Jpn. J. Appl. Phys. Vol. 38 (1999) pp. 6118–6122
Part 1, No. 10, October 1999

Direct Measurement of Fluid Mechanical Properties in Micro Space: Liquid Crystal Orientation under Shear

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(Received July 15, 1999; accepted for publication August 13, 1999)

The shear-induced molecular orientation of a nematic liquid crystal, 5CB (4-pentyl-4′-cyanobiphenyl) was studied in a newly-developed apparatus in which the liquid crystal was confined between optical windows at a film thickness that is continuously variable. The molecular orientation was measured *in situ* during shear in the presence and absence of DC electrical bias between the two surfaces. In this preliminary study we present findings for a spacing of 10 μm, which is comparable to the spacing of actual liquid crystal display technology. Fourier transform infrared time resolved spectroscopy (FTIR-TRS) synchronized with the shear motion provided the molecular orientation as a function of time during the shear cycle. Only a slight orientation along the shear direction was found in the isotropic state but, in the homeotropic state, the molecular orientations in response to shear reflected a competition process between orientation in orthogonal directions. Shear promoted orientation parallel to the confining plates, and a DC bias voltage promoted orientation perpendicular to the confining plates.

KEYWORDS: liquid crystal, confined space, mechanical properties, orientation, shear

1. Introduction

Mechanical properties are one of the important properties of materials because materials are often exposed to the mechanical forces in actual products and realistic processes. Many experimental methods have been developed to measure these properties for solid materials in various configurations. For liquid materials, sophisticated viscometers are now available for application to bulk samples. They apply a shear force or shear displacement to the liquid and measure the response. But it is not easy to apply a controlled force to liquids in tiny spaces such as micrometer-sized gaps. Because these situations are widely seen in various applications such as display devices, adhesion, dispersion and lubrication, it is important to understand mechanical behavior of the materials in these confined situations.

One of the most advanced methods to meet this requirement is a surface force apparatus equipped with a piezoelectric device shear function unit.[1–3] It gives useful information about the dynamics of molecular rearrangements within nanometer-sized plates. Though it is a powerful tool to observe mechanical responses, this technique is limited to film thickness on the order of a few nanometers in dimension. A larger gap spacing, from 1 to 10 μm, would be important for study of common realistic applications such as colloidal suspensions, emulsions, and liquid crystals.

To satisfy this need to achieve mesoscopic film spacings, we used a new experimental system that also employs a piezoelectric shear function unit. With a specially designed apparatus,[4] two separately held optical windows are brought to a parallel position at a spacing that can range from submicron to several hundred microns. Because the windows are held separately, one window can be driven parallel to the surface, and sliding motion of the window generates a shear to the samples injected between them. Within the linear response region of the piezoelectric devices, dynamic viscoelastic measurements can be performed to evaluate mechanical responses.[5,6] By adapting transparent materials as the two optical windows, this apparatus basically works as a liquid transmission cell for spectroscopy measurements, and mechanical response can also be detected by orientational measurement.

Liquid crystals have wide scientific and industrial interest.[7] The orientational behavior of liquid crystals is mainly studied as concerns electric field dependence and surface anchoring qualities.[8–11] Mechanical properties are also estimated by using electric fields in most cases.[12–15] Besides flowing liquid crystal and causing shear forces,[16–19] the use of mechanical forces as an external field is not easy to achieve in a small gap space, though a few studies have been performed in the range of single layer liquid crystal.[20–23] By applying our newly-developed equipment to the liquid crystal samples, molecular behavior confined gaps comparable to the size of an actual liquid display can be studied from the point of the dynamic viscoelasticity and mechanical shear response. This information will be useful to know domain structure between substrates, interaction with substrate surfaces, and dynamic properties. In this article we report the molecular response of 4-pentyl-4′-cyano-biphenyl (5CB) confined within parallel plates with 10 μm spacing under the action of shear forces.

