Soft elasticity and spontaneous shears

in smectic elastomers

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Abstract

Liquid crystals have various phases such as nematic, cholesteric, smectic A, smectic C with combination of the positional and orientational order. Theories about elasticity of different phases are developed intensively as well as study of phase transition. In this termpaper, properties of smectic phases in elastomers and transition from smectic A to smectic C with spontaneous shearing are presented. Experimental results are introduced to be compared with numerical results.

I. Introduction

When shape of liquid crystalline elastomer is changed without energy cost, it is called soft elastic modes [1]. Constant rotation of the distribution of chain shapes with constant entropy and nematic energy with adapting the body shape to the chains cause soft modes [2]. Deviation from ideal symmetry requirements makes semisoft property and this causes quantitatively different soft deformation [3]. Shape is changed with rotating director by soft deformation [1]. Softness is removed after the director is fixed perpendicular to the layer and loses its freedom of mobility. Since the orientation of the polymer shape tensor is not directly related to the constraint on the layer spacing in the SmC phase, additional freedom for softness is appeared in the director. Biaxial SmA has less experimental interest even though it has sufficient freedom and simple phase theoretically. In monodomains of SmA and SmC phases, the required deformation tensor is calculated to provide clear geometrical forms of soft modes in Sec. II.

Since nemaic liquid crystal has orientational order, chain shape can be elongated [4]. Spontaneous mechanical strains that are induced by order change are related to orientation and shape. Temperature and illumination can affect the order, and cause thermal or optical actuation. Spontaneous shape change decides the range of strains over which soft elasticity is occurred and is an essential property to know the anisotropy. In ideal system, shape change can be happened with no energy cost. That is, some elastic moduli are vanished and restoring forces along certain symmetry directions are absent [5]. A director **n** denotes the direction of orientational order of nematic elastomers. If strain is imposed in a plane of direction of director, the soft elasticity is occurred. Since entropy and nematic order is constant, macroscopic shape change is occurred with constant free energy [3,6].

A change of magnitude of the orientational order causes spontaneous shape change in nematic elastomers [4]. However, shape change from the transition SmA to SmC is determined by spontaneous rotations of the director of the imposing nematic order. In the SmA phase, an orientational order is parallel to the layer normal. When the AC transition is started, the director starts to rotate around the layer normal by an angle θ. The angle of molecular tilt is not simply associated with the angle of shear. Analysis from Ref. [7] shows that the tangent of the

spontaneous shear angle is same as the tilt angle times the ratio of two elastic constants for small tilts. However, a nonlinear, Lagrangian elastic analysis shows more complicated connection for the spontaneous shears at and below the SmA-SmC transition [8]. In Sec. III., this connection is investigated up to large tilts in nonlinear regime and elastomers, where layer spacing is strongly constraint and restricts spontaneous deformation, are studied. In Sec. IV., experimental results are compared with numerical results from Sec. III.

II. Smectic A and Smectic C Elastomer Model

The elastomer is composed with polymer chains and an anisotropic Gaussian distribution can express this model [1]. This model assumes that chains are long enough and cross-link matrix is rubbery and extensible. In addition, the presence of layers in smectic phases makes a periodic potential that affects to the cross-link point. Therefore, homogeneous potential of the cross-link point distribution only exists within the plane of the layers. Then shape changes of the rubber matrix induce the alteration of smectic layer spacing and smectic elastomers should have an additional modulus. Smectic elastomers, surprisingly, has rubbery-like behavior in two dimensions and solid-like in the third. When large strains occur to smectic elastomers, they show rotational instabilities. Experiment [10] and theory [9] show good agreement in SmA elastomer.
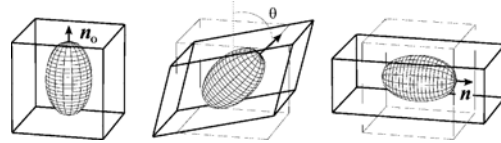

Fig. 1. The initial direction n_0 of chain shape distribution is rotated to a perpendicular n. An intermediate state direction at θ is also shown [1].

