Rapid Note

Main-chain smectic liquid-crystalline polymers as randomly disordered systems

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Abstract. We report a high-resolution X-ray lineshape study of main-chain smectic polymers. The results indicate that the layer ordering differs fundamentally from the algebraic decay typical for other smectic liquid-crystalline systems. The lineshapes are best described by broad squared Lorentzians indicating some form of short-range correlations. However, several higher harmonics are observed, which excludes simple liquid-like short-range order. This behaviour is tentatively attributed to a random field of defects associated with entangled hairpins in the main-chain polymer structure.

PACS. 61.30.-v Liquid crystals – 64.60.Cn Order-disorder transformations; statistical mechanics of model systems – 61.10.Eq X-ray scattering (including small-angle scattering)
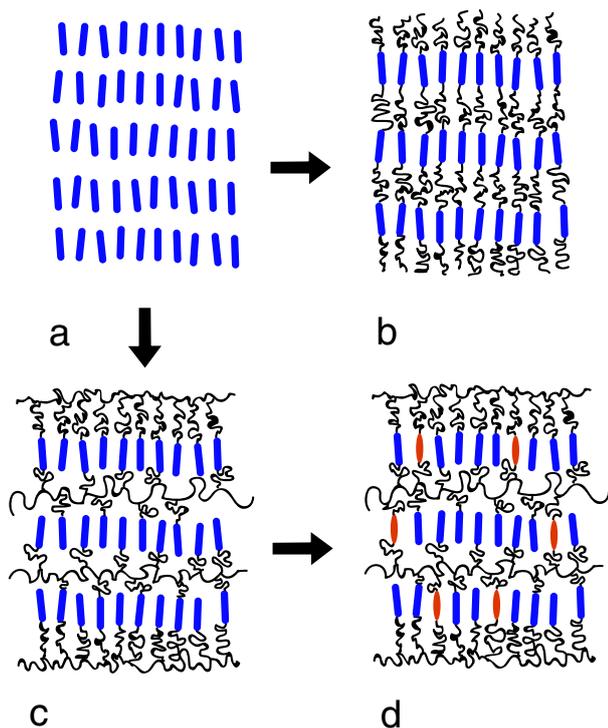
1 Introduction

The properties of condensed matter systems can be strongly influenced by a random field. The resulting disordering and the mechanisms involved constitute a source of challenging problems [1–3]. Long-range translational order is a defining quality of many systems —in 3D crystals it leads to the existence of Bragg reflections— but can be strongly disrupted by such a random field. Examples include the pinning of flux vortex lattices by impurities in superconductors, superfluid transitions in He^4 in a random environment, disordered Ising magnets, and confined smectic liquid crystals. At large enough length scales even weak disorder can destroy the translational symmetry and either only short-range order is left (exponentially decaying positional correlations) or quasi–long-range order can survive (positional correlations decaying algebraically at large distances). Smectic monomers [4] and polymers [5], which form regular stacks of fluid monolayers, provide interesting model examples because their low-dimensional order is especially vulnerable to such effects. Confinement of a smectic-monomer system in aerogels imposes a quenched random field that reduces the layer correlations to short range [6]. Crosslinking a smectic side-chain polymer into a smectic elastomer [7] provides an "internal" random field of distortions, which at large density again

leads to disorder [8]. In this work we show that main-chain smectic polymers possess by themselves an intrinsic random field restricting the correlations between the smectic layers to short range only. These observations on smectic polymers as well as elastomers lead to new insights into the fundamental aspects of their order. In addition, they are relevant for emerging applications of these materials, for example as artificial muscles [9,10] or photonic band-gap materials [11,12].

