Electrooptical Effects with Anisotropic Deformation in Nematic Gels

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Nematic polymer networks have received much interest as a hybrid material possessing both the properties of polymer networks and liquid crystals.[1,2] Macroscopic deformation of nematic networks caused by the electrically induced alignment of the constituent mesogens is an interesting property stemming from the hybrid character. The electrically driven deformation of nematic networks is expected as a promising device of soft actuators such as artificial muscle because the actuation speed is much faster due to the direct coupling of electric fields with the molecular orientation than those of the electrolyte gels based on ionic diffusion.[3] The spontaneous shape and/or volume variations in nematic networks upon the temperature-induced nematic−isotropic transition[1,2,4−6] and light radiation[7,8] were reported, but electric fields are more widely utilizable as driving forces in industrial devices. The electrical deformation of the nematic gels (nematic networks swollen by nematic solvents) with polydomain or monodomain textures were investigated, but the mesogen orientation coupled with the deformation was too small to detect or not examined in their studies.[9−12] Several groups[13−16] studied the electrooptical effect in monodomain nematic gels with global director orientation, but none of them observed a finite accompanying deformation. In these studies,[13−16] the gels were effectively sandwiched between the two electrodes, prohibiting the strain in the field direction. According to a theoretical study,[17] such external constraints significantly enhance the elastic barrier, and thus a very high electric field is required to observe a finite distortion in the directions normal to the field axis.

In this communication, we report the electrooptical and electromechanical properties of the monodomain nematic gels without external constraint. We demonstrate that in fast response to electric fields the freely suspended gels show a significant change in birefringence as well as macroscopic deformation with large anisotropy. Such electrooptical effects with anisotropic deformation reveal an interesting and important aspect in the hybrid characters of nematic gels and also extend their applicability in the industrial devices.

The side chain nematic networks with homogeneous molecular alignment were prepared using the mixture of the reactive mesogenic monomer A-6OCB, the nonreactive nematogen 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB), 1,6-hexanediol diacrylate (cross-linker), and Irgacure-784 (photoinitiator). The molecular structures of A-6OCB and 6OCB are illustrated in Figure 1. A-6OCB was synthesized in our laboratory by the method in the literature.[18] 6OCB (Sigma-Aldrich) was mixed with A-6OCB by the molar ratio of 50:50 to broaden the temperature range of the nematic phase. The concentrations of the cross-linker and initiator were 7 and 0.5 mol % in the total reactants. The reactant mixture was sandwiched between two glass plates separated by the spacers of 25 μm thickness. The plates were coated with the unidirectionally rubbed polyimide layer, yielding a homogeneous alignment of the nematic molecules. The photopolymerization was conducted at 45 °C in the monodomain nematic phase by irradiating the cell with a xenon lamp with emission at a wavelength 526 nm. The resulting gel film was carefully separated from the cell and immersed in dichloromethane to wash out the unreacted materials and nonreactive nematogen 6OCB. The swollen network was gradually deswollen by using the mixtures of dichlomethane and methanol with successive methanol contents. The fully deswollen network was dried and thereafter allowed to swell in the nematic solvent 5CB (Sigma-Aldrich) at 25 °C. The solvent (5CB) content in the fully swollen gel was evaluated to be 76 vol % from the volume change before and after swelling assuming the volume additivity. Both the constituent nematogens A-6OCB and 5CB in the swollen gel are dielectrically positive: The director of each nematogen aligns along the direction of electric fields.

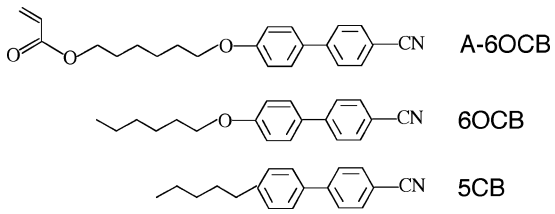

Figure 1. Molecular structures of the employed reactive mesogen and nematic solvents.

