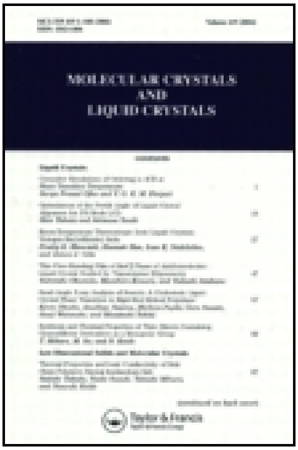

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Determination of Smectic-Nematic Phase Transitions in Liquid Crystalline Polymers Using X-ray Diffraction Methods

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Determination of Smectic–Nematic Phase Transitions in Liquid Crystalline Polymers Using X-ray Diffraction Methods

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INTRODUCTION

Phase transitions in liquid crystals are not always easily detectable. Wiegeleben and Demus [1] described methodological aspects in thermal analysis of liquid crystalline substances. There a classification of the detection of phase transitions has been given in which a division in transitions observable only by optical microscopy or/and by DSC has been made. However, there are certain cases known, where phase transitions are not detectable either by polarisation microscopy or by DSC. This is especially true, if the investigated substances have a polymeric nature. Due to polydispersity it is not always possible to obtain clear evidence for phase transitions using both methods. A special hinderence for polarization microscopy investigations is the usually high viscosity of polymeric substances and therefore the difficulties in obtaining sufficiently thin layers for the investigation. Calorimetric studies suffer from the mostly small heat of transition for smectic A- or smectic C-nematic transitions, and the small heat capacity and heat transfer coefficients of polymers.

The general difficulties in determining of phase transitions between smectic and nematic phases of polymers were the reason to perform systematically studies using X-ray diffraction techniques to characterize the smectic–nematic phase transitions, which have been previously found in liquid crystalline polymers with laterally and terminally linked mesogens [2].

EXPERIMENTAL

The substances investigated have been prepared as previously described [2]. Liquid crystalline behaviour was determined visually with a Boetius hot stage mounted on a Zeiss optical microscope. Thermal analysis has been carried out using a Perkin Elmer DSC 1C/DSC 7 with heating and colling rates of 10 K/min. Structural characterization has been performed by X-ray examination using Cu–Kα radiation monochromized by a graphite crystal monochromator. The detection device was a flat film camera or a Guinier camera from HUBER or a home made small angle camera of the KRATKY type. The samples for the flat camera investigations have been prepared in glass capillaries and oriented by permanent magnets with an approximate field strength of 0.8 T or by drawing of fibres out of the anisotropic melts. For the use of a magnetic field alignment, samples have been heated in the isotropic phase and have been cooled with a rate of 1 K/h into the nematic phase. For the Guinier and small angle investigations, unoriented samples have been prepared in between Mylar® sheets to avoid crystallisation. FWHM (full width of the half maximum) are estimated using a microdensitometer for the Guinier films.

RESULTS AND DISCUSSION

The structure of the investigated polymers is shown in Figure 1.

The phase transitions of substances are given in Table 1 [2]. As already described [2], optical microscopy does not show any texture changes below the isotropization temperatures. However, there was evidence from preliminary X-ray diffraction experiments of oriented fibres at room temperature for the existence of smectic A ($n = 4$–6)

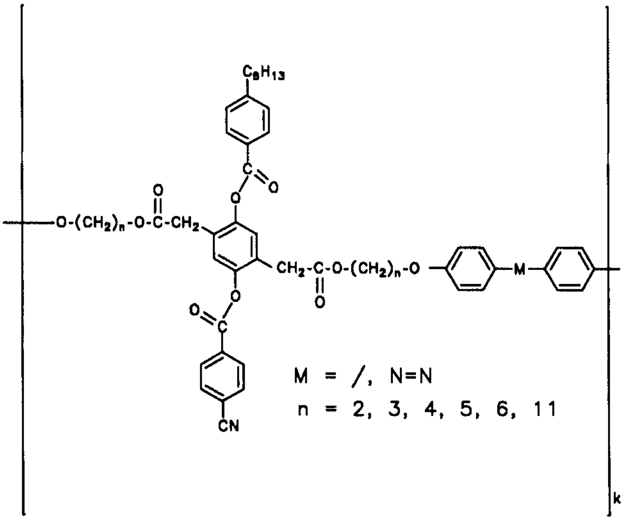

FIGURE 1 Structure of the liquid crystalline polymers with laterally and terminally linked mesogens.

