Disorder by Random Crosslinking in Smectic Elastomers

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We present a high-resolution x-ray study of the effects of disorder due to random crosslinking on the one-dimensional translational ordering in smectic elastomers. At a small crosslink density of about 5%, the elastomer network stabilizes the smectic structure against layer-displacement fluctuations, and the algebraically decaying layer ordering extends up to several micrometers. With increasing concentration of crosslinks, the finite size of these domains is strongly reduced, indicating that disordering takes over. Finally, at a crosslink concentration of 20%, the structure factor can be described by a Lorentzian, which signals extended short-range correlations. The findings are discussed in terms of recent theories of randomly quenched disorder.

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The effects of disorder by a random field on the properties of condensed matter systems constitute a source of challenging problems [1]. Usually quenched disorder is considered in which the source of the distortion is fixed in space and time. Examples include systems as different as the pinning of an Abrikosov flux vortex lattice by impurities in superconductors, disordered Ising magnets, superfluid transitions in helium, and phase transitions in smectic liquid crystals. Regarding the first example, a pioneering paper by Larkin [2] predicted that at large enough length scales, even weak disorder destroys translational order below four dimensions, resulting in exponentially decaying positional correlations. Later work recognized that the effect of the disorder was overestimated and that quasi-long-range order can survive (positional correlations decaying algebraically at large distances) [3]. This latter property is similar to the behavior of solids in two dimensions (2D), as well as of the layer correlations in smectic liquid crystals (LC). Monomer and polymer smectic LC phases consist of stacks of liquid layers in which thermally excited fluctuations cause the mean-squared layer displacements to diverge logarithmically with the system size (Landau-Peierls instability) [4]. As a result, the positional correlations decay algebraically and the discrete Bragg peaks change into Caillé line shapes with an asymptotic power-law form [5]. For monomeric smectic systems, disorder has been introduced by confinement in aerogels or alternatively by dispersion of hydrophilic aerosil. Already at small densities of the aerogels or aerosils (≈2%), the 1D smectic ordering is destroyed and persists only locally on a length scale of the order of 100 nm [6,7]. This agrees with the theoretical prediction that any quenched disorder should do so, no matter how weak [8]. In this Letter we discuss smectic elastomers in which disorder can be introduced by a random network of crosslinks.

One way to combine LC ordering with polymer properties is to attach mesogenic molecules to a polymer backbone via flexible linkages. The backbone polymer, in turn, can be weakly crosslinked to form an elastomer. The macroscopic rubber elasticity introduced via such a percolating network interacts with the LC ordering field [9]. In nematic elastomers, orientational transitions driven by the soft rubber elasticity lead to novel forms of mechanical instabilities and orientational memory effects [10]. In smectic LC elastomers [see Fig. 1(a)], the layers cannot move easily across the crosslinking points where the polymer backbone is attached. Consequently, layer-displacement fluctuations are suppressed, which stabilizes the 1D periodic layer structure [11,12]. In agreement with these predictions, this has been observed to restore true long-range ordering [13]. On the other hand, the crosslinks can provide a random network of

FIG. 1. (a) Schematic picture of smectic elastomers. (b) Chemical structures. Elastomer type I has \(X = Y = R_1\); type II has \(X = R_1\) (45%) and \(Y = R_2\) (55%).

\(X\) and \(Y\) are hydrophilic, and \(R_1\) and \(R_2\) are hydrophobic.
defects that could destroy the smectic ordering. In this Letter, we report measurements demonstrating both tendencies. Upon increasing the crosslink density, after an initial small decrease (ordering), the width of the quasi-Bragg peak corresponding to the layer structure strongly increases (disordering). Finally, at about 20% crosslinks, extended short-range order develops as evidenced by a Lorentzian line shape.

Smectic-A (Sm-A) polysiloxanes [Fig. 1(b)] were synthesized as described earlier [14]. The average degree of polymerization is about 250 with a broad distribution typical of a polycondensation reaction. Both types of elastomer contain as mesogenic groups benzoic acid phenylesters \((R_1, R_2)\) and a bifunctional hydroquinone derivative \((R_3)\) as the crosslinking agent. Type II differs from type I by the presence of a second mesogenic group \((R_2)\). The elastomers/polymers were studied in the Sm-A phase at room temperature. The Sm-A phase was identified through sharp \((00l)\) quasi-Bragg peaks along the layer normal at a wave vector \(q_n\), and a broad liquidlike peak from the in-plane short-range order. Aligned elastomer samples (typically \(40 \times 10 \text{ mm}^2\) and \(0.5 \text{ mm thick}\)) were obtained by a two-stage process. During a first crosslinking step, the networks were isotropic while solvent was still present. The solvent was slowly removed at room temperature under a uniaxial load. During this process the isotropic sample passed through a nematic phase, and subsequently became smectic. In the nematic phase, the director oriented in the direction of the uniaxial stress. This determined the long direction of the sample (coinciding with the smectic layer normal) and was fixed by a second crosslinking step. Homopolymer films were prepared at temperatures close to the smectic-isotropic transition \((65–75 \, ^{\circ}\text{C})\) by moving a spreader over a glass substrate to give films with a thickness of about \(100 \, \mu\text{m}\) and a mosaic distribution of the layer normals \(\pm 1.5^\circ\).