The fully swollen gel film with the thickness (d) of 34 μm was placed between two indium−tin oxide (ITO) coated glass slides separated by the spacers of 40 μm thickness. The cell was filled with a transparent silicone oil. In this geometry, the sample is freely suspended between the electrodes without mechanical constraint.[19] The measurements of the electrooptical and electromechanical effects were separately carried out, and the samples for these measurements were cut out from the identical gel film. The electrooptical properties were studied by measuring the transmittance through crossed polarizers with the uniaxially oriented nematic gel using a He−Ne laser (λ = 633 nm). The gel was placed such that the initial director axis is at an angle of 45° relative to the crossed polarizers. The intensity of the transmitted light (I) was measured by a photodiode detector. The ac voltages with various amplitudes (V_0) and frequencies (f) were generated by a function generator with a high-voltage amplifier. The effective birefringence (Δn_{eff}) was evaluated from the familiar relation $I/I_{\max} = \sin^2(\pi d\Delta n_{\mathrm{eff}}/\lambda)$. The maximum change in film thickness (d) under electric fields is as large as 10% in the V_0 range examined (as shown later), and thus the initial thickness was employed for simplicity in the calculation of Δn_{eff} at each V_0. The electrically induced deformation was observed with a polarizing optical microscope (Nikon E600POL). The dimensions of the gel parallel and normal to the initial director axis were measured as a function of V_0 and f.

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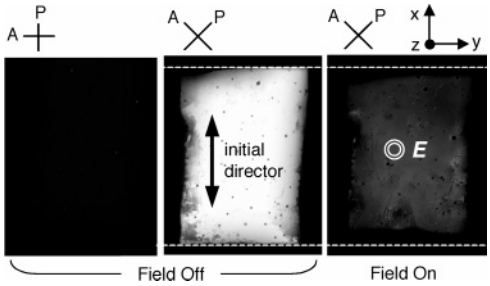

Figure 2. Optical micrographs of the uniaxially oriented nematic gel before and after applying the electric field of $V_0 =$ 750 V and $f = 1$ kHz. The gel with 34 μm thickness is freely suspended between the ITO electrodes with 40 μm gap and surrounded by a transparent silicone oil. The director in the initial state at $V_0 = 0$ aligns in x-direction. The electric field (z-direction) yields simultaneously the director reorientation in the field direction and the anisotropic deformation, ca. 10% dimensional reduction in x-direction without appreciable dimensional change in y-direction.

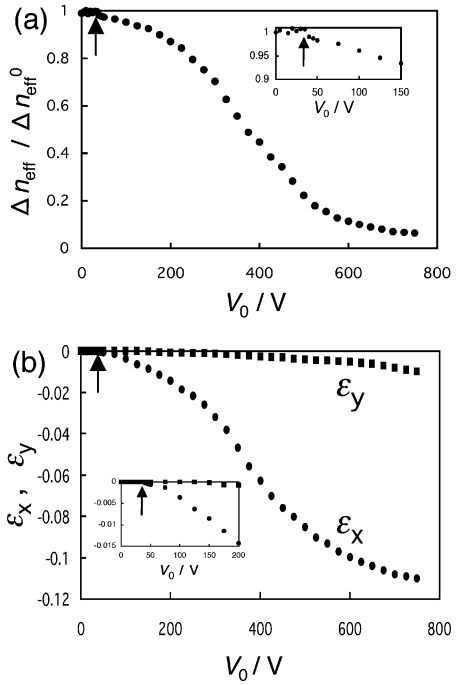

Figure 3. (a) Effective birefringence Δn_{eff} as a function of V_0 at 1 kHz. The values are reduced by the initial value of Δn_{eff} ($= 2.24 \times 10^{-2}$) at $V_0 = 0$. The arrow indicates a threshold voltage (≈35 V) to yield a finite change in Δn_{eff}. The inset presents the data at low V_0. (b) Principal strains in x- and y-directions as a function of V_0 at 1 kHz. The arrow indicates a threshold voltage (≈37 V) to yield a finite deformation. The inset displays the data at low V_0.

