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Isotropic to smectic-C phase transition in liquid-crystalline elastomers

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A phenomenological model is developed to describe the isotropic-smectic-C phase transition in liquid-crystalline side-chain elastomers. We analyze the influence of external mechanical stress on the isotropic-smectic-C phase transition. While this phase transition is first order in low-molecular-weight materials, we show here that the order of this transition does not change in liquid-crystalline elastomers. The temperature dependence of the heat capacity and the nonlinear dielectric effect in the isotropic phase above the isotropic-smectic-C phase transition in liquid crystalline elastomers are calculated. The theoretical results are found to be in good agreement with experiment.

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I. INTRODUCTION

Over the last few decades liquid-crystalline side-chain elastomers and polymer have attracted increasing attention because of their interesting optical, mechanical, and ferroelectric properties that are potentially useful for applications. Liquid-crystalline elastomers (LCEs) are rather different from low molecular weight materials in that they couple easily to external mechanical forces. Their coupling to electric fields is small or substantial. Their coupling to magnetic fields is almost zero. Thus the mechanical effects in LCEs are dominant. They show no defects in the monodomain liquid-crystalline elastomers order over macroscopic areas and can be thought of as analog of single crystals in solid state physics. The main source of defects in LCEs is the network crosslinks themselves, which are quenched in the network during the synthesis and are not able to relax and annealed very quickly. In nematic polymers the annealing of the defects will be affected by a much higher viscosity and, indeed, one may expect a very slow dynamics of relaxation. Thus such defects exist in the case of polydomain nematic elastomers since they are turbid just like a low molecular weight nematic that is not oriented.

Although the isotropic-nematic (I-N) and isotropic-smectic-A (I-SmA) phase transitions in side-chain polydomain or monodomain elastomers have been a topic active theoretical and experimental studies,^{1–21} reports on the isotropic-smectic-C (I-SmC) phase transition in LCEs are comparatively scarce. It is the goal of this paper to investigate the I-SmC phase transition in LCEs, which has been studied experimentally,^{22–24} but theoretically not at all. Sanchez-Ferrer *et al.*²² reported the synthesis of the SmC LCEs. With these novel materials a conical orientation distribution of the layer normal with respect to the director was deduced by x-ray scattering, which undergo the direct I-SmC phase transition. The I-SmC phase transition is found to be more strongly first order both for low molecular weight SmC materials^{25–28} and SmC elastomers.^{22–24} Recently published x-ray data have shown a direct I-SmC transition for SmC

elastomers.^{22,23} Cordoyiannis *et al.*²⁴ measured the temperature dependence of the heat capacity for conically distributed polydomain liquid-crystalline elastomers MCEB7Azo2-2.5 and MCEB7-10.0 both above and below the phases of the I-SmC phase transition. The analysis of the temperature dependence of the heat capacity reveals an appreciable anomalous component. The obtained heat capacity anomalies unambiguously reveal the first-order nature of I-SmC phase transition even for high cross-linking concentrations.

There is practically no theoretical work on the I-SmC phase transition in side-chain liquid-crystalline elastomers although some theoretical studies^{29–32} on low molecular weight SmC materials are available in the literature. The purpose of the present paper is to examine the nature of and the factors governing the I-SmC phase transition in LCEs within a phenomenological theory. The temperature dependence of the anomalous heat capacity is calculated in the isotropic phase of the I-SmC transition within the framework of Landau's fluctuation theory. The temperature dependence nonlinear dielectric effect in the isotropic phase above the I-SmC phase transition is calculated.

II. THEORY

A. Order parameter

The nematic order parameter originally proposed by de Gennes³³ is a symmetric, traceless second rank tensor. The layering in the SmA and SmC phases is described³³ by the order parameter $\psi(\mathbf{r}) = \psi_0 \exp(-i\Phi)$, whose modulus ψ_0 is defined as the amplitude of a one-dimensional density wave characterized by the phase Φ . The wave vector $\nabla_i \Phi$ is parallel to the director n_i in the smectic A phase. The layer spacing is given by $d = 2\pi/q_0$ with a nonzero $q_0 = |\nabla \Phi|$. The SmC order parameter has two degrees of freedom: tilt angle (magnitude) and azimuthal direction (phase). The tilt angle in the SmC phase is described by the orientational order parameter.^{30,35} Smectic-C liquid crystals are generally biaxial due to the tilt of the nematic preferred direction n_i away from the layer normal $q_0^{-1} \nabla_i \Phi$. The biaxiality is rather small and often neglected. Following,³⁰ we define the orientational

