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Monodomain liquid crystalline networks: reorientation mechanism from uniform to stripe domains

EUGENE R. ZUBAREV*, SERGEI A. KUPTSOV, TATYANA I. YURANOVA†,
RAISSA V. TALROZE and HEINO FINKELMANN‡
A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
Leninsky pr. 29, Moscow 117912, Russia
†Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka, Noginsk distr. 142432, Russia
‡Institute of Macromolecular Chemistry, Freiburg University, Sonnenstr. 5,
Freiburg 79104, Germany

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Monodomain acrylate-based networks have been synthesized by a two-step cross-linking procedure using γ-irradiation. Strain-induced reorientation of the nematic director is studied by X-ray diffraction measurements. The geometrical shape (aspect ratio) of the monodomain films is found to affect drastically the dynamics and mechanics of the reorientation transition. Uniform continuous rotation of the director occurs in narrow samples with an aspect ratio $AR = 12$ when the external mechanical field is applied perpendicular to the initial orientation. Under the same conditions, films having a lower aspect ratio ($AR = 2.5$) demonstrate the formation of stripe domains with an alternating sense of director rotation (clockwise and counter-clockwise towards the stress axis). Deformation of a square film ($AR = 1$) generates stripe domains in the geometrical centre of the sample, whereas a uniform continuous rotation is observed in other regions of the film. Finally, a comparison of experimental data and theoretical predictions is presented and discussed.

1. Introduction

Monodomain nematic networks represent a unique class of liquid crystalline polymers that possess a macroscopically uniform alignment of the mesogenic groups when no external field is applied [1–3]. This is an unusual characteristic for conventional LC polymers and networks since the monodomain alignment of mesogenic groups is thermodynamically unstable [4]. Typically, these materials spontaneously form a polydomain structure [5–11]. However, by applying an external mechanical field the macroscopic uniform orientation can be induced. This external field can be converted into an 'internal' mechanical field by incorporation of additional covalent cross-links that lock in place the extended conformation of the main chains. Due to a strong coupling between the backbone conformation and the alignment of the mesogenic side groups, these covalent cross-links prevent the restoration of the polydomain structure.

There is a great fundamental interest in monodomain LC networks due to their unusual properties which include memory effects [2], spontaneous macroscopic shape changes and shifts in phase transformations [1], which were initially predicted by theory [12, 13]. More importantly, a unique reorientation behaviour has recently been observed in these materials. For example, when stress is applied perpendicular to the original director (direction of average mesogen alignment), a discontinuous reorientation transition was reported by Mitchell *et al.* [14] for acrylate-based monodomain networks. In contrast, under similar conditions, polysiloxane LC elastomers form a periodic array of stripe domains parallel to the extensional stress [15, 16]. These stripes have a fairly regular width of several microns, and the rotation of the director occurs in opposite directions towards the axis of external stress from one stripe to another in an alternating fashion. Interestingly, both experiments were eventually described and explained by theory in spite of their contradicting results [17–23]. However, it still remains unclear which particular characteristic of the monodomain network is responsible for each of the two reorientation mechanisms. It has been proposed that such a pronounced difference is related to the network anisotropy [16] which is significantly higher for polysiloxane systems than for acrylate networks.

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*Author for correspondence. Present address: Beckman Institute for Advanced Science and Technology, University of Illinois, 405 North Mathews Ave., Urbana, IL 61801 USA; e-mail: zoubarev@staff.uiuc.edu

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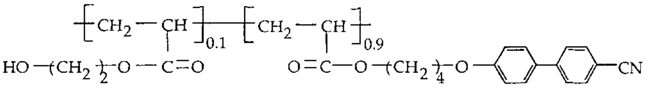
Here we report on the observation of both reorientation mechanisms in acrylate monodomain networks that were prepared by consecutive chemical and γ-induced cross-linking of a random copolymer having the following structure:



The main objective of this work was to investigate the reorientation transition in these systems and to find conditions that would allow one to regulate and control the mechanism of director rotation.

2. Results and discussion

The synthesis of monodomain networks generally involves two major steps [1–3]. First, the linear LC polymer or polydomain network is exposed to an external field that causes a uniform orientation of the mesogenic groups. The second stage is the cross-linking reaction that proceeds in the presence of an external field. In this work we explored a different pathway to monodomain networks using γ-irradiation, figure 1 (*a*). During the first step, the polydomain network prepared by chemical cross-linking is subject to uniaxial deformation at temperatures above T_g (glass transition temperature). The system is then cooled to room temperature (far below T_g) which freezes-in the strain-induced orientation. In the second stage the 'frozen' monodomain films are exposed to γ-rays that introduce covalent cross-links [9, 10, 24–26] and fix the original orientation. The resultant material is then heated above T_g. After relaxation of the residual stress, the film possesses macroscopically uniform alignment of the mesogenic groups at temperatures well above the glass transition. The monodomain structure is maintained in the absence of the external field. Figure 1 (*b*) shows the X-ray diffraction pattern of the free-standing film at 100°C. The pattern clearly indicates a monodomain structure and the orientation of mesogenic groups along the axis of the initial stress. The original direction of orientation, and the order parameter *S*, reversibly restore after the isotropic-to-nematic phase transition.

This approach has a distinct advantage compared with those described previously [1, 2], since it provides a unique opportunity to perform a multi-step fixation of any alignment of the mesogenic units. For example, if a monodomain film is subsequently exposed to an external field so that the direction of orientation changes or becomes non-uniform throughout the film, the second γ-irradiation process can fix it again and so on. Thus, this method appears to be a powerful tool for the preparation of LC networks with a variable and easily controlled distribution of local director orientations.