Figure 2 displays the optical micrographs showing the electrooptical effect with anisotropic deformation in the freely suspended nematic gel. In the initial state at $V_0 = 0$, the director of the nematic gel is uniaxially oriented in x-direction. The photographs indicate that the electric field ($V_0 =$ 750 V at 1 kHz) in z-direction drives the director reorientation in the field direction as well as an anisotropic deformation, i.e., ca. 10% dimensional reduction in x-direction without appreciable dimensional change in y-direction. The deformation and the transmittance change are repeatable when reiterating the application and removal of the fields.

Part a of Figure 3 shows the V_0 dependence of Δn_{eff} ($= n_x - n_y$ where n_x and n_y are the refractive indexes in x- and y-axes) at $f = 1$ kHz. In the figure, Δn_{eff} at each

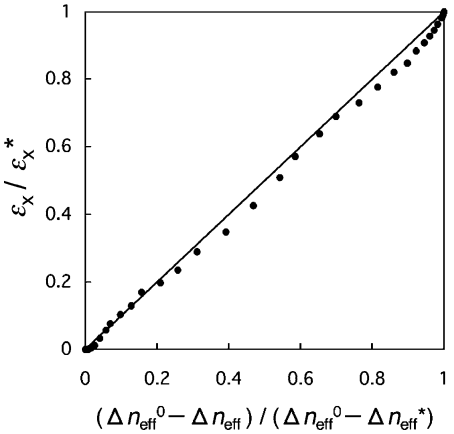

Figure 4. Relation between the reduced values of ($\Delta n_{eff}^0 - \Delta n_{eff}$) and ϵ_x. Δn_{eff}^* and ϵ_x^* are the values at the maximum V_0 (=750 V) in the present study. The slope of the straight line is unity.

V_0 is reduced by the initial value of Δn_{eff} at $V_0 = 0$ (Δn_{eff}^0). The birefringence Δn_{eff} decreases toward zero with increasing V_0, indicating the growth of the director realignment along the field direction. The value of Δn_{eff} at the maximum V_0 in the present study is less than 5% of Δn_{eff}^0, suggesting that a high degree of director reorientation is achieved. A threshold voltage ($V_c^{\Delta n} \approx$ 35 V) is identified as the point at which Δn_{eff} begins to decrease. The presence of $V_c^{\Delta n}$ was also observed for the nematic gels effectively sandwiched by the electrodes.[13−16]

Part b of Figure 3 illustrates the principal strains in x- and y-directions as a function of V_0 at $f = 1$ kHz. The strain ϵ_i ($i = x, y, z$) is defined as $\epsilon_i = (l_i - l_i^0)/l_i^0$, where l_i^0 and l_i are the dimensions in i-direction before and after deformation, respectively. The negative ϵ corresponds to a compressive strain, i.e., a reduction in dimension. As seen from the figure, the deformation is markedly anisotropic. The dimension in x-direction (initial director axis) is considerably reduced by electric fields, while the dimension in y-direction is almost unchanged even at high voltages ($|\epsilon_y| < 0.01$). The compressive strain in x-direction increases with increasing V_0 and appears to reach the plateau value of ca. 0.11 in the high V_0 region. The strain ϵ_z in z-direction (field direction) was not directly measured, but ϵ_z is estimated on the basis of the volume constancy for elastomeric materials ($\Sigma\epsilon_i = 0$ at small deformation): $\epsilon_z \approx -\epsilon_x$ because $\epsilon_y \approx 0$. Thus, the dimension in z-direction should grow with increasing V_0 and increase by ca. 10% at the high voltages. A threshold voltage ($V_c^{\epsilon} \approx 37$ V) to yield a finite deformation is also present as in the case of the electrooptical response. The value of V_c^{ϵ} is almost identical with $V_c^{\Delta n}$. Several researchers[14−16] reported that the threshold for electrooptical response in the nematic gels effectively sandwiched by the electrodes is governed by an electric field rather than a voltage.

