

Order, disorder and stretching of a smectic elastomer with ‘side-on’ mesogenic side groups

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We report an X-ray study of the order in a ‘side-on’ smectic-A elastomer in which both the polymer backbone and the mesogenic side groups are, on average, parallel to the smectic layer normal. The present system shows in all phases locally correlated structures as evidenced by systematic diffuse scattering at small angles, attributed to the fluorinated end groups of the mesogens. The elastomer shows order of the smectic layers over a limited range in spite of the relatively low crosslink concentration (4%). Upon stretching along the layer normal we find a linear increase of the smectic layer period for small loading (elastic regime). These changes parallel the stress variation for the elastic part of the macroscopic stress–strain curve and saturate at larger strains. The attendant increase in the width of the X-ray peaks indicates a decrease of the average domain dimensions. In the plastic regime no distortion of the smectic monodomain structure or layer rotation is observed. Instead the stress is relieved by ‘melting’ of the layer structure giving rise to a nematic-like state with short-range layer correlations: at the final stage about four smectic layers.

1 Introduction

Smectic liquid crystal (LC) systems provide an inexhaustible source of model examples for phase behavior, organization and transitions, mainly because of the low-dimensional character of their ordering. In the simplest case of a smectic-A system the order of the stacks of liquid layers is described by a positional correlation function that decays as $r^{-\eta}$, the exponent η being small and positive.^{1–4} This quasi-long-range order is essentially conserved in smectic polymers⁵ that combine the LC ordering of the mesogenic units with polymer properties. Fig. 1a and b describe side-chain LC polymers in which the mesogenic units are attached to a polymer backbone *via* a flexible spacer group. Alternatively in main-chain polymers these units are directly incorporated in the polymer chain (Fig. 1c and d). Conventional ‘end-on’ side-chain smectic LC polymers (Fig. 1a) have been extensively studied.⁶ In this situation the polymer backbone is approximately confined (or at least concentrated) to the two-dimensional (2-D) space in between the smectic layers,⁷ leading to a strongly oblate backbone conformation.⁸ Due to this freedom in 2-D, polymer conformations and defects are not expected to interact directly with the smectic layer order. This can be contrasted with the less studied ‘side-on’ side-chain smectic polymers^{6,9} (Fig. 1b), in which the polymer chains are on average oriented parallel to the smectic layer normal, thus connecting the layers. For these side-on smectic polymers short

spacer groups lead to considerable stretching of the polymer: ‘jacketed nematic structure’^{10a} with a strongly prolate polymer conformation.⁸ More recently also jacketed smectic and columnar structures have been reported.^{10b} Side-on LC polymers with longer spacer groups in principle allow also for smectic phases but very few cases have been reported.¹¹ The structural organization has been investigated only for one case so far.^{11c}

The signature of quasi-long-range order is provided by X-ray scattering. Instead of δ -function type Bragg peaks with diffuse tails characteristic of 3-D crystal periodicity, Caillé line shapes with an asymptotic power-law form $q^{-2+n^2\eta}$ are observed.^{4,5,12} Here n represents the harmonic number of the quasi-Bragg peak. The scaling of the exponent $\eta_n = n^2\eta$ as n^2 provides the most conclusive experimental evidence of quasi-long-range order. During the last decade the order in smectic systems has been shown to be sensitive to the effect of a random external field.

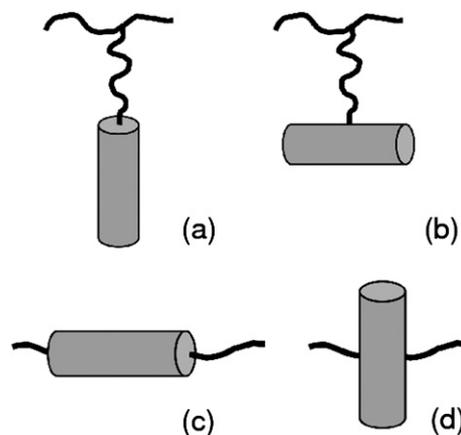


Fig. 1 Schematic representation of an LC polymer unit with the mesogens attached as side chains end-on (a) or side-on (b), and incorporated in the main-chain end-on (c) or side-on (d).