The experiments were performed at the Exxon beam line X10A at the National Synchrotron Light Source, Brookhaven National Laboratory (Upton, NY, USA) with 8 keV radiation \((\lambda = 0.155 \text{ nm})\). The wave vector transfer is given by \(q = k_f - k_i\), where \(k_f\) and \(k_i\) are the outgoing and incoming wave vector, respectively, with \(q = |q| = (4\pi/\lambda)\sin\theta\), \(2\theta\) being the scattering angle. The scattering plane \((z, x\text{ plane})\) was vertical with the \(q_z\) axis parallel to the smectic layer normal. Hence the quasi-Bragg peaks were measured along \(q_z\), while the mosaic distribution was determined by transverse (rocking) curves varying \(q_z\) at different \(q_z = q_n\). The resolution function in the scattering plane was close to a Gaussian with \(\Delta q_z = 0.003 \text{ nm}^{-1}\) (full-width-at-half-maximum, FWHM). Using a double-bounce Ge(111) monochromator and a triple-reflection channel-cut Ge(220) or Si(111) analyzer crystal, the wings were reduced to \(\sim (q_z - q_n)^{-4.5}\) at small deviations from the Bragg position, and to \(\sim (q_z - q_n)^{-3}\) further away. The resolution function along \(q_z\) could be taken as a \(\delta\) function. Out of the scattering plane, the resolution was set by slits to \(\Delta q_n = 0.02 \text{ nm}^{-1}\). The incident intensity was about \(5 \times 10^3\, \text{cts/s}\); the beam size was \(0.5 \times 1 \text{ mm}^2\) \((V \times H)\). All data were normalized, resolution corrected, and background subtracted.

We studied elastomer I for volume fractions of crosslinks \(x = 0\) (homopolymer) and \(x = 0.05\), and elastomer II for crosslink fractions \(x = 0, 0.1, 0.15, \text{ and } 0.2\). The x-ray scattering from homopolymer II shows two orders of quasi-Bragg peaks which are not resolution limited, leading to a finite-size \(L \approx 1 \mu\text{m}\) of the smectic domains. Away from the center of the peaks, a power-law behavior \((q - q_n)^{-2 + \eta_n}\) is observed [15] that can be described by the scaling law \(\eta_n/n^2 = \eta = 0.10 \pm 0.04\).

Typical x-ray profiles for elastomer II are shown in Fig. 2(a) for different orders at \(x = 0.1\). The systematic increase of the exponent \(\eta_n\) of the algebraically decaying tails follows \(\eta_n/n^2 = 0.15 \pm 0.04\). The FWHM of the quasi-Bragg peaks is not resolution limited and the central part is well described by a Gaussian. For the first-order peak this leads to a finite size along the layer normal of \(L \approx 1.6 \mu\text{m}\). Rather surprisingly, we find that the FWHM systematically increases with the order of the diffraction peak. The same behavior is observed at higher crosslink densities. The results, summarized in Tables I and II, indicate a systematic increase of the peak width along \(q_z\) as well as along \(q_n\). The central part is still well described by a Gaussian. The asymmetry seen is probably an artifact of the measurement. The central part of the peak can still be well approximated by a Gaussian [see Fig. 3(a)], and the FWHM indicates smectic domains as small as \(L \approx 400 \text{ nm}\). Similar to the case \(x = 0.1\), the FWHM increases with diffraction order. Finally at \(x = 0.20\) only a first-order diffraction peak can be
observed, which is strongly broadened along both \( q_x \) and \( q_z \). The intensity profile \( \Delta q_z \) cannot be described by a Gaussian anymore, but fits to a Lorentzian centered at \( q_0 = 2.16 \) nm\(^{-1} \) with a correlation length \( \xi \approx 50 \) nm [see Fig. 3(b)]. We conclude that for crosslink concentrations between 15% and 20%, a crossover takes place from finite domain sizes in which the positional correlations decay algebraically, to short-range positional correlations characteristic of a disordered phase. The observed behavior of all samples is summarized in Fig. 4.