It is assumed that a smectic elastomer is composed of cross-linked polymers as microscopic models of nematic elastomers [1]. The layer spacing can be described by

$$\frac{d}{d_0} = \frac{1}{\left| \underline{\underline{\lambda}}^{-T} \cdot k_0 \right|} \quad , \tag{1}$$

where $\underline{\underline{\lambda}}^{-T}$ is the inverse transpose of the deformation matrix, $\mathbf{k}_0$ denotes the initial

direction of the layer normal in the solid, $\mathbf{k}_0 = \mathbf{q}_0/q_0$ ($\mathbf{q}_0$=initial wave vector, q_0= the wave vector magnitude), d is the current layer spacing. The free energy density can be calculated by adding the smectic layer modulus to the rubber-elastic free energy terms.

$$f = \frac{1}{2}\mu Tr\left[\underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}_n^{-1}\right] + \frac{1}{2}B\left(\frac{d}{d_0} - 1\right)^2 \tag{2}$$

Here, B denotes the smectic modulus associated with deforming the layer spacing. In Eq. (2), both terms are positive. The second term should be vanished since energy cost is zero. Therefore, $d=d_0$ and $\underline{\underline{\lambda}}$ obeys following constraint.

$$k_0^T \cdot \underline{\underline{\lambda}}^{-1} \cdot \underline{\underline{\lambda}}^{-T} \cdot k_0 = 1 \tag{3}$$

In general, soft modes of nematic elastomers are expressed by

$$\underline{\underline{\lambda}} = \underline{\underline{\ell}}_n^{1/2} \cdot \underline{\underline{W}} \cdot \underline{\underline{\ell}}_0^{-1/2} \quad , \tag{4}$$

where $\underline{\underline{W}}$ denotes a general rotation matrix, $\underline{\underline{\ell}}_0$ is the initial anisotropic tensor, and $\underline{\underline{\ell}}_n$ is the current anisotropy tensor that is depend on director **n**. If one multiply $\underline{\underline{W}} \cdot \underline{\underline{W}}^T$ from the left, soft mode (4) becomes

$$\underline{\underline{\lambda}} = \underline{\underline{W}} \cdot \underline{\underline{\ell}}_{n'}^{1/2} \cdot \underline{\underline{\ell}}_0^{-1/2} \tag{5}$$

Therefore, one can know that shape change of soft deformation is determined by the particular vector **n'**. The vector **n'** can be chosen anywhere on the surface of unit sphere and the way of soft deformation of smectic phase has less freedom than that of nematic phase because smectic phase has additional constraint of the layer spacing.

By adding a biaxial polymer shape tensor, $\underline{\underline{\ell}}$, biaxial SmA elastomer can be modeled [1].

$$\underline{\underline{\ell}} = \begin{pmatrix} \ell_1 & 0 & 0 \\ 0 & \ell_2 & 0 \\ 0 & 0 & \ell_\parallel \end{pmatrix} \tag{6}$$

Rotation of director is performed through an axis perpendicular to $\mathbf{n}_0$ in the soft mode of Fig. 1. Since the layer normal $\mathbf{k}$ and the director $\mathbf{n}$ is same in SmA elastomer, Eq. (3) becomes

$$n_0^T \cdot \underline{\underline{\lambda}}^{-1} \cdot \underline{\underline{\lambda}}^{-T} \cdot n_0 = 1 \tag{7}$$

Then combination of general soft mode (4) and constraints (7) shows

$$\frac{1}{r} = n_0^T \cdot \underline{\underline{W}}^T \cdot \underline{\underline{\ell}}_n^{-1} \cdot \underline{\underline{W}} \cdot n_0 \quad, \tag{8}$$

where $r = \ell_\parallel / \ell_\perp$. So this equation has solution $\mathbf{n}=\mathbf{n`}=\underline{\underline{W}} \cdot \mathbf{n}_0$ and substituting this

$\underline{\underline{W}}$ to Eq. (4) produces the result $\underline{\underline{\lambda}} = \underline{\underline{W}}$. It means that there is no shape change in the body. Then the primary alignment director has no freedom to rotate and uniaxial SmA elastomer cannot have soft mode. However, biaxial SmA elastomer has unconstraint secondary alignment axes, so it can have soft mode. In conclusion, biaxial SmA elastomer has soft mode that can be decomposed into a body rotation, which means that the primary alignment axis is constraint but the secondary alignment axes can be deformed from their initial orientation.

The main characteristic of SmC elastomers is that the director is biased with respect to the layer normal [1]. Fig. 2 shows schematic diagram of SmC elastomers. A tilt angle θ Is described by

$$n = k \cos\theta + c \sin\theta \tag{9}$$

Fig. 2. The director **n** is biased along the layer normal, **k**, by angle theta in SmC elastomer [1].