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Clark and co-workers¹³ found that when monomeric smectic systems are confined to aerogels, the random field imposed by the confinement reduces the smectic layer correlations to short-range. An alternative way to influence the order is by weakly crosslinking a smectic LC polymer into an elastomer. In that case the macroscopic rubber elasticity of the network interacts with the smectic LC order.¹⁴ This gives rise to a rich behavior that has been well studied for smectic end-on side-chain elastomers, both theoretically and experimentally. First crosslinks suppress long-wavelength fluctuations leading to the possibility of true long-range order.^{15,16} Second crosslinks preferentially reduce the smectic density around their position, giving rise to a random field of defects that can destroy the smectic order.^{17–20} Full understanding requires a series of elastomers with varying crosslink density, which have been synthesized and studied only for a single series of end-on side-chain smectic LC siloxanes.^{19,20} In that case with increasing crosslink concentration a transition to disorder is reflected in the X-ray line shape by a gradual change in the exponent of a stretched Gaussian from 1 (simple Gaussian describing finite-size domains) for low crosslink concentrations to 0.5 (Lorentzian describing extended short-range correlations) for 20% crosslinks.

In this paper we present the first extensive X-ray study of a smectic side-on side-chain elastomer and the related homopolymer. Recently Komp and Finkelmann reported for this particular elastomer that the smectic structure stays unaffected by mechanical deformation,²¹ in contrast with the usual behavior of extensive reorientation above a certain threshold. The uniformly oriented elastomer remains essentially transparent upon deformation. We find that the present mesogens with partly fluorinated end chains show locally ‘nanophase separation’ both in the smectic and in the isotropic phase. Upon crosslinking into an elastomer the smectic order is reduced to a limited range, similarly as reported earlier for smectic end-on main-chain elastomers.²² Finally upon stretching the elastomers, for the elastic part of the macroscopic stress–strain curve the smectic layer period increases parallel to the stress variation, while the smectic layer correlation decreases (increased peak width). This behavior saturates in the plastic regime.

2 Experimental

The side-on elastomer system used in this study is depicted in Fig. 2. A particular aspect of the present material is given by the partly fluorinated end groups attached to the mesogenic central core. Oriented elastomer samples (typically $20 \times 10 \text{ mm}^2$ and 0.5 mm thick) were obtained through application of a uniaxial stress in the swollen state of the weakly crosslinked elastomer gel.²³ After completion of the network the final sample is completely transparent. The phase behavior is given by the sequence:²¹ g 10 Sm-A 42 I, in which g stands for glass, Sm-A for smectic-A and I for isotropic while the temperatures are in °C. The entropy associated with the smectic–isotropic phase transition is rather small: 2.2 J g^{-1} and 0.9 J g^{-1} for the homopolymer and the elastomer, respectively.

Preliminary X-ray data were taken using monochromatic CuK_α radiation ($\lambda = 0.1542 \text{ nm}$) under various circumstances. Fig. 3a was obtained in Freiburg using a 2-D image plate detector system. Data on the (unoriented) homopolymer (Fig. 5)

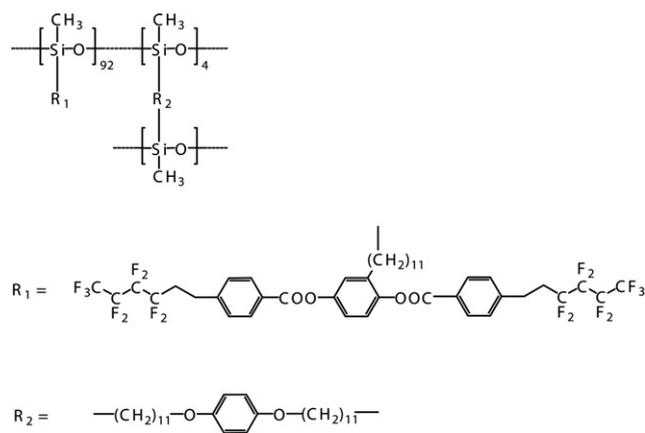


Fig. 2 Molecular structure of the smectic side-chain elastomer with 96% side-on group R_1 and 4% crosslinker R_2 .

