PHYSICAL REVIEW E VOLUME 51, NUMBER 5 MAY 1995

Light-scattering study of phase transitions in hexatic liquid-crystal films

M. S. Spector* and J. D. Litster
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307

(Received 20 October 1994)

We report on quasielastic light-scattering experiments on fluid, hexatic, and crystal phases in thin, freely suspended liquid-crystal films. The behavior of the hexatic elastic constant in the vicinity of the fluid smectic-C to hexatic smectic-I phase transition is found to change from a continuous evolution to a discontinuous jump at concentrations near the fluid-hexatic-crystal triple point in a system of mixtures of two liquid-crystal compounds. The smectic-I to crystal smectic-J transition is always found to be first order. These results represent the first experiments on films of homogeneously mixed liquid crystals.

PACS number(s): 61.30.Gd, 64.70.Md, 78.35.+c

Free-standing films of smectic liquid crystals have provided a practical system for studying a variety of concepts related to modern theories of critical phenomena [1–9]. Much of this work has centered around theories of the bond-orientationally ordered hexatic phase as an intermediate state between fluid and crystal in a two-dimensional (2D) system [10]. Since the suggestion that certain smectic phases might be three-dimensional realizations of bond-orientationally ordered phases [11], the existence of stacked hexatic phases in smectic liquid-crystal films has been clearly demonstrated using x-ray scattering [1], electron diffraction [2], and depolarized reflection microscopy [3]. Free-standing films provide an ideal quasi-two-dimensional, substrate-free system for studying these hexatic phases [4]. In addition, films of tilted smectics readily form single domain samples when a weak magnetic or electric field is applied to break the in-plane rotational symmetry. X-ray scattering experiments on tilted smectics have enabled the study of harmonic scaling of the bond-orientational order parameter [5] and dimensional crossover in the phase behavior as the film thickness is decreased [6], while light-scattering studies have revealed the presence of nonhydrodynamic coupling between the bond-orientational and tilt fluctuations [7].

Previous experiments on tilted smectic films have found the fluid to hexatic transition [12] can be either continuous or first order [5,8]. Theoretically this type of behavior can be treated in terms of a Landau theory with an additional order parameter coupled to the hexatic order parameter giving rise to a tricritical point. The additional order parameter in these systems is that due to a nearby crystal phase. Near the fluid-hexatic-crystal triple point, fluctuations of the crystalline order parameter renormalize the fourth-order coefficient in the effective free energy, changing its sign as the concentration is varied [13]. Such a theory yields a generic phase diagram such as that seen in Fig. 1(a) [13]. These predictions were qualitatively verified using x-ray scattering on the homologous series TBnA [9]. However, such experiments were restricted to single component systems and thick films. In this work, we use quasielastic light scattering to measure the behavior of the elasticity in the vicinity of the hexatic transition in thin films composed of mixtures of two liquid crystalline compounds. By studying very thin films, we expect to probe the underlying two-

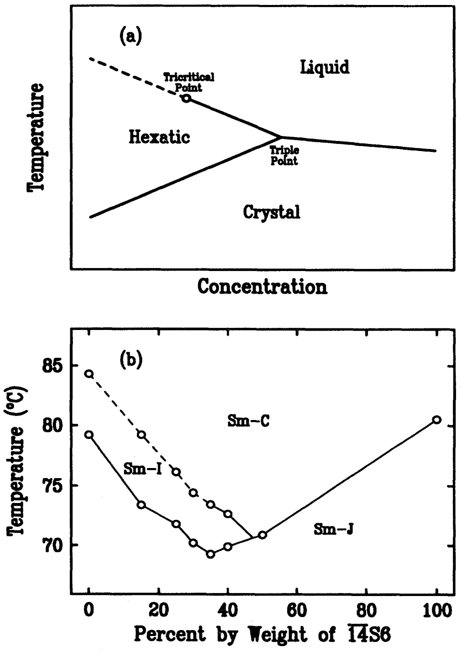

FIG. 1. (a) Generic temperature-concentration phase diagram near a fluid-hexatic-crystal triple point [13]. The broken (solid) lines indicate second- (first-) order transitions. (b) Temperature versus $\overline{14}$S6 concentration phase diagram in thin films of 8OSI/$\overline{14}$S6 mixtures. Open circles indicate experimentally determined transition temperatures in four-layer films.

