

Optical Microscopy Study for Director Patterns around Disclinations in Side-Chain Liquid Crystalline Polymer Films

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Polarizing optical microscopy is employed to study director fields around disclinations in side-chain liquid crystalline polymer films. Optical black brushes together with stripes around disclinations are observed. The stripes run parallel to the local director and thus decorate overall patterns of nematic director around disclinations. Three director patterns involving radial, spiral, and circular microstructures of a positive integer disclination with $s = +1$ and one hyperbolic pattern of a negative integer disclination with $s = -1$ are observed in the thin film. It is found that the specific configurations of a pair of $(+1, -1)$ disclinations form during the late stage of annihilation. Increasing the film thickness leads to disclination instability. We observe that black four-brushes of disclinations with $s = \pm 1$ split into black two-brushes, where two types of director patterns of disclinations with half-integer strengths of $s = \pm 1/2$ produce. Theoretical analysis is presented to explain this instability.

Introduction

Liquid crystals (LCs) are characterized by a preferred orientational order, which is described by an apolar director \mathbf{n} field. The most probable director configuration is determined by minimization of the total free energy with respect to the director field. In deformed liquid crystals, a disclination showing black brushes under polarizing optical microscopy is an orientational symmetry-breaking defect, and its strength corresponds to the number of rotations (in multiples of 2π) of the director over a path encircling the disclination.^{1,2} Knowing the disclination microstructure can shed light on defect mobility, which, in turn, affects the physical properties of LCs; for example, the alignment quality or rheological behavior.^{3,4} However, it is still far from being understood due to both the complexity of the system and the lack of suitable experimental methods.

Half a century ago, Frank predicted accurate director patterns around disclinations in his continuum theory based on Oseen's work.⁵ The detailed molecular trajectories are distinguished by disclination strength s and a value of constant parameter, c , which relates the axial position in the plane around the disclination core (polar angle θ) and the director orientation angle ϕ : in the simplest case, $\phi(\theta) = s\theta + c$. According to this theory, one negative pattern and one positive pattern for $s = \pm 1/2$, and one negative pattern and three positive patterns for $s = \pm 1$ can be expected in a two-dimensional ordered liquid crystal, as shown in Figure 1. Under polarizing optical microscopy, all these patterns exhibit black brushes due to optical effect, following a simple function $s = (\text{brush number})/4$.⁶ However, little experimental studies on direct visualization of microstructures of disclinations using optical microscopy have been reported to date.⁷

Side-chain liquid crystalline polymers are chain molecules containing a flexible polymer backbone with mesogenic units connected to it with flexible spacers, forming a comblike fashion. They present a unique class of materials with mesomorphic and viscoelastic behavior.^{8,9} Their microstructures result

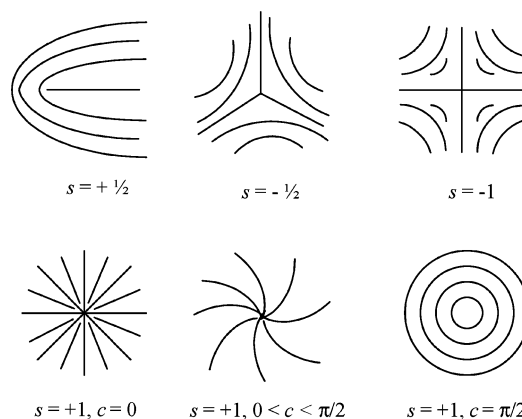


Figure 1. Frank continuum theory prediction of molecular trajectories in a two-dimensional ordered liquid crystal associated with disclinations of $s = \pm 1/2$ and ± 1 .

from the delicate balance between liquid crystalline order due to the mesogenic core and statistical disorder due to the polymer backbone entropy. The orientational properties are carried by the short mesogenic side chains, and the nature of the order parameter is then similar to the small molecule LCs.¹⁰ There are many theoretical and experimental indications that the values of elastic constants in side-chain liquid crystalline polymers are close to those in analogous small molecule LCs.^{11,12} Recently, we reported the observation of two-dimensional stripes in thin films of a side-chain polymer using transmission electron microscopy (TEM) and atomic force microscopy (AFM).^{13–15} When the samples were cooled to the smectic phase, after a holding period in the nematic phase, a characteristic pattern of stripes developed. The orientation of stripes, along the local director, was demonstrated by correlating the direction of the stripes with electron diffraction patterns. Stripes result from equilibrium instability, an analogy with the Rayleigh–Taylor instability, which in this case occurs due to the competition between the layer-alignment effect of the substrate and the planar director alignment, forcing smectic layers perpendicular to the film surface. We found that the film thickness and annealing temperature affected the stripe width and amplitude while the

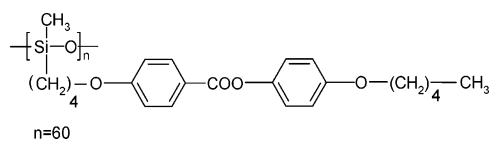
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annealing time only affected the perfection of the stripe alignment—and by implication the perfection of the underlying director pattern. Stripes serve to decorate the underlying molecular alignment, yielding a map of director fields, but do not rely on any crystallization of the polymer, unlike previous techniques for observing director fields.^{16–19} Since the stripe width could be tuneable from tens of nanometers up to micrometers, it could be possible to visualize director fields around disclinations under optical microscopy and correlate the director patterns with optical black brushes.

