

Dynamic light scattering studies of cholesteric and polymer-stabilized cholesteric liquid crystals

Redouane Borsali,^{1,2,*} Uwe P. Schroeder,¹ Do Y. Yoon,¹ and R. Pecora²
¹IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
²Department of Chemistry, Stanford University, Stanford, California 94305-5080
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Dynamic light scattering of pure cholesteric and polymer-stabilized cholesteric liquid crystals shows two relaxation modes: twist and viscous-splay (umbrella). The twist mode is diffusive, whereas the frequency associated with the viscous-splay deformation goes to a constant at zero scattering angle. In the presence of polymer networks the frequency corresponding to the twist deformation decreases as a result of an increase in the viscosity, but the frequency associated with the viscous-splay deformation increases. This is attributed to the breakup of cholesteric domains by the polymer network. [S1063-651X(98)50509-0]

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INTRODUCTION

Cholesteric liquid crystals (chiral nematics) are locally very similar to nematics. In nematics [1–4] the elongated molecules are aligned, on the average, along the nematic vector director \mathbf{n} . In cholesterics, however, in the absence of electric fields or other perturbing forces, the director is uniformly twisted along an axis called the helical axis. The distance along the helical axis for the director to twist 2π is called the pitch, denoted by $P = 2\pi/q_0$. Cholesteric liquid crystals have been utilized in many applications [5], such as twisted-nematic liquid crystal displays, thermochromic liquid crystal devices and reflective display devices.

When a cholesteric liquid crystal is sandwiched between two parallel plates with rubbed polymer surfaces, it is in the planar state (Grandjean texture) and the helical axis is perpendicular to the plates. The refractive index along the normal direction has a periodic structure and, therefore, the material reflects light for wavelength $\lambda = \langle n \rangle P$, where $\langle n \rangle$ is the average refractive index. However, in the absence of the anchoring effect of the cell surfaces, polydomains of fingerprint texture are formed and the helical axes of the domains are more or less randomly oriented throughout the cell. This is the “focal-conic” state and the material is strongly scattering because of the abrupt changes of the local refractive index.

Polymer networks can be incorporated to improve the planar and/or the focal-conic properties of cholesterics. Depending on the value of the pitch, the composite material can be used in reflective or projection displays, in which either texture can be stabilized in the off state. For values of the pitch in the infrared, light valves of two different modes can be made: the normal and reverse modes [6]. In the normal mode light valve, the strongly scattering focal-conic texture is stabilized at zero field and the material is opaque. When a field is applied, the material switches to the homeotropic texture and becomes transparent (or dark on black substrates). In the reverse mode, the planar texture is stabilized at zero field (material transparent) for visible light. When a field is applied, the material switches into the light scattering focal-

conic texture. The experiments presented here are in the reverse mode; the polymer stabilized cholesteric is transparent at zero field due to the planar texture with the pitch in the IR region.

THEORETICAL BACKGROUND

A model developed by Fan, Kramer, and Stephen [7], which has been extended to include the presence of applied external forces (electrical or magnetic fields) by Parsons and Hayes [8], describes the orientational fluctuations in an incompressible cholesteric. It shows that there are two important and dominant relaxation modes that could be observable in dynamic light scattering (DLS) experiments. They are called the twist and viscous-splay (“umbrella”) modes.

The twist mode measures the twisting oscillations about the helical axis with a restoring force given by the twist elastic constant k_{22} , and the twist viscosity γ_1 . This mode is overdamped and would therefore result in a broadening of the frequency of the scattered intensity given by

$$\Gamma_{\text{twist}} = (k_{22}/\gamma_1)q^2, \quad (1)$$

where q is the magnitude of the wave vector defined as $q = (4\pi n/\lambda_0)\sin(\theta/2)$; λ_0 is the wavelength of the incident beam, θ is the scattering angle, and n is the refractive index of the medium. The predicted line shape is Lorentzian and is most intense at momentum transfers that correspond to those required for Bragg scattering, i.e., $q = 2q_0$.

