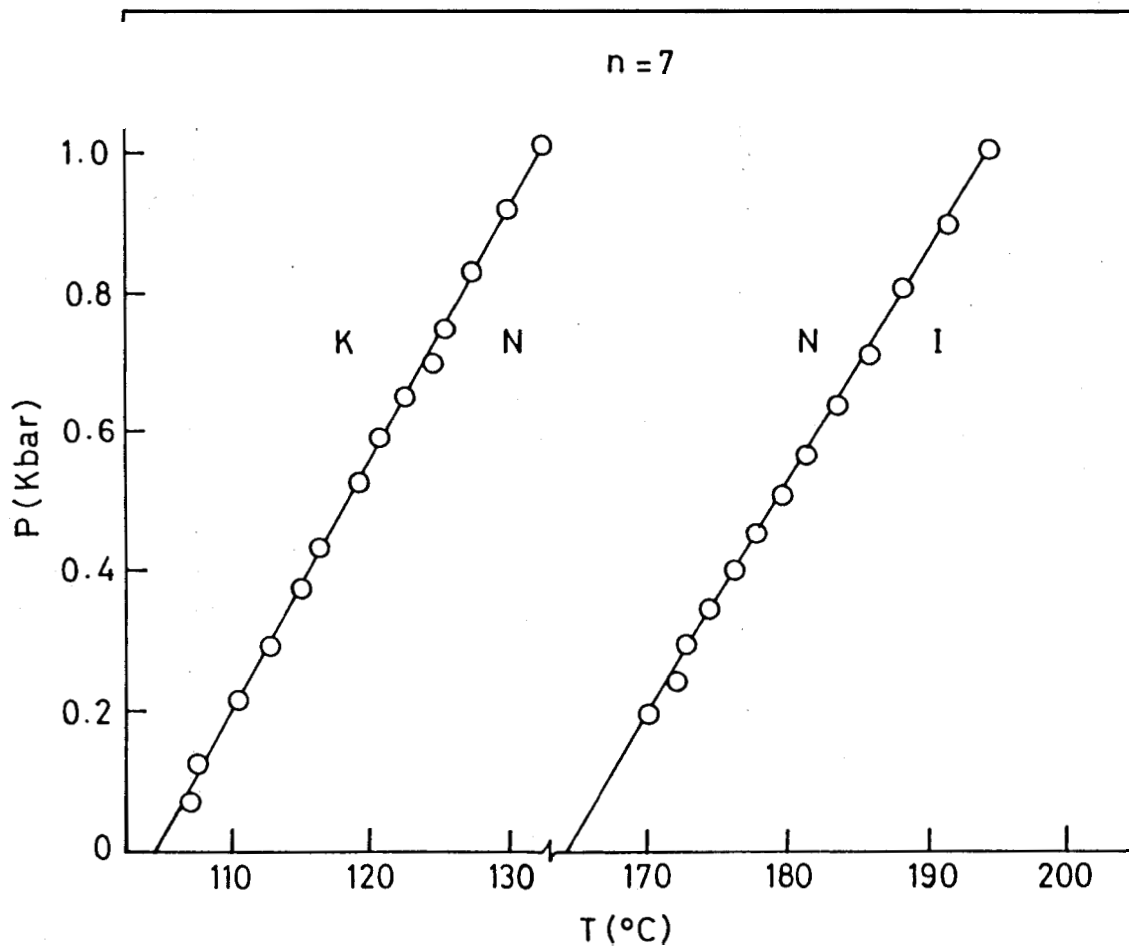


Figure 9.5

Pressure-temperature diagram of the polyester with  $n = 7$ .

