

Organization of Polymer-Dispersed Liquid Crystals from a Liquid Bridge

BYUN Myunghwan WANG Jun LIN Zhiquan*

(Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA)

Abstract: We report the organization of polymer-dispersed liquid crystals (PDLCs) into ordered concentric rings over large areas by drying a drop of bound PDLC toluene solution (i.e., confined between a spherical lens and an indium tin oxide (ITO)-coated glass substrate; sphere-on-ITO geometry). The formation of regular ring-like deposits was a direct consequence of controlled “stick-slip” cycles of three-phase contact line during the course of solvent evaporation, which was effectively regulated through the use of the sphere-on-ITO geometry. This simple approach based on controlled evaporative organization may provide a new means of processing polymer/LC mixture to produce ordered surface patterns in one step, where microscopic LCs are dispersed within the polymer matrix.

Key Words: Liquid bridge; Polymer-dispersed liquid crystal; Controlled evaporative organization; “Stick-slip” motion

Polymer-dispersed liquid crystals (PDLCs) as functional materials for a variety of advanced optical devices have recently received much attention due to their potential applications in the areas of flat-panel displays, privacy windows, microlenses, etc.^[1–7]. PDLCs composed of micrometer-sized, birefractive liquid-crystalline droplets dispersed in an optically transparent and uniform polymer matrix are typically prepared by two approaches, i.e., microencapsulation^[8] and phase-separation^[9]. The latter based on a binary mixture of homogeneous polymer and LC allows the utilization of a much wider range of chemistry, the manipulation of interfacial forces, and interfacial LC alignment^[10,11]. The phase separation of polymer/LC can be effectively induced by polymerization^[12], thermal treatment^[13], and evaporation^[14]. In the latter context, the polymer and LC are dissolved in a mutual solvent, then undergo solvent evaporation-driven phase-separation, and finally form a solid film after complete solvent evaporation. Different solubility of the polymer and LC to the solvent renders the polymer to be significantly plasticized by the dissolved LCs, thereby resulting in the formation of droplet-like LC domains in the polymer matrix. The size, shape, and distribution of LC domains on the polymer film are generally governed by the phase separation kinetics as well as the anisotropic ordering of LC as most polymer systems hardly reach a thermodynamically stable state^[6,7,15].

An emergent technique of patterning surfaces with nonvolatile solutes (e.g., polymers, colloidal particles, DNA, and carbon nanotubes) into two-dimensional structures utilizes the evaporation of a sessile droplet from a solid substrate (i.e., an unbound drop of so-

lution). However, due mainly to lack of control over the evaporation process of the drop and possible convection, the resulting structures, e.g., multiple concentric “coffee rings”^[16], fingering patterns^[17], and polygonal network structures^[18,19] are often irregular and stochastically organized^[20]. Therefore, to fully utilize the evaporation as a simple, lithography- and external field-free route to produce intriguing, well-ordered structures over large areas in a rapid, cost-effective manner that have numerous technological applications, the evaporation process that involves a wide range of parameters, including the evaporation flux, the solution concentration, and the interfacial interaction among the solvent, solute, substrate, should be precisely and systemically controlled^[21–26].

Herein, we report the organization of PDLCs into ordered concentric ring-like microstructures over large areas by allowing a drop of PDLC toluene solution to evaporate from a liquid capillary bridge formed by confining the solution between a spherical lens and an ITO-coated glass substrate (i.e., a sphere-on-ITO geometry). During the course of solvent evaporation, the combination of controlled, repetitive “stick-slip” motion of three-phase contact line at the edge of the capillary bridge due to the use of the sphere-on-ITO geometry, and spontaneous phase separation of incompatible polymer and LC at the microscopic scale led to the formation of regular ring-like deposits of PDLCs. Morphological changes of the PDLC concentric rings before and after the removal of LC was closely examined by cross-polarized optical microscope and atomic force microscopy measurements. This simple, one-step approach based on the controlled evapora-

Received: March 9, 2009; Revised: May 7, 2009; Published on Web: May 22, 2009.

