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Piezoelectric effects in cholesteric elastomer gels

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We report a piezoelectric effect in cholesteric liquid crystalline elastomer gels. When we apply a shear stress to a cholesteric elastomer gel in the direction perpendicular to its helical axis, a polarization can be induced in the direction perpendicular to both the stress and the helix. This experimental observation agrees with the theory proposed by Pelcovits and Meyer [J. Phys. II France **5**, 877 (1995)]. [S1063-651X(97)12801-X]

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INTRODUCTION

Piezoelectric materials are characterized by the appearance of an electric polarization when a suitable mechanical stress is applied. Under symmetry consideration, these materials have to be noninvariant under inversion. Chiral liquid crystals like cholesterics or chiral smectics satisfy this requirement. However, these low-molecule-weight liquid crystals are basically liquidlike and cannot sustain a static shear.

Brand [1] first noted that chiral liquid crystalline elastomers are the right candidates for studying this piezoelectric effect because these elastomers can support a static stress. He also predicted erroneously that applying a stress along the direction of the cholesteric helix can induce a polarization along the same direction. Inspired by Brand's theory, Vallerien *et al.* [2] and Meier and Finkelmann [3] were able to determine piezoelectricity in these materials.

Recently, Pelcovits and Meyer [4] wrote down the theory for piezoelectricity of cholesteric elastomers from the symmetry point of view. In that paper they showed that, if only considering the linear effect from the **E** field and the strain tensor or rotation pseudovector, the free energy density F_p for the piezoelectric effect can be written down as

$$F_p=\gamma_1 q_0 E_i \epsilon_{ijk} p_j p_l \delta^{(tr)}_{km} u_{ml}+\gamma_2 q_0 E_i p_i p_j \omega_j + \gamma_3 q_0 E_i \delta^{(tr)}_{ij} \omega_j, \tag{1}$$

where $\gamma_{1,2,3}$ are the piezoelectric coefficients, $q_0(=2\pi/\text{pitch length})$ the wave vector, ϵ_{ijk} the antisymmetric pseudotensor, $\delta^{(tr)}_{km}(\equiv \delta_{km}-p_k p_m)$ the projection operator transverse to the helical axis, p_i a unit vector along the helical axis, E_i the applied electric field, u_i the displacement field of the elastomer, u_{ij} $[=1/2(\partial u_i/\partial x_j+\partial u_j/\partial x_i)]$ the symmetric strain tensor, and ω_k $[=\frac{1}{2}\epsilon_{ijk}(\partial u_j/\partial x_i)]$ the rotation pseudovector. From this equation, they were able to conclude that compression along the helix does not produce piezoelectricity; instead, a shear stress or a local rotation can produce a polarization.

If we assume that the pitch axis is along the Z axis, i.e., $p_x=p_y=0$ and $p_z=1$, we can simplify the free energy as

$$F_p=\gamma_1 q_0 E_i \epsilon_{izk} u_{kz}+\gamma_2 q_0 E_z \omega_z+\gamma_3 q_0 (E_x \omega_x + E_y \omega_y). \tag{2}$$

Based on this equation, several experiments with different geometries can be carried out. In this paper, we will present the simplest geometry which involves the planar cell in the cholesterics. If we have a planar cell, i.e., the pitch axis of the cholesteric elastomer is perpendicular to the plates, and displace one of the plates relatively to the other in the x direction, we can induce a piezoelectric polarization in the y direction, where

$$\langle \mathbf{P} \rangle = \hat{\mathbf{y}} u_{xz} q_0 (\gamma_3+\gamma_1). \tag{3}$$

Then $\gamma_3+\gamma_1$ can be determined.

EXPERIMENT

The cholesteric liquid crystal we used was a mixture of E46, R811, and CB15 (EM Chemicals). The concentration of chiral dopants R811 and CB15 was adjusted so that the pitch length of the cholesteric liquid crystal is in the visible range at room temperature. The host E46 has a very wide temperature range in the nematic phase and has no preceding smectic *A* phase, so the pitch length of the cholesteric phase does not change much with the temperature. The acrylate monomer (I) (16.5%) was added to the cholesteric material, as was diacrylate monomer 4,4′-bisacryloyl-biphenyl (II) (0.8%) for crosslinking. In addition to these, a small amount of photoinitiator was also added to the mixture.