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order parameter in the SmC phase as

$$Q_{ij} = \frac{S}{2}(3n_i n_j - \delta_{ij}), \quad (2.1)$$

where n_i is *not* parallel to $\nabla_i \Phi$. The quantity S defines the strength of the nematic ordering. We assume flat layers in the smectic phases and take the layer normal $q_0^{-1} \nabla_i \Phi = \delta_{iz}$ as the z-axis. Then n_i is defined by

$$n_i = \delta_{iz} \cos \theta + \delta_{ix} \sin \theta, \quad (2.2)$$

where x is an arbitrary axis perpendicular to the layer normal and where θ is the angle between the layer normal and the nematic director n_i . Thus the tilt angle in the SmC phase is completely determined by the nematic order parameter.

B. The free energy

We now turn to the construction of the free energy for the I-SmC phase transition in liquid-crystalline elastomers. The first order nature of the I-SmC transition in low molecular weight liquid crystals is characterized by a density jump $(\Delta \rho / \rho)_{I-SmC} = 1.21 \times 10^{-2}$ in TB14A.²⁶ On the other hand the sharp peak of the heat capacity data indicates the first order nature of I-SmC transition in LCEs. Thus in a broad sense the Landau-de Gennes model is still valid for the I-SmC transition in LCEs. The Landau theory of phase transitions in the isotropic to the smectic mesophase transitions has been proved to be very rich in making qualitative predictions. Here we use the Landau theory for a homogeneous elastomer. The free energy can be expanded in terms of the order parameters Q_{ij} and ψ and the strain ϵ relative to the high-temperature relaxed state. Keeping terms of the quadratic order, we obtain for the generalized Ginzburg-Landau energy³⁰

$$\begin{aligned} F = F_0 &+ \frac{1}{3}a Q_{ij} Q_{ij} - \frac{4}{9}b Q_{ij} Q_{jk} Q_{ki} + \frac{1}{9}c_1 (Q_{ij} Q_{ij})^2 \\ &+ \frac{1}{9}c_2 Q_{ij} Q_{jk} Q_{kl} Q_{li} + \frac{1}{2}\alpha_1 |\psi|^2 + \frac{1}{4}\beta |\psi|^4 \\ &+ \frac{1}{3}\delta Q_{ij} Q_{ij} |\psi|^2 + \frac{1}{2}d_1 |\nabla_i \psi|^2 + \frac{1}{2}d_2 |\Delta \psi|^2 \\ &+ e Q_{ij} (\nabla_i \psi) (\nabla_j \psi^*) + 2h Q_{ij} Q_{kl} (\nabla_i \nabla_j \psi) (\nabla_k \nabla_l \psi^*) \\ &+ \frac{1}{2}u_{ijkl} \epsilon_{ij} \epsilon_{kl} + \frac{1}{3}v_{ijklmn} \epsilon_{ij} \epsilon_{kl} \epsilon_{mn} + \frac{1}{4}w_{ijklmnop} \epsilon_{ij} \epsilon_{kl} \epsilon_{mn} \epsilon_{op} \\ &- \gamma' \epsilon_{ij} Q_{ij} + \frac{2}{3}\lambda Q_{ij} Q_{ij} \epsilon_{ij} - \eta \epsilon_{ii} |\psi|^2 - \sigma_{ij} \epsilon_{ij}. \end{aligned} \quad (2.3)$$