*Corresponding author. Email: zqlin@iastate.edu; Tel: +1-515-2949967.

The project was supported by the NSF CAREER Award (NSF CBET-0844084) and the 3M Non-tenured Faculty Award.

© Editorial office of Acta Physico-Chimica Sinica

tive organization may represent a new strategy of producing ordered surface patterns of PDLC, where micrometer sized LCs are well dispersed within the microscopic polymer.

1 Experimental

1.1 Preparation of PDLC solution

Oligomeric polystyrene (PS; weight-average molecular weight, $MW=5100 \text{ g} \cdot \text{mol}^{-1}$ with polydispersity, $PDI=1.07$; Polymer Source Inc., USA) and a thermotropic liquid crystal (LC), 4-*n*-pentyl-4'-cyanobiphenyl (5CB; the nematic phase exists at temperature between 18 and 35 °C; Sigma-Aldrich Inc., USA) were used as the polymer and LC, respectively. The aspect ratio of the length (ca 1.6 nm) to the diameter (ca 0.43 nm) of 5CB is 3.7, indicating a rod-like molecule. Its director is the long axis of the cyanobiphenyl moiety. A PS and 5CB mixture at a mass (m) ratio of 50:50 was dissolved in a common solvent, toluene, at a concentration of 10% (w , mass fraction), resulting in a homogeneous solution^[7].

1.2 Construction of sphere-on-ITO geometry

The spherical lens (made from fused silica with the radius of curvature, $R=1.65 \text{ cm}$ and diameter, $D=1 \text{ cm}$) and the ITO-coated glass substrate were cleaned with a mixture of sulfuric acid and Nonchromix. After ultrasonication for 30 min, they were extensively rinsed with DI solution and blown dry with N_2 . To construct and implement a sphere-on-ITO geometry, first, both the spherical lens and the ITO substrate were firmly fixed at the top and bottom of sample holders, respectively^[7,22–35]. Subsequently, an inchworm motor was used to bring the upper sphere in contact with the lower stationary ITO substrate. Before contact, with only a few hundred micrometers between the surfaces, a 21 μL PDLC toluene solution was loaded and trapped in the sphere-on-ITO geometry. Finally, the upper sphere was brought into contact with ITO-coated glass substrate, forming a capillary-held PDLC microfluid with the highest evaporation rate at the edge of the capillary (Fig.1(a)). This geometry led to a controlled, repetitive “stick-slip” motion of the three-phase contact line, which moved towards the sphere/ITO contact center during the course of toluene evaporation. The sphere/ITO contact area was marked as the “contact center” in the far right panel of Fig.1(b). The experiments were conducted in a closed chamber to minimize possible convection, temperature variation, and humidity effects. As a result, ring-like structures were formed on surfaces of the

spherical lens and the ITO substrate. The complete evaporation took approximately 30 min.

1.3 Characterization

A polarized optical microscopy (Olympus BX51 equipped with a CCD camera, Japan; polarizer \perp analyzer) in transmission mode was used to monitor the structure formation of PDLC as well as the morphological change of PDLC after removal of LC by vacuum at room temperature. Atomic force microscopy (AFM) images of structures formed on the ITO substrate were performed using a Dimension 3100 scanning force microscope in tapping mode (Digital Instruments, USA). BS-tap300 tips (Budget Sensors, USA) with spring constants ranging from 20 to 75 $\text{N} \cdot \text{m}^{-1}$ were used as scanning probes.