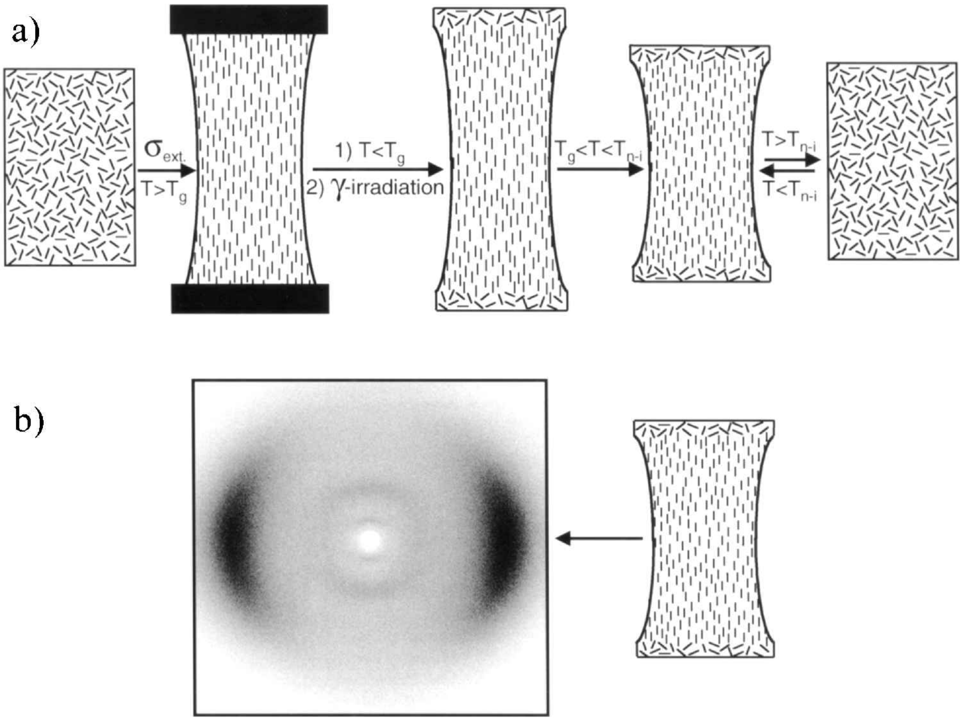


Figure 1. (*a*) Schematic representation of the synthetic route to monodomain films by the γ-irradiation approach; black rods indicate the local director orientation. (*b*) Wide angle X-ray pattern collected from the free-standing monodomain film at 100°C.

An external mechanical field applied perpendicular to the initial director of the monodomain network causes a certain finite degree of reorientation, which depends on the deformation λ. Therefore, monodomain networks represent the only class of LC materials that allow one to follow and quantitatively analyse the reorientation process using optical microscopy and X-ray diffraction measurements. Here we discuss the reorientation phenomena observed in samples having different geometrical shapes (aspect ratio AR of the film) as follows: square samples ($AR=1$), narrow strips ($AR=12$) and films with an intermediate aspect ratio ($AR=2.5$).

2.1. *Reorientation in square samples*

When the external stress is applied perpendicular to the original director axis of an optically transparent square film, a circular scattering spot emerges in the centre of the sample. Further deformation ($\lambda > 1.1$) results in splitting of the opaque circle into two equal spots which then migrate along the stress axis in opposite directions from the centre of the film to the clamps. These spots move as long as the deformation proceeds and at $\lambda = 1.3$ they reach the clamped edges. Interestingly, the spots migrate as a whole without any noticeable changes in their shape or size. The stretched film ($\lambda = 1.3$) was subsequently cooled to room temperature while held in clamps that allowed us to freeze-in the current distribution of the local director and investigate it within the glassy film. Figure 2 (*a*) shows the stretched film, which was scanned by the X-ray beam in two perpendicular directions from the point A to E (along the clamp) and from the point C to C_3 (along the deformation axis). X-ray diffraction patterns collected from the points mentioned above are represented in figure 2 (*b*). Two sharp reflections in the X-ray patterns obtained from transparent regions A and E indicate monodomain alignment of the mesogenic groups. In these areas the director rotation angle α (angle between the current and initial director) is about $+45°$ and $-45°$, respectively. In addition, during the entire deformation process, these regions remain optically transparent. Therefore, a uniform continuous rotation of the director occurs in a clockwise (point A) and counter-clockwise (point E) manner in these regions of the film, without distortion of the monodomain structure.

Diffraction patterns collected from points B and D show four reflections, but the intensity of one pair of reflections is significantly lower than that of the other. Furthermore, the X-ray pattern from the central point C shows four maxima of equal intensities. Thus, in the opaque spot, the structure appears to have a polydomain texture, where the director rotates clockwise towards the stress axis in one half of the domains and counter-clockwise in the other. Since the diameter of the X-ray beam is 800 μm, the width of the domains must be significantly smaller. In order to determine the structure of the polydomain region, the film was studied by polarizing optical microscopy. Using crossed polarizers, the stretched film displays light and dark regions which indicate non-uniform orientation of the mesogenic groups, figure 3 (*a*). In addition, figure 3 (*b*) reveals that the opaque spot is composed of stripes which are oriented preferentially along the deformation axis and have a regular width of about 15 μm. Rotation of the sample between crossed polarizers results in an alternating change in the colour of the stripes. Every light stripe turns into a dark one and *vice versa*. Moreover, at a given angle between the polarizer and the film axis, the