$$\text{(I)}\,\mathrm{CH_2{=}CH{-}CO_2{-}(CH_2)_4{-}O{-}}C_6\mathrm{H_4{-}CO_2{-}C_6H_3F}$$
$$\mathrm{-(CH_2)_4{-}CH_3}$$

$$\text{(II)}\,\mathrm{CH_2{=}CH{-}CO_2{-}C_6H_4{-}C_6H_4{-}O_2C{-}CH{=}CH_2}.$$

The cholesteric liquid crystal showed green color first. After we added those monomers, the mixture began to reflect red light. The reason for the color change is that the percentage of the chiral dopants drops because those monomers are not chiral. The center of its selective reflection band is approximately 0.62 μm, which is obtained from the reflectivity measurement. The average index of fraction of the nematic host is around 1.5, so we can get the pitch length of this cholesteric mixture. This mixture was sandwiched between two glass plates with indium tin oxide (ITO) electrodes separated by a Mylar spacer. The direction of the piezoelectric polarization was perpendicular to both the directions of the

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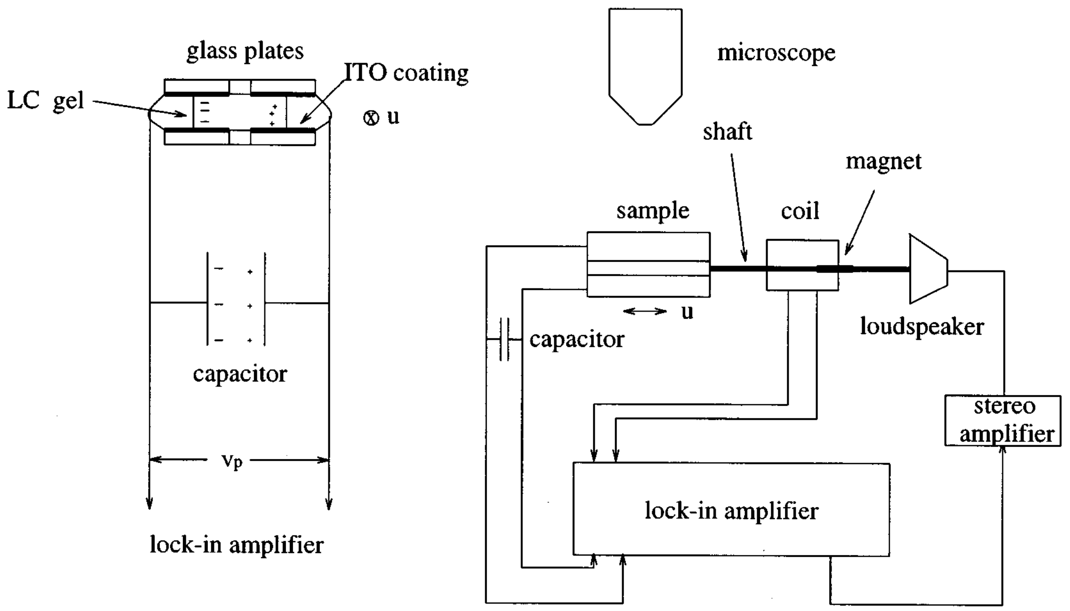

(a) (b)

FIG. 1. (a) Sample configuration; (b) Experimental setup.

helix and the shear stress. Because we were measuring the surface charges induced by electric polarization at the left side and the right side of the liquid crystal gel menisci, only the areas marked by a bold line were coated with ITO [see Fig. 1(a)]. Two thin wires were used to connect the ITO coated areas, thus forming two conductive plates at the left and right sides of the liquid crystal gel. The ITO plates were coated with PVA (polyvinyl alcohol) and rubbed unidirectionally first so that a cholesteric planar cell could be achieved. Then the cell was irradiated with UV light to polymerize the monomers and form a gel structure. Because the monomers follow the twist structure inside the cholesteric mixture, the polymer network is expected to keep the same twist structure after the polymerization. The pitch length did not change with the polymerization, again from the reflectivity measurement. The cholesteric gel was disklike in shape with a diameter of 10 mm and thicknesses of 20 μm.