2 Results and discussion

The selection of PDLCs composed of PS and 5CB as the non-volatile solute was motivated by their potential applications in flat-panel displays and other optical devices. Fig.1(a) shows a schematic illustration of the sphere-on-ITO geometry, where a small amount of 10%(w) PS/5CB (50:50) toluene solution was trapped, forming a liquid capillary bridge from which toluene was allowed to evaporate only at the capillary edge (Fig.1(a)). As toluene evaporated, the PS/5CB was transported from the solution inside to the edge of the capillary and pinned the contact line (i.e., “stick”), forming a “coffee ring” of PS/5CB. During the deposition of PS/5CB, the initial contact angle gradually decreased, due to the evaporative loss of solvent, to a critical contact angle, at which the capillary force (i.e., depinning force) became larger than the pinning force^[22], leading the contact line to jerk to next position inward (i.e., “slip”), where it was pinned again and a new “coffee ring” was thus produced. Repetitive “stick-slip” motion of the receding contact line toward the sphere/ITO contact center with elapsed time left behind regular assemblies of PS/5CB concentric rings governed by the competition between the pinning force and the capillary force, as depicted in Fig.1(b)^[22]. The ring width (W) was strongly dependent upon the pinning time of PS/5CB. While the center-to-center distance between the adjacent rings (λ) was governed by subsequent depinning of the solution front^[22].

The glass transition temperature of the PS/5CB mixture ($T_{g, \text{PS/5CB}}$) was 18 °C^[7,36]. The decrease in T_g from 64 °C for pure PS ($MW=5100 \text{ g} \cdot \text{mol}^{-1}$) to 18 °C for the PS/5CB mixture was

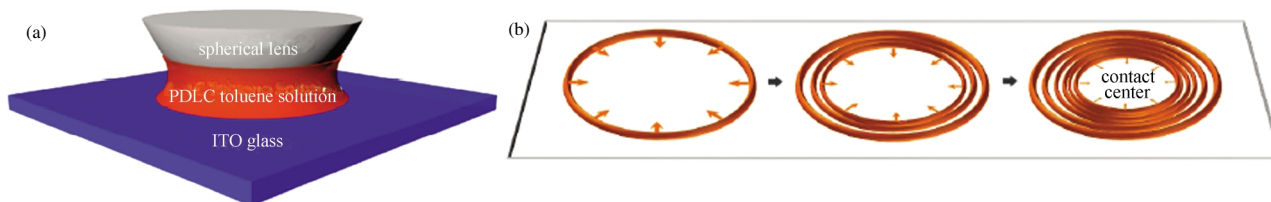


Fig.1 (a) Three dimensional illustration of a drop of polymer-dispersed liquid crystal (PDLC) toluene solution trapped between a spherical lens and an ITO-coated glass substrate (i.e., a sphere-on-ITO geometry); (b) Stepwise representation of the formation of concentric PDLC rings from the 10%(w) PDLC toluene solution ($m_{\text{PS}}/m_{\text{5CB}}=50:50$)

The sphere and ITO substrate contact area is marked as “contact center” in the far right panel.

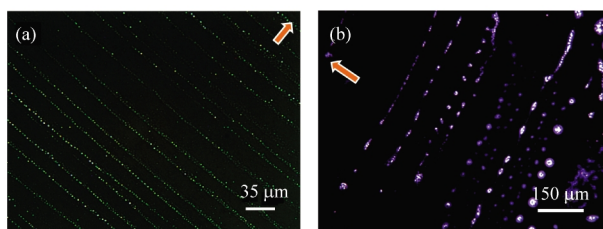


Fig.2 (a) Optical micrograph of concentric PDLC rings formed on the ITO glass by drying the 10%(w) PDLC toluene solution in the sphere-on-ITO geometry; (b) Optical micrograph of PDLC microstructures formed by drying the 10%(w) PDLC toluene solution on the ITO glass (i.e., from an unbound solution)

The images were taken under a crossed polarizer and analyzer in transmission mode. The arrow marked the direction of the movement of solution front.