TABLE 1

Phase Transition Temperatures of the Investigated Polyesters

Polymer	*M*	*n*	Phase transition temperatures(°C)
PCB 2	/	2	g 66 n 157 i
PCB 3	/	3	g 55 n 95 i
PCB 4	/	4	cr (g 60 S_A *78* n 147 i) 147 i
PCB 5	/	5	g 40 S_A *49* n 95 i
PCB 6	/	6	g 51 S_A *102* n 123 i
PCB 11	/	11	cr (g 33 S_C *71* n 83 i) 83 i
PCA 2	N=N	2	g 68 n 179 i (dec.)
PCA 3	N=N	3	g 59 n 122 i
PCA 4	N=N	4	cr (g 63 S_A *110* n 160 i) 135 n 160 i
PCA 5	N=N	5	g 49 S_A *57* n 117 i
PCA 6	N=N	6	g 50 S_A *101* n 137 i
PCA 11	N=N	11	g 36 S_C *47* n 91 i

The transition temperatures in italics are first time obtained within this investigation

and for smectic C ($n = 11$) phases below the nematic phases identified with optical microscopy (see Figures 2–4).

Therefore more precise high temperature X-ray diffraction experiments were performed to study the phase transition behaviour. With an incrase of temperature, the very distinct layer reflections of the smectic phases found at room temperature should vanish and finally disappear. Also a change in the peak position indicating a change in layer thickness could be expected. Three different methods were used for the investigation namely:

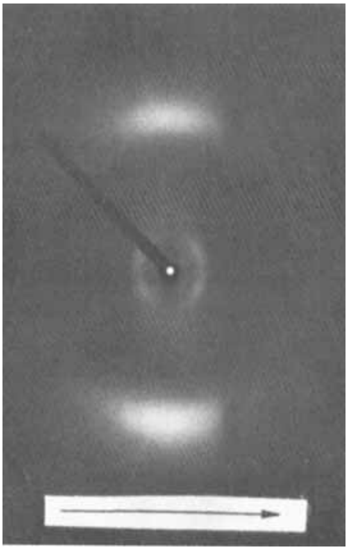

FIGURE 2 Flat camera picture of PCB 2, skewed cybotactic nematic phase [5], fiber, arrow indicates drawing direction.

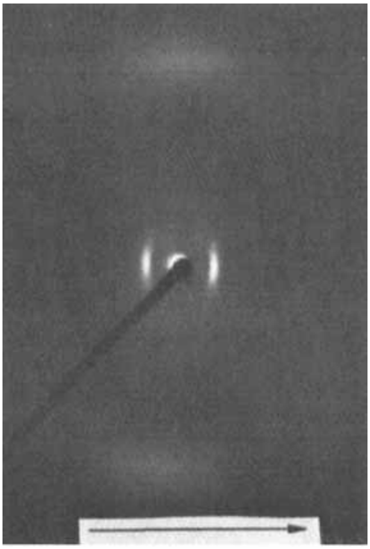

FIGURE 3 Flat camera picture of PCB 4, smectic A phase, fiber, arrow indicates drawing direction.

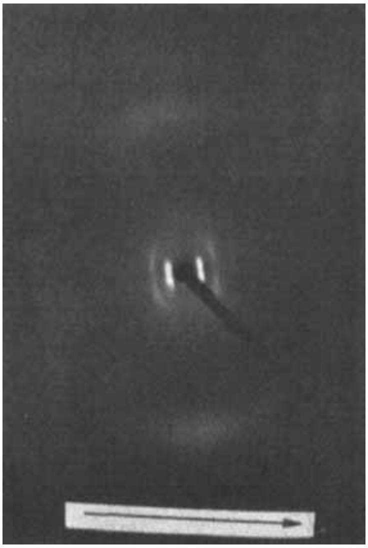

FIGURE 4 Flat camera picture of PCA 11, smectic C phase, fiber, arrow indicates drawing direction.

a. small angle diffraction using a Kratky camera

b. small and wide angle diffraction of unoriented samples using a Guinier-film camera and

c. small and wide angle diffraction of oriented samples using a flat film camera.