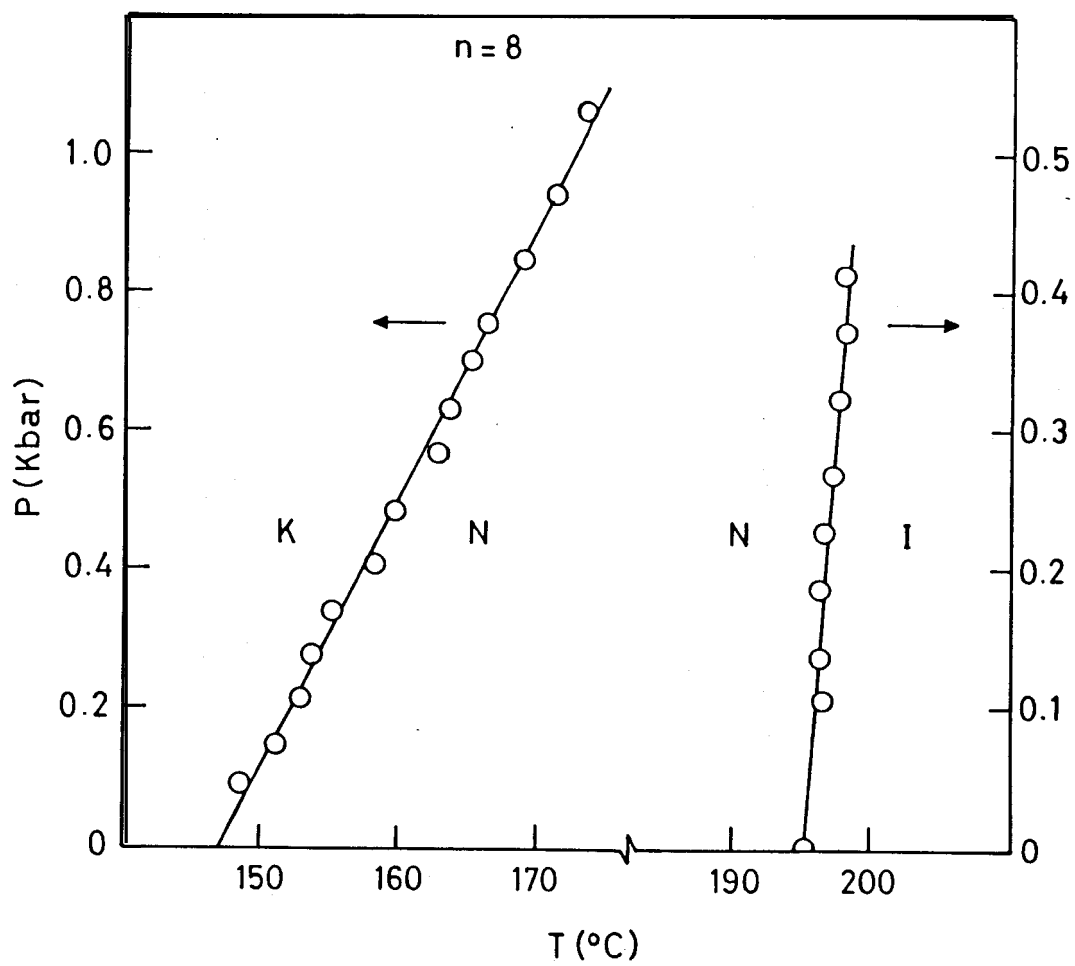


Figure 9.6

*P-T diagram of the polyester with  $n = 8$ .*

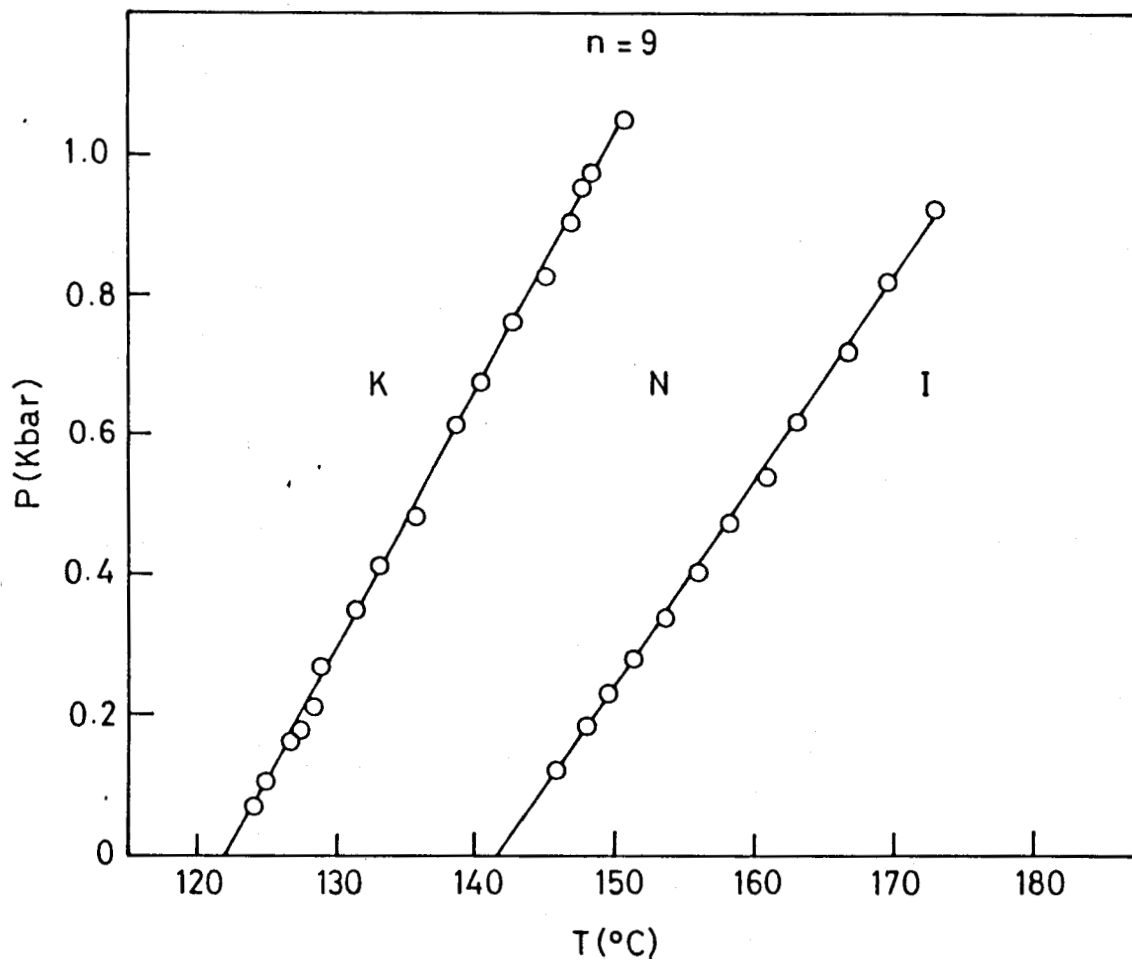


Figure 9.7

*P-T diagram of the polyester with  $n = 9$ .*

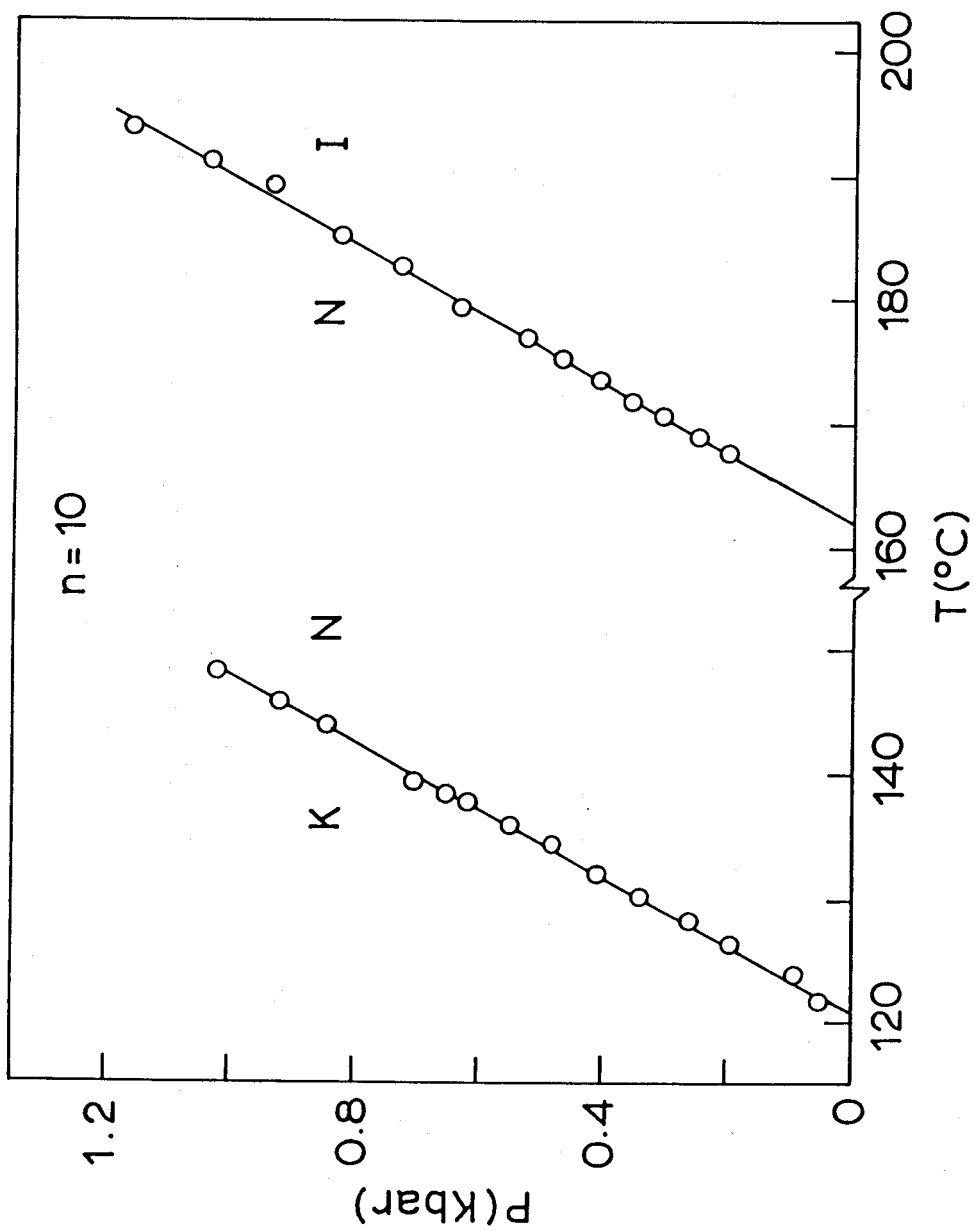


Figure 9.8. P-T diagram of the polyester with  $n = 10$ .