due to the fact that 5CB with low MW value ($MW=249 \text{ g}\cdot\text{mol}^{-1}$) acted as the plasticizer in PS. Moreover, PS and 5CB are highly incompatible. Taken together, demixing between PS and 5CB within the microscopic concentric rings took place during the course of toluene evaporation. The complete evaporation took approximately 30 min. After that, the sphere and the ITO substrate were separated. Only the concentric rings formed on the ITO substrate were further examined in the study due to the curvature effect of the upper spherical lens. The ring patterns composed of the phase separated PS and 5CB on the ITO substrate were left in air for additional 2 h to ensure the complete evaporation of residual toluene, which was confirmed by the stability of the focus under the optical microscopy. Regularly organized concentric rings of PS/5CB were yielded (Fig.2(a)), in which randomly distributed microscopic 5CB domains in green situated in the PS/5CB mixture within a ring are clearly evident, while the isotropic PS phases were not observable under the cross-polarized optical microscope. Locally, the rings appeared as the parallel stripes. By contrast, irregular concentric rings of PS/5CB were produced by drying a sessile drop of PS/5CB toluene solution placed on a single ITO substrate (i.e., unbound solution) (Fig.2(b)). The size of LCs and thus the width of rings in Fig.2(b) were larger than those formed in the sphere-on-ITO geometry (Fig.2(a)). This reflects that the use of axially symmetric sphere-on-flat geometry facilitated the control over the evaporation process and associated capillary flow, and thus yielding ordered

rings. It is worth noting that concentric rings of PS/5CB produced in the sphere-on-ITO geometry were not very highly ordered due to the use of very low MW of PS and 5CB, as compared to ordered concentric rings with unprecedented regularity obtained from other nonvolatile solutes, for example, linear conjugated polymer poly (2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), and the PS/PMMA blends, which were previously studied, in which the MW values of these polymers were high^[22,24,25,29–31,34].

Notably, when 5CB and PS solely were used as nonvolatile solutes, and their 10%(w) toluene solutions were either drop-cast on the ITO substrate (i.e., unbound droplets) or allowed to evaporate from the sphere-on-ITO geometry (bound droplets; i.e., forming a liquid capillary bridge), either chaotic structures of 5CB or continue films of PS were observed. Irregular “coffee ring” deposits of 5CB with no periodic spacing were formed, where nematic bipolar, radial, and axial configurations of 5CB with approximately circular shape^[10] and different sizes are clearly evident in the cross-polarized optical micrograph obtained in transmission mode (Fig.3(a)). The use of sphere-on-flat geometry suppressed 5CB from forming big aggregates as seen in Fig.3(a), and relatively improved the distribution of 5CB (Fig.3(b)). For PS, a continuous PS film was deposited over the entire area regardless of the use of the upper sphere. Both unbound and bound droplets of the PS toluene solutions slowly dried on the ITO surface as toluene evaporated (Fig.3(c, d)). No dewetting was observed; this may be due to the higher concentration of PS solution (10%) used in the study.

To scrutinize the surface morphologies of the PS/5CB rings and the detailed domain structures of 5CB and PS within the ring, AFM measurements were performed on the sample at the same location after selective removal of 5CB by vacuum at room temperature for different time. It should be noted that the attempt to conduct AFM imaging on the sample before the removal of 5CB was not successful due to the glass transition temperature of the PS/5CB mixture ($T_{g, \text{PS/5CB}}=18^\circ\text{C}$) lower than room temperature (25°C). The PS/5CB rings were liquid-like. By varying the vacuum treatment time, the existence of 5CB on the surface of rings can be identified. Fig.4 shows the AFM height and phase images obtained from the sample treated under vacuum