---

*Present address: Materials Research Laboratory and Department of Chemical Engineering, University of California, Santa Barbara, California 93106.

1063-651X/95/51(5)/4698(6)/$06.00

dimensional nature of the transition and minimize the influence of interlayer coupling [5].

Our samples consist of mixtures of the two liquid crystals 4-(2-methylbutyl)-phenyl-4′-(octyloxy)-(1, 1′)-biphenyl-4-carboxylate (8OSI) and 4-*n*-hexylphenyl-4-*n*-(decyloxy)-benzthiolate ($\overline{14}$S6). 8OSI has the smectic phase sequence Sm-*A* → Sm-*C* → Sm-*I* → Sm-*J*, while $\overline{14}$S6 has Sm-*A* → Sm-*C* → Sm-*J*. Both materials have a wide Sm-*A* region enabling us to pull high quality films. The bulk phase diagram for this system was previously determined by Leadbetter *et al.* [14]. The samples were mixed by heating the two components into the isotropic phase in a nitrogen environment while mechanically stirring. The samples were then immediately transferred to a two-stage optical oven before cooling to room temperature. The film is maintained in an atmosphere of 100 Torr of dry nitrogen gas; temperature stability is better than 2 mK during these scans. Further details of our film oven are available elsewhere [15]. The sample is illuminated with ~100 mW of 5145 Å light from an argon-ion laser. The depolarized component of the scattered light at a scattering angle θ is imaged onto a photomultiplier tube whose amplified output is fed into a 4-bit, 72-channel autocorrelator. All scans reported in this work were performed in the so-called bend geometry, where the scattered wave vector lies in the plane containing the director and the layer normal. In this geometry, the scattering is sensitive only to fluctuations in the azimuthal orientation ϕ of the in-plane director component and not fluctuations of the tilt angle Φ_0. The scattering intensity is then given by [16]

$$I_{\rm sc}(\boldsymbol{q}) \sim \left\langle |\delta\epsilon_{if}|^2 \right\rangle = \epsilon_a^2 \sin^2\Phi_0 \sin^2(\theta+\Phi_0) \left\langle |\phi(\boldsymbol{q})|^2 \right\rangle , \qquad (1)$$

where $\epsilon_a = \epsilon_{\|} - \epsilon_{\perp}$, $q = \frac{2\pi}{\lambda}\sin\theta$ is the in-plane component of the scattered wave vector, and we have ignored the biaxiality of the Sm-*C* director. The tilt field is aligned by a 1.2 kG SmCo$_5$ magnet so that $\langle\phi\rangle = 0$.

The two-dimensional Landau-Ginzburg free energy density appropriate for describing tilted smectic phases is a function of the complex order parameters describing the tilt orientation $\Phi = \Phi_0 e^{i\phi(\boldsymbol{r})}$ and hexatic bond orientation $\Psi_6 = \psi_6 e^{i6\theta(\boldsymbol{r})}$ and is given by [17]

$$\begin{aligned} F_{\rm 2D}(\boldsymbol{r}) = {} & \frac{1}{2}a_1|\Phi|^2 + \frac{1}{4}b_1|\Phi|^4 + \frac{1}{6}c_1|\Phi|^6 + \cdots \\ & + \frac{1}{2}l_1|\nabla\Psi_6|^2 + \frac{1}{2}a_6|\Psi_6|^2 + \frac{1}{4}b_6|\Psi_6|^4 \\ & + \frac{1}{6}c_6|\Psi_6|^6 + \cdots + \frac{1}{2}l_6|\nabla\Psi_6|^2 \\ & - h\left(\Phi^6\Psi_6^* + (\Phi^*)^6\Psi_6\right) . \end{aligned} \qquad (2)$$