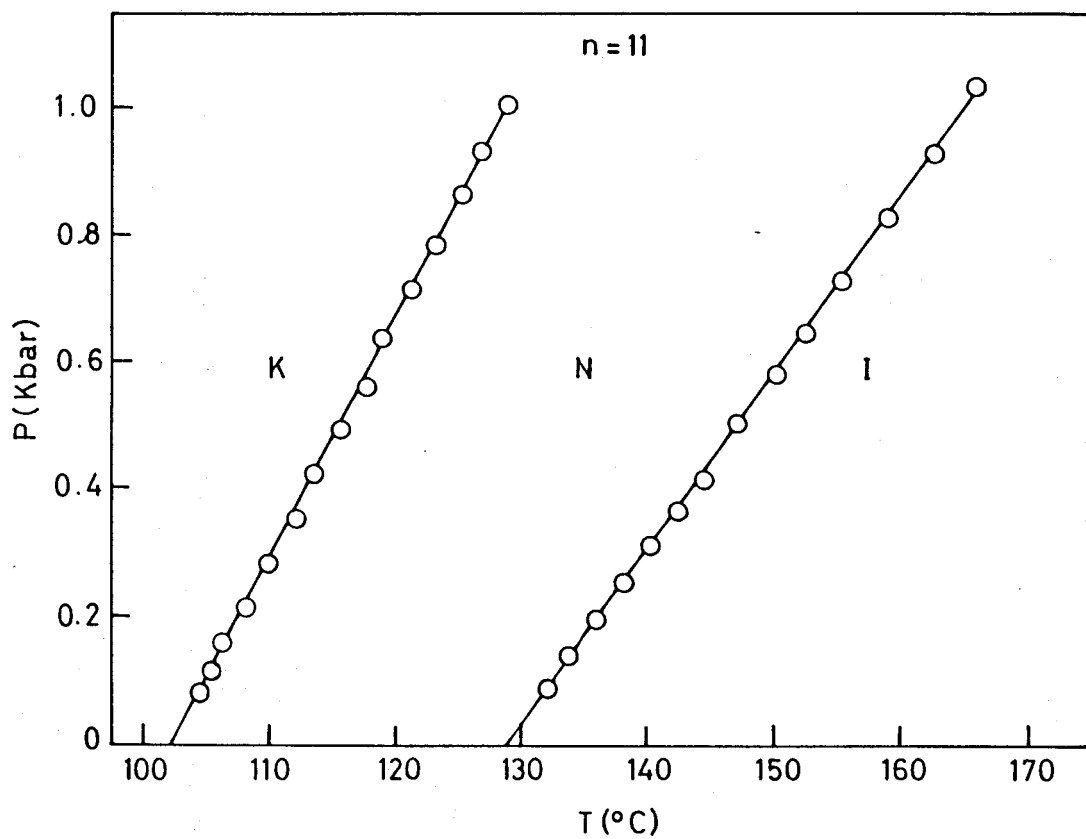


Figure 9.9

*P - T diagram of the polyester with  $n = 11$ .*

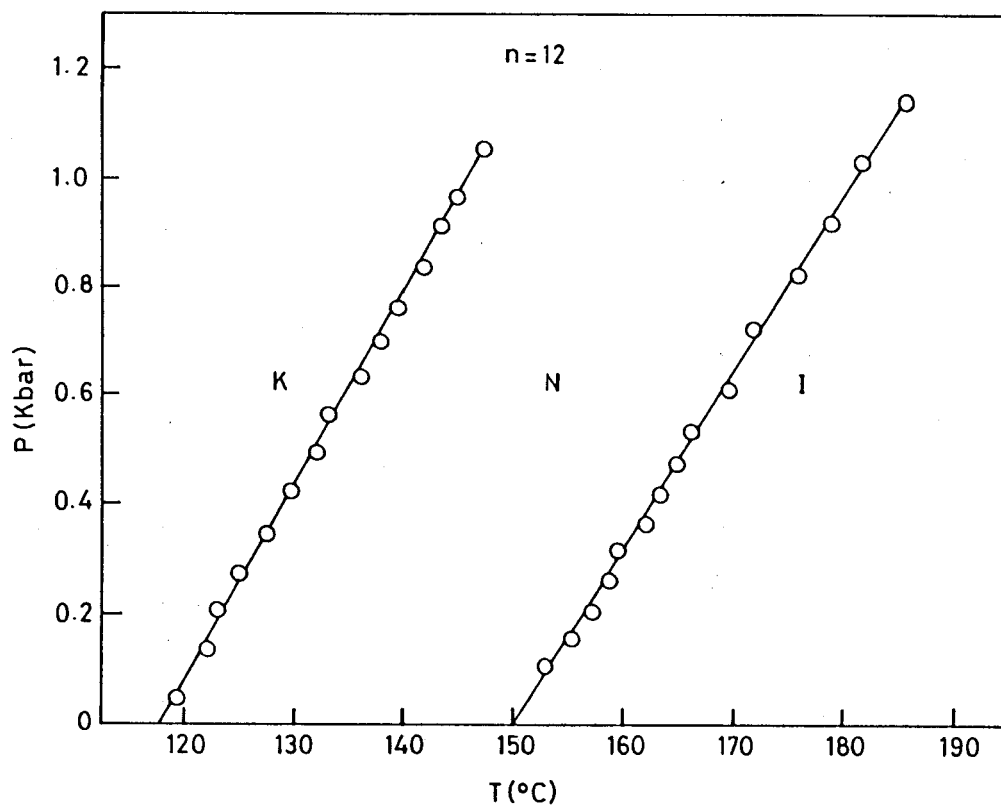


Figure 9.10

*P - T diagram of the polyester with  $n = 12$ .*

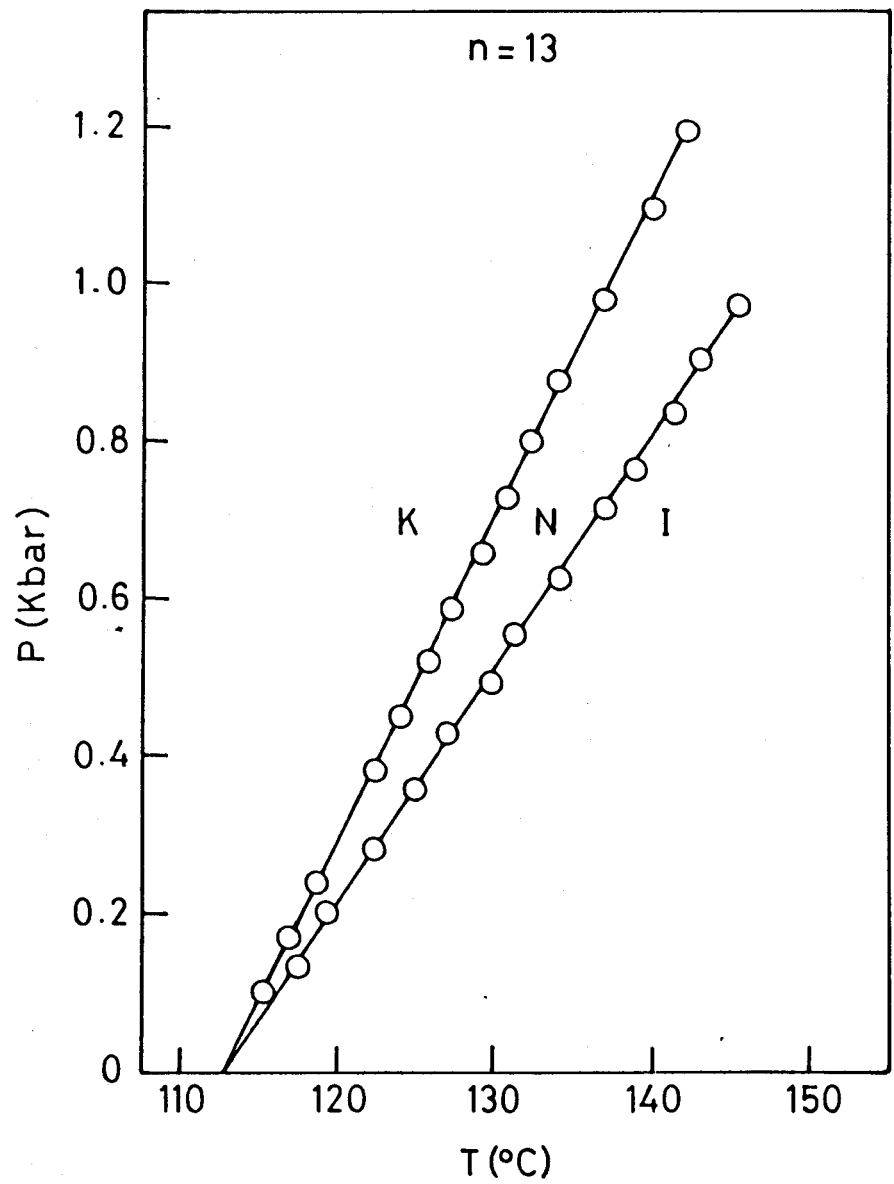


Figure 9.7.1

*P-T diagram of the polyester with  $n = 73$ .*



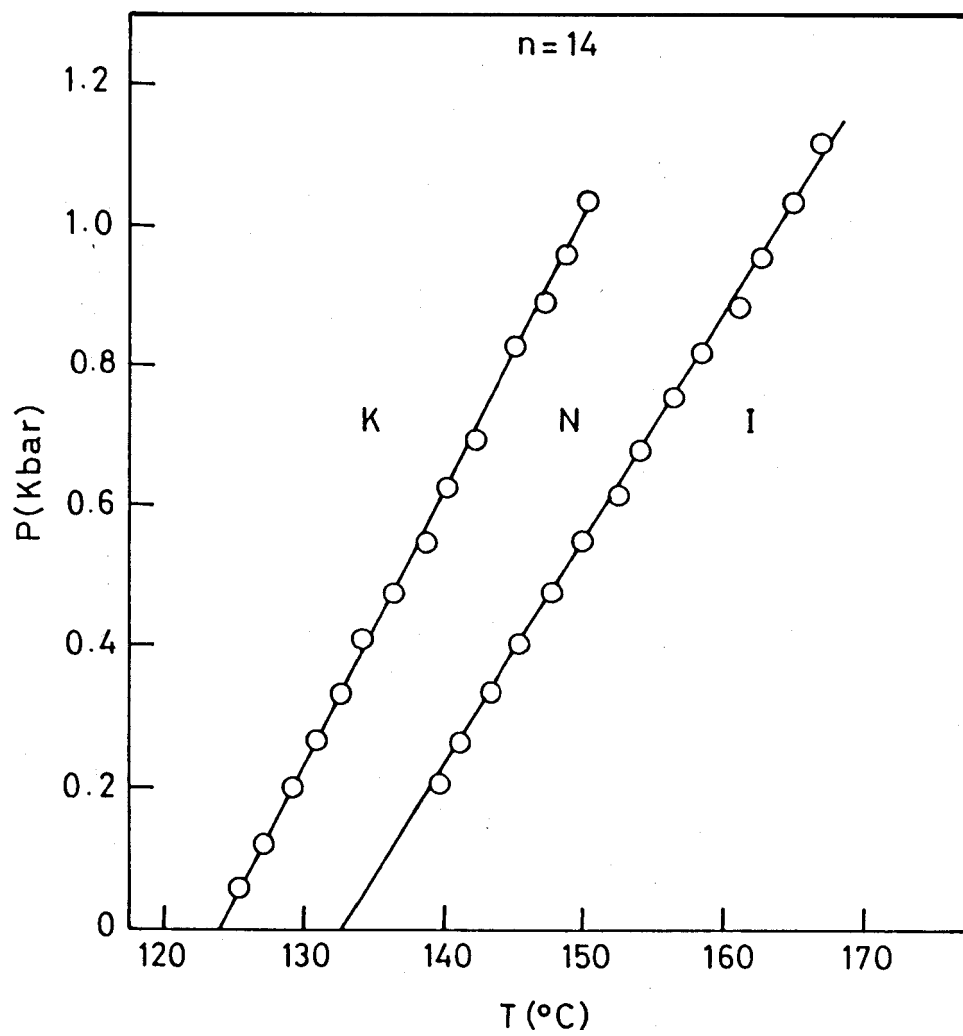


Figure 9.12

*P - T diagram of the polyester with  $n = 14$ .*

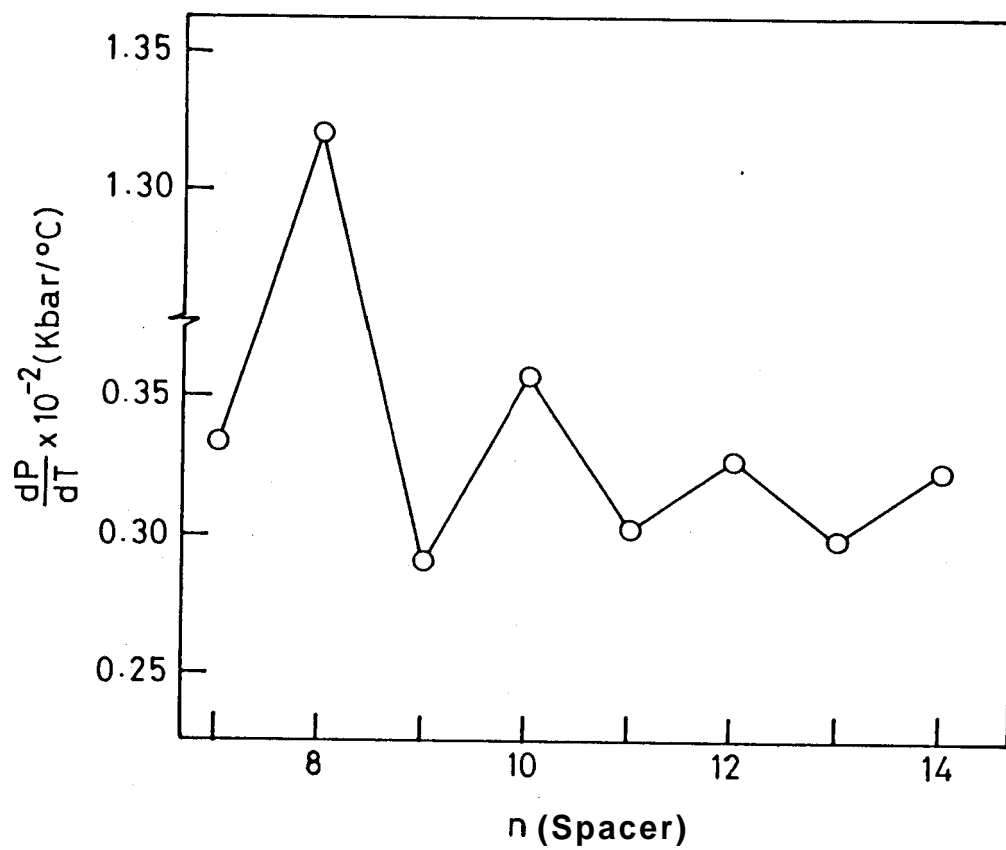


Figure 9.13

*Variation of  $dP/dT$  for the nematic - isotropic transition with  $n$ .*

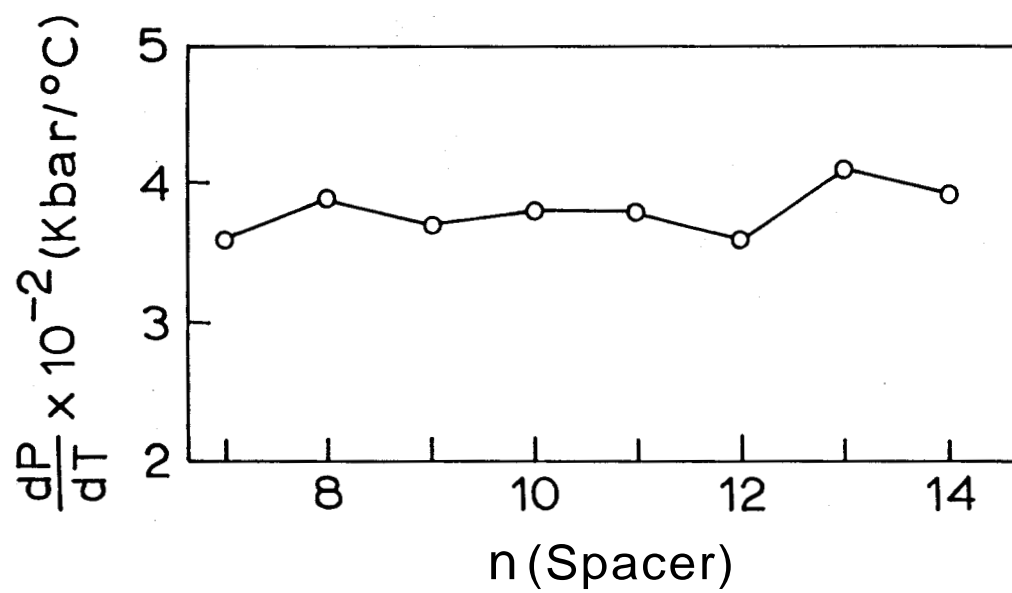


Figure 9.14

*Plot of  $dP/dT$  for the crystal-nematic (K-N) transition vs.  $n$ .*