2. Experiment

Figure 1 shows a cross sectional side view of the core parts of the apparatus. Alignment of windows and optical systems was described previously.[5,6] The detailed explanation of the parts, working mechanism bringing two windows to a micrometer gap distance, gap measurement methods, and methods to measure dynamic viscoelasticity, were also mentioned elsewhere.[4–6] Here we explain the system briefly. Circular-shaped windows, an upper window (1/2 inch diameter) and lower window (2 inch diameter), are held independently. The position of the upper window is decided by a coarse adjustment. The lower window is brought close to the upper window by the action of piezoelectric inchworms. Gap distance and parallel alignment are monitored by either optical interferometry or capacitance measurements. Gap distance can be varied from one to several hundred micrometers.

Shear motion is generated by piezoelectric bimorphs that slide the upper window against the lower window. Applying a voltage to both sides of the bimorph, the window slides over

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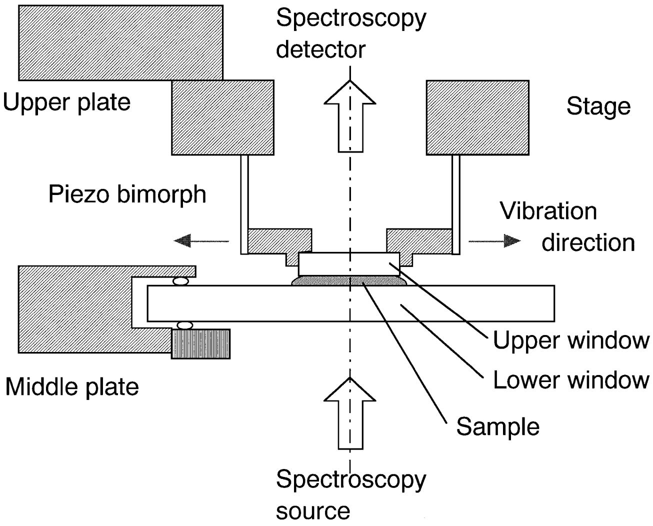

Fig. 1. Cross sectional side view of the shear unit and the optical windows. Upper and lower windows are held independently and slide horizontally, driven by a piezoelectric bimorph, to cause shear. The gap distance is exaggerated on the figure.

a distance almost proportional to the voltage. For viscoelastic measurements, sinusoidal alternating (AC) voltage can be applied to one of the bimorphs, which is used to generate shear motion (sender bimorph), and another bimorph can be used to pick up the signal (receiver bimorph) by a lock-in amplifier. Viscoelasticity of the sample between the windows can be determined by comparing phase and amplitude of sending and receiving signals.[1,2] Optical path is provided along vertical line at the center of the windows. If one chooses properly-translucent materials for the windows, various spectroscopic measurements are possible under shear.

In these experiments, we used longer bimorphs (1 inch length) than customary in this apparatus in order to obtain a relatively large shear amplitude.[1,2] This enabled us to generate 10 μm displacements, though the large voltages required to do this produced bimorph deflection that exceeded the linear region of response, and the torsion of the alternative voltage became larger. As a result the bimorphs worked just as a shear generator, and could not be used to sense viscoelasticity.

The response to shear was picked up instead by IR dichroism studies. Two mirrors were set below and above the apparatus and guided the IR beam from the FTIR instrument (Bio-Rad FTS6000) to a liquid-nitrogen-cooled MCT detector. A KRS-5 wire grid polarizer was set just below the lower window for dichroic measurements.

The electric field of the IR beam was polarized either parallel or perpendicular to the shear direction and the absorbances of specific infrared vibrations were measured in orthogonal directions ($A_\parallel$, $A_\perp$). The evaluation method of the molecular orientation from these absorbances has been well established.[7,24] Here we use dichroic ratio D and the degree of orientational order of the transition moment, S_b, to evaluate the dichroic ratio (D) and the order parameter (S):

$$D = A_\parallel / A_\perp, \tag{1}$$

$$S_\mathrm{b} = (D-1)/(D+2). \tag{2}$$

Time resolved absorbance measurements were also collected to see the orientation changes within a single cycle of shear motion.

The function and mechanism of time resolved spectroscopy (TRS) using step-scan FTIR are widely used for studying liquid crystal response to the electric field.[8–10,25,26]

In these experiments, the window material was an optical flat of germanium (Ge). Because Ge has good IR transparency and a moderately-large electrical conductivity, large enough to allow one to apply a DC bias voltage, it is widely used to study the orientational behavior of liquid crystals.