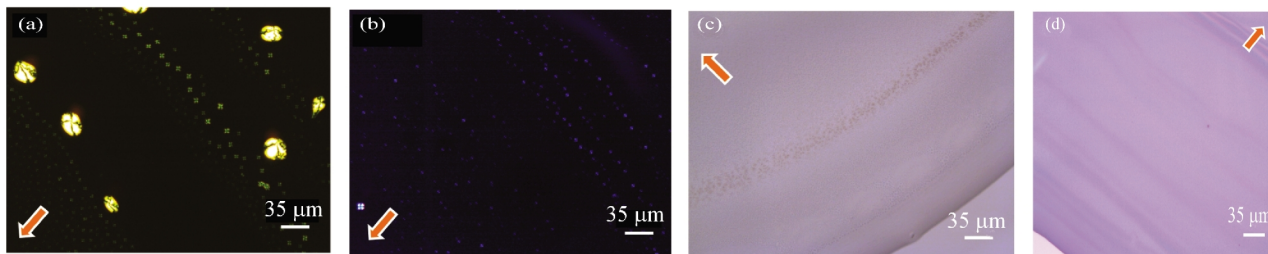


Fig.3 Optical micrographs obtained from control experiments

Optical images of 5CB formed on an ITO glass by drying (a) a drop of 10%(w) 5CB toluene solution that was cast on the ITO glass (i.e., single surface, without the use of sphere-on-ITO geometry), and (b) a drop of 10%(w) 5CB toluene solution that was originally confined in the sphere-on-ITO geometry. Optical images of PS produced on an ITO glass upon complete evaporation of (c) a 10%(w) PS toluene solution that was cast on the ITO glass, and (d) a 10%(w) PS toluene solution that was restricted in the sphere-on-ITO geometry. The arrow marked the direction of moving contact line.

for 3 h. It is noteworthy that nearly constant values of center-to-center distance between adjacent rings ($\lambda = (12.0 \pm 0.5) \mu\text{m}$) and the ring width ($W = (6.0 \pm 0.5) \mu\text{m}$) were seen over the entire deposition area. This can be attributed to the fact that a uniform height ($h = (25 \pm 5) \text{ nm}$) of the PS/5CB rings was formed on the substrate, suggesting a constant pinning time. Thus, the evaporative loss of toluene was steady, leading to the formation of concentric rings with constant λ and W . This observation was reminiscent of our recent study on evaporation-induced self-assembly of the quantum dots^[37–44] from sphere-on-flat geometry^[23]. The rings deposited over a surface area of $\pi \cdot (d'/2)^2 = \pi \cdot (8/2)^2 \approx 50 \text{ mm}^2$, where d' is the diameter of the outermost ring formed in the present study ($d' = 8 \text{ mm}$). This area is only dictated by the volume of the PDLC solution and the diameter (d) of the spherical lens used ($d = 1 \text{ cm}$). In this context, by increasing d and placing a larger amount of PDLC solution, rings over even larger areas can readily be obtained.

We noted that the 3-hour vacuum treatment was probably not long enough for 5CB to be completely extracted from the surface of PS/5CB mixture. Thus, a trace amount of liquid like 5CB may remain on the surface. As a result, scanning artificial defects appeared in the AFM images in tapping mode (Fig.4(a, c)). In this regard, AFM measurements were conducted on the sample after a lengthy vacuum treatment (i.e., suction for 24 h) to thoroughly remove 5CB on the surface, thereby eliminating the artificial defects seen in Fig.4. Randomly dispersed holes were ob-