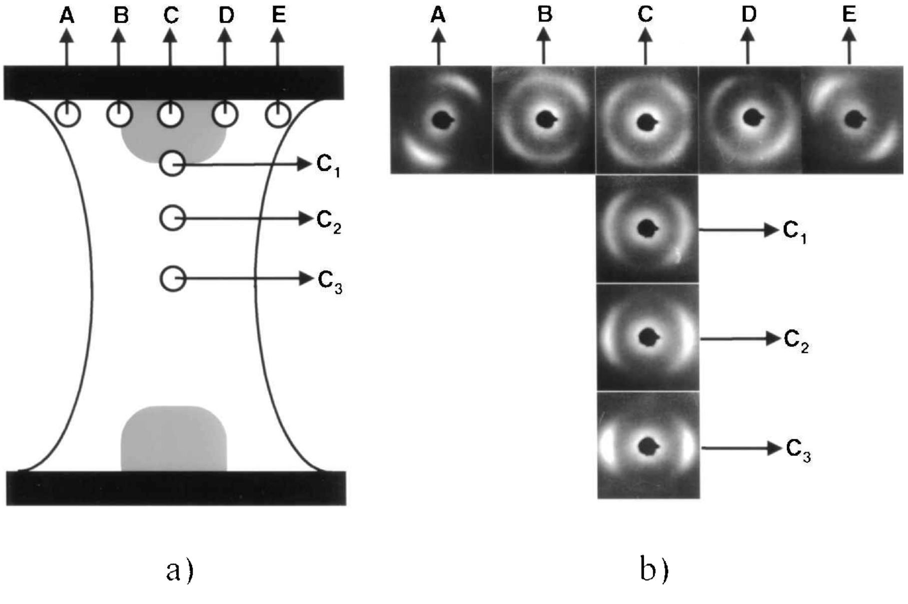


Figure 2. (*a*) Schematic representation of the film (initially $AR=1$) after deformation $\lambda = 1.3$; white circles indicate points where X-ray patterns were collected. (*b*) X-ray patterns collected from different points of the film ($T = 20°C$).

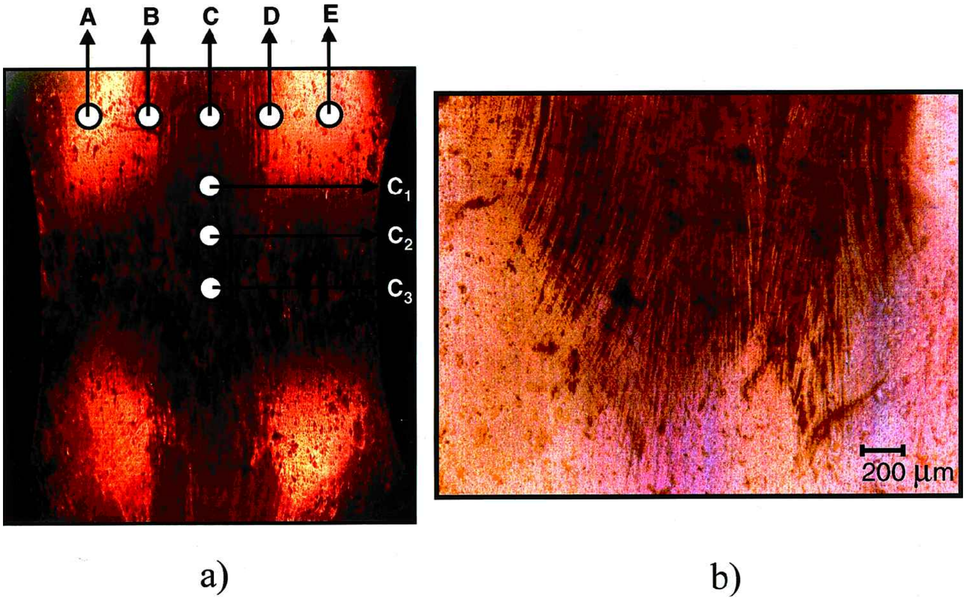


Figure 3. (*a*) Photograph of the stretched film (initial $AR = 1$) after deformation $\lambda = 1.3$ (crossed polarizers); the stress axis is parallel to polarizer. (*b*) Micrograph of the stripe domain region.

intensity of light within each domain appears to be constant along the entire stripe. These data suggest that the mesogenic units are uniformly aligned within each stripe domain and rotate continuously when an external stress is applied. The director rotation angle changes from one stripe to another in an alternating and nearly discontinuous manner from $-\alpha$ to $+\alpha$.

X-ray patterns collected from point C to C_3 reveal that reorientation of the director is complete in the geometrical centre of the film (point C_3), whereas near the opaque spot (point C_1), the director rotation angle α is still considerably smaller than 90°. However, all these regions are optically transparent which is indicative of a monodomain structure. Based on these data, we are led to the conclusion that the sample in question has a non-uniform director distribution and that the local orientation changes in a very particular way, represented in figure 5. In essence, two different reorientation mechanisms are seen within the same sample: via stripe domains in opaque spots, and uniform rotation in the other regions of the film. This can be related to the inhomogeneity of the mechanical field generated in the square sample during the deformation. The width of the film decreases in the centre at a much higher rate than it does in the clamp-constrained regions. The local stress in regions 1 and 3 (figure 4) deviates from the global deformation axis so that the angle between the external field and the initial director is no longer 90°. Due to their anisometric shape, the mesogenic units follow the shortest low energy pathway towards the local stress axis, and therefore rotate all in one direction: either clockwise (region 1) or counter-clockwise (region 3).