where  $mru$  is a mol of the repeating unit. If we consider the intercepts and slopes in equations (1) and (2) as the respective contributions of mesogen order and spacer conformational changes at the N-I transition, then it is clear that the mesogen order is much larger for  $n = \text{even}$  than  $n = \text{odd}$ .

We shall now examine the data for  $dP/dT$  obtained experimentally. According to the Clausius-Clapeyron equation,

$$\frac{dT}{dP} = T(\Delta V/\Delta H),$$

where  $\Delta V$  is the volume change at the transition. Using our values of  $dP/dT$  and  $\Delta H$  reported earlier,<sup>7</sup>  $\Delta V$  has been evaluated for both K-N and N-I transition. These are listed in Tables 9.1 & 9.2 respectively. In the case of low molecular weight liquid crystals it is generally found 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%.<sup>15</sup> In contrast, our results on main chain polyesters (Tables 9.1 & 9.2) show that  $\Delta V$  for the K-N transition is very small and comparable in magnitude to  $\Delta V$  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<sup>17</sup> on the polyester with  $n = 10$  (also generally referred to as DDA-9) indicate a collapse of crystallinity in this material for pressures

Table 9.1

Thermodynamic data for the K-N transitions

n	$(dP/dT)_{K-N}$ J/°K cm <sup>3</sup>	$S_{K-N}$ x 10 <sup>3</sup> J/g°K	$\Delta \tilde{V}_{K-N}$ x 10 <sup>3</sup> cm <sup>3</sup> /g	$T_{K-N}^{\theta}$ °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-azoxy anisole (PAA)	3.13 <sup>16</sup>	256.3 <sup>10</sup>	95.29 <sup>15</sup>	390

<sup>θ</sup>From reference 7.

