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Thermo-optic observations on a main-chain thermotropic liquid-crystal polymer

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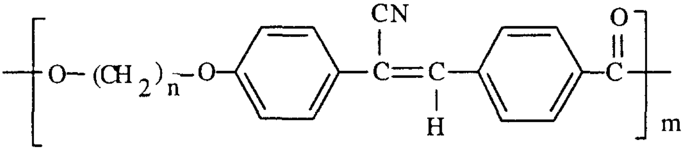
Summary

The morphological transitions of a main-chain liquid crystalline chromophoric polymer in which all of the electric dipole moments were arranged head-to-tail were investigated using the techniques of small-angle light scattering, x-ray scattering, differential scanning calorimetry and polarised optical microscopy. Above 96°C the material developed a birefringent nematic texture followed, at temperatures higher than 141°C, by a monotropic structure which was retained until the onset of thermal degradation. Under certain heating/cooling regimes non-centrosymmetric solid polymer films with low scattering characteristics could be prepared.

Introduction

Liquid crystalline polymers possessing non-centrosymmetric arrangements of electrical dipoles must be capable of forming thin films with long-term stability and low scattering characteristics if they are to be usefully employed for the fabrication of nonlinear optical devices.[1]

As part of our work on the synthesis and characterisation of new materials for nonlinear optics[2-8] we have recently reported the synthesis of a new class of main-chain liquid crystalline polymers (structure I) in which the conjugated mesogen is substituted with electron donating and electron withdrawing groups.[8] Optical microscopy showed that all the polymers exhibited an apparent isotropic texture which was retained until the true clearing transition or the onset of degradation was reached. The existence of such phases is particularly desirable if low scattering film structures are to be fabricated. A preliminary evaluation of the second order nonlinear optical properties of one of these materials in the form of a thin film has demonstrated that the polymer exhibits the expected non-linear optical behaviour. The results of these studies will be published elsewhere.[9] The transition temperatures of these materials were found to be strongly dependent upon the length of the spacer (n), the polymer with n=7 exhibiting the broadest mesophase stability range.



n = 6-12

Structure (I)

To develop a further understanding of the liquid crystalline behaviour of this polymer and to establish the best cooling regime for the fabrication of non-scattering films, we carried out a series of small-angle light scattering (SALS), wide-angle x-ray scattering (WAXS), differential scanning calorimetry (DSC), and optical microscopy (OM) experiments the

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results of which are reported here.

Experimental

The synthesis of the polymer (M_n= 6,500; M_w/M_n= 1.21) has been described elsewhere.[8] Studies of thermal properties were carried out using a DSC7 Perkin Elmer differential scanning calorimeter and a Stanton Redcroft TG-760 thermogravimetric analyser. Optical microscopy experiments were performed with an Olympus BH-2 polarising microscope equipped with a Linkam THM 600 hot-stage. The SALS apparatus consisted of a 30 mW vertically polarised He-Ne laser (λ= 632.8 nm), the light from which passed through a polariser to remove any horizontally polarised component of the incident beam. The sample in the form of a thin (*ca.* 10 μm thick) film between two cover slips was placed in a Linkam THM 600 microscope hot-stage. The incident light beam diameter was defined by a 500 μm pinhole immediately before the hot-stage. Scattered and transmitted light passed through an analyser crossed at 90° with respect to the polariser and was focused onto the active element of a CCD camera (EG and G, OmaVision).

Prior to SALS experiments the polymer sample under study was heated to 220°C, the highest temperature at which the sample was stable for up to 10 mins. A little pressure was applied in order to facilitate the formation of a film which was thin enough to allow at least 80 % of the incident light through the sample. Measurements were carried out on samples which were subjected to two different types of thermal treatment:
(a) the polymer sample was heated to 220°C at 40°Cmin^{-1} in order to form a film and then immediately cooled to room temperature at the same rate; and,
(b) the thin film was formed in the same way at 220°C, the sample was cooled to 150°C, annealed at this temperature for 45 min and finally cooled to room temperature at 40°Cmin^{-1}.
The polymer films formed were used for the SALS experiments.