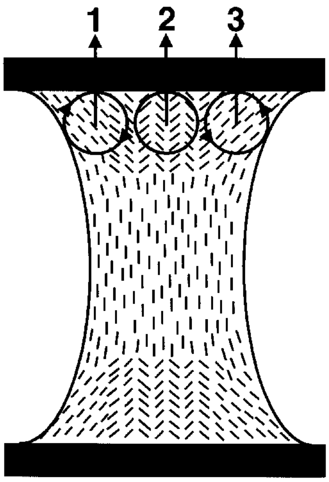


Figure 4. Schematic representation of the film (initially $AR = 1$) after deformation $\lambda = 1.3$; black rods indicate the local director orientation.

However, in the middle region 2, the local mechanical field should pass through a position strictly perpendicular to the original director. As a result, this region decays into stripes and a rotation in both directions is thus of equal probability. Interestingly, an angle close to 90° between the external stress and the initial director is a necessary condition for the formation of stripe domains according to theory [20–23]. Nonetheless, only the formation of stripes was observed in polysiloxane liquid single crystal elastomers (LSCEs), whereas Mitchell and co-workers reported on a uniform rotation of the director when the external field is applied perpendicular in the case of acrylate-based monodomain networks [14].

More importantly, the question arises as to why the opaque regions containing stripe domains are initially formed in the centre of the film and then migrate as a whole to the clamped edges. At this point we can propose the following explanation. According to both experimental observation and theoretical predictions, the reorientation process does not occur until a certain threshold strain is exceeded. Due to the square shape of the sample, the actual strain at a given point depends on the location of this point within the film. The highest degree of deformation λ should correspond to the geometrical centre of the sample where the deviation of local stress is minimal. Thus, the threshold strain λ_{th} will be reached at this point first. Consequently, the reorientation process and the formation of stripes starts in this region, while the actual strain in the upper and lower regions is still less than λ_{th} (figure 5). That is why the opaque spot has a finite size. Then, as the deformation proceeds, the reorientation in the centre becomes complete and stripes disappear at this point. Simultaneously, the reorientation begins in regions that are close to the clamps. In other words, each of these two opaque spots represents the area between the point where orientation is already complete (closer to the centre) and the point where the rotation of the director has not yet begun (closer to the clamp). The combination of all these events results in virtual motion of 'migration' of the opaque spots. In essence, this interesting reorientation behaviour reflects the gradient of strain generated within the film due to inhomogeneities of the mechanical field. Therefore, regulation of the mechanical stresses within the sample may provide a unique opportunity to control the reorientation process and separate the observed mechanisms. The easiest way to achieve this goal would be variation in geometrical shape of the sample, in particular, changes in aspect ratio (length/width) of the film, since this characteristic significantly affects the extent of the mechanical field homogeneity.

2.2. *Reorientation in narrow strip samples*

The deformation of a narrow monodomain film ($AR = 12$) reveals that the external field applied perpendicular to the director axis results in no rotation of mesogenic units until a certain value of strain ($\lambda = 1.09$) is exceeded. After this point the director starts to rotate and the transition is complete at $\lambda = 1.4$. However, the reorientation proceeds only in one direction (counterclockwise) via uniform continuous rotation and no stripe domains were observed (figure 6). Calculation of the global order parameter S based on an azimuthal distribution of X-ray diffraction intensity indicates no changes in S value (~ 0.5) within the entire range of deformation

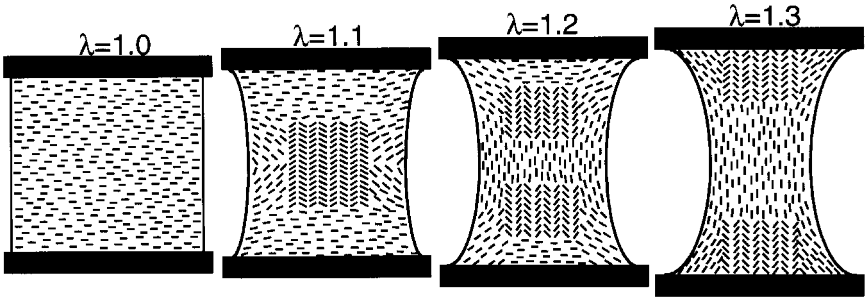


Figure 5. Strain-induced reorientation in a square monodomain film; black rods indicate the local director orientation.

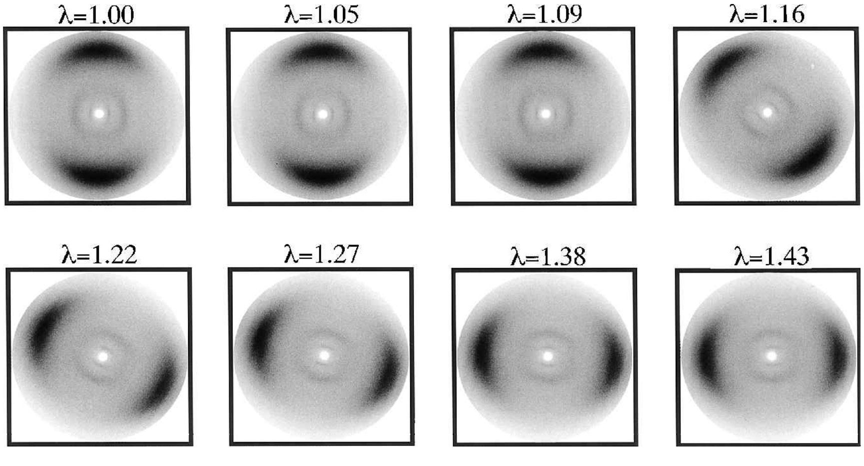


Figure 6. X-ray diffraction patterns collected from the centre of the monodomain film (initially $AR = 12$) at different strains. The external mechanical field is applied perpendicular to the original direction, $T = 90°\mathrm{C}$.