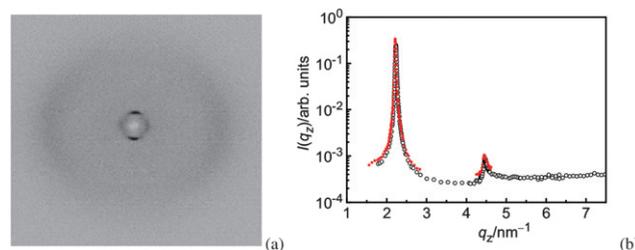


Fig. 3 (a) Two-dimensional X-ray picture of the elastomer with axially the smectic layer peaks. Note the additional diffuse ring at small angles with slight maxima in the equatorial direction. At wide angles along the equator the liquid in-plane structure can be seen. (b) Scan along one of the smectic peaks showing additional diffuse scattering at large q -values.

were obtained in Amsterdam with a rotating anode X-ray generator (Rigaku RA-H300) operating at 18 kW. By employing two parabolic multilayer mirrors (Bruker, Karlsruhe), a highly parallel beam (divergence about 25 mdeg) of monochromatic CuK_α radiation was obtained. The X-ray patterns were recorded with a Bruker Hi-Star area detector at a sample-to-detector distance of about 0.6 m. The 2-D scattering patterns were radially integrated, corrected for background, and subsequently displayed as 1-D plots.

Information on the layer correlations in the elastomer was obtained from high-resolution X-ray line shapes carried out at beamline W1 of HASYLAB (DESY, Hamburg, Germany) using 8 keV radiation corresponding to a wavelength $\lambda = 0.155 \text{ nm}$. The wave vector transfer is given by $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$, where \mathbf{k}_f and \mathbf{k}_i are the outgoing and incoming wave vector, 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 initially parallel to the smectic layer normal. Hence for a Sm-A phase quasi-Bragg peaks of harmonic number n were measured in reciprocal space along q_z at positions q_n , while the mosaic distribution was determined by transverse (rocking) curves varying q_x at different $q_z = q_n$. The instrumental resolution in the scattering plane was set by the two Si(111) monochromator crystals of the beamline and a double-reflection channel-cut Ge(220) analyzer crystal in a non-dispersive configuration. The resulting resolution function was close to

a Gaussian with $\Delta q_z = 0.004 \text{ nm}^{-1}$ (full-width-at-half-maximum, FWHM). The resolution function along q_x could be taken as a δ -function. Out of the scattering plane the resolution was set by slits to $\Delta q_y = 0.02 \text{ nm}^{-1}$. The incident intensity was about $10^{10} \text{ cts s}^{-1}$; the beam size was $0.5 \times 1 \text{ mm}^2$ ($V \times H$). Some additional data were obtained at beamline X10A of the National Synchrotron Light Source of Brookhaven National Laboratory (Upton, USA) under very similar experimental circumstances. These data are added in red in some of the figures. All data were normalized, resolution corrected and background subtracted as described elsewhere.²⁰ Stretching of the elastomer was accomplished as described in ref. 21, allowing for 30-60 min equilibration time.

3 Results

Fig. 3a shows a photographic X-ray overview of the elastomer with axially the smectic layer peaks. The corresponding layer period is 2.85 nm. In the equatorial direction we observe at wide angles the diffuse crescents corresponding to the Sm-A liquid in-plane structure. At small angles close to the smectic layer period a full diffuse ring is observed with weak maxima along the equator. A high-resolution scan along the smectic peaks (Fig. 3b) indicates a second-order harmonic and additional strong diffuse scattering. The latter scattering starts at the position of the second harmonic and stays approximately constant at larger q -values. Fig. 4 shows a linear scan of the diffuse scattering along the equatorial direction. The broad peak can be well fitted by a Lorentzian with a small correlation length $\xi \approx 2 \text{ nm}$. The X-ray results for an unoriented sample of the corresponding homopolymer (Fig. 5) give essentially the same smectic layer period as for the elastomer (see Table 1). Furthermore again strong diffuse scattering is visible at a somewhat lower q -value which survives in the isotropic phase.