To elucidate the relation between the director reorientation and macroscopic deformation, ϵ_x and the change in Δn_{eff} ($\delta n_{eff} = \Delta n_{eff}^0 - \Delta n_{eff}$) normalized using the values of ϵ_x and Δn_{eff} at the maximum V_0 are plotted in Figure 4. The data points fall on the straight line with the slope of unity, clearly indicating a strong correlation between them: The deformation is primarily caused by the electrically induced realignment of the nematogens. The macroscopic dimensional change occurs only in the $x-z$ plane where the director reorientation takes place.

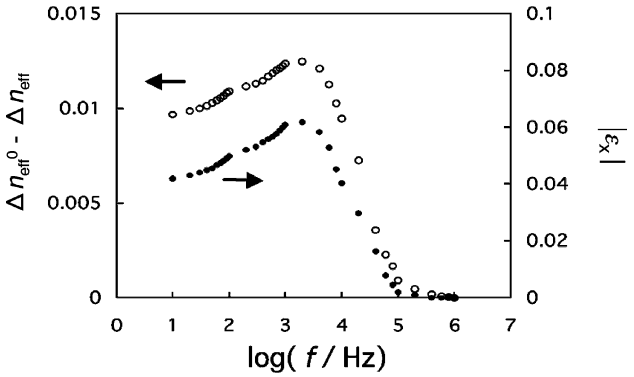

Figure 5. Principal strain ϵ_x and the change in effective birefringence ($\Delta n_{\mathrm{eff}}^0 - \Delta n_{\mathrm{eff}}$) as a function of the frequency f of the electric field with $V_0 = 400$ V.

An extensive strain in the field direction is induced by the director realignment, and a compressive strain with almost the same degree is caused in the initial director direction due to volume constancy. In contrast, almost no dimensional change takes place in y-direction (not concerned in the director realignment) normal to both the initial director and field axes. The deformation dominated by director rotation observed appears to agree with the theoretical picture[2,17] for the deformation of unconstrained nematic gels.

Figure 5 displays ϵ_x and the change in Δn_{eff} ($\delta n_{\mathrm{eff}} = \Delta n_{\mathrm{eff}}^0 - \Delta n_{\mathrm{eff}}$) as a function of f at $V_0 = 400$ V. Both δn_{eff} and ϵ_x exhibit the same features for the f dependence. At high frequencies above 10^5 Hz, neither Δn_{eff} nor ϵ_x appreciably changes before and after applying the fields. In the high f region, the field frequency is too high to induce a dipolar reorientation of the nematogens, as known in low molecular mass liquid crystals. In principle, the materials in this frequency region are expected to show the conventional electrostrictive strains, but the strains will be too small to detect. At the frequencies of $f < 10^4$ Hz, the electrooptical effects with deformation become pronounced. The reason for a finite positive f dependence of the effect at low frequencies is not known at present, and it may be due to an effect of ionic current of impurities in the system.

The response time of the nematic gel was evaluated to be 5 ms on the basis of the change in Δn_{eff} upon the application of the field of $V_0 = 400$ V and $f = 1$ kHz. This response time is comparable to that reported for the electrooptical response in a liquid crystalline gel.[16,20]

A finite electrooptical effect with deformation is also observed in the identical nematic gel effectively sandwiched by the electrodes (i.e., under the condition of $\epsilon_z = 0$),[21] but the effect is much smaller than that in the freely suspended gel. The effect saturates at the high voltages of $V_0 > 700$ V: The minimum value of $\Delta n_{\mathrm{eff}}/\Delta n_{\mathrm{eff}}^0$ is 0.4, and the maximum value of $|\epsilon_x|$ is 0.04. Thus, the mechanical constraint remarkably suppresses the electric field response of nematic gels.