Wide angle x-ray patterns were obtained with a Siemens D-5000 diffractometer. Thin films of the polymer were prepared as previously described for the SALS experiments. The x-ray diffraction pattern was recorded at room temperature.

Results and Discussion

Optical microscopy

Samples were prepared from the powdered polymer by heating between cover slips to 220°C and cooling to room temperature at 40°Cmin^{-1}. The sample was heated at 10°Cmin^{-1} and observed through crossed polars. A transition from solid to a highly birefringent liquid crystalline phase took place at 96°C. The observed texture remained unchanged until a second transition occurred at 141°C when the polymer film appeared to adopt an isotropic texture. This texture was retained until the polymer began to degrade at about 260°C. It was found that on slow cooling from 250°C (<10°Cmin^{-1}) these texture changes could be reversed and the fluid, highly birefringent liquid crystalline texture could be retained to temperatures as low as 67°C. Cooling to below this temperature resulted in the formation of a solid in which the nematic texture was retained. By contrast, the apparent isotropic texture was maintained when the sample was cooled at rates greater than 40°Cmin^{-1}. Thin polymer films which had been subjected to electrical poling[9] also exhibited an apparent isotropic texture which could be "frozen in" by cooling at rates greater than 40°Cmin^{-1}. At intermediate cooling rates, the texture adopted by the solid was dependant on the cooling rate and was inhomogeneous in appearance.

The mesophase stability range reported here is considerably broader than that previously determined[8] for a sample of the same polymer in the first heating cycle at 20°Cmin^{-1}.

Thermal analysis

The samples were conditioned using the same protocol adopted for the OM experiments.

The DSC scans for the polymer in the second heating cycle (10°Cmin^{-1}) are shown in