Smectic liquid crystals consist of stacked fluid monolayers, in which rod-like mesogenic molecules order into a density wave along the layer normal, but remain fluid in the other two directions (Fig. 1a). In such a system thermally excited fluctuations cause the mean-squared displacements of the layer positions to diverge logarithmically with the system size [13,14,2] (Landau-Peierls instability). As a result, the correlation function describing the smectic-layer periodicity decays as $r^{-\eta}$, the exponent η being small and positive. The quasi–long-range order can be studied by high-resolution X-ray scattering. Instead of delta-function–type Bragg peaks with diffuse tails characteristic of a three-dimensional crystal periodicity, Caillé lineshapes with an asymptotic power law form $q^{-2+\eta}$ are observed [15,2]. This behaviour is essentially conserved in side-chain smectic polymers [16] in which the mesogenic molecules are attached to polymer chains via a flexible spacer group (see Fig. 1c). Although the phase
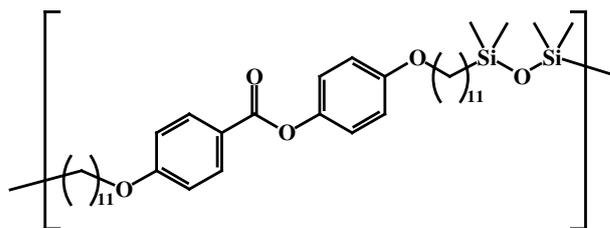
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Fig. 1. Schematic representation of (a) a smectic liquid crystal, (b) a smectic main-chain polymer, (c) a smectic side-chain polymer, (d) a weakly crosslinked smectic side-chain elastomer. For simplicity the preferred direction of the long molecular axis of the molecules in the smectic planes is taken along the layer normal (smectic-A).
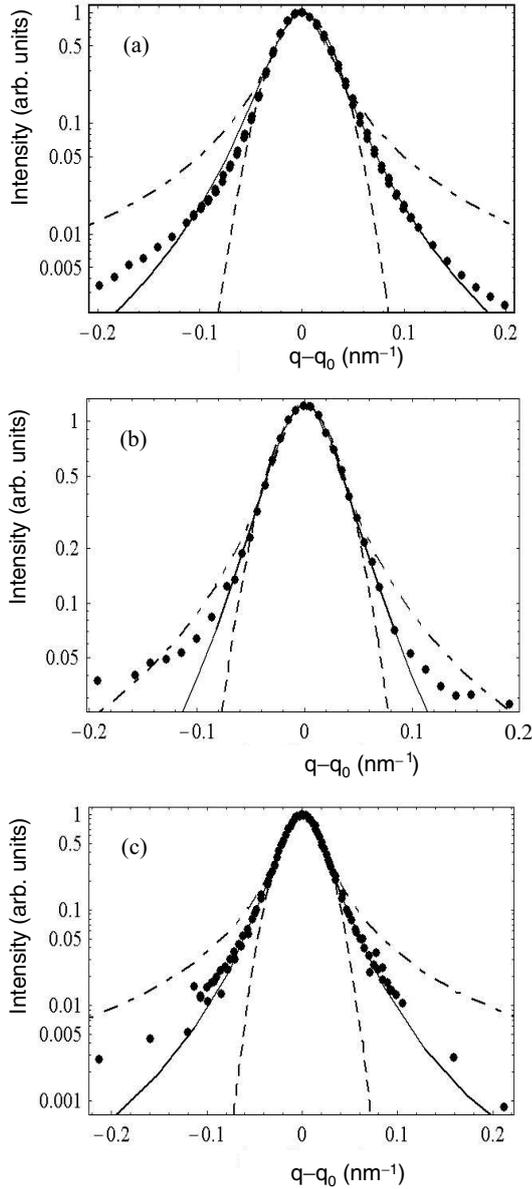

Fig. 2. Structural formula of the main-chain smectic polymer investigated.

polymers (as in the simple picture of Fig. 1b) violates the tendency of flexible polymers to randomise. The final outcome of these different driving forces is *a priori* unclear and constitutes the essential result of this investigation. We report X-ray results for main-chain smectic polymers and elastomers indicating that in both cases the order of the layers is essentially short range only.