Fig. 6a shows details of the first-order peak (FWHM = 0.035 nm^{-1}) of the uniformly oriented elastomer sample (mosaic distribution 12.5°). After correction for the scaled diffuse peak the result can be fitted well by a Lorentzian with a correlation length $\xi = 60 \text{ nm}$. Quantifying the second-order peak (Fig. 6b) is complicated because of the asymmetry due to the additional diffuse scattering at large q -values. Depending on the choice of the background, an FWHM of $0.08\text{--}0.1 \text{ nm}^{-1}$ and a Lorentzian fit giving $\xi \approx 20 \text{ nm}$ can be obtained (see Table 1). From Fig. 7b we can tentatively derive a slope at large q compatible with algebraic decay with an exponent $1 - n^2\eta$ with $\eta = 0.22$. The

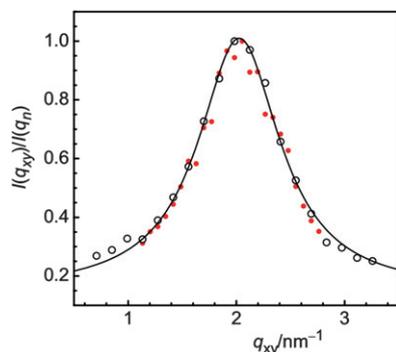


Fig. 4 Small-angle diffuse scattering peak along the smectic planes (equator). Full curve is fit to a Lorentzian.

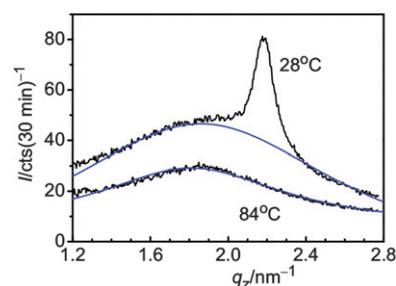


Fig. 5 X-Ray scattering of an unoriented homopolymer sample ($T_{S1} = 44^\circ\text{C}$). Note the diffuse scattering at a somewhat lower q -value than the smectic peak, which survives in the isotropic phase. The latter can be well fitted by a Lorentzian (blue lines) with a small correlation length of the order of $\xi = 1.1 \text{ nm}$ (room temperature).

Table 1 X-Ray results for the homopolymer and elastomer (room temperature). The domain size L is given by $2\pi/\text{FWHM}$. In the last column ξ refers to a Lorentzian fit

		q_0/nm^{-1}	d/nm	FWHM/ nm^{-1}	L/nm	ξ/nm
Homopolymer	Diffuse	1.86	3.4	1.8		1.1
	Smectic	2.18	2.9			
Elastomer	Diffuse	2.02	3.1	1.11		1.8
	1st order smectic	2.23	2.8	0.035	180	60
	2nd order smectic	4.45		~ 0.1	60	(20)

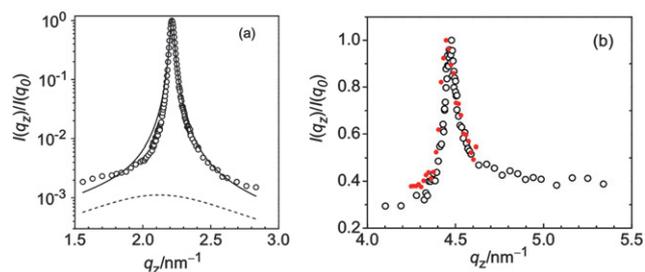


Fig. 6 First-order (a) and second-order (b) smectic layer peak of the elastomer. The dashed line is the scaled diffuse peak (see Fig. 3a and 4) as incorporated in the Lorentzian fit of the first-order peak. Fitting of the second-order peak is complicated because of the diffuse scattering at large q -values (compare Fig. 3b).

deviation from the standard exponent $2 - n^2\eta$ would indicate a random mosaic distribution.^{12,24} Though our samples had a broad mosaic distribution of 12.5° , fully random averaging should not apply. As we are also at the limit of the experimental q -range we believe this result should be considered with great caution.