Here we only consider the derivatives in Eq. (2) corresponding to bend mode fluctuations. Rewriting the fluctuating part of the free energy density in reciprocal space, we obtain

$$\begin{aligned} F_{\rm 2D}(\boldsymbol{q}) = {} & \frac{1}{2}K_1^B q^2 |\phi(\boldsymbol{q})|^2 + \frac{1}{2}K_6^B q^2 |\theta(\boldsymbol{q})|^2 \\ & - \frac{1}{36}H\cos 6(\theta-\phi) , \end{aligned} \qquad (3)$$

where $K_1^B \equiv l_1\Phi_0^2$, $K_6^{\rm I} \equiv 36\, l_6\, \psi_6^2$, and $H \equiv 36\, h\, \Phi_0^6\, \psi_6$. In general, K_1 and K_6 are anisotropic and depend on the direction of $\boldsymbol{q}$ relative to the in-plane director. However, in this paper we will only deal with scattering in the bend geometry. For $H > 0$, $\langle(\theta-\phi)\rangle = 0$ and we obtain a Sm-*I* phase. In this case, $K_6^B = K_6^I$ is the hexatic elasticity associated with type-I disclinations [18]. For $H < 0$, $\langle\theta-\phi\rangle = \frac{\pi}{6}$ and the stable hexatic phase is Sm-*F*.

In the Sm-*C* phase, where $K_6^I = 0$, $\langle|\phi(\boldsymbol{q})|^2\rangle = k_B T/(K_1^B q^2)$ so that

$$I_{\rm sc}(\theta) \sim \frac{\sin^2(\theta+\Phi_0)}{K_1^B \sin^2\theta} . \qquad (4)$$

Figure 2 shows typical scans in the Sm-*C* phase for three-layer films of pure 8OSI and $\overline{14}$S6. The solid lines indicate fits to Eq. (4). By plotting the inverse intensity times q vs q, we see that the $\overline{14}$S6 data has more downward curvature at higher q, indicating a smaller tilt angle. These fits yield a tilt angle of 18.4° for $\overline{14}$S6 and 34.2° for 8OSI. We also obtain elasticities of $K_1^B = 1.6\times10^{-13}$ and 2.9×10^{-13} ergs for $\overline{14}$S6 and 8OSI, respectively. The absolute scale for these elasticities comes from comparison of the scattered intensity to thick films of pure 8OSI [15]. However, this calibration may not hold for $\overline{14}$S6 since it depends on the square of the dielectric anisotropy, $\epsilon_a = \epsilon_{\|} - \epsilon_{\perp}$, which is not known. In typical nematic liquid crystals, the birefringence $\Delta n = 0.14 - 0.17$. Taking $\Delta n \equiv n_{\|} - n_{\perp} = \epsilon_{\|}^2 - \epsilon_{\perp}^2 \approx 2\,\epsilon_{\perp}\,\epsilon_a$, we find this could introduce an uncertainty of up to 20% in our *absolute* scale. It is, however, interesting to compare the values for films of 8OSI and $\overline{14}$S6. We can approximately scale K_1 from a bulk value using the relation $K_1 \approx l\sin^2\Phi_0 K_{\rm Bulk}$, where $l = d\cos\Phi_0$ is the layer spacing and d is the molecular length. Combining x-ray results from $\overline{14}$S6 [14] and 8OSI [19], which give molecular lengths of 40 Å and 34 Å, re-

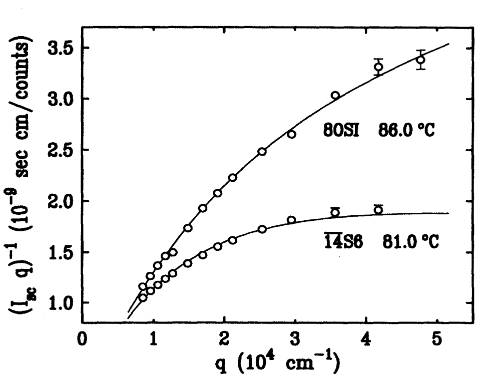

FIG. 2. Reciprocal of the intensity multiplied by q for pure 8OSI and $\overline{14}$S6 films is plotted as a function of the magnitude of q. This data is for three-layer films in the lower Sm-*C* phase. The solid lines are fits to the expected Sm-*C* behavior given by Eq. (4).