The hydrodynamic equations show several relaxation modes associated with fluctuations about the molecular director in viscous splay. These modes are also overdamped and one of them is dominant in DLS with a damping constant given by

$$\Gamma_{\text{vis-splay}} = \frac{(\alpha_2 + \alpha_4 + \alpha_5)}{\gamma_1(\alpha_4 + \alpha_5) - \gamma_2\alpha_2} [k_{33}q_0^2 + k_{11}q^2], \quad (2)$$

where k_{11} and k_{33} are the splay and bend elastic moduli (Frank elastic constants [9]), respectively. The α_i are the Leslie coefficients [10]. The line shape of this normal mode is also Lorentzian and is most intense at half the Bragg condition: $q = q_0$.

This model [7] applies to director fluctuations that propagate along the cholesteric axis, i.e., for $q_{\perp} = 0$, where q_{\perp} is

*On leave from CERMAV-CNRS and Joseph Fourier University, P.O. Box 53, F-38041, Grenoble Cedex 9, France.

the component of q perpendicular to the director. It should apply to our experimental geometry in which $q_{\perp} \ll q$.

There are no theoretical predictions for the dynamical behavior of polymer-stabilized cholesterics. The aim of this work is to characterize the dynamics in both the pure and the polymer-stabilized cholesterics, which has been done for nematics [11].

MATERIAL AND SAMPLE PREPARATION

The cholesteric liquid crystal is a mixture of 99.5% pentycyanobiphenyl (5CB) (Aldrich) and 0.5% chiral dopant R1011 (Merck). For the *in situ* polymerized polymer network-stabilized cholesteric, the sample consisted of: 4-cyano-4'[4-(6-methacryloxyhexyl)oxybenzoyl] biphenyl monofunctional mesogenic chain extender (TM6BCB) as a monomer, Benzoinmethylether (BME) (Polysciences, Inc.) as a photoinitiator, and difunctional bisphenol-A-dimethacrylate (BPADM) as crosslinker. These compounds were mixed in the weight ratio of 5% [TM6BCB:BPADM 3:1; 2% BME in toluene] in [99.5% 5CB and 0.5% R1011]. The sample preparation was performed with great care, since light scattering is extremely sensitive to defects such as dust and disclination lines in liquid crystals. The samples were filled in polyimide coated, parallel rubbed cells (made in the laboratory). The cell gap was controlled by $25 \pm 1 \mu\text{m}$ Ablefilm 539 IA (Abelstik). The filling procedure was carried out under vacuum to exclude oxygen during the polymerization process. The cell was sealed with epoxy resin. For the polymer-stabilized cholesteric, the radical polymerization process was initiated by UV irradiation from a Hg source. The radiation was filtered through neutral density filters and the exposure time of the samples was 5.5 h.

DYNAMIC LIGHT SCATTERING

DLS [12] is a powerful technique for determining relaxation times in liquid crystals. Nematics [13–16] and polymer-stabilized nematics [11] have, for example, been successfully investigated by DLS. Our apparatus uses a spectra physics model 165 argon ion laser operating at 4880 Å. The laser power was 200 mW and filters were used to reduce the incident beam intensity when necessary. The autocorrelation function of the scattered intensity was obtained using a Brookhaven BI9000 autocorrelator. The intermediate scattering function is easily related to the measured homodyne intensity autocorrelation function $C(q, t)$ [12].

Several methods have been used to analyze the DLS data, including cumulants, single and double exponential fits, and CONTIN [17]. To avoid stray light and consequent heterodyning, the cell was positioned in the index matching bath so that the spatial coherence factor was maximized. The sample temperature was controlled to ± 1 °C.