Finally we come to samples stretched along the smectic layer normal. Fig. 8a indicates first a linear increase of the smectic layer period up to a strain value $\lambda \approx 1.08$ and subsequently essentially a plateau at larger strains (with a small relaxation to lower values). The first part corresponds to the elastic region in the stress-strain curve. The two regions are also distinguished by the variation of the FWHM of the first-order peak in dependence

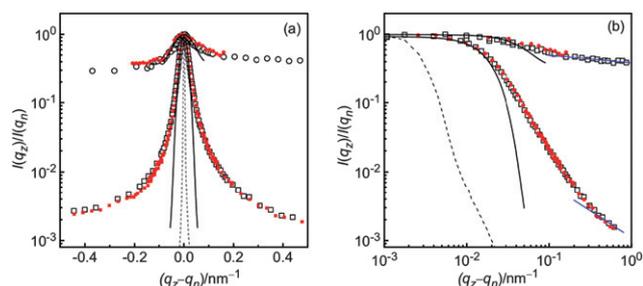


Fig. 7 First-order peak (squares) and second-order peak (circles) of the elastomer in semi-logarithmic (a) and double logarithmic plot (b, only left slope). The dashed line represents the direct beam. The full line corresponds to a Gaussian fixed to the experimental FWHM. The blue lines in (b) represent a possible fit to algebraic decay (see text).

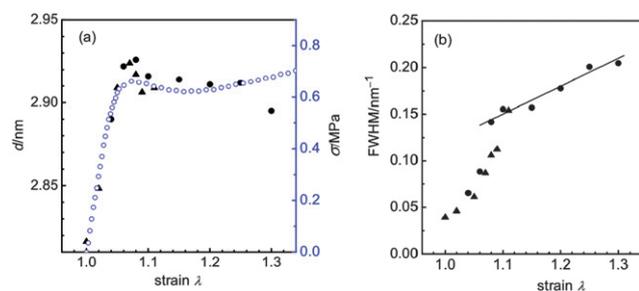


Fig. 8 (a) Variation of the smectic layer period (filled symbols, two samples as triangles and circles) compared to the stress–strain curve (blue). (b) Variation of the FWHM with the strain λ . The full line indicates that for the plastic deformation part the variation is linear.

of the strain (Fig. 8b), which increases strongly (leading to shorter correlations) in the first part of the stress–strain curve.

4 Discussion

The results as presented lead to three questions that will be discussed subsequently. The first is the nature of the diffuse scattering at low q -values that persists in all phases. Second we consider any effect of the random field of crosslinks on the smectic order. Finally we reflect on the influence of stretching on the smectic order.

Typical for the present system is strong diffuse scattering at q -values somewhat smaller than that of the smectic layers (see Table 1), both for the elastomer (Fig. 3a) and for the homopolymer (Fig. 5). From Fig. 5 we note that this scattering survives in the isotropic phase and thus it is not directly related to the smectic order. For the uniformly oriented elastomers this scattering is maximal along the equator (perpendicular to the maxima of the smectic layers). These maxima are rather weak, very broad and do not change significantly upon stretching. Therefore they represent poorly correlated structures that give rise to short-range periodicity mainly in the direction perpendicular to local long axis of the mesogens (correlation length $\xi \approx 1.8$ nm, see Table 1). We speculate that the cause of this scattering is associated with the fluorinated end groups of the mesogens. Fluorocarbons and hydrocarbons are well known to microphase separate.^{25,26} In the present situation some

‘nanosegregation’ between these two elements might occur, leading to local concentrations of fluorinated end chains. In fact it has been reported that substituting part of the hydrocarbon end groups of mesogen by fluorocarbons promotes smectic behavior, attributed to such a weak nanosegregation.²⁷ In the present situation the small correlation length associated with the diffuse X-ray scattering indicates clusters of 3–4 fluorinated end groups. In agreement with our observations, such an effect would not necessarily be restricted to the smectic phase. However, in the latter situation one would expect the local separation to be concentrated along the smectic planes (perpendicular to the mesogens and polymer backbones), in agreement with the increased scattering along the equator for the smectic elastomer sample.