corresponding to director rotation from 0° to 90°. Interestingly, opposite results were previously reported by Mitchell and co-workers [14] who observed a 30% drop in the order parameter of acrylate-based monodomain networks at $\lambda = 1.1$, followed by a continuous increase in S up to its intial value. Although the actual structure of the mesogenic species in our system is different, the polymer backbone is the same. Therefore, the question arises whether the coupling between the nematic field and the polymer matrix can be solely regulated via the mesogenic group structure. Further investigation of this phenomenon is required and will be reported elsewhere.

Scanning the sample by an X-ray beam showed that the rotation angle at a given strain λ is nearly constant within the entire film. This suggests that the uniform rotation might be caused by a slight deviation from 90° of the angle θ between the deformation axis and the initial director. In order to verify this hypothesis, the original director orientation was restored by annealing the sample in the isotropic state after the external field was removed. The position of the film was then changed by 2° clockwise with respect to the clamps. Such a slight change resulted in a uniform rotation in the opposite direction starting from the same threshold strain $\lambda_{th} = 1.09$. This experiment was reproduced several times and the uniform rotation in one direction only (either clockwise or counter-clockwise) was observed. Stripe domains did not form even in regions near the clamps. Hence, the homogeneity of the mechanical field appears to be a necessary but not sufficient condition for the formation of stripe domains. An additional question arises as to what prevents this mechanism, and why the uniform rotation of mesogenic species is preferred in the narrow strip sample. It seems unlikely that the reason is related to deviation from the right angle between the stress axis and the initial director, since uniform rotation changes from counter-clockwise to clockwise occur within a very small range of θ values ($\pm$ 1°). However, the deformation of the narrow strip is always followed by a deviation of the sample long axis from the stress axis. In other words, there is a certain degree of shear deformation. This problem is particularly difficult to avoid in the case of narrow samples in spite of the presence of clamps, which should completely prevent global shear. At this point the phenomenon in question remains an unsolved puzzle that does not fit any hypothesis or currently existing theory [17–23]. Nevertheless, we can conclude that the stripe domains mechanism can only occur when there is no deviation of the angle θ from 90° and no global shear deformation. Therefore, further investigation of the reorientation process in samples having intermediate aspect ratios ($1 < AR < 12$) is required.

2.3. *Reorientation in samples with an intermediate aspect ratio ($AR = 2.5$)*

Figure 7 shows X-ray patterns collected from a film with an initial AR of 2.5 at different strains, after the external field was applied normal to the original director. The reorientation process begins only after the threshold

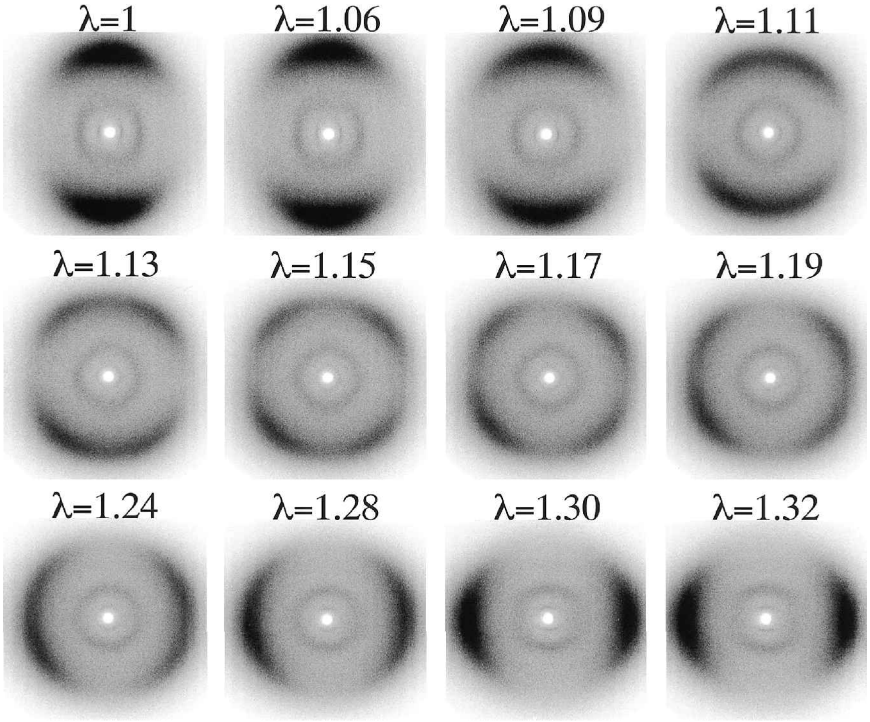


Figure 7. X-ray diffraction patterns collected from the centre of the monodomain film (initially $AR = 2.5$) at different strains. The external mechanical field is applied perpendicular to the original direction, T = 90°C.

strain $\lambda_{th} = 1.09$ is exceeded. The observed value matches that found in the previous experiment for narrow strip samples. Nonetheless, the actual mechanism is different and proceeds via splitting of the initial pair of reflections on the meridian into four distinct reflections which eventually merge into a pair of equatorial reflections. More importantly, the X-ray patterns collected from various regions of the film appear to be the same and show no difference in reorientation behaviour at a given strain. Additional confirmation was obtained by optical microscopy that revealed the formation of stripe domains within the entire film (figure 8).