F_0 is the free energy of the isotropic phase. As usual in Landau theory we assume $a = a_0(T - T_1^*)$ and $\alpha_1 = \alpha_0(T - T_2^*)$. T_1^* and T_2^* are the virtual transition temperatures. Other material parameters are assumed to be constants. The isotropic gradient terms in (2.3) guarantee a finite wavelength q_0 for the smectic density wave. The gradient terms $\sim e$ and $\sim h$ involving Q_{ij} govern the relative direction of the layering with respect to the director and lead to the tilt angle of the SmC phase. The isotropic gradient term d_1 can be positive or negative. We assume $d_1 < 0$ and $d_2 > 0$. The negative values of δ and e favors the SmA and SmC phases. We assume $h > 0$. The presence of the cubic term b and the coupling terms δ and e describes the first order character of

the SmA-SmC phase transition. The cross-coupling terms γ' , λ , and η are characterizing the coupling of the nematic and smectic order parameters to the strain tensor ϵ . σ is the effective stress acting on the elastomer, which is a combination of the applied stress and the internal stress due to anisotropic cross-linking. Thus the last term in the free energy (2.3) describes the effect of the external mechanical stress. For an isotropic medium u_{ijkl} has two independent coefficients, for example, called compressibility and shear modulus.

We consider the phases in which the nematic and smectic order are spatially homogeneous, i.e., $S = \text{const.}$ and $\psi_0 = \text{const.}$ We also consider purely dilatational deformations. It is also instructive to study the lowest order contribution of ϵ in Eq. (2.3) neglecting the cubic and quartic terms of ϵ . This is only justified as long as the applied stresses are small. The influence of such higher order terms was studied extensively by Menzel *et al.*¹⁰ In the context of phase transitions involving LCEs this issue has been discussed first by Brand.³⁴

The substitution the values of Q_{ij} and ψ in Eq. (2.3) leads to the free energy density expansion

$$\begin{aligned} F = F_0 &+ \frac{1}{2}a S^2 - \frac{1}{3}b S^3 + \frac{1}{4}c S^4 + \frac{1}{2}\alpha_1 \psi_0^2 + \frac{1}{4}\beta \psi_0^4 + \frac{1}{2}\delta \psi_0^2 S \\ &+ \frac{1}{2}\gamma' S^2 \psi_0^2 + \frac{1}{2}d_1 \psi_0^2 q_0^2 + \frac{1}{2}d_2 \psi_0^2 q_0^4 \\ &+ \frac{1}{2}e \psi_0^2 S q_0^2 (3\cos^2 \theta - 1) + \frac{1}{2}h \psi_0^2 S^2 q_0^4 (3\cos^2 \theta - 1)^2 \\ &+ \frac{1}{2}u \epsilon^2 - \gamma' \epsilon S + \lambda S^2 \epsilon - \eta \psi_0^2 \epsilon - \sigma \epsilon, \end{aligned} \quad (2.4)$$

where $c = c_1 + c_2/2$. The elimination of the equilibrium values of ψ_0 , q_0 and θ from Eq. (2.4), leads to the free energy density as a function of S and ϵ can be written as

$$\begin{aligned} F = F_0^* &+ \frac{1}{2}a^* S^2 - \frac{1}{3}b S^3 + \frac{1}{4}c^* S^4 + \frac{1}{2}u^* \epsilon^2 \\ &- \gamma' \epsilon S + \lambda^* S^2 \epsilon - \sigma^* \epsilon, \end{aligned} \quad (2.5)$$

where

$$\begin{aligned} F_0^* &= F_0 - \frac{\alpha_1^2}{4\beta}, \\ a^* &= a - \frac{\delta \alpha_1}{\beta}, \\ c^* &= c - \frac{\delta^2}{\beta}, \\ u^* &= u - \frac{3\eta^2}{2\beta}, \\ \lambda^* &= \lambda + \frac{\delta \eta}{\beta}, \\ \sigma^* &= \sigma - \frac{\eta \alpha_1}{\beta}, \\ \alpha_1^* &= \alpha_1 - \frac{d_1^2}{4d_2} - \frac{e^2}{4h}. \end{aligned}$$

The tilt angle θ in the SmC phase can be expressed as

$$\sin^2 \theta = \frac{2(S - S_0)}{3S} \quad (2.6)$$

where $S_0 = ed_2/2d_1h$. The temperature dependence of the orientational order parameter S in the SmC phase can be calculated from Eq. (2.5).

