Thermal Deformation of Imprinted Twist Nematic Elastomers

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Abstract. A nematic elastomer film with a 90° twist orientation between the top and bottom surfaces is prepared by chiral imprinting methods. The reactive achiral nematic monomers and crosslinkers are photopolymerized in the presence of a controlled amount of unreactive chiral dopant. The elastomer films possess a 90° twist orientation even after the removal of the chiral dopant. The films exhibit an elongation and contraction in the direction at an angle of 45° relative to the mesogen orientations at the top and bottom surfaces in response to cooling and heating across the nematic–isotropic transition temperature, respectively.

1. Introduction
A marked characteristic of liquid crystal elastomers (LCEs) is the strong coupling of macroscopic shape and the molecular (mesogen) orientation [1, 2]. One of the most familiar phenomena in LCEs is the large distortions induced by changes in temperature. In the case of nematic elastomers, variations in temperature around the nematic–isotropic transition temperature (T_{NI}) lead to uniaxial deformation; this deformation results from the change between uniaxial and random orientations of the constituent mesogens [1, 3–6]. In the case of smectic elastomers, shear deformation occurs when a tilt state of mesogens in the smectic layer changes due to the transition between the smectic A and smectic C phases [7]. These results clearly indicate that the mode of thermal deformation in LCEs is governed by a thermally induced change in the patterns of mesogen orientation. In this study, we focus on nematic elastomers with a 90° twist orientation between the top and bottom surfaces. The twist nematic (TN) orientation of low molecular mass LCs has been exploited in display devices [8]. Then, the following question arises: what is the thermal deformation of twist nematic elastomers (TNEs) like? This is an interesting issue in view of the coupling effects of mesogen alignment and rubber elasticity in LCEs. In addition, an understanding of the thermal deformation of TNEs will enable us to extend the possibility of the application of LCEs as thermally driven soft actuators [9].

“Chiral imprinting” provides a method of producing TNEs. The concept of imprinted chiral elastomers was envisaged by de Gennes [10], and chiral imprinting was experimentally attempted to produce achiral nonmesomorphic [11] and LC polymers [12–16]. Hassan et al. [13] first reported that when achiral LC polymers are cross-linked in the presence of a nonreactive chiral dopant (low molecular weight chiral mesogen), the resultant LCEs exhibit an imprinted chiral structure. The LCEs retain the induced chiral nematic phase after cross-linking even if the chiral dopant is removed. The physical properties of cholesteric elastomers prepared by chiral imprinting have been experimentally [14–16] and theoretically [17] studied. These cholesteric elastomers have a helical orientation with any

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windings. Broer et al. [12] prepared LC network films with a twist orientation by using the chiral imprinting method. These films—which were prepared by the homopolymerization of achiral mesogenic diacrylate with low molecular weight—were not elastomers but hard resins because of the considerably short network chains. They observed the interesting thermal deformation of these films, but it originates from the difference in thermal expansion coefficient along the thickness direction and not from the director orientation.

2. Experimental

We have prepared a side-chain-type LCE with an imprinted 90° twist orientation using the achiral mesogenic monoacrylate (A–6OCB), 1,6-hexanediol diacrylate (cross-linker) and S-811 (nonreactive chiral dopant). The chemical structures of A-6OCB and S-811 are shown in Figure 1. 4-n-Hexylxy-4'-cyanobiphenyl (6OCB) was used as a miscible nematic solvent to increase the temperature range of the nematic phase. A-6OCB was synthesized by the method specified in literature [18]. The chiral dopant and photoinitiator (Irgacure 784) were supplied by Merck Ltd., Japan, and Chiba Specialty Chemicals Co., respectively. 6OCB was purchased from Aldrich and used without further purification. The molar mixing ratio of A-6OCB and 6OCB was 1:1. The cross-linker concentration was 7 mol%.

The chiral properties of the mixtures of A-6OCB, 6OCB, and S-811 were characterized by the pitch of the resultant helicoidal structure corresponding to the distance of a 2π screw rotation of the molecular packing. The pitch was measured by the Cano wedge method [8, 19, 20]. The inverse pitch almost linearly depends on the concentration of S-811. This behavior is similar to the behaviors of conventional LC mixtures with chiral dopants. The total twist angle of the monomeric mesogens was defined as the angle between the bounding mesogenic molecules at the bottom and top substrates, whose surfaces were coated with a uniaxially rubbed polyimide layer. The chiral dopant induced a left-hand twist orientation of the mesogens. The top and bottom substrates of the glass cells used to prepare the sample were placed in such a manner that the rubbing directions could cross with each other. The concentration of the chiral dopant was adjusted such that the total twist angle could become 90° between the top and bottom substrates, the distance between the substrates being 20 µm.