In these experiments, a DC bias voltage between the upper and lower Ge windows was applied in order to align the liquid crystal vertically. The Ge was used without treatment (such as rubbing or chemical treatment adapted in other studies) except for a basic chemical cleaning of the surface.[27]

A liquid crystal, 4-pentyl-4′-cyanobiphenyl (5CB, purchased from E. M. Industries) was sandwiched between the upper and the lower windows. The temperature was kept at 24–26°C throughout the experiments. In this temperature range, 5CB is in the nematic phase. The gap distance, determined from IR interference between the opposed Ge surfaces, was around 10 μm. DC bias voltages up to 15 V were applied to the windows in some experiments. The cyclic shear frequency was fixed at 100 Hz and the shear amplitude was varied from 0 to 12 μm.

3. Results and Discussion

3.1 *DC bias dependence*

First we show the dependence of the infrared absorbance on the magnitude of DC electric field. In Fig. 2, this is shown for the C≡N stretch vibration located at 2225 cm^{-1}. Both $A_\parallel$ and $A_\perp$ are shown. Electric field dependence of 5CB orientation has, in the past, been studied extensively as concerns the homogeneous-homeotropic transition.[8–10,28] Our results basically match previous results with the difference that in our case the Ge surface was not specially treated with a rubbing process as in other works. This meant that there was no preferred molecular orientation within the plane. As a result, both $A_\parallel$ and $A_\perp$ took almost the same values. Up to 2 V, the absorbances kept the same value as at 0 V. Above 3 V they began to decrease. Because the dipole moment of C≡N stretch is parallel to the molecular long axis of 5CB,[8,29] smaller C≡N stretching intensity at both polarizations signifies that the average molecule turned increasingly upright. Beyond 6–7 V, changes of $A_\parallel$ and $A_\perp$ had saturated and showed little further change with increasing DC bias voltage. The values of the transition voltage and the saturation voltage agree well with results from previous studies.

The consequence of having no surface treatment to promote molecular alignment may be shown in the sharpness of switching at 2 V. In the absence of DC bias (0 V) the molecular orientation was not bound to any specific direction, so the change to the homeotropic state was broader and less well-defined than the clear switching seen in the previous works.

The main point of these characterization experiments was to validate that the new apparatus described here operated reliably as a simple transmission cell.

3.2 *Shear effect on liquid crystal alignment*

We now discuss the effect of shear fields. Figure 3 shows the magnitude of absorbance of the C≡N stretch vibration during shear. Cyclic shear motion at 100 Hz was applied to

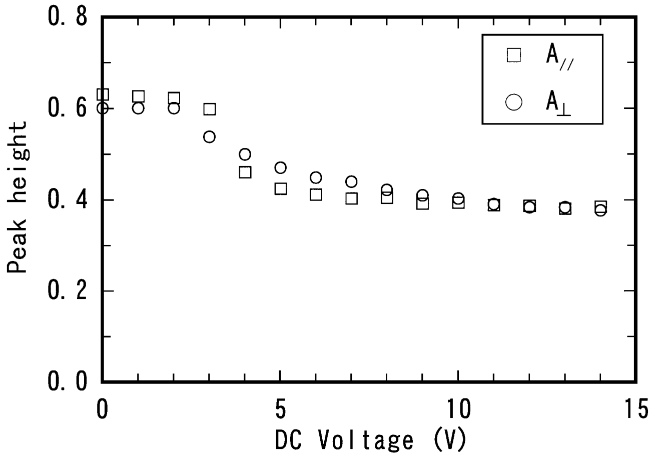

Fig. 2. Infrared absorbance of the CN stretch vibration at 222 cm^{-1} is plotted against applied DC electric field. Gap distance is 7.4 μm. The oxidized Ge surfaces were not specially treated to promote alignment in a preferred direction. The $A_{\|}$ (squares) denotes absorbance parallel to the shear direction. The $A_{\perp}$ (circles) denotes absorbance perpendicular to the shear direction.