spectively, with our measured tilt angle of 32.2° in 8OSI, we obtain

$$\frac{K_1(8\text{OSI})}{K_1(\overline{14}\text{S6})} \approx \frac{34\text{Å}\ \cos 32.2^\circ\ \sin^2 32.2^\circ}{40\text{Å}\ \cos 18.4^\circ\ \sin^2 18.4^\circ} = 2.16$$

compared with the experimental result of 1.8 from the data discussed above. Since the difference is more than 20%, the bulk elastic constant in $\overline{14}$S6 is smaller than that in 8OSI.

Upon cooling the three-layer film of pure $\overline{14}$S6, we observe a discontinuous change at 80.55 °C. The scattered intensity at small q decreased by a factor of $\sim$500 when the temperature was lowered by 50 mK, as seen in Fig. 3. We attribute this to a first-order Sm-C to Sm-J transition, as seen in the bulk. Although our light-scattering experiments do not allow us to distinguish between a Sm-J phase, where the director points toward the nearest neighbor, and a Sm-G phase, where the director points toward the second nearest neighbor, we have no reason to believe that the thin film behavior is different from that of the bulk. Figure 3 shows the scattered intensity versus temperature for data at an intermediate $q = 17\,038\ \text{cm}^{-1}$ ($\theta = 8^\circ$), which is seen to drop sharply at 80.5 °C. The scattering in the Sm-J appears to be completely uncorrelated background counts with no significant q dependence, so we are unable to determine the elastic constant in this phase. However, based on the intensity at small q, we can establish a lower limit of $\sim 10^{-10}$ ergs for the elasticity in the Sm-J phase.

Figure 3 also shows similar results for a film containing a 1:1 by weight mixture of 8OSI and $\overline{14}$S6. We find a single first-order transition at 70.9 °C, indicating the components are well mixed. While such behavior is not surprising in bulk mixtures, it is not trivial that it would occur in a thin film. Since impurities in free-standing films are known to diffuse to the edges, it is possible that one of the two components might also diffuse leaving a film purely of the other constituent. We rule out this possibility because of the significantly different transition temperatures of the mixture and the pure components. Another possibility is that the two constituents could separate into different layers. For example, the two surface layers could be pure 8OSI and the two interior layers pure $\overline{14}$S6. However, since the layers are weakly coupled, this would lead to different transition temperatures for each layer, as well as a hexatic phase for the 8OSI layers. No such behavior is seen. We conclude that our film consists of homogeneously mixed components. To the best of our knowledge, this represents the first time that a stable free-standing film of a two component mixture has been observed.

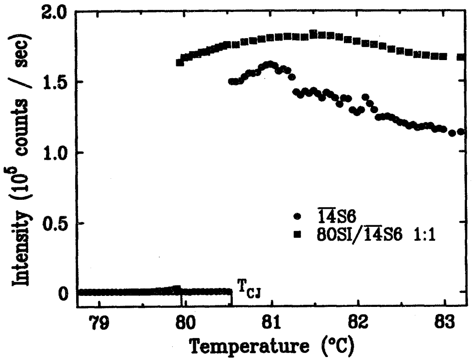

FIG. 3. Scattered intensity for a three-layer film of pure $\overline{14}$S6 and a four-layer film of a 1:1 by weight mixture of 8OSI and $\overline{14}$S6 at $q = 17\,038\ \text{cm}^{-1}$. Both films undergo discontinuous transition from the Sm-C to Sm-J phases. The transition temperatures are 80.55 °C and 70.90 °C, for the pure $\overline{14}$S6 film and 1:1 mixture, respectively. The temperatures for the 1:1 mixture have been adjusted by 9° for the convenience of display.