Photopolymerization was conducted in the cell at 45 °C—ca. 3 °C lower than the transition temperature of the nematic mixture—by irradiation for a duration of 30 min. A xenon lamp emitting at a wavelength of 526 nm was used. The cell was immersed in dichloromethane for several days until the resultant film detached from the glass substrates due to the swelling pressure. The films were allowed to swell fully in dichloromethane in order to remove the unreacted materials and chiral dopants. The swollen gel films were gradually deswollen by stepwise addition of methanol to dichloromethane. The specimens were dried and then used for the measurements. Square specimens with a thickness of ca. 15 µm—whose crossed sides were parallel to the rubbing directions at the top and bottom substrates—were cut out from the sheet sample at room temperature which was below \( T_{\text{NI}} \) (103 °C) and the glass transition temperature (ca. 35 °C) [21].

The phase behavior and thermal deformation of the TNEs were observed by means of a polarized optical microscope with a Mettler FP-82 hot stage. The mesogen orientation was characterized by an FTIR spectrometer Jasco 4200ST with a custom-made temperature-controllable box. The adsorption band for the stretching vibration of the terminal cyano group that was parallel to the long axis of the mesogen was used to characterize the mesogen orientation. The absorbance \((A)\) of the unpolarized incident light normal to the film surface was measured as a function of temperature.
Figure 2. Optical micrographs of the specimen placed between two parallel polarizers at 93 °C (=T_{NI}−10 °C). The optical axis of the parallel polarizers is (a) parallel and (c) normal to the rubbing direction (R.D.) for the top surface and (b) at an angle of 45° to the crossed rubbing directions.

3. Results and Discussion

Figure 2 shows the optical micrographs of the specimen. These micrographs confirm a 90° twist mesogen orientation. The sample is placed between two parallel polarizers. When the optical axis of the parallel polarizers coincides with the rubbing direction at the top or bottom surface, the sample appears dark. A bright image is observed when the optical axis of the polarizers is inclined 45° to the crossed rubbing directions. A similar twist orientation is observed at temperatures less than T_{NI}. This twist orientation is recovered when repeating the cycle of the nematic-isotropic transition. This result indicates that the elastomers can retain the 90° twist mesogen orientation during cross-linking, even after the chiral dopant is removed. The off-square shape of the specimen shown in Figure 2 is a result of thermal deformation, which is described below.

Figure 3 shows the optical micrographs of thermal deformation driven by a temperature change across T_{NI}. When the specimen is heated across T_{NI}, the almost square shape of the cross section normal to the thickness direction (at 40 °C) changes to a diamond-like shape (at 130 °C). Cooling across T_{NI} induces a reverse change in shape. It should be noted that each side of the cross section shown in Figure 3a is almost parallel to the direction in which the bounding mesogens are oriented (which corresponds to the rubbing direction) at the top or bottom surface of the films. The shape of the specimen at 40 °C was almost similar to the shape of the specimen cut out from the sample sheet at 25 °C because the glass transition temperature is around 35 °C. On cooling (heating), the elastomer appears uniaxially stretched (compressed) along the diagonal a. We characterize the thermal deformation on the basis of the variations in the length along the diagonals a and b, which are shown in Figure 3.
in Figure 3. The dimensional ratios $\lambda_a$ and $\lambda_b$, whose reference state is taken in the high-temperature isotropic state, can be defined as follows: $\lambda_i = l_i/l_i^0$ ($i = a, b$), where $l_i$ is the dimension in the state of interest and the superscript 0 denotes the isotropic state at 130°C. The corresponding dimensional ratio in the thickness direction ($\lambda_c$) was calculated using the formula $\lambda_c = Z_{ab}/Z_{ab}$, where $Z_{ab}$ is the cross-sectional area of the $a-b$ plane evaluated from video analysis; in this case, the volume of the rubbery specimen was assumed to be constant.