The experimental setup [5] is shown in Fig. 1(b). A lock-in amplifier (EG&G 124) with preamplifier (EG&G 119) was used to measure the induced voltage, also as the signal generator. The sinusoidal signal from the internal oscillator was magnified by the stereo amplifier, and then drove the loudspeaker, causing the membrane of the loudspeaker to vibrate. The upper plate of the sample was connected to the membrane by a shaft, so the upper plate also moved sinusoidally. We put a large capacitor ($C=21.3$ nF) in parallel with the two conductive plates as shown in Fig. 1(a), so we can ignore the small capacitance of the coaxial cables and the input capacitance of the lock-in amplifier. Then we used the lock-in amplifier to measure the charges on this capacitor. We can treat the amount of charges on the capacitor equal to those surface charges on the liquid crystal gel because of the large capacitance of this capacitor and the high input resistance ($R=100$ MΩ) of the lock-in amplifier. We attached a magnet to the shaft and put a coil around it, so that we were able to determine the phase shift between the motion of the upper plate and the piezoelectric signal. We used an optical microscope to monitor the shear motion and measure the shear displacement.

RESULTS

We started the shear experiment with a nematic gel. As expected, only a tiny residual voltage appeared. Then we tried a cholesteric cell without polymers. A voltage in the range of microvolts showed up across the cell. This polarization was induced by the shear flow which could break the symmetry of the twist distortion. It is hard to get an accurate measurement here because of the fluidlike property of the cholesteric liquid crystals. Finally we tried the cholesteric gel. This time the gel did not flow at all; it only distorted along the direction of the shear stress. The same magnitude of voltage appeared steadily.

The induced voltages (V_p) from the piezoelectric polarization as a function of the shear frequency are shown in Fig. 2. Here the amplitude of displacement is fixed at $u_x=10$ μm. This figure clearly shows that there is a frequency dependence on the induced voltage, which increases with increasing shear frequency and then gradually saturates. Figure 3 shows the dependence of piezoelectric polarization on the amplitude of the shear displacement with two different shear frequencies. When the displacement is small, the polarization increases with the increasing displacement linearly as the theory predicts. When the displacement becomes larger, V_p increases at a decreasing rate. This could be due to nonlinear effects. Since the sample is only 20 μm thick, the

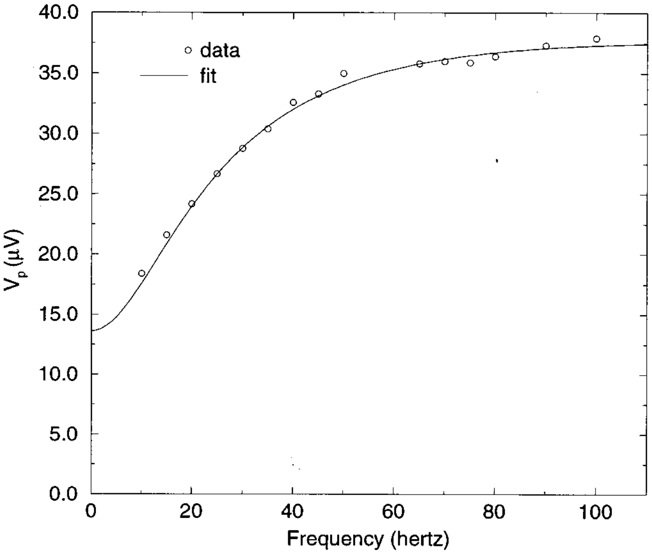

FIG. 2. Induced voltage from piezoelectricity as a function of shear frequency with fixed shear displacement. The solid line is the fitting curve which will be explained later.

larger displacements (above 20 μm) are beyond the consideration of the linear theory. At large displacements, the helix may also be disrupted. If we make a linear fit to the first few data points of the two sets of data shown in Fig. 3 and use Eq. (3), we can calculate the piezoelectric coefficients $|\gamma_1+\gamma_3|$ to be 3.0×10^{-5} statC/cm and 4.5×10^{-5} stat C/cm for 20 Hz and 75 Hz, respectively.

In liquid crystals, it is known that splay-bend distortion can produce a polarization due to the flexoelectric effect [6]:

$$\mathbf{P}=e_s\mathbf{n}(\nabla\cdot\mathbf{n})-e_b[\mathbf{n}\times(\nabla\times\mathbf{n})], \tag{4}$$

where e_s and e_b are flexoelectric coefficients. In their paper, Pelcovits and Meyer wrote down the structure of the director for planar geometry due to the shear stress as

$$\mathbf{n}(z)=\hat{\mathbf{x}}\cos\psi+\hat{\mathbf{y}}\sin\psi+\hat{\mathbf{z}}\alpha u_{xz}\cos\psi \tag{5}$$

for small value of u_{xz}, where α is a measure of the coupling of the director to the strain and $\psi=q_0z+\psi_0$, ψ_0 a phase constant. They were able to write down