We now discuss results from films of mixtures containing a higher percentage of 8OSI, where an intermediate Sm-I phase is found. Experiments were performed on four-layer films containing 15%, 25%, 30%, 35%, and 40% by weight $\overline{14}$S6. In the Sm-I phase we must consider the full free energy of Eq. (3). This energy density is equivalent to that of two 1D coupled harmonic oscillators. Diagonalizing this free energy in terms of two normal modes with coordinates $\theta_+ = (K_1^B\,\phi + K_6^I\,\theta)\,/\,(K_1^B + K_6^I)$ and $\theta_- = \theta - \phi$, we can rewrite Eq. (3) as [17]

$$F_{2\text{D}}(\boldsymbol{q}) = \frac{1}{2} K_+^B\, q^2 \left|\theta_+(\boldsymbol{q})\right|^2 + \frac{1}{2}\left(K_-^B\, q^2 + H\right)\left|\theta_-(\boldsymbol{q})\right|^2 ,$$

where $K_+^B = K_1^B + K_6^I$, $K_-^B = K_1^B\,K_6^I\,/\,(K_1^\text{B} + K_6^\text{I})$, and we have expanded $\cos 6\,\theta_-$ to lowest order. We immediately see that θ_+ corresponds to the normal acoustic mode where θ and ϕ fluctuate in phase, while θ_- corresponds to an optic mode where θ and ϕ beat and the spectrum is expected to have a gap with value H. Since fluctuations of each of these modes couple to the scattered light through their dependence on ϕ, we might expect to see two decays in the autocorrelation function as was previously found in other light-scattering studies [7]. However, we find that all correlation functions in these samples appear single exponential. None of the Sm-I correlation functions showed evidence of a second dynamic mode from the optic fluctuations. This suggests that even near the triple point, the coupling field H is large enough that these fluctuations occur on a time scale faster than our experimental resolution ($\sim$ 0.5 μsec). This is the case for pure 8OSI where the optic fluctuations are only seen in very thick films [15]. In all cases we obtained the acoustic mode elasticity as a function of temperature by fitting the amplitudes of the measured correlation functions for the acoustic mode to Eq. (4), where K_1^B is now replaced by K_+^B. The resulting elasticities are shown as a function of temperature in Fig. 4. This figure represents the central result of this work. The transition temperatures in this figure have been shifted for the convenience of display. The actual values are given in Table I. We find that in films with $\overline{14}$S6 concentration $\lesssim$ 35%, K_+^B evolves continuously in the vicinity of the Sm-C to Sm-I transition temperature T_{CI} and a single transition is seen.

In order to analyze the data presented in Fig. 4, we need a quantitative expression for the elastic constant K_6 near the hexatic to liquid transition in the presence

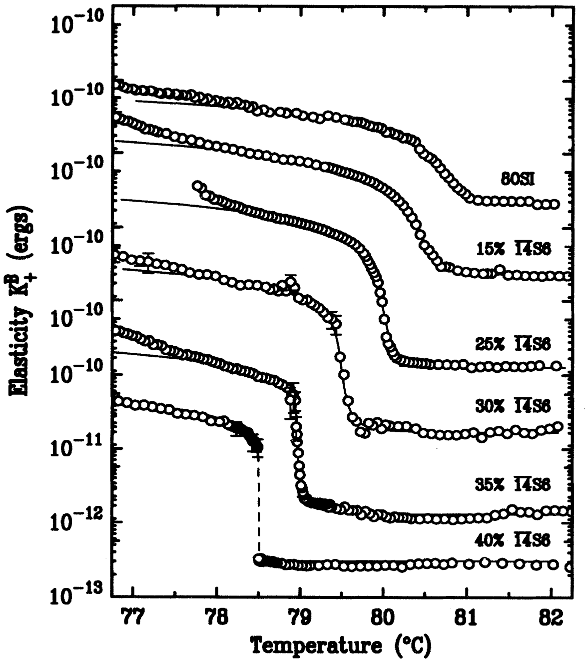

FIG. 4. Bend elasticity K_+^B in the vicinity of T_{CI} for 80SI/$\overline{14}$S6 mixtures. Solid lines are fits to $K_6 = a\psi_6^2$, where ψ_6 is found by minimizing Eq. (5). The fit parameters are given in Table I. The transition temperatures have been adjusted for convenience of display.