RESULTS AND DISCUSSION

Dynamics of cholesteric liquid crystals

The cell was positioned so that the wave vector \mathbf{q} was parallel to the vector director \mathbf{n} of the helix for all the scattering angles to avoid any contamination of the dynamics due to different modes propagating in other directions. Both

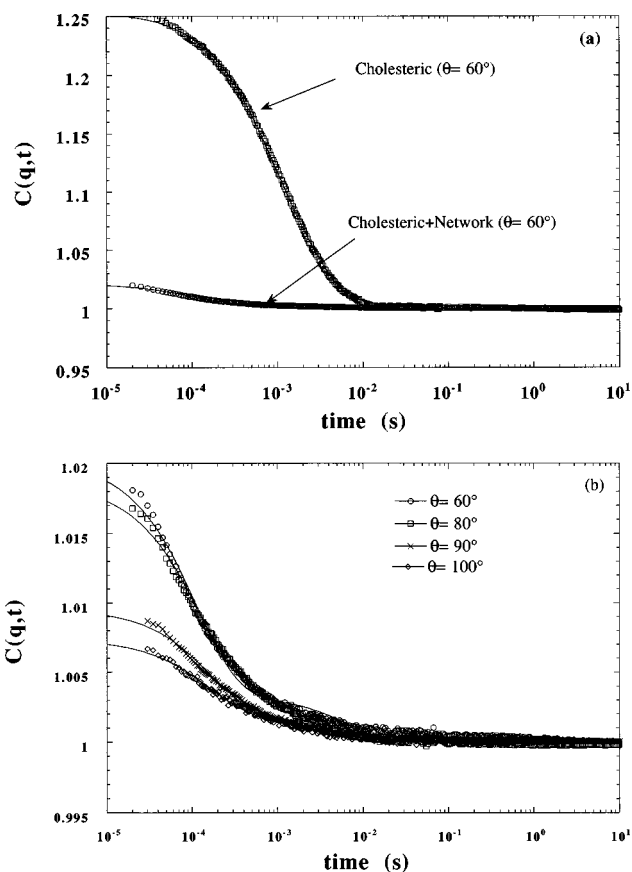


FIG. 1. (a) Typical DLS autocorrelation functions from the cholesteric liquid crystal (99.5% 5CB+0.5% chiral agent) with and without the polymer network at $T=25$ °C and $\theta=60^\circ$. The dots represent the experimental data and the solid line the double-exponential fit. (b) Typical DLS autocorrelation functions from the cholesteric liquid crystal in the presence of the polymer network at $T=25$ °C and the different scattering angles shown. The dots represent the experimental data and the solid line the double-exponential fit.

polarized and depolarized experiments (which gave the same relaxation times) were performed at $T=25$ °C and scattering angles ranging from 40° to 120° in steps of 5° . The results show that the dynamics is well described mainly (see below) by two relaxation modes at all investigated angles and geometries (polarized and depolarized). Typical intensity autocorrelation functions of the cholesteric with and without the polymer network at the scattering angle $\theta=60^\circ$ are shown in Figs. 1(a) and 1(b). The dots represent the experimental data and the solid line represents a two-exponential fit that was confirmed by CONTIN analysis ($\pm 2\%$ error). The same data treatment was used for the other angles. We noted, however, the existence of an extra-fast mode that was very difficult to resolve (very high frequency) and whose amplitude vanished as q increased. The amplitude of this fast mode was always less than 5%.

The variations of the frequencies of the two relaxation modes in the pure cholesteric liquid crystal with q^2 are shown in Fig. 2. The slower mode can be identified with the twist mode, given by Eq. (1). Its frequency shows a q^2 dependence (diffusive) and $(k_{22}/\gamma_1)_{\text{choles}} = 1.90 \times 10^{-9} \text{ cm}^2/\text{s}$.

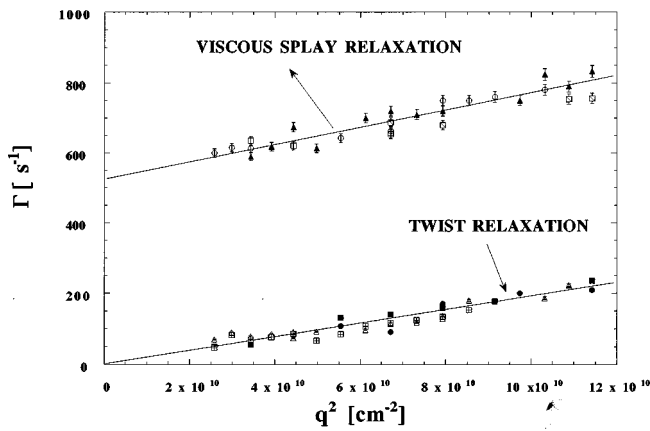


FIG. 2. Variations of the frequencies of the twist and viscous-splay modes as functions of q^2 for the pure cholesteric. The different symbols on the same solid line refer to polarized and depolarized DLS experiments done at different times over an eight-month period.