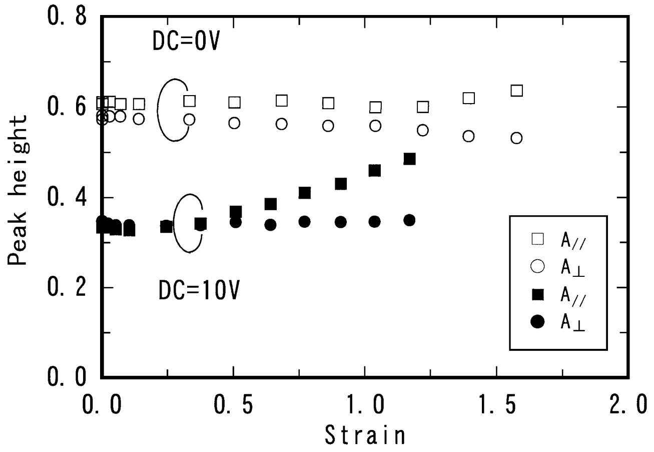

Fig. 3. Infrared absorbance of the CN stretch vibration is plotted against relative strain during periodic at 100 Hz. Strain is defined as shear displacement normalized by film thickness. Filled symbols show the response when 10 V DC voltage was applied to the windows.

the sample. The shear magnitude is quantified as the maximum strain during the cyclic motion (strain shear displacement normalized by thickness of the liquid crystal sample). In the absence of a DC bias voltage, 5CB had no preferred nematic direction and at zero strain the magnitude of absorbances were $A_{\|} \approx A_{\perp} \approx 0.6$. This is essentially the same value as at 0 V in Fig. 2. A small discrepancy between $A_{\|}$ and $A_{\perp}$ is seen in the low strain region, but it is hard to tell whether it comes from shear effect, because the magnitude of this scatter is the same as the difference between these measurements and the measurement at 0 V DC bias in Fig. 2. The slight difference may result from the initial flow of liquid into the sample cell, or might reflect memory of a previous shear experiment. At any rate, infrared intensities did not show significant change as the strain increased up to a magnitude of 1. Then $A_{\|}$ became slightly larger than $A_{\perp}$, suggesting slight orientation along the shear direction. But as a whole the absorbances still remained around 0.6. So it is considered that the molecular orientations were almost the same as at rest, with only a slight tendency to align in the shear direction.

When DC bias voltage was applied, the situation was different. Here 10 V DC bias voltage was applied between the upper and lower windows with 10.8 μm gap distance. The electric field was therefore large enough to place the sample in a homeotropic state, as can be seen from Fig. 2. So at zero strain both $A_{\|}$ and $A_{\perp}$ show smaller values than for the case of 0 V DC bias and the molecules were aligned preferentially in the vertical direction between the windows. As the shear amplitude increased, the values of $A_{\perp}$ remain unchanged, but $A_{\|}$ began to increase above 0.3 strain, and at 1.2 strain it exceeded $A_{\perp}$ by 40%. This means the molecular longer axis tended to align in the shear direction. When one considers that the magnitude of $A_{\perp}$ remained constant, one concludes that the change must have been from the vertical toward the shear direction, independent of the perpendicular direction.

3.3 *Time-resolved analysis in one shear cycle*

The previous section analyzed the average molecular orientation that prevailed during many shear cycles; all information about detailed changes occurring with individual shear cycles was lost. In this section, we address dynamic changes of orientation within a single cycle of shear motion.

To see the details of these changes, we employed time-resolved spectroscopy (TRS) under the periodic shear motion. Figures 4 and 5 show the time resolved absorbances of the C≡N stretch vibration. The spectra were collected with 62.5 μs time resolution. The shear frequency was 100 Hz, so 10 ms corresponded to the one whole cycle. Time zero is set at zero displacement of the upper window.

Figure 4 shows TRS under 0 V DC bias. When the strain was small, $A_{\|}$ and $A_{\perp}$ showed almost the same values, and they kept essentially these same values during the shear cycle. So with this small external mechanical disturbance, there was no significant change in the liquid crystal state (though a small response was observed from precise analysis).[12] At the largest strains, it is apparent that $A_{\perp}$ decreased while $A_{\|}$ increased. This was seen already in Fig. 3 at the higher strain region. In addition to the preference under shear, we can now scrutinize this change from the point of view of kinetics.

Though the absorbance changed little during the cycle, one can recognize a small maximum in $A_{\|}$ and that there may be a minimum in $A_{\perp}$. This small dynamic information was averaged and disappeared in the normal scan mode, and this is one of the benefits of the TRS function. From these results we can summarize that 5CB was still in an unoriented state under small strain and that, under large amplitude oscillatory strain, there was a slight increase in the number of domains whose molecular axis aligned in the shear direction. Because the TRS absorbances were almost flat, we conclude that the orientation changed little with time.