In the derivation of Eq. (2.5) with respect to strain, we find

$$\epsilon = \frac{\sigma^* + \gamma' S - \lambda^* S^2}{u^*}. \quad (2.7)$$

Equation (2.7) shows the strain changes with temperature since S changes with temperature. Elimination of ϵ in the free energy expansion (2.5) yields

$$F = F_0^{**} - \frac{\gamma' \sigma^*}{u^*} S + \frac{1}{2} a^{**} S^2 - \frac{1}{3} b^{**} S^3 + \frac{1}{4} c^{**} S^4, \quad (2.8)$$

where

$$\begin{aligned} F_0^{**} &= F_0^* - \frac{\sigma^{*2}}{2u^*}, \\ a^{**} &= a^* - \frac{\gamma'^2}{u^*} + \frac{2\lambda^*}{u^*} \sigma^*, \\ b^{**} &= b - \frac{3\gamma'\lambda^*}{u^*}, \\ c^{**} &= c^* - \frac{2\lambda^{*2}}{u^*}. \end{aligned}$$

By inspection of Eq. (2.8), it is evident that the influence of the external mechanical stress on SmC liquid crystals in LCEs results in two main effects. First, the mechanical stress produces a shift of the transition temperature T_{I-SmC}^* which is proportional to the mechanical stress

$$\Delta T_{I-SmC}^*(\sigma) = m\sigma \quad (2.9)$$

with $m = \frac{2\lambda^*}{a_0^* u^*}$ and $a_0^* = a_0 - \frac{\delta \alpha_0}{\beta}$. So the I-SmC transition line further shifts to the right side of the coordinate a in the $a - \alpha$ plane. The striction couplings renormalized the Landau coefficients. Thus one expect anomalously small value of the cubic coefficient b . The quantitative determination of b^{**} will reflect how strongly the first order character of the I-SmC transition. This result indicates that it is the strong coupling between the order parameters and the strain which induces a first order character of the I-SmC transition in liquid-crystalline elastomers. Second, the mechanical stress induces weak orientational ordering in the isotropic phase. The orientational order induced by a mechanical stress in the isotropic phase is calculated to a first approximation ($b^{**} = 0$, $c^{**} = 0$) from Eq. (2.8) and can be expressed as

$$S(\sigma) = \frac{\gamma' \sigma}{a_0^* u^* (T - T^*)}, \quad (2.10)$$

where

$$T^* = (1/a_0^*) \left[a_0 T_1^* - \frac{(\delta + \frac{2\lambda^* \gamma}{u^*})}{\beta} \left(\alpha_0 T_2^* + \frac{d_1^2}{4d_2} + \frac{e^2}{4h} \right) + \frac{\gamma'^2}{u^*} \right].$$

The first order I-SmC transition temperature in LCEs can be calculated from the implicit equation

$$g_1 f_2 + g_2 (f_1^2 - g_1 k_1)^{1/2} = g_2 k_1 + g_1 (f_2^2 - g_2 k_2)^{1/2}, \quad (2.11)$$

where

$$\begin{aligned} g_1 &= (16/3) [-3a^{**} c^{**} + b^{**2}], \\ f_1 &= -(4/3) [2a^{**} b^{**} - 18\sigma^* c^{**} \gamma'/(1/u^*)], \\ k_1 &= (16\sigma^*/3u^*) [12\sigma^* + \gamma' b^{**}], \end{aligned}$$

$$\begin{aligned} g_2 &= (4/9) [36\sigma^* c^{**} + \gamma' b^{**}], \\ f_2 &= -2[a^{**} \gamma' + 4\sigma^* b^{**}], \\ k_2 &= 4\sigma^* [4a^{**} + (3\gamma'^2/u^*)]. \end{aligned}$$

The I-SmC transition temperature for a low molecular weight liquid crystals can be expressed as

$$\begin{aligned} T'_{I-SmC} &= \left(1 - \frac{\delta_0}{\delta} \right)^{-1} \left[T_2^* + \frac{d_1^2}{4\alpha_0 d_2} + \frac{e^2}{4\alpha_0 h} \right. \\ &\quad \left. - \frac{\delta_0}{\delta} \left(T_1^* + \frac{2b^2}{9\alpha_0 c^*} \right) \right] \end{aligned} \quad (2.12)$$

with $\delta_0 = a_0 \beta / \alpha_0$. Inspecting Eqs. (2.11) and (2.12) we see that two expressions differ by the term σ^* and the renormalized coefficients b^{**} and c^{**} . These terms in Eq. (2.11) appear due to the strong coupling between the order parameter S and elastic strain ϵ . However, since the Eq. (2.11) is not a definite form, we can not proceed further on this issue. The quantitative estimation of the discontinuity of the I-SmC transition in LCEs is not possible due to the lack of experimental data.