Since the SmC phase has two different directions, the polymer shape shows anisotropy. Therefore shape tensor is also biaxial. However, when the biaxial arrangement of a uniaxial $\underline{\underline{\ell}}$ is biased at a certain angle perpendicular to the layer, soft elasticity is already found. At first, to describe general form of soft mode for SmC elastomer, a new vector $\mathbf{w}_0$ is induced.
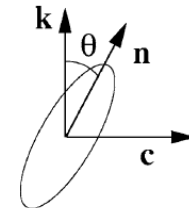
$$w_0 = \underline{\ell}_{=0}^{-1/2} \cdot k_0 = k_0 + \left(\sqrt{r}-1\right)\cos\theta n_0 \tag{10}$$

n_0, **k0**, and w_0 is located in the same plane and w_0 is located between n_0 and k_0 when r >1. If one use w_0 into the general soft mode (4) with Eq. (3), one obtains

$$w_0^T \cdot \underline{\underline{W}}^T \cdot \underline{\ell}_{=n}^{-1} \cdot \underline{\underline{W}} \cdot w_0 = 1 \tag{11}$$

Using $w_0^2 = 1+(r-1)\cos\theta$, the equation of two planes where the point of the director **n** is located can be expressed by

$$\left(\underline{\underline{W}} \cdot w_0\right)^T \cdot n = \pm\sqrt{r}\cos\theta \tag{12}$$

Therefore, they are located at distance $\pm 1/(1+1/r\tan^2\theta)^{1/2}$ from the origin and have vectors perpendicular to the $\underline{\underline{W}} \cdot w_0$ direction. The transformed layer wave vector $q = \underline{\underline{\lambda}}^{-T} \cdot q_0$ is normalized and

$$k = \frac{\underline{\underline{\lambda}}^{-T} \cdot k_0}{\left|\underline{\underline{\lambda}}^{-T} \cdot k_0\right|} \rightarrow \underline{\underline{\lambda}}^{-T} \cdot k_0 \tag{12}$$

When d/d₀=1, Eq. (3) is satisfied equally. But in case of a specific soft deformation, a particular $\underline{\underline{W}}$ in Eq. (4) should be chosen. At first, soft modes are analyzed without $\underline{\underline{W}}$ and then modes that include $\underline{\underline{W}}$ are studied following part.
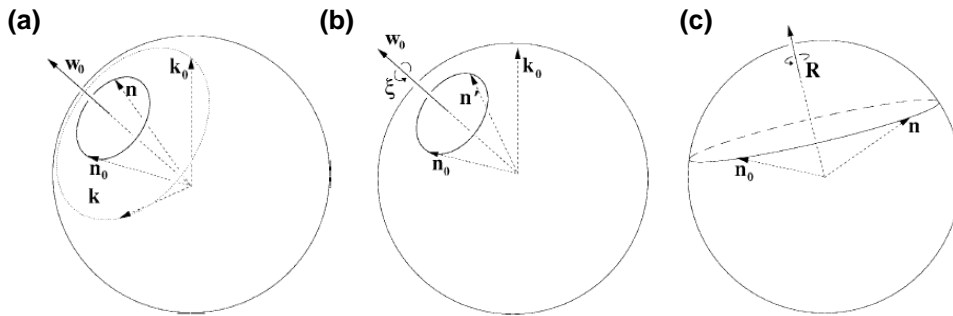

Fig. 3. (a) An illustration of soft mode of SmC elastomer without $\underline{\underline{W}}$ [1].

(b) The first stage of a general soft mode: rotating the initial director n_0 around to **n** [1].

(c) The second stage of a soft mode: rotating with respect to the axis **R** [1].