Figure 9 shows azimuthal profiles of X-ray diffraction intensity obtained at different deformations of the film. Curves corresponding to strains within the range $1 < \lambda < 1.09$ coincide and no differences were detected. However, a sharp drop in the intensity occurs when the strain becomes greater than 1.09 and the initial peak splits into two maxima of slightly different intensities. This is an interesting observation, which most likely means that the number of mesogenic groups rotating clockwise is not equal to that rotating in the opposite direction. Nevertheless, it should be pointed out that the X-ray beam covers only a limited area of the sample and the width of the stripes varies in a fairly broad range from 10 to 20 μm. Thus, local inhomogeneities in stripe width may be responsible for the observed difference in the intensities of the two reflections which emerge after splitting of the initial peak. There is also a possibility of a slight deviation of the angle θ from 90°. According to theoretical predictions [20], this deviation should result in formation of stripes with different

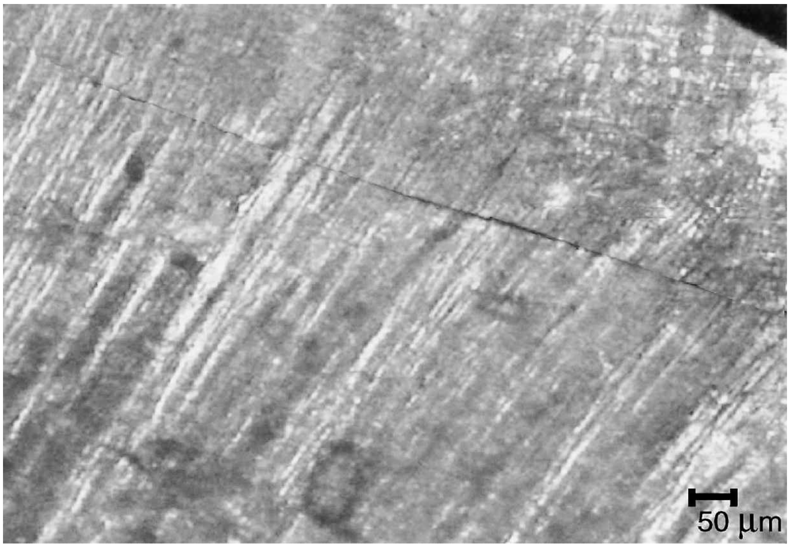


Figure 8. Polarized micrograph of the stripe domains at $\lambda = 1.5$ in a film with initial $AR = 2.5$; the angle between the stress axis and polarizer is 45°.

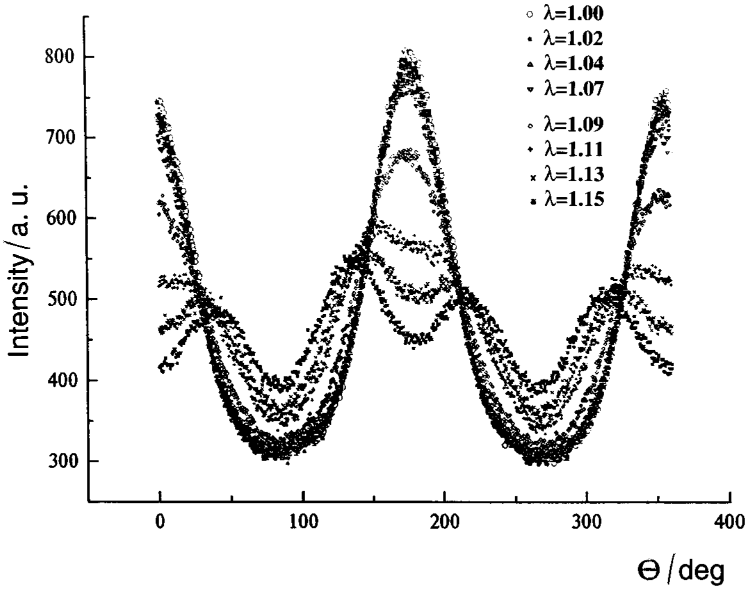


Figure 9. Azimuthal profiles of X-ray diffraction intensity obtained from the centre of the film (initially $AR = 2.5$) at different strains indicated on the plot.

width, when one half of them is thicker and contains a greater number of mesogenic units than the other set of thinner stripes. Based on these data, we can conclude that reorientation in monodomain films with an intermediate aspect ratio proceeds exclusively via the stripe domain mechanism and is characterized by a threshold strain $\lambda_{\text{th}} = 1.09$. The interval of deformations where the rotation of the director occurs is very narrow and lies within the range $1.09 < \lambda < 1.32$.

At this point it is particularly interesting to compare the networks in question and the polysiloxane-based LSCEs described earlier [15]. First, the threshold strain observed in our experiments is very close to that reported by Kundler *et al.* [16, 21] for polysiloxane systems ($\lambda_{\text{th}} = 1.07$). However, the 'window' of strains where the reorientation occurs was found to be significantly broader and typically covers the range of $1.07 < \lambda < 1.7$. These data are in good qualitative agreement with Warner–Terentjev theory [20], which suggests the director rotation should proceed within the interval of $\lambda_{\text{th}} < \lambda < \lambda_{\text{th}} \times \sqrt{r}$, where $r \equiv \langle l_{\|}/l_{\perp} \rangle$ is the mean ratio of chain dimensions parallel and perpendicular to the local director. Therefore, the observed difference in reorientation strain interval of the two systems is solely related to the difference in their intrinsic network anisotropy r. The latter can be determined experimentally either by small angle neutron scattering measurements (SANS) [27, 28] or via thermal expansion measurements of monodomain films, so that the average anisotropy [29]:

$$\langle r \rangle \approx (L/L_0)^3 \qquad (1)$$

where L is the length of sample at a given temperature and L_0 is the length in the isotropic state, which is almost constant and virtually independent of temperature.