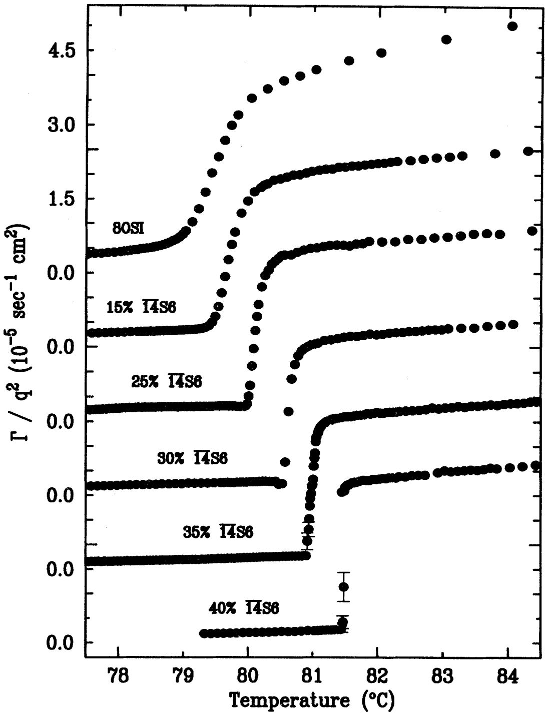

FIG. 5. Bend mode linewidth in the vicinity of T_{CI} for 80SI/$\overline{14}$S6 mixtures. Note the pretransitional slowing down above T_{CI}. The transition temperatures have been adjusted for convenience of display.

of a field. In two dimensions, K_6 has been theoretically predicted to scale as the square of the *positional* correlation length ξ_p for the Sm-J phase [18], and experiments have found this behavior in thick films [15].

We assume that ξ_p is small near T_{CI} and there is a direct enhancement of K_6 by the hexatic order parameter ψ_6; in a mean field approximation we would expect $K_6 = a\psi_6^2$. We calculate ψ_6, the real part of the hexatic order parameter, by minimizing a sixth-order Landau free energy with a linear coupling to the field

$$F = \frac{1}{2}t\psi_6^2 + \frac{1}{4}b\psi_6^4 + \frac{1}{6}c\psi_6^6 - H\psi_6, \tag{5}$$

where $t \equiv (T - T_{CI})/T_{CI}$. Equation (5) is not expected to be exact, but it is simple, and is the only expression we have which includes a field and a tricritical point. The expression provides a satisfactory representation of ψ_6 in thick films [5] up to $\psi_6 = 0.8$ and $T_{CI} - T = 1.25\,^\circ$C and gives the parameter $c = 0.01$. (A parametric equation of state can predict specific heat behavior, but only mimics the first-order transition with a very small critical exponent β [20].)

We fixed K_1^B to its value in the lower Sm-C phase and used Eq. (5) to calculate the enhancement of $K_6 = a\psi_6^2$. As Eq. (5) has many parameters, we fixed $c = 0.01$. (Changing c results in proportional changes in a, b, and H, but no change in the fit quality.) The fit parameters are then a, b, H, and T_{CI}. The results of these fits are summarized in Table I. As the values of the transition temperatures T_{CI} are those determined in the fits to Eq. (5), care should be taken when comparing these values to other experiments where the transition temperature was

TABLE I. Summary of results for films of 8OSI/$\overline{14}$S6 mixtures. All films are four-layer except the pure $\overline{14}$S6, which is three layers. The value of $K_6^I = K_+^B - K_1^B$ is that measured 2° below T_{CI}. The values of a, b, H, and T_{CI} are from the fits described in the text. All elasticities and a are given in ergs.