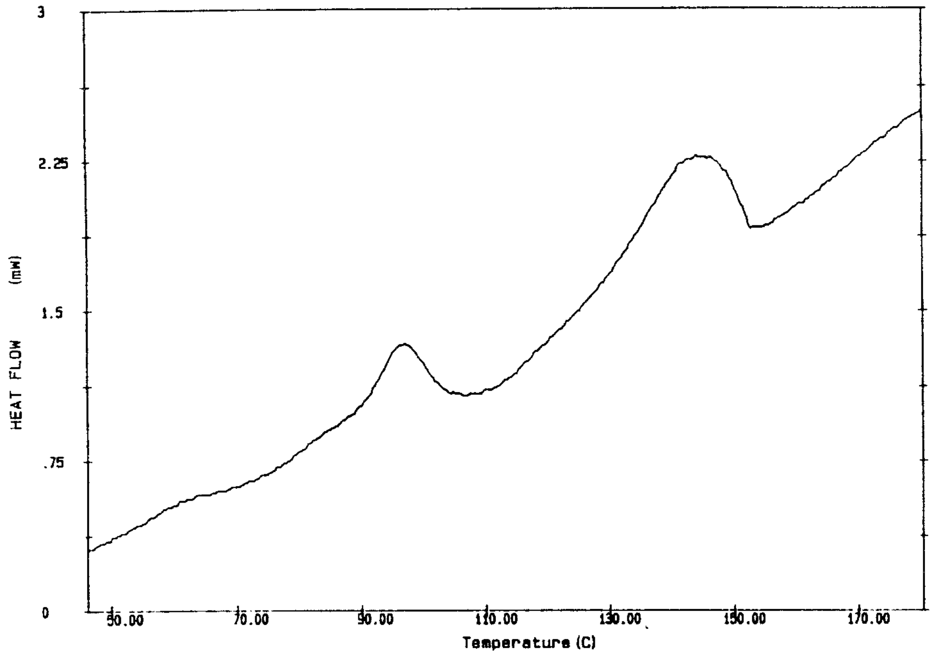


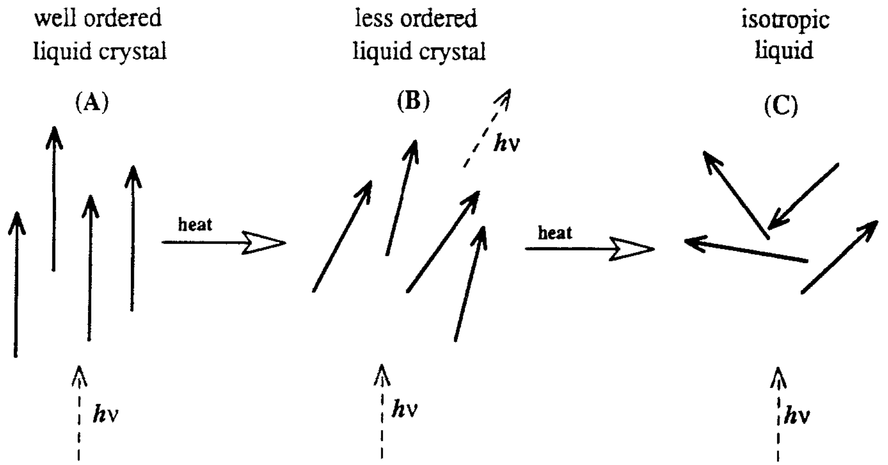
Figure 1. DSC thermogram for the polymer in the second heating cycle (heating rate:10°Cmin^{-1}).

figure 1. On heating the material exhibited two broad endotherms with peaks at 96°C and 141°C.

Thermogravimetric analysis (air; 10°Cmin^{-1}) demonstrated that the polymer begins to degrade above 260°C.

SALS analysis

Liquid crystals are optically anisotropic systems which alter the plane of polarisation of incident light. Small-angle light scattering experiments are commonly used for the study of such materials since they can yield information not only about the optical anisotropy of the system from the scattered intensity but also about the size and shape of the scattering entities from the intensity variation with scattering angle.[10-12] Usually, for liquid crystalline systems, as the temperature is increased, the amount of disorder also increases. For a system which alters the plane of polarisation of the incident light, there would be an associated decrease in the depolarised scattering intensity as the degree of disorder increases. However, there are liquid crystalline anisotropic systems which do not behave in this manner. For example, for a highly anisotropic, monotropic liquid crystalline polymer, one in which all the optical axes are aligned parallel to the incident vertically polarised light, there would be no change in the plane of polarisation of the scattered light. Consequently, under crossed polars, the depolarised scattered intensity would be approximately zero. This general behaviour is depicted in scheme 1; for **A** and **C**, zero depolarised scattered intensity would be detected, whereas **B** would result in a definite SALS pattern under crossed polars. As the monotropic system becomes more disordered, the optical axes deviate from their parallel alignment with the plane of polarisation of the incident light, resulting in an increase in depolarised scattering intensity. Thus, in this case, an increase in intensity is observed as the amount of disorder increases until the true isotropic state is reached.



Scheme 1. Idealised scattering behaviour of a liquid crystal film between crossed polars and at various states of order: (**A**) no change in the plane of polarisation of the incident beam; (**B**) detectable change in the plane of polarisation; and, (**C**) fully depolarised scattered light (the directors are represented by the solid arrows)

SALS investigation of the polymer under study showed that the processes depicted in scheme 1A and **B** operate but that decomposition occurs before the isotropic state is reached. Figure 2 shows the overall depolarised light intensity variation as a function of temperature for a sample subjected to treatment (a). Heating the sample from 100°C resulted in a gradual increase in scattered intensity which eventually reached a maximum at 260°C (the onset of degradation). The weak scattering characteristics observed at 100°C can be explained in terms of a monotropic liquid crystalline structure as described earlier. As expected for such a system, the depolarised light intensity increased with temperature. Further heating to above the clearing temperature should result in no light being detected, see scheme 1C. Owing to degradation before the clearing transition this was not observed.