$$\langle\mathbf{P}\rangle=\hat{\mathbf{y}}u_{xz}q_0\alpha\frac{e_b-e_s}{2} \tag{6}$$

and identify γ_1 as $\alpha(e_b-e_s/2)$ for the case of $\partial u_x/\partial z=\partial u_z/\partial x$. The value of the flexoelectric coefficients, e_b-e_s, was measured for 4′-octyloxy-4-cyanobiphenyl (8OCB) to be approximately 5.0×10^{-4} stat C/cm [7]. Using this result as an estimate, we found the range of α to be approximately on the order of 0.1. This coupling is physically not unreasonable.

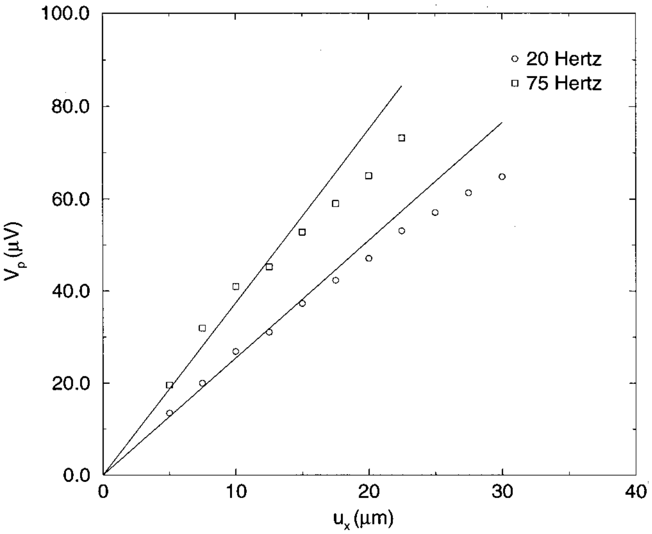

FIG. 3. Induced voltage from piezoelectricity as a function of shear displacement with two different frequencies. Note that the induced voltage saturates at larger shear displacement.

After we got these data, we heated the liquid crystal gel to its isotropic state, and the induced voltage dropped dramatically. After the gel went back to its cholesteric phase, the voltage came back, but it was not as large as it used to be, indicating that the alignment is a key role for this polarization measurement. The polarization will reach the maximum when the helical axis is perpendicular to the plates.

THEORY

In order to understand the frequency dependence, we have to write down the torque equation for n_z, which is the small deviation of the director along the z direction or the angle by which the helix rotates about the Y axis caused by the stress:

$$\mathbf{n}=\hat{\mathbf{x}}\cos q_0z+\hat{\mathbf{y}}\sin q_0z+\hat{\mathbf{z}}n_z(z). \tag{7}$$

If we only consider the linear coupling between the director and the shear strain, as Pelcovits and Meyer did in their theory, the dynamic equation under shear stress can be written as [8]

$$K\left(q_0^2n_z-\frac{\partial^2n_z}{\partial z^2}\right)-(\sigma_1+\sigma_2)\cos q_0z=-\Gamma\frac{\partial n_z}{\partial t}-\alpha_3\frac{v}{d}\cos q_0z, \tag{8}$$

where $K(=K_1=K_3$, for simplicity,) is the elastic constant, $\Gamma(=\alpha_3-\alpha_2)$ the rotational viscosity, $v(=\partial x/\partial t, x=$ shear displacement) the shear velocity, and d the sample thickness. The terms in σ_1 and σ_2 represent the stresses on the director due to deformation of the polymer network. σ_1 is the stress from the fraction of the gel network that can sustain a static strain and σ_2 represents the stress from polymer coils that are free to relax after deformation:

$$\sigma_1=A\frac{x}{d} \tag{9}$$

and

$$\sigma_2=-\tau_P\frac{\partial\sigma_2}{\partial t}+B\frac{v}{d}, \tag{10}$$

where A and B are constants, and τ_P the relaxation time constant of the polymers. Note that a term comparable to that for σ_2 would also arise from a direct coupling of shear flow in the liquid crystal to stress on the director, as shown by

Prost [9]. The dependence of $\cos q_0 z$ on the shear stress term in Eq. (8) describes that the interaction from the shear strain to the director is the largest when the shear stress is parallel to the molecular orientations; it is zero when the shear stress is perpendicular to the molecular orientations. The static solution for Eq. (8) can be described as

$$n_z = \phi \cos q_0 z. \tag{11}$$

Comparing Eq. (11) with Eq. (5), ϕ can be identified as αu_{xz}.