vskip 2pt

% $\overline{14}$S6	T_{CI} (°C)	T_{IJ} (°C)	K_1^B ($\times 10^{-13}$)	K_6^I ($\times 10^{-11}$)	a ($\times 10^{-11}$)	b ($\times 10^{-3}$)	H ($\times 10^{-5}$)	Φ_0 (Sm-C)	Φ_0 (Sm-I)
0	83.56 ± 0.05	79.2	3.92	0.60	9.5 ± 0.4	19 ± 7	3.9 ± 0.8	32.2°	38.6°
15	79.11 ± 0.01	73.4	4.13	1.66	3.2 ± 0.1	5.7 ± 0.2	6.0 ± 0.4	31.6°	40.6°
25	76.10 ± 0.02	71.8	2.44	3.94	5.1 ± 0.2	2.9 ± 0.4	2.6 ± 0.8	23.8°	36.0°
30	74.38 ± 0.01	70.2	3.91	4.68	5.7 ± 0.2	0.68 ± 0.03	2.2 ± 0.5	26.2°	33.0°
35	73.38 ± 0.01	69.3	2.28	5.94	4.8 ± 0.3	-0.74 ± 0.04	2.3 ± 0.4	23.0°	29.0°
40	72.63 ± 0.01	69.9	3.07	5.34	5.2 ± 0.1	-5.2 ± 0.1	3.2 ± 1.5	24.0°	27.0°
50	70.9 (T_{CJ})		2.89					22.0°	
100	80.5 (T_{CJ})		1.58					18.4°	

determined differently. Other transition temperatures in Table I are determined by the discontinuous changes in the scattered intensity.

The resulting fits are shown as solid lines in Fig. 4. We restricted the range of data fit to within approximately two degrees of the transition. The fit is not good at lower temperatures, due to a combination of the enhancement proportional to ξ_p^2 becoming important and the failure of Eq. (5). The main value of fitting to Eq. (5) is that in capturing the correct qualitative physical behavior it demonstrates that the coupling field is roughly constant and shows a clear evolution in the parameter b. With our samples, it appears that the tricritical point occurs about 33% $\overline{14}$S6 in four-layer films. We find that the elastic constant associated with fluctuations on the in-plane director (K_1^B) is relatively insensitive to the composition of the film, while that associated with fluctuations of the hexatic bond angle (K_6^I) increases approximately tenfold as the concentration of $\overline{14}$S6 in the films is increased. The proportionality constant a also has little dependence on $\overline{14}$S6 concentration, indicating that the large increase we observe in K_6 is due to a corresponding increase in the positional correlation length. Finally, we find that in all samples the tilt angle Φ_0 also increases at the Sm-C to Sm-I transition.

The acoustic mode linewidth in the vicinity of T_{CI} for the six mixtures is shown in Fig. 5. We again adjust the transition temperatures for the display. This data confirms the sharpening of the transition with increasing $\overline{14}$S6 concentration. We observe that in all the mixtures there is some pretransitional slowing down above T_{CI}. This reflects an increase in the viscosity just above the transition. In the 40% mixture, we find that Γ_B jumps discontinuously at T_{CI} reflecting the same behavior as K_+^B. However, there is a small amount of pretransitional behavior seen in the dynamics which is not seen in K_+^B.

In this paper, we have presented results from dynamic light scattering on thin films of 8OSI/$\overline{14}$S6 mixtures. We found that in all mixtures there is a single transition, which indicates the constituents are homogeneously mixed within the layers; thus, no evidence of phase separation was seen. Using this system we were able to study the generic crystal-hexatic-liquid phase diagram of Fig. 1(a). We observed that at high concentrations of $\overline{14}$S6 ($\geq$ 50%) the film has a first-order Sm-C to Sm-J transition. At lower concentrations of $\overline{14}$S6, an intermediate hexatic phase is present. As the concentration of $\overline{14}$S6 is increased, we were able to observe a sharpening of the Sm-C to Sm-I transition until this transition becomes first order at a tricritical point near 35% $\overline{14}$S6. The continuous behavior of the bend elasticity is well fit by a power law whose exponent decreases with increasing $\overline{14}$S6 concentration. We also found the bond-orientational elastic constant K_6^I increases tenfold as the $\overline{14}$S6 concentration is increased.