Now the free energy density (2.8) associated with the long wavelength part of the orientational order parameter fluctuation in the isotropic phase can be expressed as

$$\begin{aligned} F &= F_0^{**} - \frac{\gamma' \sigma^*}{u^*} S(\mathbf{r}) + \frac{1}{2} a^{**} S^2(\mathbf{r}) - \frac{1}{3} b^{**} S^3(\mathbf{r}) \\ &\quad + \frac{1}{4} c^{**} S^4(\mathbf{r}) + \frac{1}{2} D [\nabla S(\mathbf{r})]^2. \end{aligned} \quad (2.13)$$

Here D is the stiffness constant of the degree of order S .

Applying the same method as adopted by Mukherjee,³⁵ the excess heat capacity in the isotropic phase above the I-SmC transition due to the fluctuation in the Gaussian model ($b^{**} = 0$, $c^{**} = 0$) with zero mechanical stress ($\sigma = 0$) is given by

$$\Delta C_P(T) = C_1 T^2 (T - T^*)^{-1/2}, \quad (2.14)$$

where $C_1 = \frac{k_B}{16\pi} (a_0^*/D)^{3/2}$.

Equation (2.14) shows that the heat capacity strongly depends on the behavior of the shear modulus. Thus the anomalous behavior of the heat capacity above the I-SmC transition temperature in LCEs occurs due to the anomalous behavior of the shear modulus.

III. NONLINEAR DIELECTRIC EFFECT

We will now calculate the temperature dependence of the nonlinear dielectric effect (NDE) in the isotropic phase above the I-SmC transition in LCEs. Generally only swollen nematic elastomers show a considerable director reorientation at reasonably low electric field.³⁶ Menzel *et al.*³⁶ showed that fine-tuned prestretching of nematic elastomers may allow a considerable electric field induced director reorientation and resulting elastic deformations. For the determination of the NDE in the isotropic phase above the I-SmC transition in LCEs, we consider a prestretching of SmC elastomers. The NDE denotes the change in the dielectric permittivity of a material that originates from the application of strong static electric field E . The NDE is widely analogous to the electro-optic Kerr effect which applies to the case of optical

frequencies.^{37–39} The transition from the isotropic to SmC phase is associated with a pronounced pretransitional NDE since the aligning electric field E couples to the critical fluctuations. Then in the presence of a static electric field E the free energy density (2.8) can be written as

$$F = F_0^{**} - \frac{\gamma' \sigma^*}{u^*} S + \frac{1}{2} a^{**} S^2 - \frac{1}{3} b^{**} S^3 + \frac{1}{4} c^{**} S^4 - \frac{1}{3} \varepsilon_0 \Delta \varepsilon_0 E^2 S, \quad (3.1)$$

where ε_0 is the vacuum permittivity and $\Delta \varepsilon_0$ is the anisotropy of the dielectric permittivity. The order parameter induced by an electric field in the isotropic phase is calculated to a first approximation ($b^{**} = 0$, $c^{**} = 0$) with zero mechanical stress ($\sigma = 0$) and can be expressed as

$$S(E) = \frac{1}{3} \frac{\varepsilon_0 \Delta \varepsilon_0 E^2}{a^{**}}. \quad (3.2)$$

The dielectric permittivity in the isotropic phase is written as

$$\Delta \varepsilon(E) = \varepsilon(E) - \varepsilon(0) = \Delta \varepsilon_0 S(E), \quad (3.3)$$

where $\varepsilon(E)$ and $\varepsilon(0)$ are the dielectric permittivities observed with and without the strong static aligning field $E \gg 0$. Combining Eqs. (3.2) and (3.3), we find

$$\varepsilon_{NDE} = \frac{\varepsilon(E) - \varepsilon(0)}{E^2} = \frac{M}{T - T^*}, \quad (3.4)$$

where $M = \frac{\varepsilon_0 \Delta \varepsilon_0^2}{3a_0^2}$.