The ratio L/L_0 reveals spontaneous macroscopic elongation of a monodomain film at the nematic-to-isotropic phase transition. Based on thermal expansion experiments for polysiloxane systems, the parameter $\langle r \rangle$ was found to be up to 3.4 depending on the temperature and cross-link density of the elastomer [16]. The temperature dependence of L/L_0 obtained for our system is shown in figure 10. Within the entire range of the liquid crystalline phase, spontaneous elongation remains fairly low and reaches the highest value of 1.2 in the vicinity of the glass transition temperature ($T_g = 62$°C). Hence, in accordance with equation (1) the intrinsic anisotropy $\langle r \rangle$ remains less than $(1.2)^3 = 1.73$. In fact, polyacrylate-based networks generally exhibit very low anisotropy and the value of the parameter $\langle r \rangle$ obtained is also in good agreement with SANS experiments performed for a linear LC homopolymer containing the same mesogenic groups [30]. It is believed that the significantly lower anisotropy of polyacrylate systems results from the higher rigidity of their polymer chain in comparison with that of polysiloxane elastomers. Alternatively, the presence of highly polar cyano groups in our system favours formation of smectic-like clusters, which also reduce the mean anisotropy of the network. Moreover, it has been recently proposed that even cross-link density can affect parameter $\langle r \rangle$ [21].

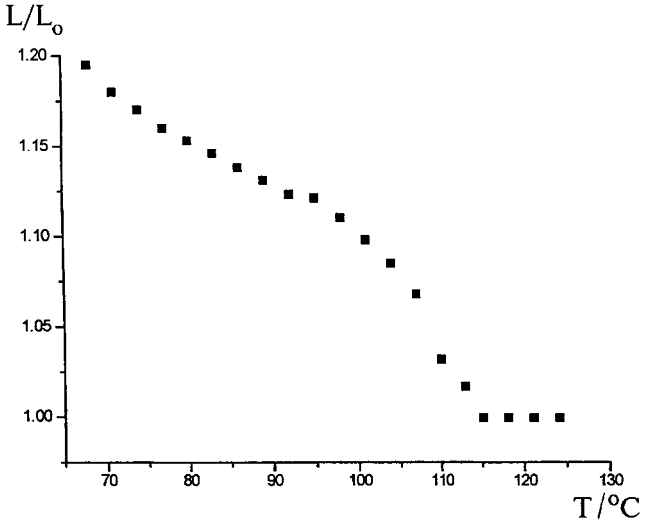


Figure 10. Spontaneous macroscopic elongation L/L_0 of the monodomain film ($AR = 2.5$) as a function of temperature.

The reorientation experiment under consideration was carried out at 90°C. The spontaneous macroscopic elongation L/L_0 corresponding to this temperature is 1.13 (see figure 10). Thus, according to equation (1) the intrinsic anisotropy $\langle r \rangle$ is equal to 1.44, and therefore the theoretical interval of reorientation covers the range from 1.09 to $1.09 \times \sqrt{1.44} = 1.31$, which is in excellent agreement with the experimental data. More importantly, azimuthal profiles of X-ray diffraction intensities obtained for different strains allow us to calculate the director rotation angle α and plot it as a function of strain λ. On the other hand, Warner theory [20] describes the dependence of $\alpha(\lambda)$ as follows:

$$\alpha = \pm \arcsin\left[\frac{\langle r \rangle}{\langle r \rangle - 1}\left(1 - \frac{\lambda_{\text{th}}^2}{\lambda^2}\right)\right]^{1/2} \qquad (2)$$

where $\langle r \rangle$ is the mean anisotropy at a given temperature and λ_{th} is the threshold strain. In essence, the theory operates with only two parameters, $\langle r \rangle$ and λ_{th}, which can be determined experimentally. Therefore, we can compare the theoretical curve plotted for $\langle r \rangle = 1.44$ and $\lambda_{\text{th}} = 1.09$ with experimental data based on the calculation of α from azimuthal X-ray diffraction profiles (figure 11). Such a surprising coincidence reveals the universality of the Warner–Terentjev model, which perfectly describes not only this particular system, but also polysiloxane LC elastomers [21]. Moreover, it suggests

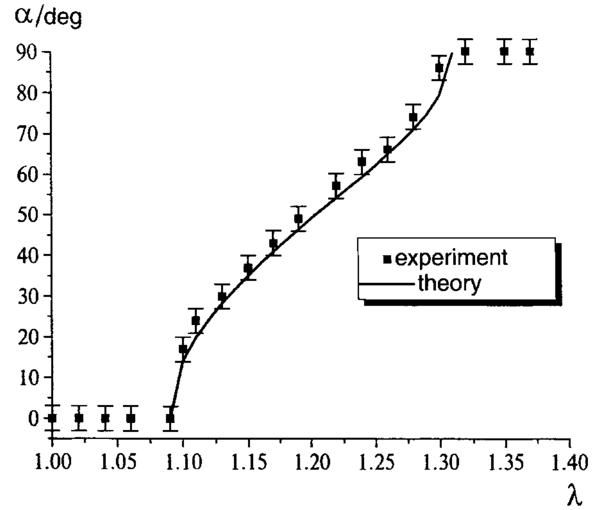


Figure 11. Director rotation angle α as a function of strain λ. The plot shows experimental points obtained from azimuthal X-ray profiles and the theoretical curve from equation (2) plotted for $\langle r \rangle = 1.44$ and $\lambda_{th} = 1.09$. The experimental error in the angle determination is ± 3°.

that the reorientation transition in monodomain networks is basically regulated by coupling between the elastic matrix and the nematic field, rather than chemical structure of the mesogens or the polymer backbone.