Soft modes of a SmC elastomer without $\underline{\underline{W}}$ matrix indicate that the final director should be located on the intersection of the unit sphere and the planes of Eq. (12) [1]. Fig. 3(a) shows an illustration of this. If the final orientation of director **n** does not lie on the circle of solid line in Fig. 3(a), a proper $\underline{\underline{W}}$ should be included. From Eq. (5), we can replace **n** to **n`** and Fig. 3(b) shows a director **n'**. A matrix $\underline{\underline{W}}$ can be decomposed by two rotations, $\underline{\underline{W}} = \underline{\underline{W}}_R \cdot \underline{\underline{W}}_{w_0}(\xi)$ where the latter is a rotation by ξ about **w**$_0$ and takes **n`** to **n**$_0$, and $\underline{\underline{W}}_R$ takes **n**$_0$ to **n**. Then,

$$\underline{\underline{\lambda}} = \underline{\underline{W}}_R \cdot \underline{\underline{W}}_{w_0}(\xi) \cdot \underline{\underline{\ell}}_{n'}^{1/2} \cdot \underline{\underline{\ell}}_0^{1/2} \tag{13}$$

In this equation, soft mode is parameterized by the angle ξ and final director is determined by **n**=$\underline{\underline{W}}_R \cdot$ **n**$_0$. As one can see Fig. 3(c), final director is not limited to the circle.

III. Spontaneous deformations on SmA to SmC Transitions

Monodomain samples are needed to get spontaneous distortions that are induced by order change caused thermally [4]. If chains are cross-linked in nematical order or surface alignment in thin samples is exploited, one can have nematic monodomain elastomers. However, Finkelmann [12]'s method is widely used. At first, sample is partially cross-linked therefore it shows enough rigidity to hold. When it is stretched uniaxially, cross-linking
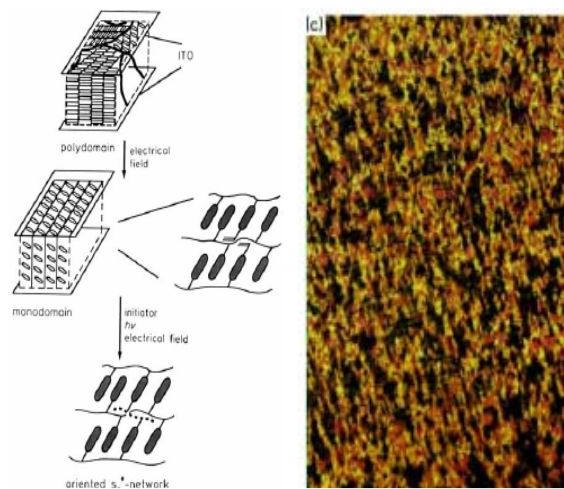

Fig. 4, Schematic diagram for preparation of smectic monodomain and optical micrograph of elastomer [11].

is completed. Then it is released to have a new stress-free, equilibrium state. This state can be a standard state for the measurement of any strains due to temperature change. Applied stresses should change this equilibrium state. The fraction ξ of chains are linked in the first stage and they are under tension. Although previous state tend to contract, the fraction (1- ξ) linked in the second stage do not want to contract. Since it makes them to extent in the plane normal to the stretch direction, their energy would be increased. Actually, these residual strains are almost same as the fraction (1- ξ) of the second stage linkage strain. The deformation gradient is $\underline{\underline{\lambda}} = \partial X / \partial X_0$, where **X** is the current position(in the target space) and **X**$_0$ is original position(in the reference space). In the case of uniform distortion, the diagonal elements of $\underline{\underline{\lambda}}$ indicate the ratio of a current dimension to the imposing original dimension. The off-diagonal elements are described by simple shears. The deformation gradient $\underline{\underline{\lambda}}_1$ is applied after the first step and this is a simple, constant volume, and layer-preserving shear.

$$\underline{\underline{\lambda}}_1 = \underline{\underline{\delta}} + \lambda_1 mn_0 \rightarrow \begin{pmatrix} 1 & 0 & \lambda_1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{13}$$

Here, $\underline{\underline{\delta}}$ denotes unit tensor, **m** is the direction in the smectic planes of displacement in the shear, and **n**$_0$ is the initial director which is parallel to the layer since we start in the SmA phase. From Ref. [13], free energy density for isotropic rubber of multistage linking is

$$f = \frac{1}{2} \mu Tr \left[\underline{\underline{A}} \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}_n^{-1} \cdot \underline{\underline{\lambda}} \right] \tag{14}$$

Here $\underline{\underline{\lambda}}$ denotes the total deformation and $\underline{\underline{A}}$ is the composite second-rank tensor. Deformation connecting the initial state and relaxed state is denoted $\underline{\underline{\lambda}}^r$. Deformation related with relaxed shape is $\underline{\underline{\lambda}}'$. Therefore,

$$\underset{=}{\lambda} = \underset{=}{\lambda}' \cdot \underset{=}{\lambda}^r \tag{15}$$