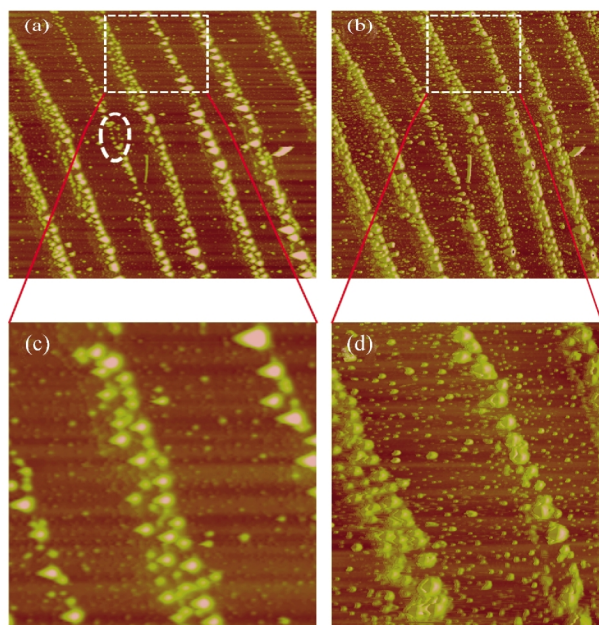


Fig.4 AFM height (a, c) and phase images (b, d) of concentric PDLC rings produced from the drying-mediated self-organization of the 10%(w) PDLC toluene solution after the 3-hour vacuum treatment

The scan sizes are $80 \mu\text{m} \times 80 \mu\text{m}$ in (a, b), and $25 \mu\text{m} \times 25 \mu\text{m}$ in (c, d). Close-up AFM images in (a) and (b) are shown in (c) and (d), respectively. The white dashed ellipse in (a) indicated that the image after the 3-hour and 24-hour (Fig.5(a)) vacuum treatments to remove 5CB were taken at the same location.

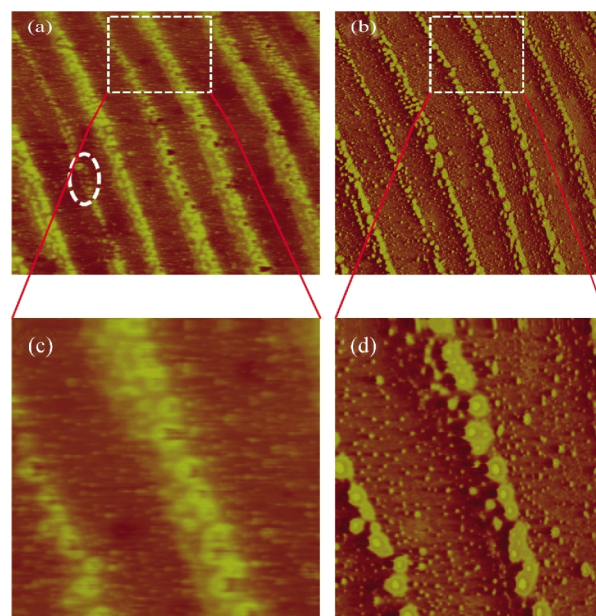


Fig.5 AFM height (a, c) and phase images (b, d) of concentric PDLC rings produced from the drying-mediated self-assembly of the 10%(w) PDLC toluene solution after the 24-hour vacuum treatment

The scan sizes are $80 \mu\text{m} \times 80 \mu\text{m}$ in (a, b), and $25 \mu\text{m} \times 25 \mu\text{m}$ in (c, d). Close-up AFM images in (a) and (b) are shown in (c) and (d), respectively.

served within the microscopic rings as shown in Fig.5(a, c). By comparing with the close-up AFM images of ring patterns shown in Fig.4(c, d), these holes can be assigned to the locations where 5CB originally situated (Fig.5(c, d)). Some PS/5CB dot-like domains were deposited between two adjacent rings on the ITO substrate (Figs.4 and 5). This is not surprising in light of the fact that ultralow MW PS (i.e., oligomer, no chain entanglements) and 5CB were used; and the depinning force was not strong enough to cause the three-phase contact line to jump to a new position inward^[34]. Fig.6(a) shows a cross-polarized optical micrograph of concentric rings obtained in a reflection mode after 24-hour vacuum suction. No distinctive 5CB microdomains were observed under cross-polarized optical microscope in a transmission mode (Fig.6(b)), signifying that anisotropic 5CB was successfully extracted from the PS matrix after a lengthy vacuum process, leaving behind isotropic PS on the surface as shown in Fig.6(a).