3. Conclusion

We have explored a new synthetic pathway to monodomain LC networks using γ-irradiation. This versatile approach provided insight into regularities which control the reorientation behaviour of these rare materials. Two different mechanisms of director reorientation were observed for the first time in a polyacrylate-based system: via uniform rotation, and stripe domains. This suggests that the actual chemical structure of the mesogenic groups or the polymer backbone is not the only characteristic responsible for one or the other reorientation mechanism. The homogeneity of the external mechanical field and the global shear deformation can play a key role in the reorientation process. Variation in geometrical shape of the polyacrylate monodomain films gives a unique opportunity either to separate different mechanisms or to observe them both simultaneously. Good qualitative agreement of the experimental data with theoretical predictions indicates the universality of director reorientation behaviour in a wide range of nematic elastomers.

Our findings can serve as a basis for further investigation of LC networks, particularly chiral systems where the coupling between the LC director orientation and the external field may allow the observation of specific effects like piezoelectricity and non-linear optical susceptibility.

4. Experimental

4.1. *Characterization of the linear copolymer*

The mesogenic monomer and linear copolymer were synthesized as described in [24]. The molecular mass characteristics of the copolymer were determined by gel-permeation chromatography (GPC) using a Waters liquid-phase chromatograph equipped with an R401 differential refractometer ($\bar{M}_w = 140\,000$, $\bar{M}_w/\bar{M}_n = 3.02$). The glass transition temperature T_g and nematic to isotropic transition temperature of the copolymer were measured by differential scanning calorimetry (DSC) to be 62 and 112°C, respectively. The composition was determined by UV spectroscopy to be $x = 0.9$ and $y = 0.1$ (see the structure).

4.2. *Synthesis of polydomain networks*

Polydomain chemically cross-linked networks were obtained by casting a 30% solution of the linear copolymer in 1,2-dichloroethane/acetonitrile, 4:1 by volume, containing 2.4 mol % of the cross-linking agent (4,4′-methylenediphenyl diisocyanate) onto a polyamide substrate. The cross-linking reaction proceeded at room temperature and was monitored by the disappearance of the melting peak of the cross-linking agent (DSC) and by swelling experiments using the 1,2-dichloroethane/acetonitrile mixture. Under conditions of complete consumption of the mol-fraction of cross-linking agent, the average molecular mass of the polymer chain per cross-link was calculated from the stoichiometric ratio indicated below:

$$\bar{M}_c = m_{cop}/2\nu_c$$

where m_{cop} is the mass of the copolymer and ν_c is the number of moles of the cross-linking agent. The cross-link density indicating the average number of cross-links per macromolecular was estimated as $\bar{M}_w/\bar{M}_c = 23.2$. After completion of the reaction and successive annealing at 120°C, the polydomain film was peeled from the support. The thickness of the films was in the range 250–300 ± 5 μm.

4.3. *Preparation of monodomain networks*

The polydomain chemically cross-linked samples were stretched at 90°C up to $\lambda = 1.5$ and then cooled to room temperature (40°C below T_g) while secured in the clamps. The films possessing the ‘frozen’ monodomain structure were then placed into ampoules which were evacuated for 1 h at room temperature at 0.133 Pa. The ampoules were sealed under vacuum and γ-irradiated with a 2 MGy dose at 20°C. The dose rate was 0.048 MGy h^{-1} (γ-radiation from a ^{60}Co source). The gel dose was determined by the standard technique from the gel fraction versus dose plots. To characterize the cross-link density in the networks formed under the action of γ-radiation, we used the parameter $\bar{M}_c$ calculated according to the following expression:

$$\bar{M}_c = \bar{M}_w (R_g/R)$$

where R_g and R are the gel and the exposure doses, respectively. The sample was then heated to 100°C and after complete relaxation of residual stresses, transparent films were obtained, possessing uniform alignment of the mesogenic groups in the direction of the initial deformation without any external field. The samples for reorientation experiments were cut perpendicular to the director axis to form samples of the following sizes: $5 \times 5\,\mathrm{mm}^2$ ($AR = 1$), $3 \times 36\,\mathrm{mm}^2$ ($AR = 12$) and $7 \times 17.5\,\mathrm{mm}^2$ ($AR = 2.5$).

4.4. *Characterization*

The DSC measurements were carried out using a Mettler TA-4000 at heating rates of 15, 10, 5, and $2\,\mathrm{K\,min}^{-1}$. The nematic to isotropic transition temperature was determined by extrapolating to a $0\,\mathrm{K\,min}^{-1}$ heating rate. X-ray scattering measurements were performed using a Cu X-ray tube (wavelength = 0.154 nm) coupled with a graphite monochromator and a 0.8 mm collimator. The incident beam was normal to the surface of the films. The scattered X-ray intensity was detected by the Image Plate system. The order parameter was calculated by an azimuthal scan applied to the nematic intermesogen-reflections [31].

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