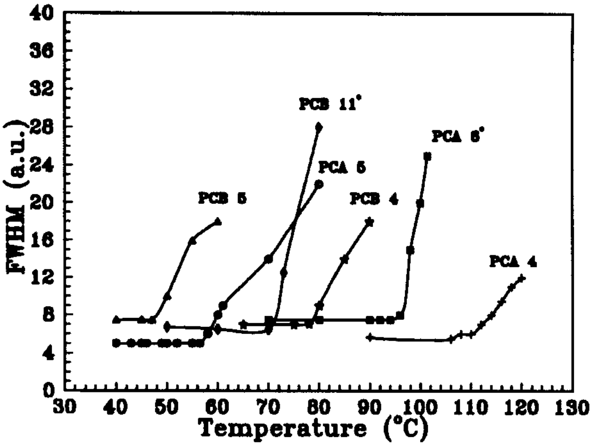

FIGURE 5 Plot of the FWHM of the layer reflection against temperature.

Only some samples have shown sufficient high signal-to-noise ratios to observe the layer reflections using the small angle camera ($M = /, n = 11$; $M = \mathrm{N{=}N}, n = 6$, both marked in Figure 5 with an *).

All other samples could be examined using the Guinier Film camera. An example of a Guinier film is shown in Figure 6.

In general, an increase of the FWHM has been observed with increasing temperatures (see Figure 5). The FWHM is nearly constant from 25°C up to the phase transition temperature. Upon the phase transition the FWHM steadily increases until no distinct reflection is observable any longer. The transition temperatures could finally be determined from the intersection of the lines describing the temperature dependence of the FWHM in both phases. The obtained transition temperatures are in a good agreement with those obtained from subsequent DSC experiments using sample weights of 40–60 mg [2]. The X-ray results, obtained by the Kratky and Guinier technique have been confirmed using a flat film camera. Distinct patterns were recorded in temperature steps of 2 K crossing the phase transition temperatrue. They

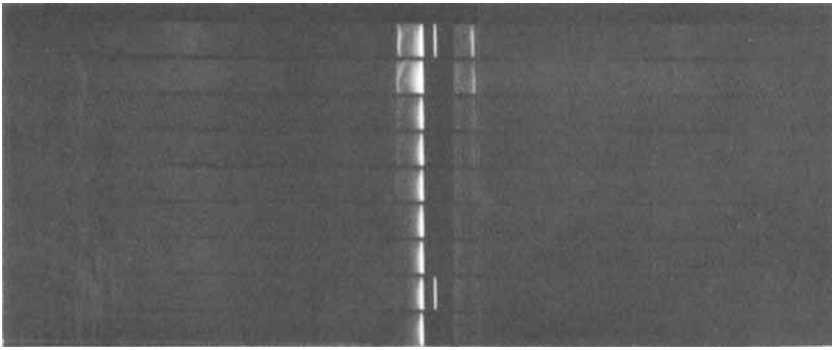

FIGURE 6 Guinier picture of PCA 4, temperatures indicated in the Figure.

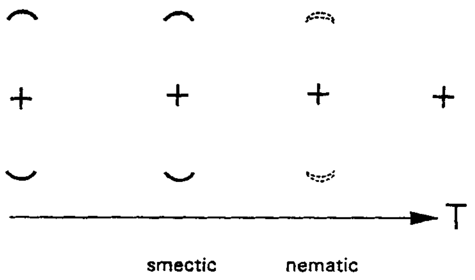

FIGURE 7 Schematic picture of the smectic A—nematic transition as recorded by flat plate pictures.

show a disappearance of the sharp layer reflections at the phase transition temperature also. Figure 7 shows the principle X-ray pattern obtained.

Also a shift of the position of the layer reflection for a transition from the smectic to the nematic phase towards larger angles has been observed (Figure 8).

The shift in the position of the layer reflection could be related due to the increased thermal motion, and a melting of the alkyl chains in the tail and the spacer groups. At the temperatures of investigation a transition from an *all-trans* to a *gauche* confirmation would lead to a decrease of layer thickness and therefore explain the shift towards larger angles. Experiments using dielectric spectroscopy have shown in the case of $n = 4, 5, 6$ and 11, a decrease in absorption intensity with decreasing temperatures [3,4]. This effect should be connected with a smectic like preorder in the nematic phases (cybotactics [5,6]) for the investigated polyesters. A dielectric investigation at lower temperatures was not possible due to the stronger influence of the conductivity at