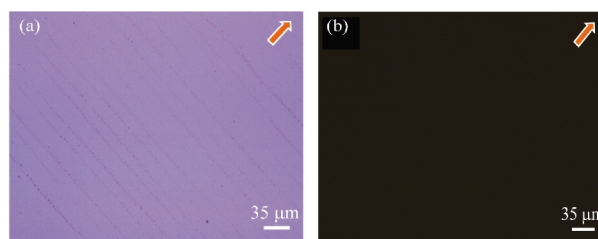


Fig.6 Cross-polarized optical micrographs of concentric PDLC rings in reflection mode (a) and in transmission mode (b) after the 24-hour vacuum treatment

3 Conclusions

In summary, we describe a simple, one-step method based on controlled evaporation from a confined geometry to organize PDLCs into regular concentric ring-like microstructures over large areas. These self-organized microstructures were resulted from two simultaneous processes, involving the controlled, repetitive “stick-slip” motion of the contact line and the spontaneous phase separation of polymer and LC. Morphological changes of these LC-containing concentric rings before and after the removal of LCs by vacuum were visualized by cross-polarized optical microscope and atomic force microscopy measurements. We would like to be able to exert more control over the regularity of ring-like PDLC deposits by increasing the MW of PS. This work is currently under investigation. Although here we use the sphere-on-ITO geometry to harness the evaporation process, this concept, in principle, should be applicable to other confined geometries with different shapes of upper surface to yield a wide spectrum of intriguing yet highly ordered structures.