Using (15) to Eq. (14),

$$f = \frac{1}{2} \mu Tr \left[(\underset{=}{\lambda}^r \cdot \underset{=}{A} \cdot \underset{=}{\lambda}^{rT}) \cdot \underset{=}{\lambda}^{'T} \cdot \underset{=}{\ell}_n^{-1} \cdot \underset{=}{\lambda}' \right]$$
$$= \frac{1}{2} \mu Tr \left[\underset{=}{\ell}_r \cdot \underset{=}{\lambda}^{'T} \cdot \underset{=}{\ell}_n^{-1} \cdot \underset{=}{\lambda}' \right] \tag{16}$$

A shear deformation $\underset{=}{\lambda}_1$ occurred in second stage cross-linking indicates that a sample cannot have its original shape again, but retains a residual deformation $\underset{=}{\lambda}^r$ [4]. For small shears, extensions and contractions that are projected into the layer planes are same. So nothing is happened. However, for large shears, the extension diagonal lies on close to the layer plane and the system tends to contact with the in-plane direction when released. The value of λ_1^2 determines the magnitude of contraction.
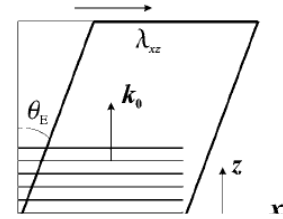

Fig. 5. Bold shape represents SmA elastomer with λ_{xz} shear and faint line represents initial shape [4].

Since layer spacing is constant, xx is the only possible contraction reaction. The final relaxed shear λ^r_{xz} is less than λ_1 because of this contraction. The director is parallel to the layer in the SmA phase. This director is evenly anchored to the equilibrium rotate angle and can be endured with other mechanical pressure. With the deformation gradient $\underset{=}{\lambda}'$, of the relaxed SmA state, the free-energy density becomes

$$f = \frac{1}{2}\mu \left(\begin{array}{l} 1 + (r-1)\sin^2\theta - 2(r-1)\lambda'_{xz}\sin\theta\cos\theta + {\lambda'_{xz}}^2 \left[r - (r-1)\sin^2\theta \right] \\ + \sqrt{1 + \gamma\lambda_1^2} \left[\frac{{\lambda'_{xx}}^2}{r} \left[r - (r-1)\sin^2\theta \right] + \frac{1}{{\lambda'_{xx}}^2} \right] \end{array} \right) \tag{17}$$

To minimize free energy, one can get following relations.

$$\lambda'_{xz} = (r-1)\sin\theta\cos\theta / \left[r - (r-1)\sin^2\theta \right] \tag{18}$$

$$\lambda'_{xx} = r^{1/4} / \left[r - (r-1)\sin^2\theta\right]^{1/4} > 1 \tag{19}$$

Substituting these deformations to the free energy, one can get free energy induced by rotating the director:

$$f = \frac{1}{2}\mu\left(\frac{r}{r-(r-1)\sin^2\theta} + 2\frac{\sqrt{1+\gamma\lambda_1^2}}{r^{1/2}}\left[r-(r-1)\sin^2\theta\right]^{1/2}\right) \tag{20}$$

Nonideality is appeared when compositional fluctuation and rigid rod cross-links are combined to ideal model [4]. This is called semisoft. It seems that nonideality has no large effect and it is indicated by the degree of semisoftness, α. Then free energy for nonideal soft elasticity becomes

$$f_\alpha = \frac{1}{2}\mu\alpha Tr\left[\underline{\underline{B}} \cdot \underline{\underline{\lambda}}^T \cdot ss \cdot \underline{\underline{\lambda}}\right]$$

$$\underline{\underline{B}} = \xi n_0 n_0 + (1-\xi)\underline{\underline{\lambda}}_1^{-1} \cdot n_0 n_0 \cdot \underline{\underline{\lambda}}_1^{-T} \rightarrow \begin{pmatrix} (1-\xi)\lambda_1^2 & 0 & -(1-\xi)\lambda_1 \\ 0 & 0 & 0 \\ -(1-\xi)\lambda_1 & 0 & 1 \end{pmatrix} \tag{21}$$