The second mode (fast) goes to a constant as $q \rightarrow 0$ and is identified as the viscous-splay (umbrella) mode given by Eq. (2). The intercept of $\Gamma_{\text{vis-splay}}$ gives $\Gamma_0(q=0) = 524.16 \text{ s}^{-1}$ and a slope equal to $3.22 \times 10^{-9} \text{ cm}^2/\text{s}$. We believe that this is the first time these cholesteric deformations have been observed using DLS. They are, at least qualitatively, in good agreement with the theoretical predictions of Fan, Kramer, and Stephen [7]. It is interesting to compare the twist viscosities of the 5CB in the nematic and cholesteric phases. For the nematic phase [14–16] $(k_{22}/\gamma_1)_{\text{nem}} = 5.0 \times 10^{-7} \text{ cm}^2/\text{s}$. Using this and our value for the cholesteric phase, we find the ratio $[(k_{22}/\gamma_1)_{\text{nem}}]/[(k_{22}/\gamma_1)_{\text{choles}}]$ is about 263. Since the values of the elastic constants do not vary much from one phase to the other, the high value of this ratio is probably due to the large difference in the twist viscosities in the two phases. The intercept and the slope of the viscous-splay frequency allow the determination of the ratio $(k_{11}/k_{33}) = 0.24 \times 10^{-3}$, using an estimated value for the pitch of $10 \text{ }\mu\text{m}$.

Dynamics of polymer-stabilized cholesteric liquid crystals

The autocorrelation functions shown in Fig. 1(b) were also well described by two relaxation times. The frequencies of both modes in both systems are shown in Figs. 3(a) and 3(b). In the polymer-stabilized cholesteric $(k_{22}/\gamma_1) = 1.19 \times 10^{-9} \text{ cm}^2/\text{s}$. The second mode goes to a nonzero constant as $q \rightarrow 0$, as in the case of the pure cholesteric. The intercept of $\Gamma_{\text{vis-splay}}$ gives $\Gamma_0 = 3542.2 \text{ s}^{-1}$ and a slope equal to $2.28 \times 10^{-8} \text{ cm}^2/\text{s}$. Thus, the presence of the polymer network slows down the twist mode and speeds up the so-called viscous-splay deformation. For the twist mode, one might ascribe this decrease of the frequency or (k_{22}/γ_1) by about 70% to the increase of the twist viscosity. The frequency associated with the viscous-splay mode increases in the presence of the network. This may be due to a breakup of cholesteric domains into smaller helical domains that could exhibit faster collective dynamics.