Let us discuss the theoretical context of the results observed. The elastic free energy of a smectic system is described by the layer-displacement field \( u(r) = u_x(\mathbf{r}_\perp, z) \) along the layer normal \( z \). The mean-squared fluctuations are given in the harmonic approximation by

\[
\langle u^2(q) \rangle = \frac{k_B T}{Bq_z^2 + Kq_z^4},
\]

(1)

where the elastic moduli \( K \) and \( B \) describe bending and compression of the layers, respectively, and \( k_B T \) is the thermal energy. A conventional smectic with liquid layers has no resistance to shear, and a term \( \nabla_\perp u(r) \rightharpoonup \) is not allowed in the deformation energy. Only higher-order contributions \( \sim (\Delta u(r))^2 \), corresponding to layer curvature, are energetically penalized. As a result, in the long-wavelength limit \( q \to 0 \), fluctuation modes have a much higher amplitude than in a three-dimensional solid, for which the analogous mean-square average is proportional to \( k_B T/(Cq_z^2) \). However, in a smectic elastomer, the underlying elastic network couples to the layer displacements and the smectic degeneracy with respect to uniform layer rotations is lost. Though the resulting expression for the free energy as a function of layer displacements is rather complicated, the essential physics can be seen from the dispersion law for the elastomer phonon modes [12]:

\[
\langle u^2(q) \rangle_\perp = \frac{k_B T}{B^*q_z^2 + 2C_{q_z}^*q_z^4 + 2C_{q_z}^{\text{eff}}(q_z^2/q_z^2)},
\]

(2)

where \( B^* \) and \( C_{q_z}^* \) are renormalized bulk compression and shear moduli, respectively. The elastic modes now feature a solidlike elastic energy proportional to an overall squared power \( q_z^2 \). This can lead to reestablishment of true long-range order, even though the translational order is still 1D, like in a noncrosslinked smectic polymer [9].

So far, the crosslinks—pinning the smectic layers in a number of points—were not supposed to alter the smectic density. However, the crosslinks are also expected to disturb the layer structure itself, which effect will become more important with increasing concentration. A preferential reduction of the smectic density around a crosslink can be modeled by a local random field that adjusts the phase of the smectic density wave [16]. A full theory of such a system—still to be developed—might need a correlation function that is a product of two independent terms describing size and strain effects, respectively. Such possibilities have been discussed for various defect situations by Krivoglaz [17]. This problem

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<th>TABLE I. Summary of linewidth results for elastomer I.</th>
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<td>Concentration crosslinks ( x )</td>
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<th>TABLE II. Summary of linewidth results for elastomer II.</th>
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<td>Concentration crosslinks ( x )</td>
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![FIG. 3. First harmonic line shape of elastomer II for (a) crosslink density \( x = 0.15 \), and (b) \( x = 0.2 \). The dashed line is the best fit to a Gaussian, the full line to a Lorentzian.](image)

![FIG. 4. Summary of the peak width \( \Delta q_z \) as a function of the crosslink density; squares: first harmonic, triangles: second harmonic, circle: third harmonic.](image)
is also well known in metal physics, were this type of decoupling is used to describe strain-induced line shape broadening increasing with \( q \) and thus with the order of the reflection [18].

Let us analyze our findings (Fig. 4) in more detail in the context sketched. At small crosslink concentration \( x = 0.05 \), the finite size of the smectic domains is 2–4 times larger than in the corresponding homopolymer. Evidently the elastomer network enhances the stability of the layered structure in agreement with the predictions of layer pinning theory, Eq. (2). With increasing concentration of crosslinks, the disorder gradually takes over as indicated by broadening of the x-ray peaks both along and perpendicular to the layer normal. For the higher harmonics, the width of the peaks along \( q_z \) increase quadratically with \( n \); the observed broadening of the mosaic distribution is somewhat more complicated (compare Table II for \( x = 0.1 \) and various \( n \)). The observed broadening with different orders of diffraction is attributed to strain due to the layer displacements around the crosslinks (or other types of defects generated by the crosslinks) that are not small anymore in comparison with the layer spacing. The observed behavior also resembles that predicted for the elastic field of distant dislocations or other topological defects [19].

At a crosslink concentration \( x = 0.15 \), the finite size of the smectic domains has diminished to a few hundred nm, but within the domains the algebraic decay of the smectic layer correlations is still preserved. At higher crosslink densities, the finite-size domains give way to extended short-range correlations. The structure factor is now given by an anisotropic Lorentzian characteristic of a positionally disordered nematiclike phase. Though this behavior is consistent with the general predictions for randomly quenched disorder, it is remarkable that the algebraic decay survives within the domains up to large random amount, which causes large displacements of the smectic layer correlations is still preserved. At higher densities of crosslinks (or other types of defects generated by the crosslinks) that are not small anymore in comparison with the layer spacing. The observed behavior also resembles that predicted for the elastic field of distant dislocations or other topological defects [19].

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