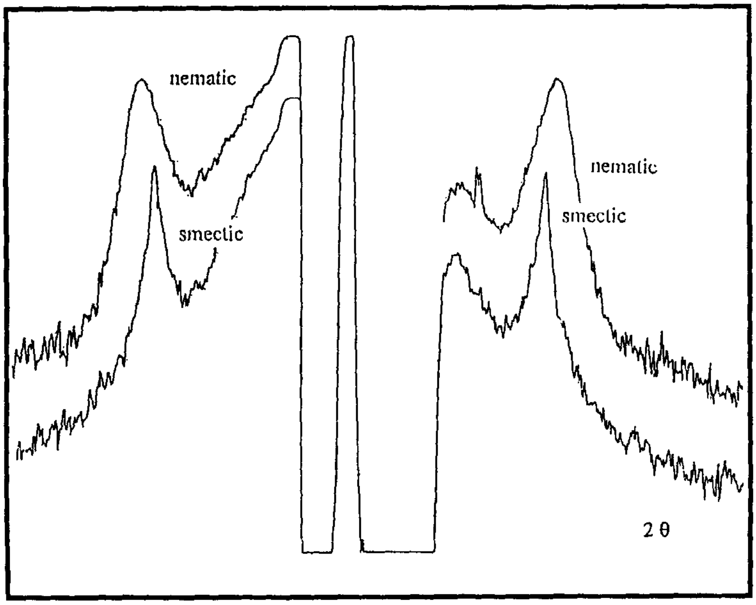

FIGURE 8 Microdensitometer traces of a Guinier Film showing a smectic A phase and a nematic phase.

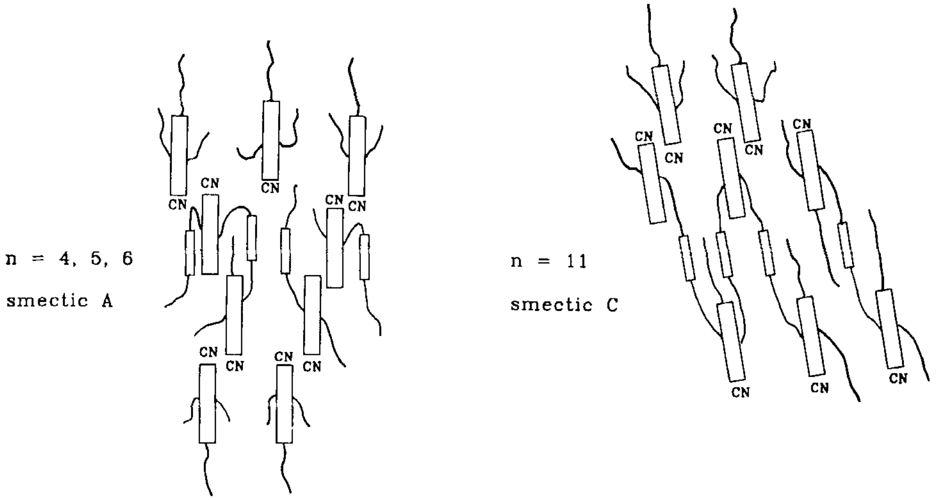

FIGURE 9 Proposed structures for the smectic A and smectic C phases.

lower temperatures. However, an anti parallel orientation of the dipoles is favored [3, 4]. Also a parallel arrangement of the laterally and terminally linked mesogens is more favoured due to the simple X-ray pattern. A proposal for the structures in the two smectic phases is shown in Figure 9.

Only in the case of the undecyl spacer is there enough space to build two distinct layers of each type of the mesogens. This can be deduced from the weaker second order reflections from the X-ray diffraction pattern. Therefore a different arrangement is present and the molecules are tilted in the layers. In the case of the shorter mesogens due to the strong dipolar interaction of the cyano-groups, the formation of a smectic A phase is more favoured.

SUMMARY

Smectic–nematic phase transitions have been determined using different methods of X-ray diffraction investigations. The transition temperatures could be extrapolated from the intersection of the lines describing the temperature dependence of the FWHM in the smectic phase (constant) and in the nematic phase (steady increase). This procedure is especially usefull in the case of liquid-crystalline polymers, where the phase transitions are usually difficult to observe by means of polarization microscopy and DSC. Subsequent DSC runs with unusually high sample amounts (40–60 mg) confirmed the X-ray determined phase transition temperatures.

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