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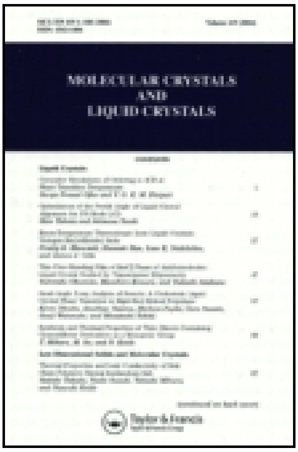

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High Resolution X-Ray Measurements of the Nematic-Smectic C Phase Transition in the Polymeric Liquid Crystal C-6 Polysiloxane

Ehud Nachaliel [a], Edward N. Keller [a], Dan Davidov [a], Herbert Zimmermann [b] & Moshe Deutsch [c]

[a] Racah Institute of Physics, Hebrew University, Jerusalem, Israel

[b] Max-Planck Institut für Medizinische Forschung, Heidelberg, West Germany

[c] Department of Physics, Bar-llan University, Ramat, Gan, Israel

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High Resolution X-Ray Measurements of the Nematic-Smectic C Phase Transition in the Polymeric Liquid Crystal C-6 Polysiloxane[†]

EHUD NACHALIEL, EDWARD N. KELLER and DAN DAVIDOV
Racah Institute of Physics, Hebrew University, Jerusalem Israel

and

HERBERT ZIMMERMANN
Max-Planck Institut für Medizinische Forschung, Heidelberg, West Germany

and

MOSHE DEUTSCH
Department of Physics, Bar-Ilan University, Ramat Gan Israel

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We report on high-resolution X-ray measurements of the nematic to smectic C phase transition in the polymeric liquid crystal, C-6 polysiloxane. Preliminary results show that smectic fluctuations measured in the nematic phase are roughly consistent with a Chen and Lubensky type of theory, as was developed for monomeric liquid crystals. The phase transition in C-6 polysiloxane shows pre-transitional smectic fluctuations at least 30° C above the phase transition temperature, T_{NC}, where $T_{NC} = 37.84 \pm 0.05$°C. At T_{NC}, there is a weak first order phase transition to the smectic C phase.

Keywords: polysiloxane C-6, phase transition (nematic-smectic), high resolution, x-ray, flexible spacer, flexible backbone

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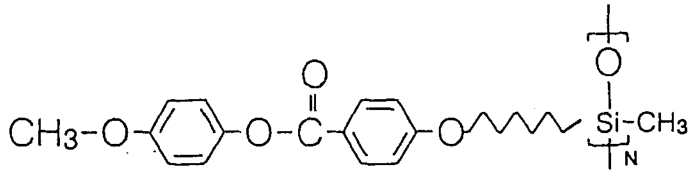

G —— 8°C —— S_c — 37.84±.05°C — N — 90°C —— I

FIGURE 1 Upper Panel: Chemical structure of C-6 polysiloxane. Lower Panel: Phases and phase transition temperatures of C-6 polysiloxane. Note that there is evidence that the smectic C phase is metastable with respect to the crystalline state.[6] I denotes isotropic phase, N, the nematic phase, S_c, the smectic C phase, and G, the glass phase.

INTRODUCTION

In recent years, there have been several high resolution X-ray measurements of phase transitions in monomeric liquid crystals. Most work has concentrated on the 2nd order nematic to smectic A transition (see e.g., Refs. 1–3). One work by Safinya, *et al.*[4] measured the nematic to smectic C phase transition for mixtures of $\bar{8}S5_{1-x}-\bar{7}S5_x$. However, no high resolution X-ray measurements have been done to date on polymeric liquid crystals on either a nematic to smectic A or nematic to smectic C transition.

There is interest in comparing the phase transitions of monomers and polymers. Such a study should help determine the effect of the polymeric backbone on the liquid crystalline phase transitions. To study this effect, we have undertaken a study of C-6 polysiloxane.

Low resolution x-ray measurements of Zugenmaier[5] identified the crystalline phase of this material as a tilted phase. We were able to identify the smectic phase also as a tilted phase, viz., smectic C. Figure 1 lists the phases and phase transition temperatures of this material. The structure of C-6 polysiloxane allows us to make several predictions about its behaviour in the nematic phase. First of all, there is evidence that the siloxane backbone is flexible.[6] A study of the monomeric liquid crystal 4OP10OB,[7] which resembles the mesogenic groups of C-6 polysiloxane, has shown that the $(CH_2)_6$ alkyl group is itself very flexible. We expect, therefore, that polysiloxane C-6 should behave quite closely to monomeric liquid crystals, at least at the high temperatures of the nematic phase.

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EXPERIMENT

The heating element of the oven used for this experiment is a thermoelectric device. Although we use a single-stage oven, the temperature does not drift more than 0.02° C in 24 hours. In order to align the sample, the C-6 polysiloxane was placed in a 9.2 kG magnetic field and was allowed to sit for a week at a temperature 10°C below the isotropic-nematic phase transition, T_{NI} ($T_{NI} = 90°$ C). The long period of annealing seems to be critical for the sample's alignment. The sample was then brought to 70° C at a rate of 3° C per hour (after which, long data taking scans were commenced). In this way, we obtained a mosaicity of 2 degrees full width half maximum. We were therefore able to relax the in-plane resolution of our spectrometer (described in reference (7)) to 5.7×10^{-3} Å^{-1}. The vertical resolution was calculated by a detailed raytracing program to be 0.16 Å^{-1}.