2 Experimental

The macromolecular systems used in this study are the smectic main-chain polymer depicted in Figure 2 and a corresponding elastomer. In these systems the preferred direction of the long molecular axis in the smectic layers is tilted with respect to the layer normal (smectic-C). The smectic-C phase was identified through a set of degenerate quasi-Bragg peaks at an angle of 31° to the layer normal and a broad liquid-like peak from the in-plane short-range order. The material was studied in the smectic-C phase around 60 °C, well below the smectic-isotropic transition around 99 °C and above another phase transition at 55 °C. Oriented polymer samples were obtained by spreading and annealing a film on a glass substrate (thickness approximately 200 μm, no solvent). Alternatively, an oriented fibre could be pulled from the melt by tweezers. Finally, oriented elastomer samples (typically $20 \times 10 \, \mathrm{mm}^2$ and 0.5 mm thick) were obtained via a two-stage crosslinking process. In all cases the resulting mosaic distribution of the layer structure was of the order of 4°–6°.

X-ray lineshapes typical for the layer correlations were measured at beamline W1 of Hasylab (DESY, Hamburg, Germany) at a wavelength of 0.155 nm. The wave vector transfer was given by $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$, where $\mathbf{k}_f$ and $\mathbf{k}_i$ are the outgoing and incoming wave vectors, respectively, with $q = |\mathbf{q}| = (4\pi/\lambda)\sin\theta$, 2θ being the scattering angle. The scattering plane ((z,x)-plane) was vertical with the q_z-axis parallel to the smectic-layer normal. Hence quasi-Bragg peaks at harmonic number n were measured in reciprocal space along q_z at positions q_n The instrumental resolution in the scattering plane was set by the double-bounce Si(111) monochromator and analyser crystals. The resulting resolution function was close to a Gaussian with $q_z = 0.003 \, \mathrm{nm}^{-1}$ (full-width-at-half-maximum, FWHM). The results for the polymers film on a substrate were obtained in a reflectivity configuration, the other ones in transmission. All data were normalized and background subtracted.

transition temperatures can differ significantly from those of its monomeric counterpart due to the coupling between the layer structure and the ensemble of polymer chains, in such systems the formation of smectic layers by the mesogenic side groups is still the dominant feature.

Side-chain liquid-crystalline polymers can be weakly crosslinked into an elastomer network (Fig. 1d) with almost no change in the phase transition temperatures. The macroscopic rubber elasticity introduced via such a network [7] interacts with the liquid-crystalline order. This gives rise to a rich behaviour, predicting two opposing tendencies that have been both observed experimentally. i) Crosslinks pin the smectic layers in a number of points, thus suppressing long-wavelength layer fluctuations. If the suppression of the fluctuations is strong enough this can restore true long-range order [17,18]. ii) Crosslinks preferentially reduce the smectic density around their position, giving rise to a random field of defects that can destroy the smectic order [19,8].

The situation described so far is rather different for main-chain smectic polymers, in which semi-rigid liquid-crystal groups alternate with flexible "spacers" (Fig. 1b). The standard picture shown suggests that the layers are coupled through the polymers themselves, even though they have some freedom to slide along each other. This could lead to quenching of the layer fluctuations and possibly to improved order. However, full stretching of the

Fig. 3. X-ray lineshape of the first-order peak of (a) the polymer film on a substrate, (b) the polymer fibre and (c) the elastomer sample. Fits are to a Gaussian (broken line), a squared Lorentzian (solid line) and a Lorentzian (dash-dotted line).

3 Results

The essential results for the smectic-layer peak are displayed in Figure 3 for the polymer film on a substrate, the polymer fibre and the elastomer sample, respectively. The peak positions indicate a periodicity of 3.69 nm for the polymer and of 3.59 nm for the elastomer. Crosslinking leading to the elastomer hardly influences the order, which seems to be only fixed by this process. In all cases the experimental FWHM is surprisingly broad corresponding typically to a size of $2\pi/\mathrm{FWHM} \approx 120$ nm, only some tens of layers. As this is an order of magnitude larger than the instrumental resolution, no resolution corrections are required for the peak fitting. In Figure 3 such fits