According to Fig. 6a the first-order smectic layer peak is well described by a Lorentzian. However, the corresponding correlation length $\xi = 60$ nm is rather large, indicating correlation over about 18 smectic layers. Moreover, for true short-range order the FWHM of the second-order peak should be four times larger (quadratic increase with harmonic number). Experimentally the value is about three. This leaves as the most plausible explanation that the Lorentzian line shape is due to a broad exponential-like distribution of domain sizes in the sample, similar to as found for some main-chain smectic polymers.²² The average domain size along layer normal can be estimated from the Gaussian reproducing the central part of the X-ray peak (Table 1) as $L = 2\pi/\text{FWHM} \approx 180$ nm.²⁸ In this picture the broadening of the smectic peaks with increasing harmonic number n is due to non-uniform strain in the sample associated with multiple defects of the layer structure. Algebraic decay seems to be absent (Fig. 7b). That the present side-on system is structurally very similar to main-chain end-on smectic elastomers²² is not surprising. In both cases mesogenic units and polymer backbone are on average parallel to the layer normal with the backbone connecting adjacent layers. However, in the present situation this behavior is already found at a rather low crosslink concentration (4%) and does not change much going to 10%.²⁹

The present situation is rather different from end-on side-chain elastomers. In that case with increasing crosslink concentration a transition to disorder is reflected in the X-ray line shape by a gradual change from a simple Gaussian describing finite-size domains to a Lorentzian describing extended short-range correlations for 20% crosslinker.²⁰ In the present system liquid-like behavior is already obtained at much lower crosslink concentration (4%). We attribute this difference to the fact that for the present side-on situation the original homopolymer is probably already rather disordered due to the different preferred directions of the aliphatic spacers and the mesogenic groups. This strongly favors nematic behavior, but creates problems for a smectic organization. Neutron data indicate for a side-on smectic-C system that the polymer backbone is partly distributed in the middle of the mesogenic layers.³⁰ In addition the nanoseparation of the fluorinated end groups is expected to contribute to the disorder. These ideas are supported by the rather low enthalpy associated with the smectic–isotropic transition.

The elastic properties of the present elastomeric compound have been reported by Komp and Finkelmann.²¹ Most remarkably the sample remains transparent when stretching either parallel or perpendicular to the director. This can be contrasted

with the usual behavior reported so far, in which above a threshold the smectic elastomer domains break up into stripes leading macroscopically to a cloudy appearance. Upon stretching the present sample parallel to the director a linear regime exists up to a threshold strain $\lambda = 1.08$ with a modulus of $E_z = 14$ MPa. This deformation scales nearly affine with the macroscopic dimensions of the sample. Physically this means that the crosslinks—which create and define the rubbery solid—are strongly pinned to the smectic layers. The associated modulus is therefore not rubbery but rather the modulus B associated with compression/dilation of the smectic layers. For higher strain values $\lambda > 1.08$ the slope first decreases somewhat and finally stabilizes at a magnitude $E_z \approx 0.4$ MPa comparable to the value in the isotropic state, quite remarkably without any layer reorientation. The authors attribute the behavior in the latter regime to an increase of the number of smectic layers that can glide past each other due to the highly defective structure.²¹

The picture sketched above can be refined by the present X-ray measurements. First we find that the elastic part of the stress–strain curve up to about $\lambda = 1.08$ corresponds to a small but significant linear increase of the smectic layer period of about 3% (Fig. 8a). This clearly reflects dilation of individual smectic layers which can be described by deformation energy

$$\Delta F = \frac{1}{2}B\left(\frac{\partial u}{\partial z}\right)^2 = \frac{1}{2}B\varepsilon^2 = \frac{1}{2}B\left(\frac{\Delta d}{d}\right)^2$$

where u is a layer displacement and $\varepsilon = \lambda - 1$. From the inclination of the linear part of the stress–strain curve we derive $B \approx 14$ MPa, about 40 times larger than isotropic (rubber) moduli. This behavior is in line with the general theory of the elasticity of smectics.³¹ Variation of a smectic period is rare and to the best of our knowledge only one case has been reported. Stannarius *et al.*³² reported for a freely suspended UV-crosslinked smectic elastomer film (thickness hundreds of nm) a reversible decrease in the layer period of about 30% upon stretching perpendicular to the layer normal. The interpretation of these results is still a matter of debate and our situation is obviously very different. According to Fig. 8b in the elastic regime the width of the smectic peak increases more than linearly, reflecting enhanced internal strain upon stretching.

