Phase Transitions of Nematic Main-Chain Polyesters Under High Pressure

V. N. Raja; R. Shashidhar; S. Chandrasekhar; A. Blumstein; R. B. Blumstein; S. Kumar

a Raman Research Institute, Bangalore, India
b Department of Chemistry, University of Lowell, Polymer Science Program, Lowell, MA, USA

First published on: 01 February 1988


To link to this Article: DOI: 10.1080/00268948808070392

URL: http://dx.doi.org/10.1080/00268948808070392

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
PHASE TRANSITIONS OF NEMATIC MAIN-CHAIN POLYESTERS UNDER HIGH PRESSURE

V.N. RAJA, R. SHASHIDHAR, S. CHANDRASEKHAR
Raman Research Institute, Bangalore 560080, India, and

A. BLUMSTEIN, R.B. BLUMSTEIN, S. KUMAR
Polymer Science Program, Department of Chemistry,
University of Lowell, Lowell, MA 01854, USA

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 \( \frac{dP}{dT} \) for the NI transitions show an odd-even alternation with \( n \), consistent with the previously reported alternation of \( T_{NI} \) and \( AH_{NI} \). The characteristic temperature \( T^* \) calculated for \( n = \text{odd} \) is approximately 300 K, similar to the values for noncybotactic nematics. On the other hand, for \( n = \text{even} \), \( T^* \) could not be reliably calculated, perhaps due to the existence of cybotactic ordering. At the KN transition there is no such clear alternation in \( \frac{dP}{dT} \). 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. The phase transitions were detected by the optical transmission technique. Light from a helium-neon laser was incident normally 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 $1^\circ\text{C}/\text{min}$. 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 \( \frac{dP}{dT} \) for the nematic-isotropic transition with \( n \).
Fig. 4. Plot of the nematic-isotropic transition temperature \(T_{NI}\) and enthalpy of transition \(\Delta H\) \(_{NI}\) measured at 1 bar vs. \(n\).

According to the Clausius-Clapeyron equation

\[
\frac{dT}{dP} = \frac{T(\Delta V/\Delta H)}{P},
\]

where \(\Delta V\) is the volume change at the transition. Using our values of \(dP/dT\) and the \(\Delta H\) data reported earlier, \(\Delta V\) 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

<table>
<thead>
<tr>
<th>$n$</th>
<th>$(dP/dT)_{K-N}$</th>
<th>$\Delta S_{K-N}$</th>
<th>$\Delta V_{K-N}$</th>
<th>$T_{K-N}$ $^\circ$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3.64</td>
<td>17.87</td>
<td>4.92</td>
<td>371.3</td>
</tr>
<tr>
<td>8</td>
<td>3.93</td>
<td>18.76</td>
<td>4.73</td>
<td>409.8</td>
</tr>
<tr>
<td>9</td>
<td>3.70</td>
<td>47.69</td>
<td>12.88</td>
<td>394</td>
</tr>
<tr>
<td>10</td>
<td>3.77</td>
<td>49.65</td>
<td>13.15</td>
<td>391.2</td>
</tr>
<tr>
<td>11</td>
<td>3.77</td>
<td>55.17</td>
<td>14.63</td>
<td>373.8</td>
</tr>
<tr>
<td>12</td>
<td>3.58</td>
<td>41.74</td>
<td>11.65</td>
<td>383.8</td>
</tr>
<tr>
<td>13</td>
<td>4.15</td>
<td>53.82</td>
<td>12.97</td>
<td>379.8</td>
</tr>
<tr>
<td>14</td>
<td>3.92</td>
<td>45.96</td>
<td>11.72</td>
<td>394</td>
</tr>
<tr>
<td>P-azoxyanisole (PAA)</td>
<td>3.13 $^7$</td>
<td>256.3$^{(8)}$</td>
<td>95.29$^{(9)}$</td>
<td>390 $^8$</td>
</tr>
</tbody>
</table>

$^8$From reference 1.
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 \(\Delta V\) 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\(^{11}\) 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.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(T_{\text{N-I}}^\circ\text{K})</th>
<th>((\text{d}P/\text{d}T)_{\text{N-I}}) J/cm(^3) (\circ\text{K})</th>
<th>(\Delta S_{\text{N-I}} x10^{-3}) J/g(\circ\text{K})</th>
<th>(\Delta V_{\text{N-I}} x10^{-3}) cm(^3)/g</th>
<th>(T^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>437.6</td>
<td>3.35</td>
<td>12.82</td>
<td>3.82</td>
<td>305</td>
</tr>
<tr>
<td>8</td>
<td>461.3</td>
<td>13.2</td>
<td>30.11</td>
<td>2.28</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>417.0</td>
<td>2.92</td>
<td>13.74</td>
<td>4.70</td>
<td>391</td>
</tr>
<tr>
<td>10</td>
<td>436.5</td>
<td>3.57</td>
<td>31.78</td>
<td>8.90</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>405.8</td>
<td>2.78</td>
<td>16.61</td>
<td>5.97</td>
<td>329</td>
</tr>
<tr>
<td>12</td>
<td>416.8</td>
<td>3.27</td>
<td>33.44</td>
<td>10.23</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>395.8</td>
<td>2.99</td>
<td>17.94</td>
<td>6.00</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>407.0</td>
<td>3.23</td>
<td>34.40</td>
<td>10.65</td>
<td>-</td>
</tr>
<tr>
<td>PAA</td>
<td>408.0</td>
<td>2.17</td>
<td>5.68</td>
<td>3.799</td>
<td>280</td>
</tr>
</tbody>
</table>

Pentamer p-oxy-benzoate\(^{10}\) - - 8.8 - 306
Finally, according to the Flory-Rona theory\textsuperscript{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

$$
T^\# = \frac{\Delta H^0}{RS(1 - S^2)}
$$

where $S$ is the order parameter, $\Delta H^0$ is the N-I transition enthalpy of the homologues $\Delta H^0_{N-I}$ extrapolated to $n \to 0$. For homologues with $n$ odd, $\Delta H^0 = 0.94 \text{ kJ/mru}$ or 3.01 J/g (see Ref. 13). $\Delta H^0$ was corrected for the change in specific volume ($\Delta V$) at the N-I transition. The mesogen order parameter $S$ was obtained from PMR spectra.\textsuperscript{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 $\Delta V(n)$ 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.\textsuperscript{14}

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

ACKNOWLEDGEMENT

This work was supported in part by NSF grants DMR 8600029 and INT-8207204.

REFERENCES

1. A. Blumstein and O. Thomas, Macromolecules, 15, 1264 (1982); A. Blumstein, Polymer J. (Japan), 17, 277 (1985)