Figure 4 shows the temperature dependence of $\lambda_i$ ($i = a, b, c$). No appreciable difference in $\lambda_i$ between the cooling and heating processes is observed. In the nematic state, the specimen undergoes anisotropic deformation ($\lambda_i \neq 1$). As the temperature decreases, $\lambda_a$ increases while $\lambda_b$ and $\lambda_c$ decrease. The solid lines in Figure 4 represent the values of $\lambda_b$ (= $\lambda_c$) calculated from the experimental values of $\lambda_a$, assuming simple uniaxial stretching in the $a$-direction ($\lambda_b = \lambda_c = \lambda_a^{-1/2}$), i.e., the intermediate direction between the directors of the top and bottom surfaces. The induced deformation is roughly approximated by uniaxial stretching, although a finite difference between the experimental values of $\lambda_b$ and $\lambda_c$ indicates that the real deformation is more complicated. The diagonal $a$ corresponds to the direction of the summation of the local directors (for the constituent cross sections normal to the helical axis), which gradually rotate by 90° between the top and bottom surfaces. Each cross section is subjected to uniaxial stretching along the local director, but each cross section cannot deform independently of the distortion of the other cross sections. The constituent cross sections in TNEs are strongly bounded by rubber elasticity; this, however, is not the case with low molecular mass LCs or uncrosslinked LC polymers with a similar twist orientation. Therefore, elastomers are expected to exhibit maximum elongation along the direction corresponding to the summation of the local directors.

The inset of Figure 5 shows the $T$ dependence of the absorbance $A$ for the stretching vibration of the terminal cyano group. The absorbance in the figure is reduced by $\lambda_c$ at each $T$ to consider the change in the thickness with variations in $T$. In the nematic state ($T < T_{NI}$), a reduction in $T$ results in an increase in $A/\lambda_c$. An increase in $A/\lambda_c$ leads to a decrease in the tilt angle ($\theta$) of the mesogen with respect to the $a-b$ plane, because $A/\lambda_c$ is proportional to $<\cos^2\theta>$ as $A/\lambda_c = p <\cos^2\theta>$, where $p$ is a constant and the bracket denotes the average over the specimen. Each constituent cross section (normal to the helical axis and parallel to the $a-b$ plane) of the twist nematic texture is simply expected to have a uniaxial mesogen alignment with almost the same degree of orientation, whereas the local directors gradually rotate between the top and bottom layers. The orientational order parameter for each cross section is expressed by $S_{\text{local}} = [3<\cos^2\psi> - 1]/2$, where $\psi$ is the angle between the
The quantity $\langle \cos^2 \psi \rangle'$ may be approximated by $\langle \cos^2 \theta \rangle$ because of the symmetry of uniaxial orientation, and then $S_{\text{local}}$ is correlated with $A$ as $S_{\text{local}} = \left[3A/(p\lambda_c)\right]^{-1/2}$. The constant $p$ is determined by the value of $A$, and $S_{\text{local}} = 0$ in the isotropic state with random orientation.

As observed in Figure 5, $S_{\text{local}}$ in the nematic state increases with decreasing $T$. In Figure 6, the ratios $\lambda_a/\lambda_b$ and $\lambda_c/\lambda_b$ are given as functions of $S_{\text{local}}$. It can be observed that a growth in $S_{\text{local}}$ increases the anisotropy for the deformation in the $a$–$b$ plane, and that the ratio $\lambda_a/\lambda_b$ is almost linearly proportional to $S_{\text{local}}$. In contrast, an increase in $S_{\text{local}}$ induces no appreciable anisotropy for the deformation in the $b$–$c$ plane.

A TNE with a desired twist angle (for example, $180^\circ$ and $270^\circ$) can be prepared by the chiral imprinting method. The thermal deformation behaviors of TNEs with different twist angles will provide a further basis to explain the types of deformation driven by the twist orientations. The findings of the deformation induced by the twist orientation and the dependence of the deformation on $S_{\text{local}}$ can be applied to the theoretical study of liquid crystal elastomers.

4. Summary
We have shown that a $90^\circ$ twist nematic elastomer (TNE) prepared by chiral imprinting exhibits macroscopic deformation when the temperature is varied across the nematic–isotropic transition temperature ($T_{\text{NI}}$). The macroscopic deformation reflects the change in mesogen alignment between the twist nematic and random orientations. The macroscopic deformation is roughly approximated by a uniaxial deformation in a direction at an angle of $45^\circ$ relative to the mesogen orientations at the top and bottom surfaces. The distortion increases with a reduction in temperature, i.e., an increase in orientational order.

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[21] Specimens with a square cross section in the high-temperature isotropic state are more suitable for straightforward demonstration of thermal deformation. However, we were unable to prepare such specimens due to the difficulty involved in cutting the samples at high temperatures above 100 °C.