Table 9.2

Thermodynamic data for the N-I transition

n	$T_{N-I}^e$ °K	$(dP/dT)_{N-I}$ J/cm <sup>3</sup> °K	$S_{N-I}$ x 10 <sup>3</sup> J/g°K	$\Delta\tilde{V}_{N-I}$ x 10 <sup>3</sup> cm <sup>3</sup> /g	T*
7	437.6	3.35	12.82	3.82	305
8	461.3	13.20	30.11	2.28	-
9	417.00	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	2.10 <sup>16</sup>	5.60 <sup>10</sup>	3.79 <sup>15</sup>	280
Pentamer p-oxy- benzoate	-		8.8	-	306

<sup>e</sup>From Ref. 7

greater than 4 kbar.

Finally, it is known from Flory-Ronca theory<sup>18</sup> that  $T^*$ , 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,  $\Delta H^{\circ}$  is the N-I transition enthalpy of the homologous,  $\Delta H_{N-I}$  extrapolated to  $n = 0$ . For homologs with  $n_{\text{odd}}$ ,  $\Delta H^{\circ} = (0.94 \text{ kJ/mru})$  or  $3.01 \text{ J/g}$  (see Ref. 14).  $\Delta H^{\circ}$  was corrected for the change in specific volume ( $\Delta \tilde{V}$ ) at the N-I transition. The mesogen order parameter  $S$  was obtained by PMR spectra.<sup>14</sup> The value of  $T^*$  calculated for  $n = \text{odd}$  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  $n = \text{even}$  systems,  $\Delta \tilde{V}(n)$  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.<sup>19</sup> Further studies on other main chain polyesters would be of considerable interest.

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## CHAPTER X

### A THERMOTROPIC BIAXIAL NEMATIC LIQUID CRYSTAL

#### 10.1 INTRODUCTION

Following the discovery of the biaxial nematic liquid crystal by Yu and Saupe<sup>1</sup> in an amphiphilic system (potassium laurate + 1-decanol + D<sub>2</sub>O) there have been a number of investigations on this phase in similar lyotropic materials.<sup>2-14</sup> In these systems, the constituent units are micelles whose size and shape are sensitive to temperature and concentration. Over a range of temperature/concentration the biaxial nematic (N<sub>b</sub>) phase intervenes between two uniaxial (N<sub>u</sub>) phases, one composed of rod-shaped micelles and the other of disk-shaped micelles. Evidence of biaxiality has also been found in certain nematic polymers.<sup>15,16</sup> There are obvious advantages in having a thermotropic N<sub>b</sub> phase in a simple low molecular weight system in order to be able to carry out detailed physical studies. It was suggested by Chandrasekhar<sup>17</sup> that a convenient method of achieving this would be by 'bridging the gap between rod-like and disk-like mesogens', i.e., by preparing a mesogen that combines the two features in the molecular structure. Such compounds have been synthesized in our laboratory by Dr. B. K. Sadashiva. The structural formula of the complexes with R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub> and OC<sub>3</sub>H<sub>7</sub> is shown in Fig. 10.1a. These complexes

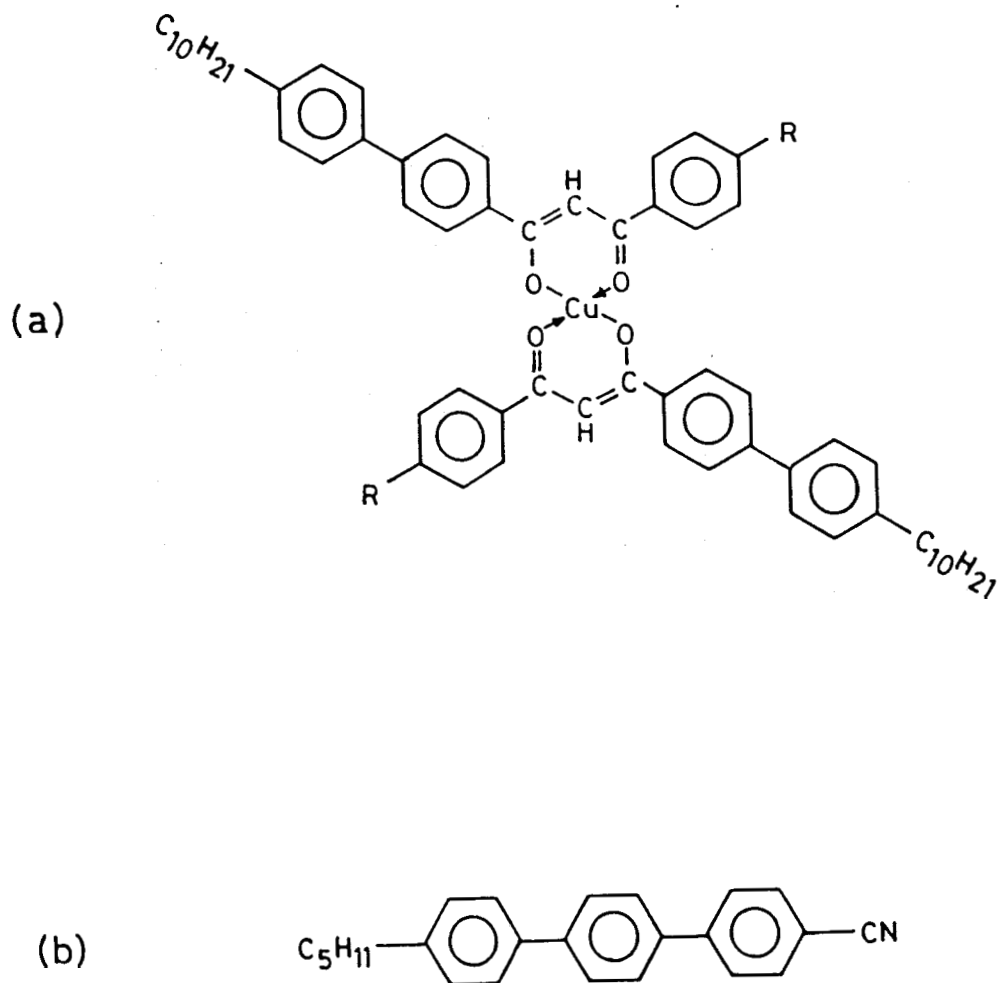


Figure 10.1

Structural formulae of (a) the complex A: bis[1-(p-n-decylbiphenyl) 3-(p-substituted phenyl)propane-1,3-dianoato]copper(II), and (b) 4''-n-pentyl-4-cyano-p-terphenyl (5CT).

exhibited nematic phase with paramagnetic properties.<sup>18,19</sup> Since then careful conoscopic observations have been conducted on the complex with  $R = OC_2H_5$ . These observations clearly revealed the occurrence of the  $N_b$  phase in this complex\*. Addition of a very small quantity of a uniaxial nematogen, viz., 4''-n-pentyl-4-cyano-p-terphenyl (5CT) results in the appearance of an optically positive  $N_u$  phase between I and  $N_b$  and thereby resulting in an interesting uniaxial to biaxial nematic phase transition. The results of our conoscopic studies on the complexes with  $R = OC_2H_5$  as well as its mixtures with 5CT constitute the subject matter of this chapter.