Table 1. Experimental peak width (FWHM) and correlation length from a fit to a squared Lorentzian for the various diffraction orders of the polymer film.

| Harmonic n	FWHM (nm^{-1})	Correlation length ξ (nm)
1	0.049	26
2	0.085	15
3	0.16	8
4	0.21	6

are displayed to a Gaussian, a Lorentzian, and a squared-Lorentzian lineshape. For the polymer film four harmonics have been observed, for the pulled fibre only two. The latter can be attributed to the smaller intensity for the fibre (compare Fig. 3b) due to the limited amount of material in the beam. Attempts to fit the wings of the first-order and second-order peak of the film (the best-quality data) to a Caillé lineshape were not successful. The first-order peak gives an effective exponent $2 - \eta \gtrsim 2$, which cannot give a scaling relation with the second-order one. In Table 1 we present the FWHM of the various orders of diffraction of the film, which is most remarkably roughly proportional to the harmonic number n. We found the reported behaviour to be hardly dependent on temperature, while it was also observed for a similar compound with shorter flexible linkers (C_7 instead of C_{11}). The transition to the isotropic phase was characterized by a strong decrease in the intensity of the smectic peak.

4 Discussion

According to Figure 3 the best (though not perfect) fit to the first-order peaks corresponds to a squared Lorentzian of the form

$$I(q) \propto \left[(q - q_0)^2 + k^2 \right]^{-2}, \qquad (1)$$

in which $\xi = k^{-1}$ is the correlation length. The lineshapes of the higher-order diffraction peaks are rather similar to the first-order one. The results for ξ from fitting the various orders of the polymer film are given in Table 1 alongside the purely experimental FWHM. The structure factor of equation (1) corresponds in 3D to positional correlations decaying exponentially, in this case typically over 7 layers only. Thus, an obvious first attempt to interpret the experimental results would be in terms of smectic-layer correlations restricted to short range (or, in other words, as a nematic state with the extended smectic-like fluctuations). Such behaviour is typical for several disordered systems like smectics in aerogels [6], random Ising magnets [3], etc. However, in this situation ξ should decrease quadratically with the harmonic number n, which is why higher-order peaks are hardly observed in short-range–ordered systems. In our situation we find that ξ is roughly inversely proportional to n. An alternative interpretation of the lineshape could involve dislocation-induced broadening, in which case the width of the peak harmonics
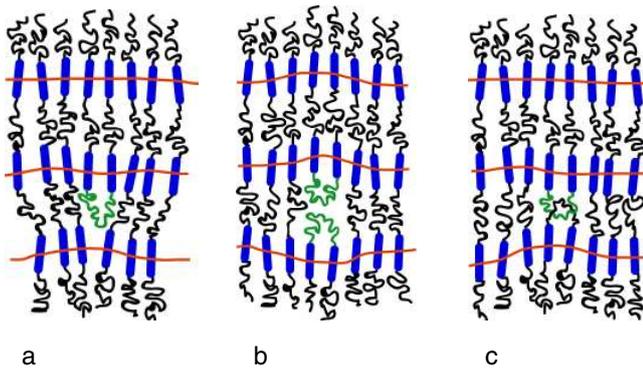
Fig. 4. Various types of possible hairpin defect in the main-chain smectic structure limiting the correlation length of the layer periodicity. External stress is not expected to remove the entangled hairpins in case (c).

should scale as $n^{4/3}$ [20]. This would lead to an alternative fitting of the various peaks by a Gaussian central part, indicating finite domain sizes, plus some squared or other Lorentzian from diffuse scattering by randomly distributed dislocations. The latter interpretation is similar to that given for the scattering from a random-field Ising magnet [3]. Unfortunately, the accuracy with which the higher-order peaks were obtained is not sufficient to decide on the exact lineshape in the wings of the peaks. We plan further measurements at lower resolution that will allow taking the wings of the broad peaks with better statistics.