RESULTS

Figure 2 shows contours of equal scattering intensity from C-6 polysiloxane at two temperatures within the nematic phase. The smectic C fluctuations appear clearly as two peaks along $q_\perp$ corresponding to the intersection of a ring of scattering with the scattering plane (see e.g., Ref. (4)). The tilt angle, ϕ, determined from the separation of the two peaks is equal to 15 degrees at $T = T_{NC}$. Notice that the peaks in Figure 2 sharpen with lower temperature. This means that the correlation length is increasing with decreasing temperature.

Attempts were made to fit the data, as a function of temperature, to the Chen and Lubensky (CL)[8] and Chu and McMillan (CM)[9] theories of the nematic-smectic C phase transition. We can justify fitting our data to these theories, which were developed for monomeric liquid crystals, for the following reasons: (1) The mesogenic group of C-6 polysiloxane is attached to the backbone by an extremely flexible $(CH_2)_6$ spacer, and (2) the siloxane backbone is also very flexible. Criteria 1 and 2 suggest that C-6 polysiloxane may be modeled by monomeric liquid crystal theory, at least in the nematic phase (where the molecules are the most flexible). The predicted scattering intensity near the NC transition for the CL model has the general form,[8]

$$I(k) \sim \frac{1}{\bar{a} + D_\parallel(k_\parallel^2 - q_\parallel^2)^2 + D_\perp(k_\perp^2 - q_\perp^2)^2} \qquad (1)$$

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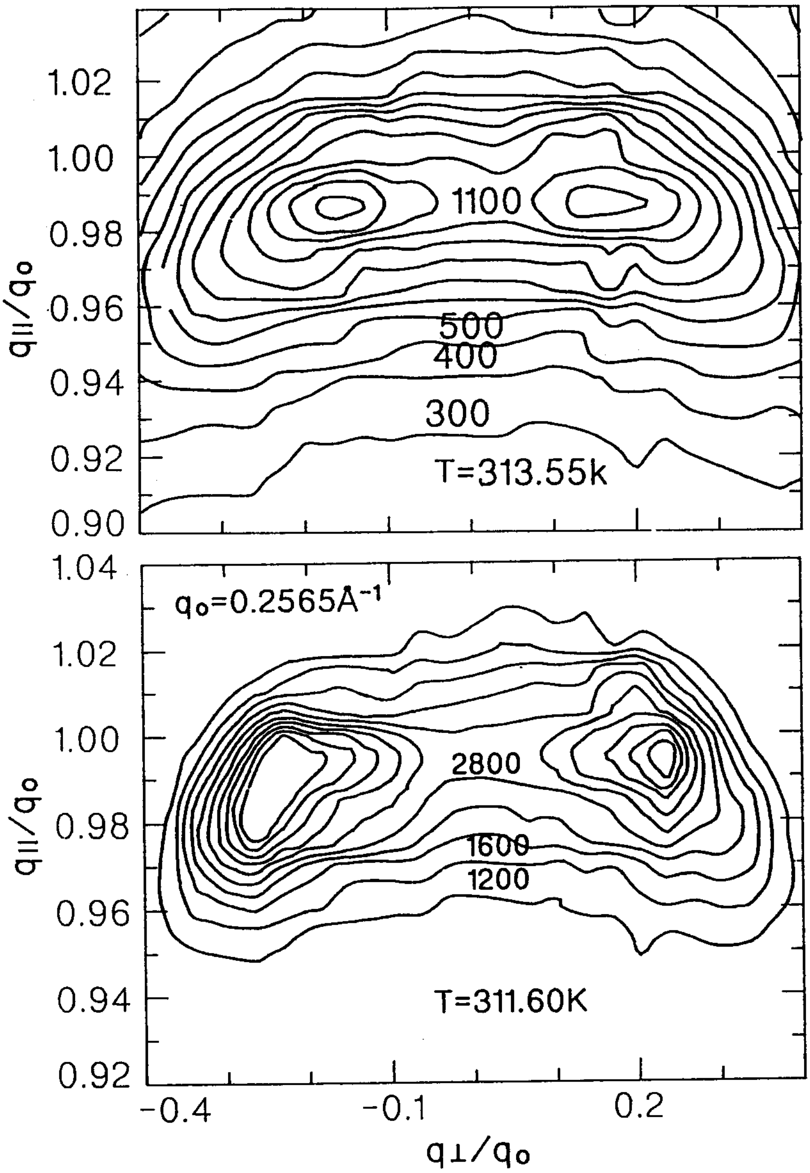

FIGURE 2 Q-space x-ray scattering scans showing smectic C fluctuations in the nematic phase. The two peaks correspond to the intersection of the smectic C ring with the scattering plane. Upper panel: q-space scan at T = 313.55 K (t = 0.0087). The correlation lengths at this temperature were computed to be $q_0\xi_\parallel = 65 \pm 7$ and $q_o\xi_\perp = 7.2 \pm 1$. Lower panel: q-space scan at T = 311.60 K (t = 0.0024). The correlation lengths are $q_0\xi_\parallel = 83 \pm 8$, $q_0\xi_\perp = 11 \pm 1$. The correlation lengths $\zeta_\parallel$ and $\zeta_\perp$ are defined in reference 4.