## 10.2 MATERIAL

The material studied was bis[1-(p-n-decylbiphenyl) 3-(p-ethoxy phenyl) propane-1,3-dionato]copper(II), hereafter referred to as **A**. 5CT is a very well known material whose structure is given in Fig. 10.1b. The transition temperatures of **A** are melting: 186.6°C, isotropic-nematic: 168.5°C. 5CT has the melting transition at 130.3°C and the isotropic-nematic transition at 237.7°C.

## 10.3 EXPERIMENTAL

In order to make reliable conoscopic observations, it is extremely important that the alignment of the sample should be

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\* It should be pointed out that there is another report<sup>20</sup> of the observation of the thermotropic biaxial nematic phase. In this case, the sequence of transitions, viz.,  $I \rightarrow N_b \rightarrow N_u$  was observed,  $N_b$  occurring at a temperature higher than  $N_u$ .

perfect. After trying various techniques it was finally found that the best alignment of the copper complex could be achieved by .the combined effect of silane (octadecyl tetramethoxy silane) coating and a 3 KHz AC electric field. In order to prevent possible **electrohydrodynamic** motion it was decided to ensure that the active surface of the electrode was not in direct contact with the material. This was done in the following manner. The sample was sandwiched between two coverslips (each of thickness 100  $\mu\text{m}$ ). The coverslip surface which was in contact with the sample was coated with a silane solution (which promotes homeotropic alignment) while the other surface had electrically conducting tin-oxide coating to facilitate application of the electric field. Cooling the sample from the isotropic phase in the presence of a 3 KHz AC field yielded an excellent alignment of the sample in the nematic phase. The **"degree of perfectness"** of the alignment was checked by visual observation as well as by monitoring the intensity of the light transmitted by the sample between crossed polaroids under orthoscopic conditions. Usually visual observation for a good alignment showed no textures in the field of view even at a magnification of 400. For the intensity measurements, light from a He-Ne laser was incident normally on the sample and the transmitted light intensity was measured using a photo-diode. The orientation of the **polarizers** was adjusted for complete extinction in the isotropic phase. In the nematic phase, the intensity was measured as a function of

voltage. To begin with, the intensity was very high for low voltages. But with the increase in the voltage, intensity decreases and then saturates, the saturated intensity being equal to that measured in the isotropic phase. This saturation in the intensity indicated the perfect alignment of the sample. Typically, the saturation voltage necessary for perfect alignment was about 200 V across a sample of thickness 125  $\mu\text{m}$ . There was evidence of chemical decomposition on repeated heating of the material, and therefore only fresh samples were used for the experiments. All the conoscopic observations were found to be reproducible with well aligned samples in freshly prepared cells. Also, the conoscopic pattern was independent of the applied voltage for voltages greater than the saturation value. These observations were made using Leitz Orthoplan polarizing microscope (the numerical aperture of the objective used being 0.40) equipped with a hot stage (Mettler FP82) and a microprocessor controlled temperature controller (Mettler FP800).

#### **10.4 RESULTS AND DISCUSSION**

The conoscopic figure for the nematic phase of complex A is shown in Fig. 10.2. The biaxiality can be seen quite clearly. In this case, the transition takes place directly from the isotropic phase to  $N_b$ . Occasionally 'zig-zag' disclinations were seen in the  $N_b$  phase but these appeared quite unpredictably and we did not regard it as conclusive evidence of biaxiality.

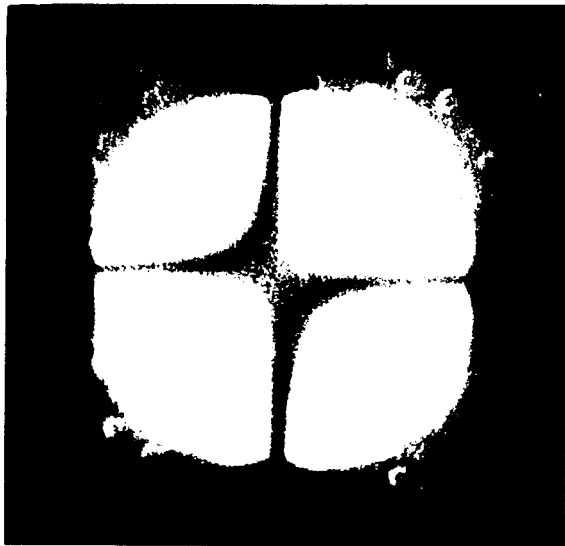


Figure 70.2

*Conoscopic figure showing the biaxiality of the nematic phase of complex A.  $T_{NI} - T = 1.5^\circ\text{C}$ . Film thickness  $\sim 125 \mu\text{m}$ , homeotropic alignment. Numerical aperture of the objective used = 0.40.*

Addition of even a very small quantity of the uniaxial nematogen 5CT results in the appearance of an optically positive  $N_u$  phase between I and  $N_b$ , and the sequence of transition, on cooling, is then  $I \rightarrow N_u \rightarrow N_b$ . It should be remarked here that the optical textures of  $N_u$  and  $N_b$  are virtually indistinguishable. It was observed that for 0.2% 5CT (by weight)  $N_u$  exists for  $\sim 1^\circ\text{C}$  and for 0.4% 5CT it exists for  $\sim 3^\circ\text{C}$ . Fig. 10.3 shows the conoscopic figures for the uniaxial and biaxial phases of a mixture with 0.25% 5CT. The  $N_u - N_b$  transition occurs reversibly in both heating and cooling modes, and the biaxiality increases as the temperature of the  $N_b$  phase is lowered. This is illustrated in the sequence of photographs shown in Fig. 10.3. The phase diagram for the binary system for the concentration (X) range 0 - 1% of 5CT is shown in Fig. 10.4. It can be seen that the temperature range of  $N_u$  increases rapidly with increasing concentration of 5CT. For  $X = 1\%$ , the meso-phase remains uniaxial throughout till the sample crystallizes.