Under 10 V of DC bias voltage, 5CB was oriented in the homeotropic state relative to the surface and Fig. 3 showed that the average orientation changed with shear amplitude. Next we will see what happened in one shear cycle. Figure 5 shows the TRS absorbances of C≡N stretch under 10 V DC bias. It is obvious that one sees large changes with time for $A_{\|}$ but not $A_{\perp}$. In Fig. 3 the averaged absorbances already suggested alignment toward the shear direction. From TRS data it is clear that the change was actually dynamic, not static.

The dipole moment of C≡N stretch is parallel to the molec-

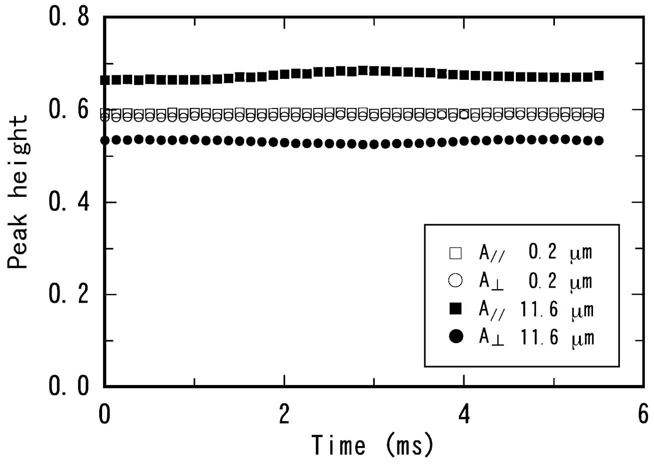

Fig. 4. Time-resolved infrared absorbance of the CN stretch band during cyclic shear is plotted against time during the shear cycle in the absence of external DC bias. The film thickness was 10.3 μm and shear frequency was 100 Hz. Open symbols show the case of 0.2 μm shear amplitude. Filled symbols show the case of 11.6 μm shear amplitude.

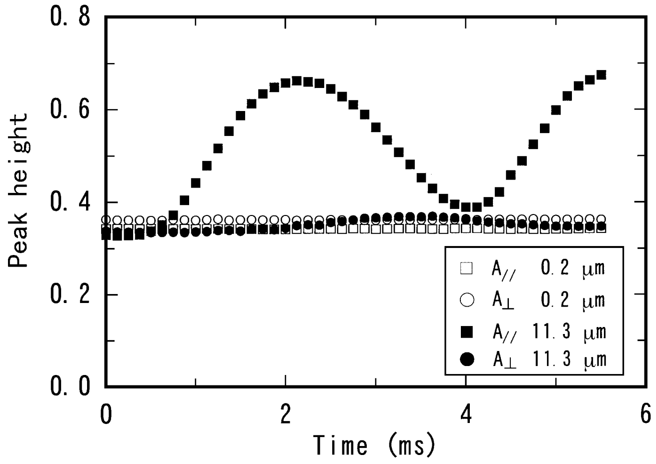

Fig. 5. Time-resolved infrared absorbance of the CN stretch band during cyclic shear is plotted against time during the shear cycle in the presence of 10 V DC voltage between the windows. The film thickness was 10.3 μm and shear frequency was 100 Hz. Open symbols show the case of 0.2 μm shear amplitude. Filled symbols show the case of 11.3 μm shear amplitude.

ular long axis.[14,19] So large $A_{\parallel}$ means the molecules were aligned along the shear direction. When the strain amplitude was small, TRS absorbances were almost flat at small $A_{\parallel}$ and $A_{\perp}$ values. This means the molecules remained oriented in the vertical orientation direction during each shear cycle. When large strain amplitude was applied, $A_{\parallel}$ showed large change synchronized with the strain during the cyclic shear. Because $A_{\perp}$ was almost steady during this period, the changes must come from the vertical direction to the shear direction. This means that the molecular movement is like tilt motion toward the shear direction. The molecules bound to the vertical direction by DC bias rotate to the shear direction by the strain temporarily, but the molecules quickly recovered to vertical orientation.