The shear displacement x is a function of shear frequency $f(=\omega/2\pi)$. By substituting $\phi e^{i(\omega t+\theta)}\cos q_0 z$ into Eq. (8) and assuming that α_3 is small in the low frequency range where the experiment was conducted, we are able to calculate ϕ:

$$\phi = \frac{1}{2Kq_0^2}\frac{x}{d}\frac{1}{\sqrt{1+\omega^2\tau_{\mathrm{LC}}^2}}\left(A^2+\frac{2AB\omega^2\tau_P+B^2\omega^2}{1+\omega^2\tau_P^2}\right)^{1/2}, \tag{12}$$

where $\tau_{\mathrm{LC}} = \Gamma/2Kq_0^2$ is the relaxation time constant of the cholesteric liquid crystals.

By combining Eq. (6) and Eq. (12), using the value of $e_b - e_s$ of 8OCB as an approximation, and extrapolating the first few data linearly to $\omega = 0$, we are able to get $|A| = 1.2\times 10^3$dyn/cm^2. The rest of the parameters can be obtained by using Eq. (12) to fit the data shown in Fig. 2. It turns out that $|B| = 11$ poise, $\tau_P = 5$ ms, and $\tau_{\mathrm{LC}} = 0.3$ ms. The values of $|B|$ and τ_P justify the assumption that α_3 can be ignored in the low frequency range. These values indicate that, in the frequency range we studied, the frequency dependence is mainly from the polymers. The polymer network is stretched by the shear stress, and part of it relaxes with the time constant τ_P. The liquid crystal molecules basically follow the strain of the polymer network and some of them relax quickly. This τ_{LC} dependence should become dramatic at higher frequency, which can decrease the value of ϕ. The result of fitting is shown as the solid line in Fig. 2.

In Pelcovits and Meyer's theory, they only considered the situation of static shear, which is the low frequency limit in our experiment. When $\omega = 0$, and $\phi = |A|/2Kq_0^2(x/d)$, we can get $|\alpha| = \phi/u_{xz} = |A|/Kq_0^2 = 0.06$, and $|\gamma_1 + \gamma_3| = 1.4\times 10^{-5}$ stat C/cm. This finite value of ϕ verifies the major difference between shearing the cholesteric liquid crystals and cholesteric gels: when ω goes to zero, in the former case, the polarization will go to zero; but in the latter case, it will go to a finite value due to the existence of the shear strain (σ_1) term.

The values of A and α should have the same sign depending on the value of θ, the phase difference between the piezoelectric signal, and the shear strain, at $\omega = 0$, where positive α (or A) means that the director will rotate towards the elongation direction. We measured θ by comparing the phase difference of two signals from the sample and the coil. The value of θ is negative in our measurement; it decreases with increasing shear frequency and then reaches the minimum, which is about $-90°$. Our theoretical expression for A either positive or negative does not agree with this. Therefore, at this time we cannot confirm the sign of A.

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[1] H. R. Brand, Makromol. Chem. Rapid Commun. **10**, 441 (1989).

[2] S. U. Vallerian, F. Kremer, E. W. Fischer, H. Kapitza, R. Zentel, and H. Poths, Makromol. Chem. Rapid Commun. **11**, 593 (1990).

[3] W. Meier and H. Finkelmann, Makromol. Chem. Rapid Commun. **11**, 599 (1990); Macromolecules **26**, 1811 (1993).

[4] R. A. Pelcovits and R. B. Meyer, J. Phys. II France **5**, 877 (1995).

[5] P. Pieranski, E. Guyon, and P. Keller, J. Phys. France **36**, 1005 (1975).

[6] R. B. Meyer, Phys. Rev. Lett. **22**, 918 (1969).

[7] I. Dozov, I. Penchev, Ph. Martinot-Lagarde, and G. Durand, Ferroelectrics Lett. **2**, 135 (1984); I. Dozov, Ph. Martinot-Lagarde, and G. Durand, J. Phys. Lett. **43**, L365 (1982).

[8] J. S. Patel and R. B. Meyer, Phys. Rev. Lett. **58**, 1538 (1987); J. S. Patel and S.-D. Lee, J. Appl. Phys. **66**, 1879 (1989).

[9] J. Prost, J. Phys. France **39**, 639 (1978).