The broadening of the smectic peaks with increasing harmonic number n is very similar as observed in smectic side-chain elastomer systems. In that case the broadening has been attributed to strain induced by the crosslinks. On the basis of this analogy we speculate that in the present case also an intrinsic random field that causes disorder is present. The crucial question concerns the nature of a disordering field. A prime candidate is the formation of hairpins [21], a form of coiling of the polymer chain compatible with the smectic-layer structure (see Fig. 4). However, stress-strain experiments on nematic main-chain networks indicate that during the formation of a monodomain sample, simple hairpins are probably removed by the mechanical strain and might play only a minor role [9]. On the other hand, this argument does not hold anymore for entangled hairpins as depicted in Figure 4c. The presence of such defects would be compatible with a plateau in the stress-strain curve.

In summary, we have found evidence that the layer correlation in main-chain smectic polymers differs from that of other smectic liquid-crystalline systems. It is essentially short range, probably due to a random field of defects that has tentatively been associated with entangled hairpins in the main-chain polymer structure. The experimental observations violate the conventional textbook picture of main-chain smectic liquid crystals in use up to now. The precise nature of the origin of the limited smectic correlations is under further investigation.

References

1. G. Blatter, M.V. Feigel'man, V.B Geshkenbain, A.I. Larkin, V.M. Vinokur, Rev. Mod. Phys. **66**, 1125 (1994).
2. P.M. Chaikin, T.C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, New York, 1995).
3. R.J. Birgeneau, J. Magn. & Magn. Mater. **177-181**, 1 (1998).
4. P.G. de Gennes, J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon Press, Oxford, 1993).
5. V.P. Shibaev, L. Lam (Editors), *Liquid Crystalline and Mesomorphic Polymers* (Springer, New York, 1994).
6. T. Bellini, R. Radzihovsky, J. Toner, N.A. Clark, Science **294**, 1074 (2001).
7. M. Warner, E.M. Terentjev, *Liquid Crystal Elastomers* (Clarendon Press, Oxford, 2003).
8. D.M. Lambreva, B.I. Ostrovskii, H. Finkelmann, W.H. de Jeu, Phys. Rev. Lett. **93**, 185702 (2004).
9. H. Wemter, H. Finkelmann, E-polymers 013 (2001).
10. Y. Yusuf, J.H. Huh, P.E. Cladis, H.R. Brand, H. Finkelmann, S. Kai, Phys. Rev. E **71**, 061702 (2005).
11. H. Finkelmann, S.T. Kim, A. Munoz, P. Palffy-Muhoray, B. Taheri, Adv. Mater. **13**, 1069 (2001).
12. J. Schmidtke, S. Kniesel, H. Finkelmann, Macromolecules **38**, 1357 (2005).
13. L.D. Landau, Phys. Z. Sowjetunion **11**, 545 (1937).
14. R.E. Peierls, Helv. Phys. Acta, Suppl. II, **7**, 81 (1934).
15. J. Als-Nielsen *et al.*, Phys. Rev. B **22**, 312 (1980).
16. E. Nachaliel, E.N. Keller, D. Davidov, C. Boeffel, Phys. Rev. A **43**, 2897 (1991).
17. E.M. Terentjev, M. Warner, T.C. Lubensky, Europhys. Lett. **30**, 343 (1995); M.J. Osborne, E.M. Terentjev, Phys. Rev. E **62**, 5101 (2000).
18. G. Wong, W.H. de Jeu, H. Shao, K. Liang, R. Zentel, Nature **389**, 576 (1997).
19. P.D. Olmsted, E.M. Terentjev, Phys. Rev. E **53**, 2444 (1996); E.M. Terentjev, Macromol. Symp. **117**, 79 (1997).
20. V.M. Kaganer, B.I. Ostrovskii, W.H. de Jeu, Phys. Rev. A **44**, 8258 (1991).
21. M.H. Li, A. Brûlet, J.P. Cotton, P. Davidson, C. Strazielle, P.J. Keller, J. Phys. II **4**, 1843 (1994).