One interesting point is that at the maximum the $A_{\parallel}$ were around 0.65 and not larger than the $A_{\parallel}$ without DC bias. So this amplitude of shear oriented the molecules along the shear direction, but was not so strongly as to cause overall alignment of the molecules.

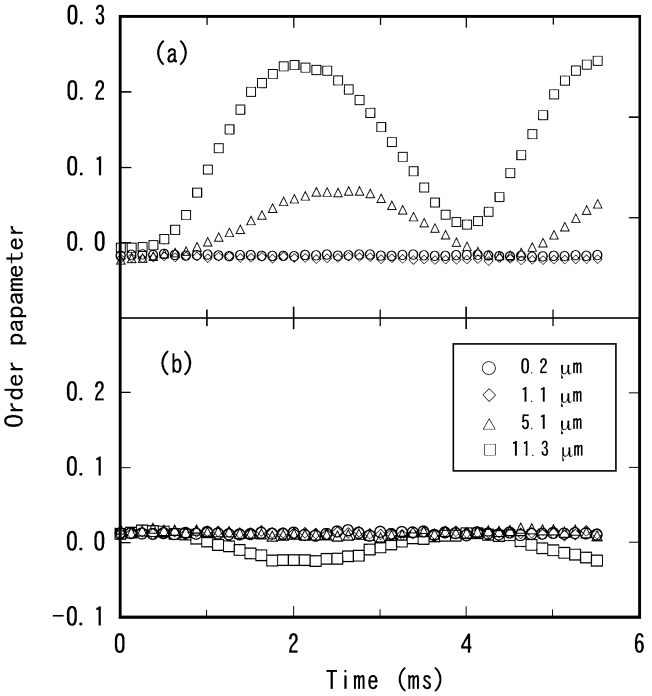

Fig. 6. Time-resolved order parameter of two infrared vibrations is plotted against relative period during the shear cycle in the presence of 10 V DC voltage between the Ge windows. The gap distance was 10.3 μm and shear frequency was 100 Hz. (a) Phenyl stretch at 1485 cm^{-1}. (b) CH wagging vibration at 812 cm^{-1}.

Also worth emphasizing is that $A_{\parallel}$ was proportional to the strain, not to the shear velocity. A liquid crystal is a viscous material and one might have expected its alignment to be proportional to the shear velocity. If this were the case, maximum tilt would be observed at zero displacement position, but it was observed at the maximum displacement position. Considering the fact that the shear alignment was so large under DC bias, this effect should be related to details of the anchoring interaction between the liquid crystal domains and the solid surfaces under DC bias voltage. But this point requires further study for precise explanation.

We can see the same kind of molecular dynamics for other vibrational bands under 10 V DC bias. In Fig. 6 we summarize the time dependence of phenyl C–C stretching at 1606 cm^{-1} and phenyl CH wagging at 812 cm^{-1}. Here, rather than show the raw data (absorbance), we plot the order parameter of bond orientation S_b. The phenyl C–C stretch has a dipole moment parallel to the molecular long axis, just as does the CN stretch,[28,29] and we observed the same type of change as for the C≡N stretch. The order parameter took a maximum value (largest alignment along shear direction) at the maximum shear displacement, and was almost zero (no alignment along shear direction) at the minimum shear displacement.

On the other hand, the phenyl CH wagging vibration has dipole moment perpendicular to the molecular axis,[28,29] and showed a minimum value of orientation at the maximum strain displacement. Because the dipole is perpendicular to the shear direction at maximum strain, the molecular axis is parallel to it, so the observation concerning this vibration is consistent with our results for the other infrared vibrations.

In summary, within a micrometer-sized confined geometry between parallel plates, the mechanical response of a nematic liquid crystal to shear and electric fields was measured using this newly-developed experimental system. FT-IR dichroism was used to evaluate the molecular orientation. Combined with step-scan time-resolved methods (TRS), it provided new information about the molecular orientation under cyclic shear field. The multidomain nematic liquid crystal (5CB) was found to align only slightly in the shear direction except in the presence of a DC bias. But under DC bias, in its homeotropic state, the molecules showed large periodic changes, which were in phase with the displacement.

