



A transition is observed from an oblate backbone conformation ( $N$  and  $S_{Ad}$ ) to a prolate conformation ( $N_r$ ). Using the model of Wang and Warner [5], the  $N$  phase can be identified with the  $N_I$  phase and the  $N_r$  phase with the  $N_{III}$  phase. Quasi-elastic neutron scattering measurements of Benguigui *et al.* [7], give additional support to this interpretation. The objective of this work is to study the backbone conformation of PA-CN using high resolution X-ray diffraction.

## 2. Experimental

The X-ray source was an Enraf Nonius GX-21 rotating anode generator operated at 6 kW. A standard triple-axis spectrometer was used with Ge(111) crystals at the monochromator and analyser positioned to select the  $CuK_{\alpha 1}$  line. The longitudinal resolution (parallel to the director) could be described by a lorentzian with a HWHM of  $2.6 \times 10^{-4} \text{ \AA}^{-1}$ , the transversal out of plane resolution by a trapezium with a HWHM of  $2.6 \times 10^{-2} \text{ \AA}^{-1}$ , and the transversal in-plane resolution by a lorentzian with a HWHM of  $1.3 \times 10^{-5} \text{ \AA}^{-1}$ .

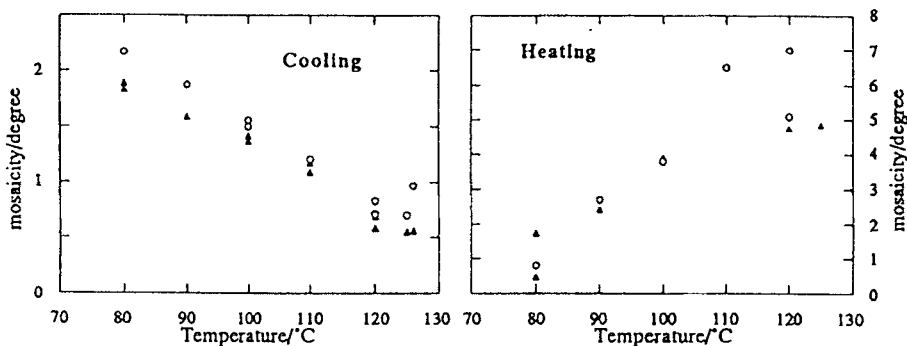
To obtain good alignment of the director of the side groups, a magnetic field of 0.9 T was applied by two permanent cobalt-samarium magnets equipped with pole caps concentrating the field. The sample was contained in a sealed glass capillary with a diameter of 2 mm. The temperature of this capillary was controlled in a two stage oven, with a stability of 0.1°C. Good alignment was reached by keeping the sample for 12 h in the nematic phase just below  $T_{NI}$ .

The PA-CN sample studied had a number averaged molecular mass  $\bar{M}_n = 18\,000$  and a polydispersity, expressed by the ratio of the weight averaged and the number averaged molecular mass,  $\bar{M}_w/\bar{M}_n = 3.4$  [8–10]. It should be realized that the average molecular weight and its distribution can strongly affect the phase behaviour [11].

## 3. Results

Between 78°C and 127°C, a smectic  $A_d$  peak was observed, the position of which changed from  $q_0 = 0.1915 \text{ \AA}^{-1}$  at low temperatures to  $q_0 = 0.1968 \text{ \AA}^{-1}$  at higher temperatures. These values are in agreement with some values reported in the literature [12], but higher than  $q_0 = 0.187 \text{ \AA}^{-1}$  as reported by other groups using low resolution X-ray scattering [6, 9]. A second harmonic was found, which has an intensity of 10 per cent (close to the nematic phases) to 30 per cent (around 110°C) of that of the first order peak. A much weaker third harmonic was present around 100°C with an intensity of about 1 per cent of the first order peak. All these peaks were found to be resolution limited in the longitudinal direction. We did not further study the broad reflections at larger angles reported in [6, 12].

On cooling the oriented sample from the nematic phase, the narrowest mosaicity was obtained just below the  $NS_{Ad}$  phase transition: the value was 0.66° HWHM. Upon further cooling through the  $S_{Ad}$  phase, the mosaicity became broader and reached values slightly larger than 2° HWHM just above the transition to the  $N_r$  phase (see the figure). Interestingly, once in the  $N_r$  phase, good alignment of the sample could again be obtained, by leaving it for 12 h at 75°C. Upon heating the sample up to 80°C in the  $S_{Ad}$  phase, a narrow mosaicity of 0.44° HWHM was found. It was essential to leave the sample for such a long time in the  $N_r$  phase in order to achieve alignment of this quality. For example, after 1 h at 75°C and subsequent heating to 80°C, the mosaicity did not improve at all. When the well oriented sample was heated from 80°C up to 120°C, the mosaicity broadened to 7° HWHM. These measurements were repeated with different counting, heating, and cooling times, with the same results. This makes it unlikely that dynamical effects play a role.



Changes in the mosaicity in the  $S_{Ad}$  phase of PA-CN upon cooling from the  $N$  phase and upon heating from the  $N_r$  phase. Triangles and circles represent values as obtained from the first and second harmonic of the Bragg peak, respectively.

#### 4. Discussion

According to Noirez *et al.* [6], the backbone in PA-CN is perpendicular to the side groups in the  $N$  and  $S_{Ad}$  phase and parallel in the  $N_r$  phase. This transition from an  $N_I$ -like to an  $N_{III}$ -like local structure would mean that the backbone conformation undergoes a giant change at the  $N_r/S_{Ad}$  phase transition. In principle, the possibility should be considered that the variations in the mosaicity in the smectic phase are a signature of the backbone conformation already changing in the smectic phase. The observed differences in mosaicity upon heating and cooling then would indicate that the backbone conformation in the smectic phase depends on the temperature history of the sample. This seems rather unlikely, since upon heating and cooling, neither differences in the ratio of the intensities of the first and second harmonic of the Bragg peak nor in the layer thickness have been found. In addition, the variations in the mosaicity are of a similar magnitude to those that also occur in monomeric liquid crystals upon changing the temperature over ten's of degrees in the smectic phase. In combination with the possibility of aligning the  $N_r$  phase, it seems most likely that the transition from an oblate backbone conformation to a prolate backbone conformation happens in the  $N_r$  phase during the pretransitional effects associated with the phase transition to  $S_{Ad}$ . Then the  $N_r$  phase can indeed be identified as an  $N_{III}$  phase, while in contrast, the smectic fluctuations have the perpendicular  $N_I$ -like backbone conformation. In that case, the change of the backbone conformation from  $N_{III}$  to  $N_I$ -like occurs with the growth of the smectic fluctuations. From the packing point of view, it seems intuitively difficult to impose a smectic density modulation upon a  $N_{III}$ -like structure, which could provide the driving force for the change in backbone conformation.

#### 5. Conclusions

From measurements of the mosaicity in the  $S_{Ad}$  phase and the possibility of aligning the polymer sample PA-CN in both nematic phases, it is concluded that the change in the backbone conformation from  $N_{III}$  to  $N_I$ -like occurs in the  $N_r$  phase parallel to the growth of the  $S_{Ad}$  fluctuations.

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