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Citation	PHYSICAL REVIEW E (2009), 79(5)
Issue Date	2009-05
URL	http://hdl.handle.net/2433/109857
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Type	Journal Article
Textversion	publisher

Electrically driven director-rotation of swollen nematic elastomers as revealed by polarized Fourier transform infrared spectroscopy

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(Received 29 January 2009; published 8 May 2009)

We have investigated the director reorientation behavior of unconstrained nematic gels (nematic elastomer swollen by low molecular mass liquid crystals) under electric fields by means of polarized Fourier transform infrared (FTIR) spectroscopy. The polarized FTIR reveals that the director rotates about the (y) axis normal to the original director (x axis) and field directions (z axis), and the nematic order remains unchanged in the plane where the director stays confined during rotation. The rotation angle of director (θ) is estimated as a function of imposed voltage amplitude on the basis of the absorbances of the cyano group which is aligned along the long axis of the mesogen for light linearly polarized in the x and y directions. The director-rotation drives a two-dimensional macroscopic deformation which is characterized by a contraction along the x axis, an extension in the z direction, and nonappreciable length change along the y axis. The strain in the x direction is linearly proportional to $\sin^2 \theta$ in agreement with the expectation of soft or semisoft elasticity theory for thin nematic elastomer films where the shear contribution becomes negligibly small.

DOI: [10.1103/PhysRevE.79.051702](https://doi.org/10.1103/PhysRevE.79.051702)

PACS number(s): 61.30.Vx, 82.70.Gg

I. INTRODUCTION

Liquid crystal elastomers (LCEs) exhibit intriguing stimulus-response behaviors due to their hybrid characters of liquid crystals (LCs) and elastomers [1,2]. The unique stimulus-response behaviors of LCEs originate from the strong coupling of macroscopic shape (deformation) and molecular orientation of constituent mesogens. In particular, a finite and fast deformation induced by electric fields is an attractive property in view of the applications to electrically driven soft actuators and microelectromechanical systems (MEMS) [3–11]. The LCEs in the neat (dry) states need unrealistically high electric fields for actuation but the nematic elastomers swollen by low molecular mass LCs show a finite distortion under moderate electric fields because of a considerable softening without the loss of liquid crystallinity. In previous papers [9–11], we showed that the swollen “monodomain” nematic elastomers with global orientation exhibited a two-dimensional deformation as well as a large change in optical birefringence in fast response to electric fields when the elastomer films were placed between rigid electrodes without mechanical constraint (i.e., with a gap larger than the film thickness). The movie in the supporting information of Ref. [11] demonstrates this electro-optomechanical effect. When the elastomers are effectively sandwiched between electrodes to prohibit the strain in the field direction, the director-rotation is considerably suppressed, and such frustration leads to inhomogeneous or complicated deformations [12–16]. The two-dimensional deformation under the unconstrained geometry is characterized by a contraction along the original director (x direction in Fig. 1), an extension in the field direction (z direction), and nonappreciable dimensional change in the y direction normal

to the original director and the electric field (i.e., the axis about which the director rotates) [9,10]. This deformation dominantly results from the director-rotation in the x - z plane toward the field direction rather than usual electrostrictive effects [17]. A linear correlation was observed between the strain in the x direction (γ_x) and $\sin^2 \theta$ (θ : the rotation angle of director) which was estimated from the birefringence [10]. This linear relation was confirmed for the specimens with various degrees of swelling whereas the induced deformation increased with swelling. The linear correlation observed was in agreement with the expectation of soft or semisoft elasticity concept for sufficiently thin nematic elastomer films where the shear contribution becomes negligibly small [1,10,17–19]. The relationship between γ_x and θ is an important key to understand the coupling of the deformation and director-rotation in nematic elastomers.

Techniques currently employed to characterize the rotation angle of the director θ include optical birefringence and polarized Fourier transform infrared (FTIR) spectroscopy [20–22]. In the previous study [10], θ was estimated from the

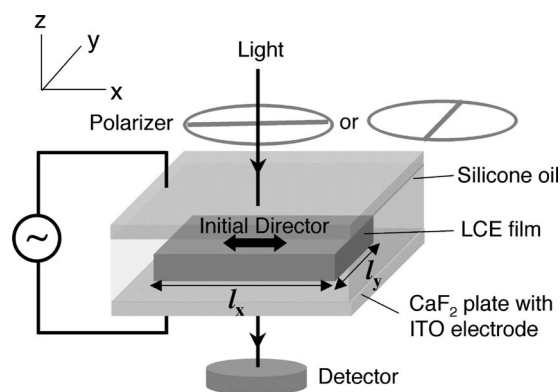


FIG. 1. Experimental setup of polarized FTIR for swollen nematic elastomers under electric fields.