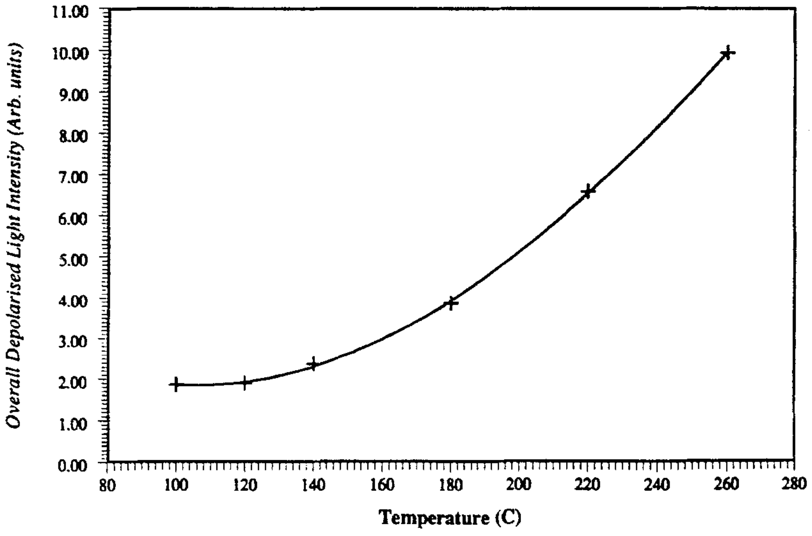


Figure 2. Overall depolarised light intensity variation as a function of temperature for samples subjected to treatment (a) and heated from 100°C to the onset of degradation.

On the basis of the observed SALS behaviour the highly birefringent texture is attributed to a biaxial nematic order in which both the long axes and the flat faces of the cyanostilbene chromophore lie parallel to each other. The monotropic structure is assigned to a uniaxial nematic orientation in which the long axes are parallel and there is a random distribution of the nitrile dipoles around this axis.

Figure 3 shows the overall depolarised scattered light intensity as a function of temperature for a sample prepared according to treatment (b) and heated to 260°C at 10°Cmin^{-1} and then cooled at the same rate. The low depolarised light intensity observed from room temperature up to 260°C is indicative of a highly monotropic system since we have shown above that an isotropic state is never attained. This suggests that the annealing process at 150°C for 45 minutes and the subsequent cooling to room temperature at 40°Cmin^{-1} had effectively "frozen in" this well ordered structure. Optical microscopy work validated this suggestion. Only upon heating to above 260°C did the equilibrium disordered arrangement appear, as demonstrated by a large increase in depolarised intensity (figure 3). Upon subsequent cooling, a decrease in depolarised scattering intensity was observed with temperature. This is analogous to the SALS intensities observed for the heating run of samples subjected to treatment (a), figure 2, indicating that formation of this structure is thermodynamically reversible.

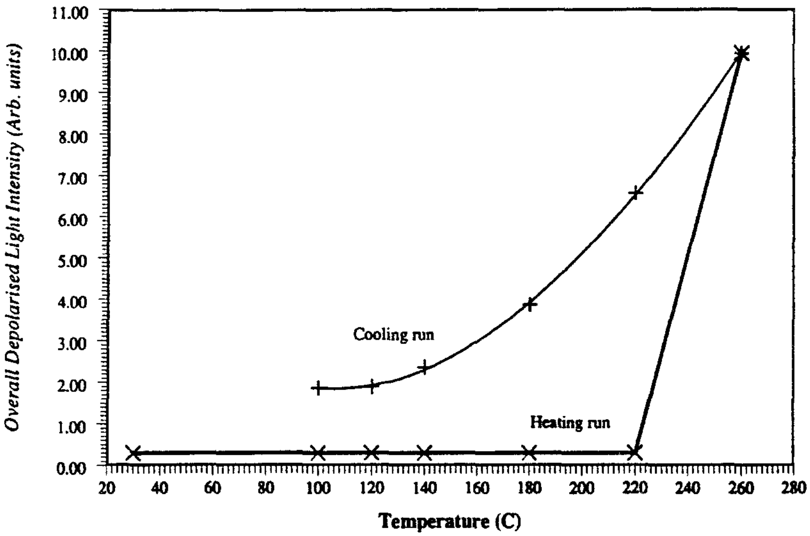


Figure 3. Overall depolarised light intensity variation as a function of temperature for samples subjected to treatment (b) heated to 260°C at 10°Cmin^{-1} and cooled to room temperature at the same rate.