Acknowledgements

The authors thank to Mrs. Yoon-Kyong Cho and Mr. Everett Geizer for contributions to this work. Support was provided through the National Science Foundation and Department of Energy under Award No. DEFG02-ER9645439, through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign.

1) J. Peachey, J. Van Alsten and S. Granick: Rev. Sci. Instrum. **62** (1991) 463.
2) S. Granick, H.-W. Hu: Langmuir **10** (1994) 3857.
3) S. H. J. Idziak; I. Koltover; J. N. Israelachvili and C. R. Safina: Phys. Rev. Lett. **76** (1996) 1477.
4) A. Dhinojwala, S. Granick: J. Chem. Soc. Faraday Trans. **4** (1996) 619.
5) I. Soga, A. Dhinojwala, Y.-K. Cho and S. Granick: *Proc. Dynamics in Small Confining Systems IV*, eds. M. Drake, S. Troian, R. Kopelman and Y. Klafter (Materials Research Society, 1997).
6) I. Soga, A. Dhinojwala and S. Granick: Langmuir **14** (1998) 1156.
7) H. Okano and S. Kobayashi: *Ekisho* (Liquid Crystal) (Baifukan, Tokyo 1992) [in Japanese].
8) H. Toriumi, H. Sugisawa and H. Watanabe: Jpn. J. Appl. Phys. **27** (1988) L935.
9) T. Nakano, T. Yokoyama and H. Toriumi: Appl. Spectrosc. **47** (1993) 1354.
10) V. G. Greogoriu and R. A. Palmer: Macromol. Symp. **94** (1995) 75.
11) J. Stelzer, R. Hirning and H.-R. Trebin: J. Appl. Phys. **74** (1993) 6046.
12) H. Toriumi and T. Akahane: Jpn. J. Appl. Phys. **37** (1998) 608.
13) H. Schmiedel, R. Stannarius, M. Grigutsch, R. Hirning, J. Stelzer and H.-R. Trebin: J. Appl. Phys. **74** (1993) 6053.
14) O. Nakagawa, M. Imai, H. Naito and A. Sugimura: Jpn. J. Appl. Phys. **35** (1996) 2762.
15) M. Imai, H. Naito, M. Okuda and A. Sugimura: Jpn. J. Appl. Phys. **33** (1994) L119.
16) C. R. Safinya, E. B. Sirota, R. J. Plano and F. R. Bruinsma: J. Phys. Condens. Matter. **2** (1990) SA365.
17) C. R. Safinya, E. B. Sirota and R. J. Plano: Phys. Rev. Lett. **66** (1991) 1986.
18) C. R. Safinya, E. B. Sirota, R. F. Bruinsma, C. J. Robert, R. J. Plano and L. J. Wenzel: Science **261** (1993) 588.
19) S. Masuda, T. Nose, R. Yamaguchi and S. Sato: Jpn. J. Appl. Phys. **34** (1995) 4129.
20) S. H. J. Idziak, C. R. Safinya, R. S. Hill, K. E. Kraiser, M. Ruths, H. E. Warriner, S. Steinberg, K. S. Liang and J. N. Israelachvili: Science **264** (1994) 1915.
21) S. H. J. Idziak, I. Koltover, J. N. Israelachvili and C. R. Safinya: Phys. Rev. Lett. **76** (1996) 1477.
22) C. D. Dushkin and K. Kurihara: Rev. Sci. Instrum. **69** (1998) 2095.
23) C. D. Dushkin and K. Kurihara: Colloids & Surf. A **129/130** (1997) 131.
24) C. L. Khetrapel, *et al.*: *Liquid Crystals Applications and Uses*, ed. B. Bahaudur (Academic Press, London, 1979) Sepctroscopic Applications of Liquid Crystals.
25) R. E. Murphy, F. H. Cook and H Sakai: J. Opt. Soc. Am. **65** (1975) 600.
26) H. Sakai and R. E. Murphy: Appl. Opt. **17** (1978) 1342.
27) P. Frantz and S. Granick: Langmuir **8** (1992) 1176.
28) V. G. Greogoriu, J. L. Chao, H. Toriumi and R. A. Palmer: Chem. Phys. Lett. **179** (1991) 491.
29) A. Hatta: Mol. Cryst. Liq. Cryst. **74** (1981) 195.