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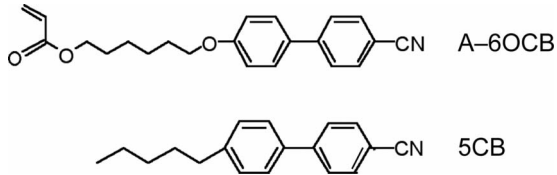


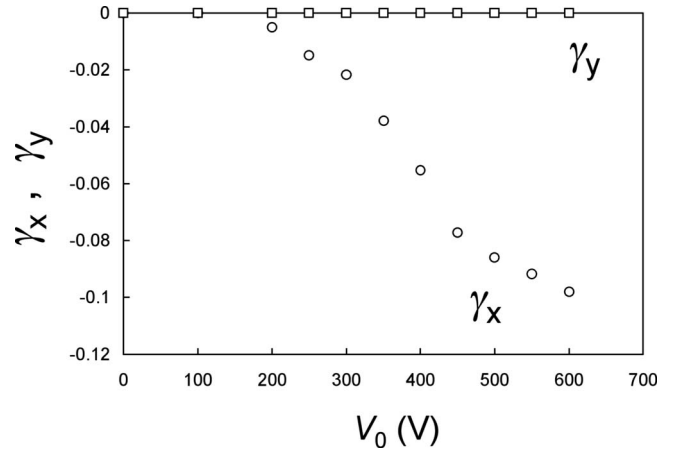
FIG. 2. Chemical structures of A-6OCB and 5CB.

optical birefringence ($\Delta n = n_x - n_y$, where n is the refractive index) under the condition of sufficiently small birefringence satisfying $\Delta n \ll n_y$. Polarized FTIR techniques have been employed to study molecular reorientation and mobility in monodomain LCEs in response to external mechanical fields [20,21] or to investigate the effect of strain-induced compression of molecular layers in smectic LCE films [22]. The dependence of the absorbance A of a characteristic band on the polarizer angle reflects the average orientation of the bond: A is proportional to $\langle (\mu E)^2 \rangle$, where the vectors μ and E denote the molecular transition dipole moment and the electric field of the IR beam, respectively, and the bracket represents the averaging over all molecules in the measured region. In the present study, we investigate the mesogen reorientation behaviors in swollen nematic elastomers under electric fields by means of polarized FTIR. A merit of this method is that we can obtain more detailed information about the reorientation behavior of mesogens: in the case of usual optical birefringence measurements, the obtained information is the only difference of the contributions in the two directions ($n_x - n_y$). The characterization by polarized FTIR gives further and unambiguous basis about the electrically driven director-rotation in nematic elastomers.

II. EXPERIMENTAL SECTION

The sample employed in this study is essentially the same as one of the specimens in the previous study [10] although there is a small difference in film thickness. A side chain type monodomain nematic elastomer with global uniaxial orientation was prepared by the photopolymerization of monoacrylate LC monomers (A-6OCB) and diacrylate crosslinker (1,6-hexanediol diacrylate) in a glass cell whose surfaces were coated by uniaxially rubbed polyimide layer. The details of the method were described elsewhere [23]. The crosslinker concentration was 7 mol % in feed. The elastomer film was allowed to swell fully in a low molecular mass LC (5CB). The chemical structures of A-6OCB and 5CB are shown in Fig. 2. 5CB was chosen as a swelling solvent because of the good miscibility and large positive dielectric anisotropy both of which were needed for a finite electrical deformation. The 5CB content and thickness of the swollen elastomer film were 78 vol % and 43 μm , respectively.