Upon increasing the strain a threshold of plastic deformation is reached (see Fig. 8) above which the elastomer still remains transparent. Following ref. 21 we assume that at this stage smectic layers move in, relieving the external strain without any need for reorientation. This is a rather unusual process and we assume that it is only possible because of the highly defective nature of the elastomer system. From Fig. 8b we see that the FWHM of the smectic scattering peak increases during the process from 0.035 nm^{-1} to 0.14 nm^{-1} at the threshold and subsequently to 0.20 nm^{-1} at the highest strain of $\lambda = 1.3$. This corresponds to a decrease of the average domain size from the original 180 nm down to about 45 nm at the threshold. At this level we have a transition to a highly disordered nematic-like state, signaled by the change in inclination of the curve in Fig. 8b. Finally at the highest reached strain $\lambda = 1.3$ the X-ray peak clearly should be interpreted as short-range order, with a correlation length $\xi \approx 10$ nm corresponding to about four smectic layers. Interestingly a discontinuity seems to appear in the

FWHM around $\lambda = 1.08$, indicating that the transition is not continuous. Independent of the precise nature of the transition, effectively short-range order is reached which allows easy readjustment of the number of smectic layers upon stretching. Such a process is consistent with a much smaller increase in the FWHM of the smectic peak above the threshold where the smectic layer period more or less stabilizes.

Finally we will try to account qualitatively in some detail for the unique behavior observed. First we note that in many metal and semiconductor crystals plastic behavior starts at certain stress threshold and proceeds *via* multiplication and movement of dislocations.³³ The present side-on smectic system is initially already very defective due to mutual disorientation of all three constituent fragments: polymer backbones, aliphatic spacers and stiff partly fluorinated mesogenic groups. The random field associated with crosslinks adds further disorder and creates certain constraints on elasticity. This all can be expected to lead to a high density of edge dislocations (dislocation loops). Such dislocations are a source of non-uniform strain in smectic elastomers which shows up in broadening of the smectic peak with harmonic number. We assume that this leads for the present system to a rather low threshold for dislocation multiplication. This would allow the dislocation density to start growing directly at the initial stage of stretching. The crosslinks are covalently linked to the polymer backbone which presents an obstacle for dislocation gliding. As a result the dislocations can move only locally, over dimensions not exceeding distances between crosslinks. This distinguishes smectic elastomers from low molecular mass smectics and smectic end-on polymers in which dislocations are rather mobile. Distant dislocations may interact and can form domain boundaries, thus minimizing the elastic strain.³⁴ This leads to domains of a finite size, which in turn give a broadening of the X-ray peak as observed (Fig. 8b). Multiplication of dislocations during stretching may trigger a process of consecutive diminishing domain sizes, resulting in a non-linear increase of the peak width with strain. At a certain value of the domain size local stresses lead to ‘melting’ of the layered structure, giving rise to a disordered nematic-like state with only short-range layer correlations. In this interpretation the final plastic regime of the stretching of the elastomer involves simply deformation of the network of crosslinks. We speculate that such a process could occur rather generally when smectic main-chain elastomers are stretched to reach a transparent uniformly oriented state.³⁵

5 Conclusions

We have reported on the (dis)order of a side-on smectic polymer and elastomer, in which the polymer chains are on average oriented parallel to the smectic layer normal. Strong diffuse scattering occurs in all phases and is attributed to local ‘nanosegregation’ between the fluorinated end groups of the mesogens and the hydrocarbon environment. Crosslinking the homopolymer leads to further disorder of the smectic layering. Upon stretching the elastomer we find that in the linear elastic regime the smectic layer period increases parallel to the stress–strain curve, which behavior saturates in the plastic regime. In addition an increase in the width of the X-ray peaks indicates decreasing average domain dimensions. In the plastic regime no distortion

of the smectic monodomain structure or layer rotation is seen which requires an increase of the number of smectic layers upon stretching. This unusual process can be understood by ‘melting’ of the layered structure at certain strain threshold, giving rise to disordered nematic-like state with short-range layer correlations. At the final stage of stretching true short-range order is reached with a correlation length of about four smectic layers. Accordance to this scenario in the plastic regime the elastomer stretching corresponds to deformation of the nematic polymer network. The unusual response to mechanical deformation of the present elastomer is attributed to its specific defective structure.

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