On the basis of the SALS experiments it is not possible to speculate as to whether the polymer chains are aligned in a parallel or antiparallel fashion. Pockels effect measurements have however demonstrated that both electrically poled films and samples subjected to treatment (b) exhibit second-order nonlinear optical responses of similar magnitude.[9] Since such properties can only be observed on samples possessing a non-centrosymmetric arrangement of dipoles it is concluded that a statistical parallel alignment of the dipoles predominates.

Throughout the temperature range of the experiments the observed SALS patterns were circularly symmetric about the incident beam indicating random orientation fluctuations about the thus defined axis. Occasionally and at temperatures higher than 180°C sharp streaks of low intensity were observed. Such patterns have been noted previously with other liquid crystalline samples[12,13] and although their origins have not as yet been identified possible reasons for their development may be sample thickness fluctuation, interdomain interference, enhanced mobility due to reduced surface restraints of the cover glass sandwich and annealing effects or orientation due to surface forces.

WAXS data

The wide-angle x-ray scattering profile of a polymer film cooled from 220°C to room temperature at 10°Cmin^{-1} is shown in figure 4. The polymer was subjected to treatment (a). Inspection under the polarising microscope demonstrated that the film texture was analogous to that observed in the birefringent nematic state. The scattering profile is characterised by the presence of a broad peak at $2\theta = 11.740$ (corresponding to a d-spacings of 7.532 Å) and an "amorphous halo" at a higher angle. The observed d-spacing is consistent with the structure assigned on the basis of the SALS experiments and is attributed to the intermolecular distance between the centres of gravity of neighbouring cyanostilbene chromophores.[10]

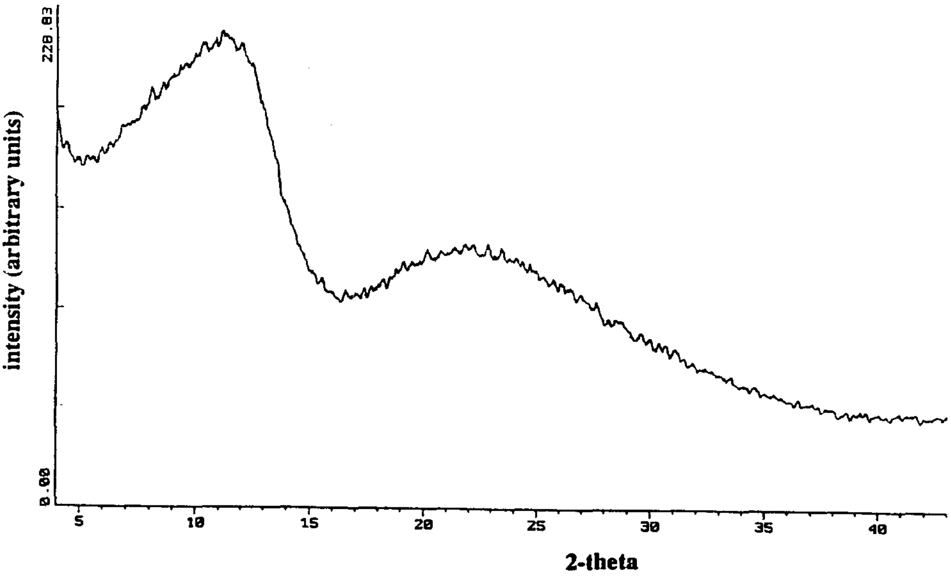


Figure 4. WAXS profile of a polymer film at room temperature.

Solid polymer films subjected to treatment (b) exhibited identical scattering profiles.

Conclusions

The morphological changes of a conjugated, unsymmetrically substituted main-chain liquid crystalline polymer have been investigated. The material exhibited a biaxial nematic texture followed by a uniaxial monotropic structure throughout the temperature range. SALS measurements along with optical microscopy investigations confirmed the existence of this monotropic structure. Annealing of a polymer sample at 150°C for 45 mins and subsequent cooling to room temperature at 40°Cmin^{-1} resulted in a solid which possessed a non-centrosymmetric arrangement of dipoles and exhibited weak scattering characteristics. Strong interactions between the carbonyl and hydroxyl end groups of the polymer chain and the glass surface may be responsible for the monotropic structure observed.

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