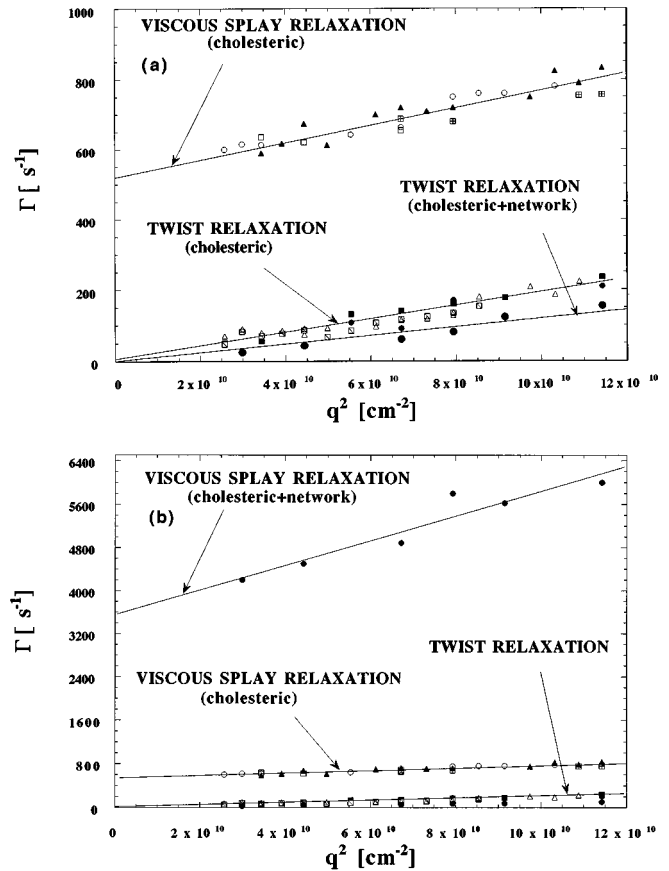


FIG. 3. (a) Variations of the frequencies of the twist and viscous-splay modes as functions of q^2 for both the pure cholesteric and the polymer-stabilized cholesteric samples. The symbols are the same as described in Fig. 2. (b) Same as (a), at a different scale.

CONCLUSION

We have made polarized and depolarized DLS observations of the twist and viscous-splay relaxation modes in both pure and polymer-stabilized cholesterics. Both modes exhibit a q^2 dependence in their relaxation frequencies, but the viscous-splay frequency approaches a nonzero constant as $q \rightarrow 0$. When a polymer network is present both relaxation modes are substantially modified. It is found that the twist frequency is decreased, which is most likely due to an increase in the twist viscosity. The frequency of the viscous-splay mode increases, possibly because of a breakup of helical domains by the polymer network. The resulting domains of cholesteric helical structures become smaller and, therefore, the dynamics may become faster. These effects have direct consequences for threshold voltages and switching times of display devices.

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- [1] S. Chandrasekhar, in *Liquid Crystals, Their Physics, Chemistry and Applications*, edited by G. Hilsum and E. P. Raynes (The Royal Society, London, 1983).
- [2] D. Demus, in *Liquid Crystals, Applications and Uses*, edited by B. Bahadur (World Scientific, Singapore, 1990).
- [3] P. G. Collings, *Liquid Crystals, Nature's Delicate Phase of Matter* (Adam Hilger, Bristol, 1990).
- [4] P.-G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, Oxford, 1993).
- [5] *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks*, edited by G. P. Crawford and S. Lumer (Taylor & Francis, London, 1996).
- [6] D.-K. Yang, L.-C. Chien, and J. W. Doane, *Appl. Phys. Lett.* **64**, 1905 (1992).
- [7] C. Fan, L. Kramer, and M. J. Stephen, *Phys. Rev. A* **2**, 2482 (1970).
- [8] J. D. Parsons and C. F. Hayes, *Phys. Rev. A* **9**, 2652 (1974).
- [9] F. C. Frank, *Discuss. Faraday Soc.* **25**, 19 (1958).
- [10] F. M. Q. Leslie, *J. Appl. Math. Mech.* **19**, 357 (1966).
- [11] D. F. Gu, A. M. Jamieson, and L.-C. Chien, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **287**, 295 (1996).
- [12] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).
- [13] Orsay Liquid Crystal Group, *J. Chem. Phys.* **51**, 816 (1969).
- [14] M. S. Sefton, A. R. Bowdler, and H. Coles, *Mol. Cryst. Liq. Cryst.* **129**, 1 (1985).
- [15] D. Gu, A. M. Jamieson, M. Kawasumi, M. Lee, and V. Percec, *Macromolecules* **25**, 2155 (1992).
- [16] R. Borsali, D. Y. Yoon, and R. Pecora, *J. Phys. Chem.* (to be published).
- [17] S. W. Provencher, *Comput. Phys. Commun.* **27**, 213 (1982); **27**, 239 (1982).