The relaxation due to cross-linking and that created by increasing tilt on cooling in the SmC phase are presented here [4]. Fig. 6(a) shows in-plane elongation of SmC elastomers by biased angle θ on cooling. Same shear, λ_1=0.3 at second stage linking, is used for both systems r=2.5 and r=4.5. Nonideality fraction α=0.3 and a first linkage fraction ξ=0.5 are used in this calculation. Fig. 6(b) shows simple shear caused by the director tilt. These results are also observed by experiments [14]. It is predicted that shear approaches its maximum with increasing tilt angle. The angle of shear distortion, θ_E, recorded after relaxation on second linkage is shown in Fig. 6(c). Same cross-linking shear is imposed for each pair of curves. The dashed line means how mechanical and molecular tilts diverge from each other because of cross-linking. For large tilt one can see that the slope $d\theta_E/d\theta_X$ shows lower than 1/2. These results are identically reproduced by experiment [14].
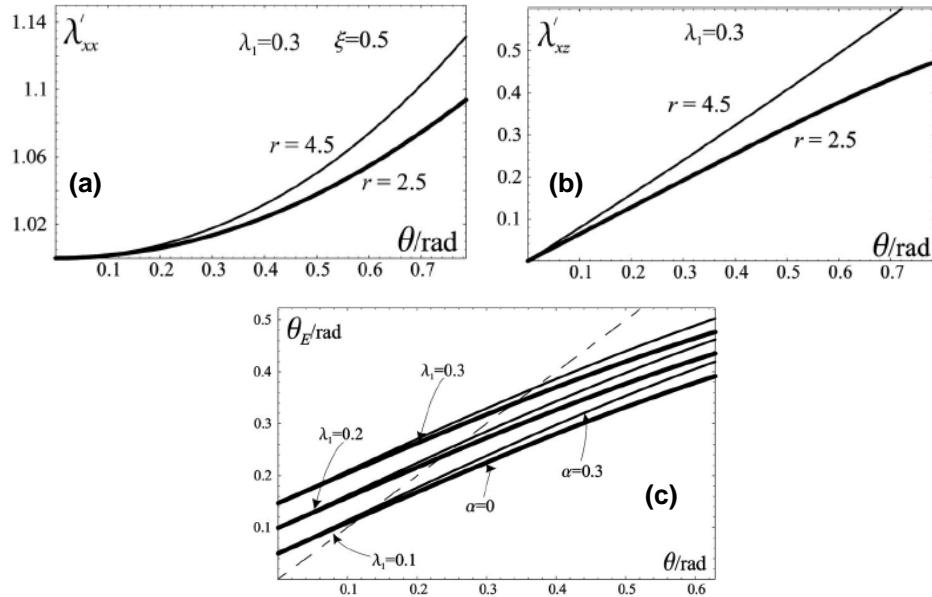
Fig. 6. (a) In-plane elongation caused by tilt θ on cooling into the SmC phase [4].

(b) Simple shear induced by tilt θ on cooling into the SmC phase [4].

(c) Shear angle θ_E of SmC against director tilt θ [4].

IV. Experimental Results

The deformation of chiral smectic C (SmC*) elastomers are not studied well yet [14]. The monodomain SmC* elastomer produced by a mechanical shear field shows a biaxial shape memory effect. This means that by heating and cooling process during phase transitions spontaneous and reversible

Fig. 7. Schematic model shows relation between macroscopic shape of elastomer and molecular realignment [14].