The film specimen was placed between the CaF_2 plates (transparent to infrared light) with indium tin oxide electrodes. The almost square sheet specimens with each side of ca. 3 mm and ca. 1 mm were used for the FTIR measurement and the observation of deformation, respectively. Each specimen was cut out from the same sample sheet. The cell with a

FIG. 3. Strains in the x and y directions as a function of imposed voltage amplitude.

gap of 50 μm (larger than the film thickness) was filled with silicone oil which was a nonsolvent for the specimen. In this geometry, the specimen has no mechanical constraint from rigid electrodes. The frequency of the imposed square ac electric fields was 1 kHz. The electrically driven deformation was observed by an optical microscope. The dimensional changes in the x and y directions were measured in the steady state as a function of imposed voltage amplitude (V_0). The FTIR measurement was conducted with a spectrometer Jasco 4200ST. The beam spot was ca. 1 mm in diameter. The absorption band regarding the stretching vibration of the terminal cyano group parallel to the long axes of the mesogens of LCE (A-6OCB) and solvent (5CB) at around 2225 cm^{-1} was used to characterize the director-rotation. The absorbances of the incident polarized light parallel and normal to the initial director axis (denoted by A'_x and A'_y , respectively) were evaluated from the area of the corresponding peak as a function of V_0 . The absorbance by the silicone oil at around the wavelength of interest (2225 cm^{-1}) was negligibly small. The CaF_2 cell filled with the silicone oil without the specimen was employed for the background measurement. In the fully swollen films, the LCE and 5CB are completely miscible, and they form a single nematic phase, which is confirmed by a single nematic-isotropic transition temperature [24]. The absorbances A'_x and A'_y reflect the total contributions from the mesogens of LCE and solvent, and we employ them to analyze the director-rotation behavior. The absorbance of the incident light polarized at angles other than 0° and 90° relative to the initial director was not measured. This is related to the limited time required for the measurements under high electric fields to prevent electric short circuits. However, as demonstrated later, A'_x and A'_y provide sufficient information about the director-rotation because the director simply rotates about the y axis.

III. RESULTS AND DISCUSSION

Figure 3 shows the dependence of the strain γ_i in the i direction ($i=x, y$) as a function of V_0 . The strain γ_i is defined by $\gamma_i = (l_i - l_i^0) / l_i^0$, where l is the length and the superscript 0

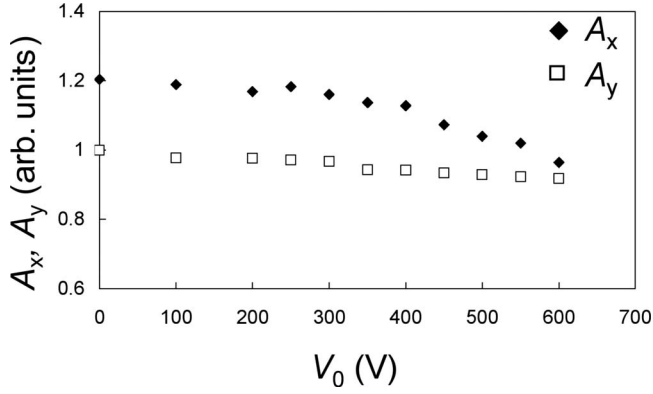


FIG. 4. Reduced absorbances A_x and A_y as a function of imposed voltage amplitude.

denotes the state without field. The voltages of $V_0 > 200$ V result in a finite contraction in the x direction, and the strain reaches ca. 10% at the highest V_0 in this study. No appreciable dimensional change was observed in the y direction even at high V_0 , i.e., $\gamma_y(V_0) \approx 0$. These features are identical with those of the similar sample in our previous paper (Fig. 4 in Ref. [10]). The detailed characterization of the threshold voltage amplitude was given in Ref. [10]. The dimensional ratio $\lambda_z (=l_z/l_z^0)$ was calculated by $\lambda_z = 1/[(1+\gamma_x)(1+\gamma_y)] \approx 1/(1+\gamma_x)$ assuming volume conservation.

Figure 4 shows the V_0 dependencies of the reduced absorbances $A_x [=A'_x/(\lambda_z A'_{y0})]$ and $A_y [=A'_y/(\lambda_z A'_{y0})]$, where A'_x and A'_y are reduced by λ_z to consider a variation in effective thickness by deformation, and A'_{y0} is the value of A'_y at $V_0 = 0$. The absorbance A reflects the average orientation of the C \equiv N bond parallel to the long axis of the mesogens. A finite difference in A_x and A_y at $V_0 = 0$ (denoted as A_{x0} and A_{y0} , respectively) reflects the initial uniaxial orientation (original director) in the x direction. As V_0 increases, the difference in A_x and A_y becomes smaller whereas A_y remains almost unchanged. Furthermore, A_x becomes nearly equal to A_y at the high V_0 . When a uniform reorientation of mesogens in the specimen is assumed, A_x and A_y correspond to the long and short axes of the intersection in the x - y plane at $z=0$ for the absorption ellipsoid of the director which rotates about the y axis by an angle of θ (Fig. 5). The absorbances A_{x0} and A_{y0} at $\theta=0$ give the long and short axes of the ellipsoid, respectively. The shape of the intersection varies from ellipse ($A_{x0} > A_{y0}$) to nearly circle ($A_x \approx A_y$) with almost no change in the short axis ($A_y \approx A_{y0}$). The relation $A_x \approx A_y$ at the high V_0 shows a nearly 90° rotation of the director. In addition, $A_y(V_0) \approx A_{y0}$ indicates that the director rotates around the y axis with no appreciable change in the orientational order in the plane where the director stays confined during rotation. No macroscopic distortion in the y direction under electric fields ($\gamma_y \approx 0$) results from this type of director-rotation.