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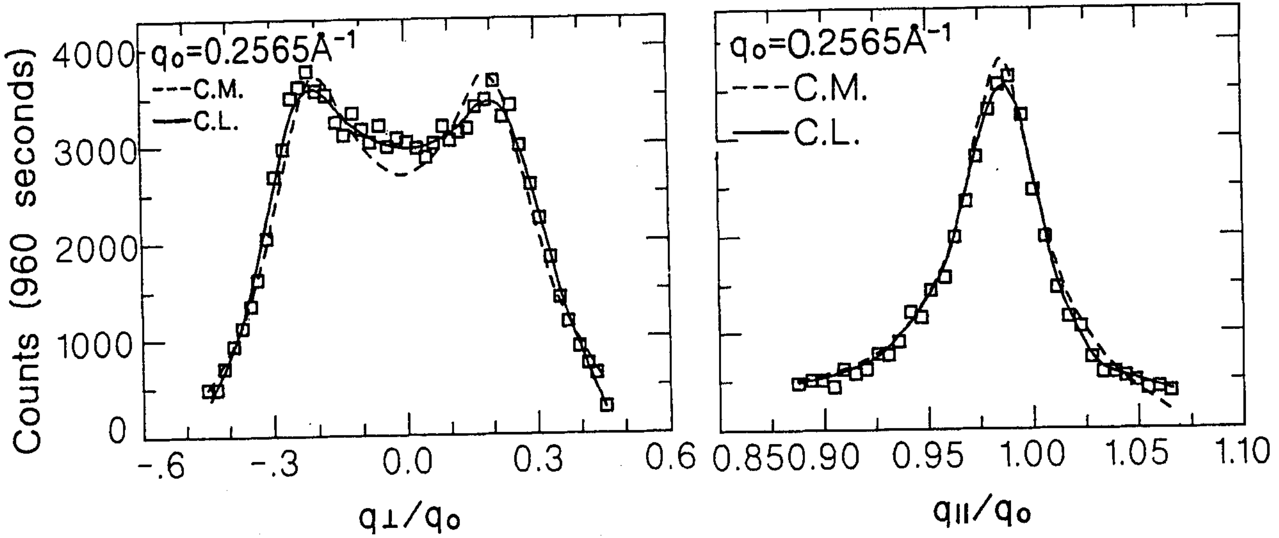

FIGURE 3 Sections of q-space at T = 311.30 K (t = 0.0015) showing the least square best fits to the data using the Chen and Lubensky theory (solid line), and the Chu and McMillan theory (dashed line). The NC phase transition temperature was experimentally determined to be 310.84 ± .05 K. Left panel: scan along $q_\perp$ with $q_\parallel/q_o = 0.984$. Right panel: scan along $q_\parallel$ with $q_\perp/q_o = -0.21$.

where $q_\parallel^2 = C_\parallel/2D_\parallel$ and $q_\perp^2 = |C|_\perp/2D_\perp$, and $C_{\parallel(\perp)}$ are parameters in the free energy. The predicted form for $I(k)$ from the CM theory is,[9]

$$I(k) \sim \frac{A\xi_\parallel^2}{\sqrt{1+\xi_\parallel^2(k_\parallel-q_\parallel)^2+\xi_\perp^2(k_\perp-q_\perp)^2}\sqrt{1+\xi_\parallel^2(k_\parallel-q_\parallel)^2+\xi_\perp^2(k_\perp+q_\perp)^2}} \tag{2}$$

Figure 3 shows least square fits of the CL and CM theories (convoluted with the instrumental resolution) to sections in $q_\parallel$ and $q_\perp$ at the reduced temperature, $t = 0.0015$, where $t = (T-T_{NC})/T_{NC}$ and $T_{NC} = 37.84$°C. These preliminary results suggest that the Chen and Lubensky theory fits our data better than the Chu and McMillan theory. It is interesting to note that Safinya, *et al.*[4] had similar conclusions for the mixtures: $\bar{8}S5_{1-x}-\bar{7}S5_x$.

CONCLUSION

Our preliminary measurements shows that the nematic-smectic C transition in polysiloxance C-6 is quite similar to the transition measured for mixtures of monomeric liquid crystals, $\bar{8}S5-\bar{7}S5$. This might have important consequences for theories about ordering of the smectic C phase. That is to say, since smectic C fluctuations in the nematic phase seem to be little perturbed by the polymeric backbone, this implies that one can ignore the contribution of the flexible alkyl groups to the smectic C ordering.

Acknowledgment

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