deformation is occurred. Shear deformation related with molecular tilting in the smectic phases is observed in this section. Using X-ray scattering observation, the
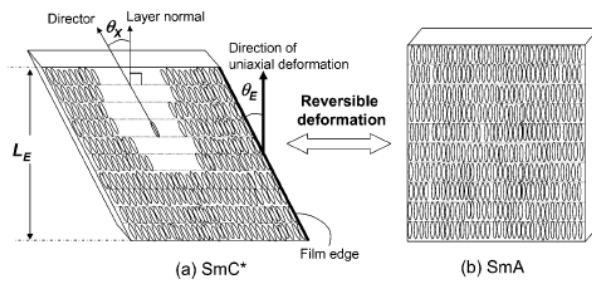
fundamental of the spontaneous and reversible deformations of the SmC* elastomers are studied. For monodomain SmC* elastomer, the shape of the elastomer film determines the macroscopic symmetry and the X-ray scattering shows that this symmetry matches to the local symmetry induced by molecular alignment.
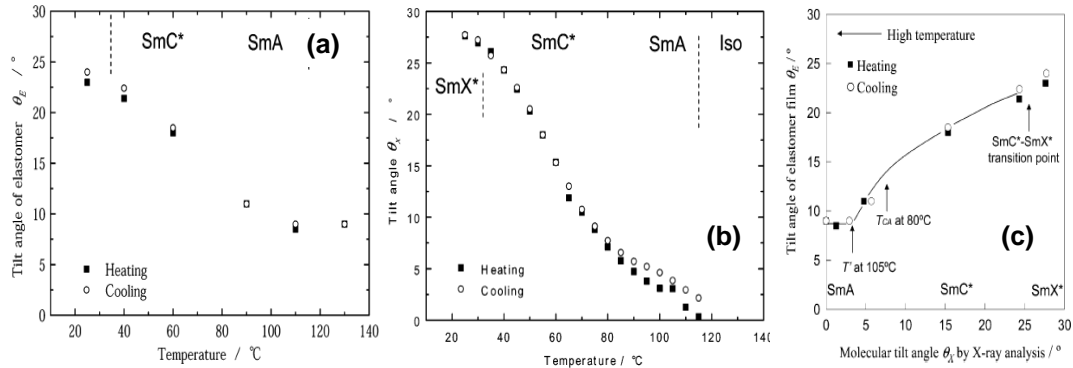

Fig.8. (a) The tilt angle θ_E is plotted as a function of temperature [14].

(b) The molecular tilt angle θ_X measured by X-ray scattering is plotted as a function of temperature [14].

(c) Nonlinear relation between the molecular tilt angle θ_X and tilt angle θ_E of elastomer film [14].

The distance between polyimide tapes is symbolized as the sample length L_E and angle between the edge of the film and the direction of the first uniaxial deformation is denoted by tilt angle θ_E [14]. Fig. 8(a) shows the behavior of tilt angle of elastomer as a function of temperature. Tilt angle at around 40℃ decreases as temperature increases during SmC*-SmA transition and tilt angle is around 10° in the SmA phase. In the reverse order, tilt angle shows same value as heating process and it gets initial condition again. It seems that SmC* elastomer can restore its shape spontaneously. Furthermore, this shape memory effect is a biaxial deformation procedure caused by the spontaneous shear deformation. For the next step, X-ray scattering is performed to find out the relation between macroscopic shape changes and molecular re-alignment process. The behavior of molecular tilt angle θ_X with respect to various temperatures is in Fig. 8(b). At room temperature (25℃) the tilt angle is about 25° and it decreases quickly as temperature increases in the SmC* and SmA phases. This curve shows same manner as the tilt angle of elastomer film θ_E. Therefore, the shape of elastomer film

is closely related to local symmetry of elastomer. It also shows same behavior that tilt angle on cooling process is very similar with that on heating process. Fig. 8(c) shows change of θ_E as a function of θ_X. In this figure, nonlinear relation between θ_E and θ_X can be observed. According to their hypothesis, emergent of nonlinearity is not because of mesogens but because of the topology of cross linkers. The slope of curve is steep in the temperature region between T` and T_{CA}. In this region, topology of cross links causes internal shear stress and retains the layer tilting despite the constant layer thickness. Therefore, it turns out that cross linkers dominate the tilting condition due to constant tilt angle of mesogens. The deformation of cross linkers causes the shape change because cross linkers make polymer networks to form sample shape. Meanwhile, the slope becomes slow in region less than T_{CA}. In this region, number of mesogens almost eight times larger than number of cross linkers, so mesogens start to dominate deformation with a decreasing layer thickness.

V. Conclusions

A geometrical analysis of the soft modes for two phases of smectic elastomers have introduced in this paper [1]. The director has only one soft trajectory as a result of limitation of fixed layer. Monodomains of SmA and SmC were studied to understand soft modes. The two-step cross-linking of smectic elastomers with shearing have also modeled [4]. When thermal transition between SmA and SmC is occurred, smectic elastomer shows spontaneous elastic shear deformation. If shears are large, nonideal theories should be included. Lagrangian elasticity models can explain nonlinearity of soft elasticity [8]. A molecular-based model which can also show theoretical evidence for nonlinearity have introduced in this paper. Experimental results [14] have compared with numerical results [4] and they made good agreement.

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