The absorbance data provide a basis to evaluate the rotation angle of director θ . In this geometry, $A_x(\theta)$ can be expressed by [25]

$$A_x(\theta) = a \left[\frac{1-S}{3} + S \cos^2 \theta \right], \quad (1)$$

where a is a constant of proportionality and S is the orientational order parameter of the mesogens. The parameter S is

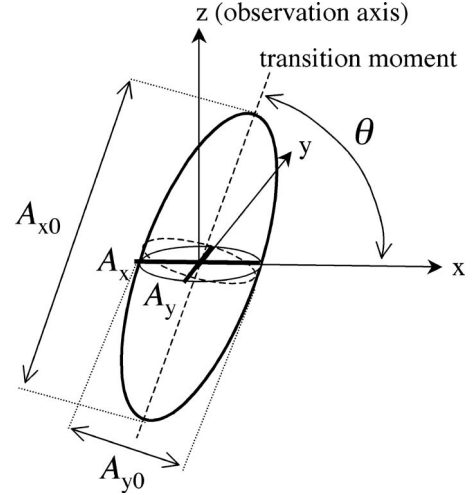


FIG. 5. Absorbance ellipsoid and geometry in polarized FTIR measurements. The coordinate system is the same as Fig. 1.

defined by $S = [3\langle \cos^2 \phi \rangle - 1]/2$, where the bracket denotes the spatial average and ϕ is the angle between the mesogen and the director. The parameter S is related with A_{x0} and A_{y0} as [25]

$$S = \frac{A_{x0} - A_{y0}}{A_{x0} + 2A_{y0}}. \quad (2)$$

From Eqs. (1) and (2), we obtain [22,26,27]

$$A_x(\theta) = A_{x0} \cos^2 \theta + A_{y0} \sin^2 \theta. \quad (3)$$

Equation (3) can be rewritten as

$$\sin^2 \theta = \frac{A_{x0} - A_x}{A_{x0} - A_{y0}}. \quad (4)$$

Equation (4) indicates that θ is obtained from A_x at each V_0 , A_{x0} , and A_{y0} . Figure 6 shows the V_0 dependence of θ evaluated from Eq. (4). In the calculation of θ at each V_0 , we employed the value of A_y at the corresponding V_0 as A_{y0}

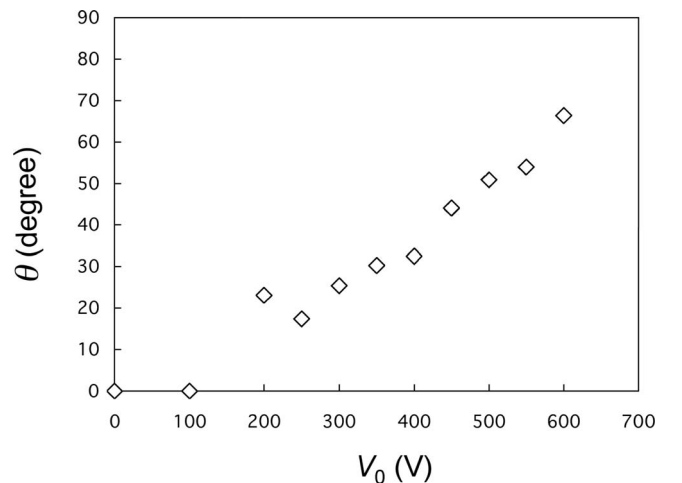


FIG. 6. Rotation angle of the director as a function of imposed voltage amplitude.