In conclusion, we have demonstrated the electrooptical effects with anisotropic deformation for uniaxially aligned nematic gels in the freely suspended state. In fast response to electric fields, the gels exhibit concurrently the large changes in birefringence and the markedly anisotropic deformation. The macroscopic strain strongly correlates with the degree of director reorientation. The enhancements in dielectric anisotropy and initial orientation degree of constituent mesogens will increase the magnitude of the electric field response of nematic gels. The monodomain nematic gels hold promise for fast soft actuators with electrooptical effects.

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References and Notes

(1) Finkelmann, H.; Brand, H. R. *Trends Polym. Sci.* **1994**, *2*, 222.
(2) Warner, M.; Terentjev, E. M. *Liquid Crystal Elastomers*; Oxford University Press: Oxford, 2003.
(3) Calvert, P. In *Electroactive Polymer (EAP) Actuators as Artificial Muscles − Reality, Potential, and Challenges*; Bar-Cohen, Y., Ed.; SPIE: Bellingham, WA, 2001.
(4) Urayama, K.; Okuno, Y.; Kohjiya, S. *Macromolecules* **2003**, *36*, 229.
(5) Urayama, K.; Okuno, Y.; Nakao, T.; Kohjiya, S. *J. Chem. Phys.* **2003**, *118*, 2903.
(6) Urayama, K.; Arai, Y. O.; Takigawa, T. *Macromolecules*, in press.
(7) Cviklinski, J.; Tajbakhsh, A. R.; Terentjev, E. M. *Eur. Phys. J. E* **2002**, *9*, 427.
(8) Yu, Y.; Nakano, M.; Ikeda, T. *Nature (London)* **2003**, *425*, 145.
(9) Zentel, R. *Liq. Cryst.* **1986**, *1*, 589.
(10) Kishi, R.; Kitano, T.; Ichijo, H. *Mol. Cryst. Liq. Cryst.* **1996**, *280*, 109.
(11) Huang, C.; Zhang, Q.; Jákli, A. *Adv. Funct. Mater.* **2003**, *13*, 525.
(12) Urayama, K.; Kondo, H.; Arai, Y. O.; Takigawa, T. *Phys. Rev. E*, in press.
(13) Hikmet, R. A. M.; Boots, H. M. J. *Phys. Rev. E* **1997**, *51*, 5824.
(14) Chang, C.-C.; Chien, L.-C.; Meyer, R. B. *Phys. Rev. E* **1997**, *56*, 595.
(15) Terentjev, E. M.; Warner, M.; Meyer, R. B.; Yamamoto, J. *Phys. Rev. B* **1999**, *60*, 1872.
(16) Ren H.; Wu, S. T. *Appl. Phys. Lett.* **2002**, *81*, 1432.
(17) Terentjev, E. M.; Warner, M.; Bladon, H. *J. Phys. II* **1994**, *4*, 667.
(18) Shivaev, V. P.; Kostromin, S. G.; Plate, N. A. *Eur. Polym. J.* **1982**, *18*, 651.
(19) In the geometry employed, the field strength effectively acting on the gel (E_{g}) is related to that between the electrodes (E) separated by the distance d_{t} as $E_{\mathrm{g}} = Ed_{\mathrm{t}}/\{d + (D_{\mathrm{g}}/D_{\mathrm{s}})d_{\mathrm{s}}\}$, where D_{g} and D_{s} are the dielectric constants of the gel along the field axis and the silicone oil, respectively, and d_{s} ($= d_{\mathrm{t}} - d$) is the length occupied by the oil. The value of D_{g} changes with E due to the nematogen reorientation, which markedly complicates the accurate estimation of E_{g}. Thus, we employ the voltage amplitude V_0 between the electrodes for the discussion.
(20) Mizoshita, N.; Hanabusa, K.; Kato, T. *Adv. Mater.* **1999**, *11*, 392.
(21) The surfaces of the electrodes were sufficiently lubricated to allow the gel to deform smoothly in the directions normal to the field axis.

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