It should be emphasized here that the method suggested a few years ago by Chandrasekhar<sup>17</sup> of obtaining a low molecular weight thermotropic  $N_b$  phase has been demonstrated to be efficacious in a practical case. Such a phase offers a very convenient system for investigating the physics of the biaxial nematic liquid crystals and for verifying some important theoretical predictions that have been made concerning phase transitions,<sup>21-32</sup> hydrodynamics,<sup>33,39</sup> topological defects,<sup>40-45</sup> etc. For example, Saupe<sup>36</sup>



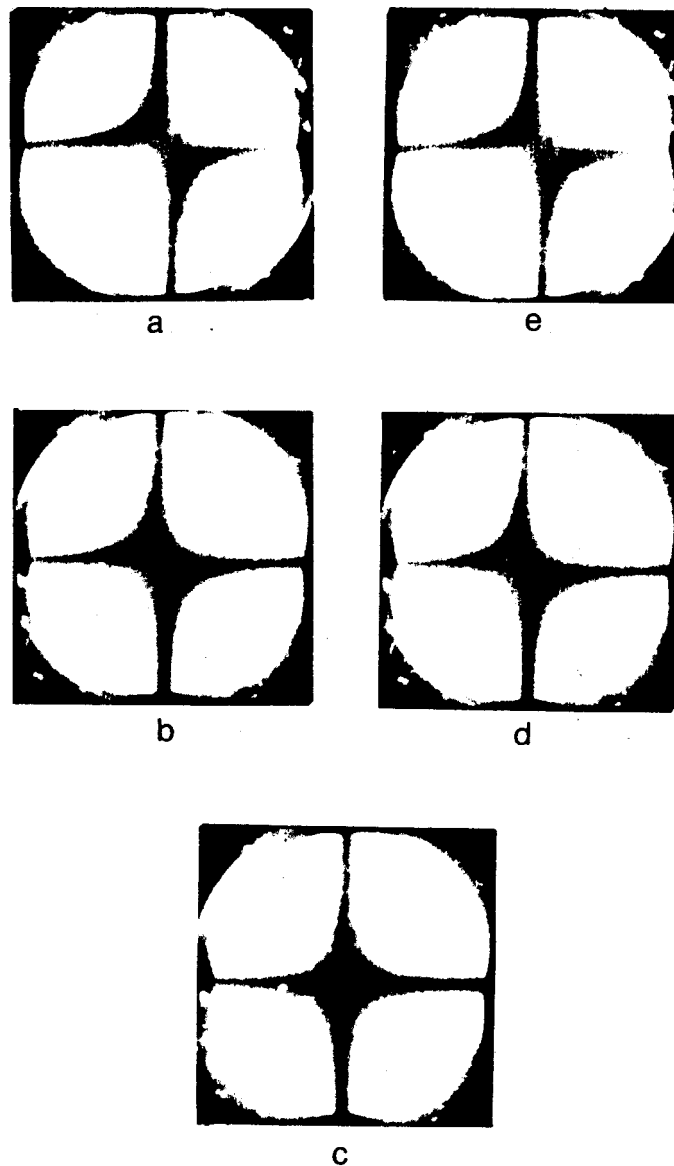


Figure 10.3

Sequence of photographn showing the reversibility of the  $N_b$ - $N_u$  transition on heating and cooling in a binary mixture of 0.25 % (by weight) of 5CT in A. Heating mode: (a)  $N_b$  at 165.5°C, (b)  $N_b$  at 167.0°C, (c)  $N_u$  at 167.8°C; Cooling mode: (d)  $N_b$  at 167.2°C, (e)  $N_b$  at 166.3°C. The biaxiality of  $N_b$  can be seen to decrease on approaching the  $N_b$ - $N_u$  transition at 167.5°C. Film thickness  $\sim 125 \mu\text{m}$ , homeotropic alignment.

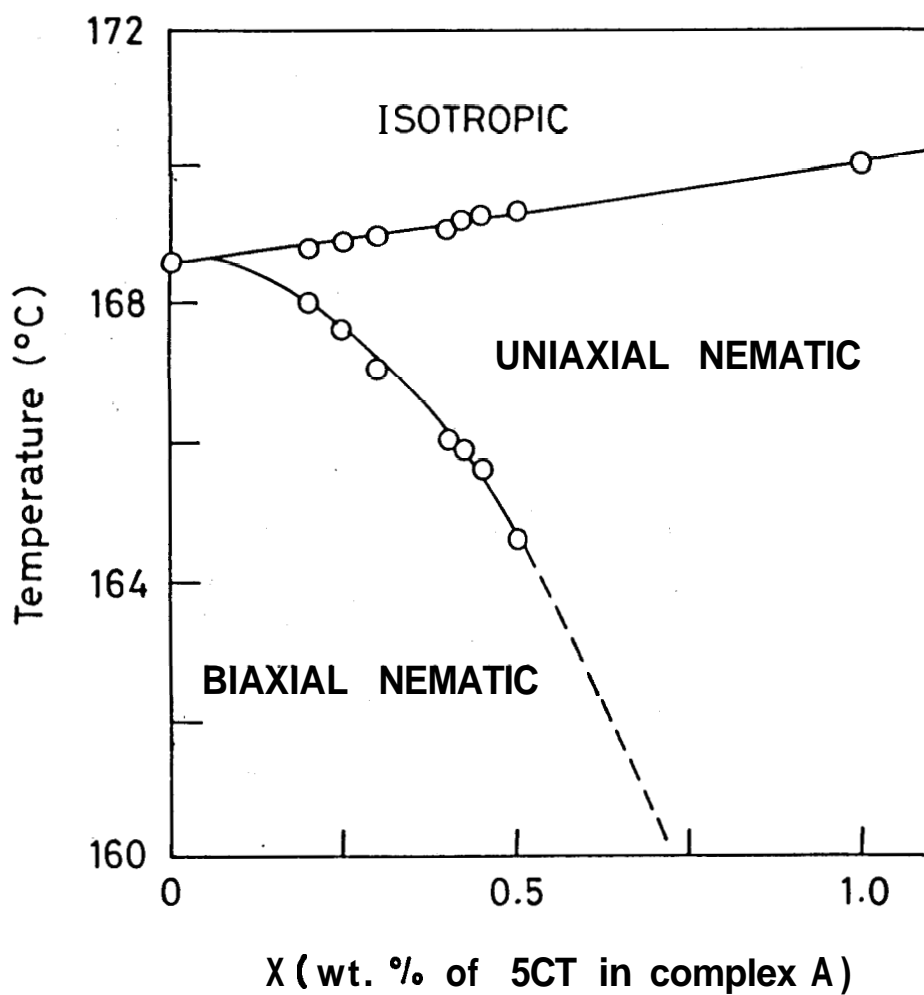


Figure 10.4

*Partial phase diagram of the binary mixture of A and 5CT in the concentration range 0-1% 5CT, showing the  $I-N_u$  and  $N_u-N_b$  phase boundaries. The dashed portion of the curve represents an extrapolation.*

and Kini<sup>37</sup> who used different theoretical approaches, have both concluded that the orthorhombic  $N_b$  has 15 curvature elastic and 15 viscous constants. Again, a remarkable conclusion of the homotopy theory is that the usual law of coalescence of two defects breaks down in the  $N_b$  phase. The combination rule is now non-Abelian. Moreover, there can arise an entanglement of disclination lines, which may lead to what Toulouse describes as 'topological rigidity':<sup>40-44</sup> These and other ideas are yet to be investigated experimentally. The availability of a simple thermotropic biaxial nematic phase makes it possible to carry out physical studies and to test some of these predictions.

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