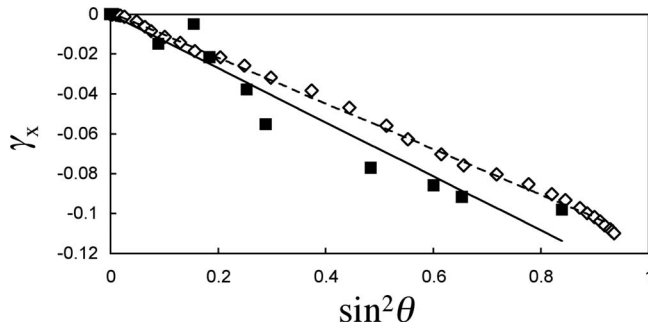


FIG. 7. Strain in the x direction as a function of $\sin^2 \theta$, where θ is the rotation angle of director. The slope of the solid line is -0.13 . The open symbols represent the data of the similar sample in Ref. [10] where $\sin^2 \theta$ was estimated from the optical birefringence. The slope of the dotted line is -0.12 .

[although $A_y(V_0) \approx A_{y0}$]. The rotation angle θ appears to increase almost linearly with V_0 above the threshold voltage amplitude.

In Fig. 7, we replot γ_x against $\sin^2 \theta$ estimated from Eq. (4). A nearly linear relation between γ_x and $\sin^2 \theta$ is observed, which is similar to the result in the previous study using $\sin^2 \theta$ estimated from the optical birefringence [10]. For comparison, the corresponding data for the similar sample in the previous work [10] are also shown in the figure. The slope obtained by the least square method (-0.13) is almost identical with that (-0.12) for the previous result. The main features of the θ dependence of the deformation, i.e., $\gamma_x(\theta) \sim \sin^2 \theta$ and $\gamma_y(\theta) \approx 0$, accord with the expectation of a soft or semisoft elasticity theory for sufficiently thin nematic elastomer films [10]. The deformation induced by director-rotation is theoretically expected to include shear distortion [1,17–19] but the shear contribution becomes negligibly small in sufficiently thin films [10]. The ratios l_z^0/l_x^0 and l_z^0/l_y^0 for the samples are in the order of 10^{-2} . The linear coefficient in Fig. 7 is correlated with the chain anisotropy k ($\equiv r^{1/2}$ in the original theory [1,17]) or orientational order parameter S_B of network backbones [10,17]:

$$\gamma_x = -(1 - k^{-1})\sin^2 \theta, \quad (5)$$

$$k^2 = (1 + 2S_B)/(1 - S_B). \quad (6)$$

The value of k for the results in Fig. 7 is 1.15, which leads to $S_B \approx 0.1$. This S_B value is comparable to the order parameter of the mesogens S (≈ 0.1) estimated from Eq. (2) with A_{x0} and A_{y0} . The similar value of S_B (≈ 0.2) is also obtained from the shape anisotropy in anisotropic swelling using the Warner-Gelling-Vilgis elastic free energy for nematic elastomers [28] (Eq. 9 in Ref. [23]). In the case of side chain type nematic elastomers, S_B is expected to be smaller than S ($S_B = bS$ with $b < 1$) and b depends on the chemical structures [29]. However, the similar values of S_B and S obtained from different characteristics support the validity of Eqs. (5) and (6). The values of S_B and S of this specimen are modest, which is likely due to the swelling effect because S in the dry state is 0.3–0.4 that is comparable to the values of typical side chain type LCEs [29].

IV. CONCLUSIONS

The polarized FTIR reveals that the director of free nematic elastomers under electric fields rotates about the axis normal to the field direction and original director, and sufficiently high fields result in an almost 90° of director-rotation. A linear relation between the macroscopic contractive strain along the original director and $\sin^2 \theta$ is observed, which is similar to the earlier result by optical birefringence measurements. The correlation between the director rotation and deformation is satisfactorily explained by a soft or semisoft elasticity theory for thin nematic elastomer films, and the linear coefficient is related to the nematic order parameter.

ACKNOWLEDGMENTS

The authors thank a referee for the valuable comment on Eq. (4). This work was partly supported by the Grant-in-Aid on Priority Area “Soft Matter Physics” (Grant No. 19031014) and that for Scientific Research (B) (Grant No. 16750186) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan. This research was also supported in part by the Global COE Program “International Center for Integrated Research and Advanced Education in Materials Science” (Contract No. B-09) of MEXT of Japan, administrated by the Japan Society for the Promotion of Science. P.K. thanks the Deutsche Forschungsgemeinschaft (KO 3618/1–1) for financial support.

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