IV. COMPARISON WITH EXPERIMENT

The temperature dependence of the heat capacity in the isotropic phase of the I-SmC transition of liquid-crystalline elastomers was reported by Cordoyiannis *et al.*²⁴ As can be observed from the Fig. 2 of Cordoyiannis *et al.*,²⁴ the normal heat capacity is much higher than anomalous contribution. The strong large magnitude of the normal component relative to the anomalous contribution renders it progressively more difficult to separate out the anomalous part as one gets further away from the transition temperature. We have therefore fitted Eq. (2.14), plus a normal component C_0 representing the normal component, to the measured data over a restricted temperature range above the I-SmC transition using C_0 , C_1 , and T^* as fit parameters. $C_0 = 1.94 \text{ J K}^{-1} \text{ g}^{-1}$ was selected for the good fit. The fit (line) and the measured data (filled circle) are shown in Fig. 1. As can be observed, the agreement of the measured data with functional form of the heat capacity (2.14) predicted by theory is reasonably good. The fit yields $C_1 = 1.90 \times 10^{-6} \text{ J K}^{-5/2} \text{ g}^{-1}$, $T^* = 327 \text{ K}$.

We also observe that the amplitude of the order parameter (tilt angle or orientational ordering) fluctuations increases abnormally near the I-SmC transition and brings about the anomalous increment in heat capacity. This may be caused by a macroscopically inhomogeneous distribution of bulk impurities. From Eq. (2.14) it is clear that the heat capacity has a square root divergence in the isotropic phase. The NDE expression (3.4) gives the exponent $\gamma = 1$. Thus the critical ex-

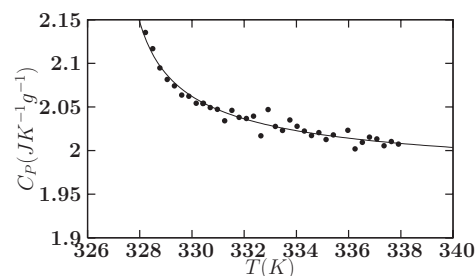


FIG. 1. The anomalous part of the measured heat capacity $C_P(T)$ of the liquid crystal MCEB7azo2-2.5 in the isotropic phase above the I-SmC transition in liquid-crystalline elastomers. The measured data (filled circle) are from reference Ref. 24, and line is the best fit of Eq. (2.14).

ponents $\gamma = 1$ and $\alpha = 0.5$ which is same value as the I-N and I-SmA transitions in low molecular weight liquid crystals and indicate the fluid-like analogy in the isotropic phase of the I-SmC transition in liquid-crystalline elastomers.

It should be pointed out that the heat capacity data²⁴ shows a curvature change as the temperature is reduced. For temperature moderately above the I-SmC phase transition temperature the contributions to the cubic and quartic terms must be taken into account in the heat capacity calculation to obtain the curvature detected experimentally. Further the term such as $(\Delta_z u)^2$ must be added into the free energy (2.8) to explain the curvature change in the experimental curve. Here u is the displacement of the smectic layers in the z direction.

V. CONCLUSION

We have presented here a Landau theory analysis to describe the I-SmC transition in liquid-crystalline elastomers. The anomalous behavior of the heat capacity in the isotropic phase of the I-SmC transition is calculated. The analysis shows that the I-SmC transition in liquid-crystalline elastomers is always a first order similar to the low molecular weight I-SmC transition. The effect of shearing strain on the I-SmC transition strongly depends on the character of the transition and renormalizes the I-SmC transition temperature. The heat capacity strongly depends on the behavior of the shear modulus. The present theory shows that a first order theory is sufficient to explain the anomalous behavior of the heat capacity in the isotropic phase above the I-SmC transition. The same pretransitional phenomena is observed in the isotropic phase of the I-SmC transition in LCEs similar to the I-N and I-SmA transitions in low molecular weight liquid crystals. The analysis presents the first theoretical support with experimental observation.

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