The liquid crystals used in this work were synthesized by Sandra Keast and Mary Neubert at the Liquid Crystal Institute, Kent State University. We would like to thank Sam Sprunt and George Nounesis for many valuable discussions. This research was supported by the National Science Foundation under Grant No. DMR-9014886.

[1] R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981); S. C. Davey, J. Budai, J. W. Goodby, R. Pindak, and D. E. Moncton, *ibid.* **53**, 2129 (1984).

[2] M. Cheng, J. T. Ho, S. W. Hui, and R. Pindak, Phys. Rev. Lett. **59**, 1112 (1987).

[3] S. B. Dierker, R. Pindak, and R. B. Meyer, Phys. Rev. Lett. **56**, 1819 (1986).

[4] C. Y. Young, R. Pindak, N. C. Clark, and R. B. Meyer, Phys. Rev. Lett. **40**, 773 (1978).

[5] J. D. Brock, A. Aharony, R. J. Birgeneau, K. W. Evans-Lutterodt, J. D. Litster, P. M. Horn, and G. B. Stephenson, Phys. Rev. Lett. **57**, 98 (1986); J. D. Brock, D. Y. Noh, B. R. McClain, J. D. Litster, R. J. Birgeneau, A. Aharony, P. M. Horn, and J. C. Liang, Z. Phys. B **74**, 197 (1989).

[6] E. B. Sirota, P. S. Pershan, L. B. Sorenson, and J. Collett, Phys. Rev. A **36**, 2890 (1987).

[7] S. B. Dierker and R. Pindak, Phys. Rev. Lett. **59**, 1002 (1987); S. Sprunt and J. D. Litster, *ibid.* **59**, 2682 (1987).

[8] S. Amador *et al.*, Phys. Rev. A **39**, 2703 (1989).

[9] D. Y. Noh, J. D. Brock, J. D. Litster, R. J. Birgeneau, and J. W. Goodby, Phys. Rev. B **40**, 4920 (1989).

[10] B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); **41**, 519 (E) (1978); D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979); A. P. Young, *ibid.* **19**, 1855 (1979).

[11] R. J. Birgeneau and J. D. Litster, J. Phys. (Paris) Lett. **39**, 1399 (1978).

[12] Strictly speaking, this may not be a phase transition, as the field due to the tilt can suppress a continuous transition in the same way that a magnetic field can suppress the phase transition in a ferromagnet. However, if the field is weak enough the characteristics of the underlying transition may still be observed.

[13] A. Aharony, R. J. Birgeneau, J. D. Brock, and J. D. Litster, Phys. Rev. Lett. **57**, 1012 (1986).

[14] A. J. Leadbetter, P. A. Tucker, G. W. Gray, and A. R. Tajbakhsh, Mol. Cryst. Liq. Cryst. **1**, 19 (1985).

[15] S. Sprunt, M. S. Spector, and J. D. Litster, Phys. Rev. A **45**, 7355 (1992).

[16] M. S. Spector, S. Sprunt, and J. D. Litster, Phys. Rev.

E **47**, 1101 (1993).

[17] D. R. Nelson and B. I. Halperin, Phys. Rev. B **21**, 5312 (1980).

[18] S. Ostlund and B. I. Halperin, Phys. Rev. B **23**, 335 (1984).

[19] J. D. Brock, Ph.D. thesis, Massachusetts Institute of Technology, 1987.

[20] C. W. Garland, J. D. Litster, and K. J. Stine, Mol. Cryst. Liq. Cryst. **170**, 71 (1989).