References

- Mucha, M. *Progress in Polymer Science*, **2003**, **28**: 837
- Zhang, H.; Lin, Z.; Yan, D.; Yang, Y. *Sci. China Ser. B*, **1997**, **40**: 128
- Lin, Z.; Zhang, H.; Yang, Y. *Macromol. Theory Simul.*, **1997**, **6**: 1153
- Lin, Z.; Zhang, H.; Yang, Y. *Phys. Rev. E*, **1998**, **58**: 5867
- Lin, Z.; Zhang, H.; Yang, Y. *Macromol. Chem. Phys.*, **1999**, **200**: 943
- Xia, J. F.; Wang, J.; Lin, Z. Q.; Qiu, F.; Yang, Y. L. *Macromolecules*, **2006**, **39**: 2247
- Wang, J.; Xia, J.; Hong, S. W.; Qiu, F.; Yang, Y.; Lin, Z. Q. *Langmuir*, **2007**, **23**: 7411
- Drzaic, P. S. *J. Appl. Phys.*, **1986**, **60**: 2142
- Doane, J. W.; Vaz, N. A.; Wu, B. G.; Zumer, S. *Appl. Phys. Lett.*, **1986**, **48**: 269
- Erdmann, J. H.; Zumer, S.; Doane, J. W. *Phys. Rev. Lett.*, **1990**, **64**: 1907
- Yamaguchi, T.; Kawata, Y.; Mori, Y. *Appl. Phys. Lett.*, **1998**, **72**: 1170
- Lee, J. C. *Phys. Rev. E*, **1999**, **60**: 1930
- Chiu, H. W.; Kyu, T. *J. Chem. Phys.*, **1995**, **103**: 7471
- Higgins, D. A. *Adv. Mater.*, **2000**, **12**: 251
- Chiu, H. W.; Kyu, T. *J. Chem. Phys.*, **1999**, **110**: 5998
- Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature*, **1997**, **389**: 827
- Pauliac-Vaujour, E.; Stannard, A.; Martin, C. P.; Blunt, M. O.; Nottingher, I.; Moriarty, P. J.; Vancea, I.; Thiele, U. *Phys. Rev. Lett.*, **2008**, **100**: 176102
- Nguyen, V. X.; Stebe, K. J. *Phys. Rev. Lett.*, **2002**, **88**: 164501
- Rabani, E.; Reichman, D. R.; Geissler, P. L.; Brus, L. E. *Nature*, **2003**, **426**: 271
- Adachi, E.; Dimitrov, A. S.; Nagayama, K. *Langmuir*, **1995**, **11**: 1057
- Ming, T.; Kou, X.; Chen, H.; Wang, T.; Tam, H.; Cheah, K.; Chen, J.; Wang, J. *Angew. Chem. Int. Ed.*, **2008**, **47**: 9685
- Xu, J.; Xia, J.; Hong, S. W.; Lin, Z. Q.; Qiu, F.; Yang, Y. L. *Phys. Rev. Lett.*, **2006**, **96**: 066104
- Xu, J.; Xia, J.; Lin, Z. Q. *Angew. Chem. Int. Ed.*, **2007**, **46**: 1860
- Hong, S. W.; Xia, J.; Lin, Z. Q. *Adv. Mater.*, **2007**, **19**: 1413
- Hong, S. W.; Byun, M.; Lin, Z. Q. *Angew. Chem. Int. Ed.*, **2009**, **48**: 512
- Byun, M.; Laskowski, R. L.; He, M.; Qiu, F.; Jeffries-EL, M.; Lin, Z. Q. *Soft Matter*, **2009**, **5**: 1583
- Hong, S. W.; Xu, J.; Xia, J.; Lin, Z. Q.; Qiu, F.; Yang, Y. L. *Chem. Mater.*, **2005**, **17**: 6223
- Lin, Z. Q.; Granick, S. *J. Am. Chem. Soc.*, **2005**, **127**: 2816
- Hong, S. W.; Giri, S.; Lin, V. S. Y.; Lin, Z. Q. *Chem. Mater.*, **2006**, **18**: 5164
- Hong, S. W.; Xu, J.; Lin, Z. Q. *Nano Lett.*, **2006**, **6**: 2949
- Hong, S. W.; Xia, J.; Byun, M.; Zou, Q.; Lin, Z. Q. *Macromolecules*, **2007**, **40**: 2831
- Hong, S. W.; Jeong, W.; Ko, H.; Kessler, M. R.; Tsukruk, V.; Lin, Z. Q. *Adv. Funct. Mater.*, **2008**, **18**: 2114
- Byun, M.; Hong, S. W.; Qiu, F.; Zou, Q.; Lin, Z. *Macromolecules*, **2008**, **41**: 9312
- Byun, M.; Hong, S. W.; Zhu, L.; Lin, Z. Q. *Langmuir*, **2008**, **24**: 3525
- Byun, M.; Wang, J.; Lin, Z. *J. Phys.: Cond. Matt.*, **2009** (in press)
- Boussoualem, M.; Roussel, F.; Ismaili, M. *Phys. Rev. E*, **2004**, **69**: 031702
- Xu, J.; Wang, J.; Mitchell, M.; Mukherjee, P.; Jeffries-EL, M.; Petrich, J. W.; Lin, Z. Q. *J. Am. Chem. Soc.*, **2007**, **129**: 12828
- Xu, J.; Xia, J.; Wang, J.; Shinar, J.; Lin, Z. Q. *Appl. Phys. Lett.*, **2006**, **89**: 133110
- Wang, J.; Xu, J.; Goodman, M. D.; Chen, Y.; Cai, M.; Shinar, J.; Lin, Z. Q. *J. Mater. Chem.*, **2008**, **18**: 3270
- Goodman, M. D.; Xu, J.; Wang, J.; Lin, Z. Q. *Chem. Mater.*, **2009**, **21**: 934
- Lin, Z. Q. *Chem. Eur. J.*, **2008**, **14**: 6294
- Zimnitsky, D.; Jiang, C.; Xu, J.; Lin, Z. Q.; Tsukruk, V. V. *Langmuir*, **2007**, **23**: 4509
- Zimnitsky, D.; Jiang, C.; Xu, J.; Lin, Z. Q.; Zhang, L.; Tsukruk, V. V. *Langmuir*, **2007**, **23**: 10176
- Zimnitsky, D.; Xu, J.; Lin, Z.; Tsukruk, V. *Nanotechnology*, **2008**, **19**: 215606