In this work, we extend the stripe-decoration technique to study director distortions around disclinations in thin films of a side-chain liquid crystalline polymer using polarizing optical microscopy. We study effect of the film thickness on disclination instability. In thin films, we observe four types of patterns of disclinations with integer strengths of $s = \pm 1$, using optical microscopy for the first time. Each pattern is accompanied by optical black four-brushes. By controlling the annealing time in the nematic phase, and thus the average separation of pairs of disclinations with opposite sign move together and annihilate via a certain special configuration. Increasing the film thickness results in disclination instability. We observe optical black four-brushes of disclinations with $s = \pm 1$ are separated into optical black two-brushes, where two types of director patterns of disclinations with half-integer strengths of $s = \pm 1/2$ produce. We put forward arguments that explain why the film thickness induces disclination instability.

Experimental Section

The polymer in this work is an end-on fixed side-chain liquid crystalline polysiloxane denoted as SCP-4. The material was kindly prepared for us in house by Dr. A. R. Tajbakhsh. The detailed procedure can be found in the pioneering work of Finkelmann and Rehage.²⁰ Its chemical structure is as follows:



Its phase behavior was studied by differential scanning calorimetry (DSC) and polarizing optical microscopy. The polymer has a glass transition T_g at 12 °C, a smectic–nematic transition at 82 °C, and a nematic–isotropic transition at 97 °C. The phases were identified by the characteristic textures observed under polarizing optical microscope.

Thin films were prepared by the spin-coating method by spinning onto the glass slides from a 1–10% chloroform solution of the polymer at a speed of 2000–3500 rpm. Film thickness was controlled by changing the sample concentration and spinning speed. After completing solvent evaporation, the thin films were heated to the nematic phase at 90 °C for different times to develop the texture and subsequently quenched into room temperature. As a result, the typical Schlieren nematic texture was locked within the polymer. The samples were then directly used for observation of polarizing optical microscope (Zeiss Axioplan).

Results and Discussion

Integer Disclinations. Figure 2 shows a typical optical micrograph for a thin film of ~ 500 nm thickness, annealed in a nematic phase at 90 °C for 1 h and then quenched to room temperature, deep into the smectic state. One can immediately see black four-brushes of a Schlieren texture emanating from singularities typical of the nematic phase under polarizing optical microscopy. They are disclinations with integer strengths of s

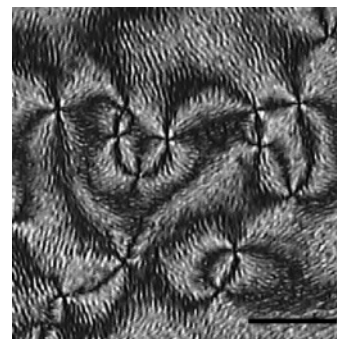


Figure 2. Polarizing optical micrograph of a typical Schlieren texture of ~ 500 nm thin films annealed at a nematic phase of 90 °C for 1 h and then quenched into room temperature. The scale bar is 30 μm .

$= \pm 1$.^{6,8} The black brushes are regions where the local optic axis is perpendicular to the plane of polarization of the incident light. In other region, the plane of polarization could be parallel to the local director. Accompanying optical black four-brushes, surface stripes were observed under optical microscopy. The periodic stripes are more or less parallel to each other. The average periodicity of the strips is about 1 μm . The stripes were apparent with or without crossed polars and did not change their orientation when rotating the crossed polars. As the director of the mesogenic groups is parallel to the direction of the stripes,¹³ the orientation of stripes reveals the actual directions of the trajectories of the directors around each disclination.

The physical origin of stripes in this work is simple and general. As well-known, the nematic director in thin films of side-chain polymers preferentially lies parallel to the surface, whereas the smectic layer has a natural affinity to a flat surface and the director is thus perpendicular to it.^{8,9} When the polymer undergoes the nematic–smectic transition, there is a competition between the planar director alignment and the layer-aligning effect of the substrate. Since the polymer is essentially incompressible, there is a geometric requirement of deformation parallel to the surface, which requires flow of materials. Because the chains have limited mobility in the smectic phase, a modulation of the director (and smectic layers) develops in order to minimize the lateral mechanical displacement in the film. This modulation manifests itself in both the out-of-plane director and surface topographic profile, leading to observed stripes along the director. This mechanism is, in its spirit, very close to the famous Rayleigh–Taylor instability, as described in detail.¹³ As this polysiloxane is known to have a prolate backbone conformation, this direction is also the long axis of anisotropic polymer chains in the film.

Figure 3 shows optical micrographs of four typical super-molecular microstructures around disclinations with strengths of $s = \pm 1$ in isolation. One can immediately observe the pattern of contrasting stripes, which evidently follow the director pattern around each disclination. We found three different patterns of disclinations with a strength of $s = +1$ including radial (R), spiral (S), and circular (C) patterns, (Figure 3a–c) and only one type of disclination with a strength of $s = -1$. This negative disclination has a hyperbolic structure (H) with 4-fold symmetry (Figure 3d). For positive disclinations, Frank theory predicts that radial and circle patterns occur when the constant c is 0 and $\pi/2$, respectively, whereas for other values of c , between $-\pi/2$ and $\pi/2$, spiral patterns occur, which may have either sense (right- or left-handed).⁵ In our work, we found that the average numbers of left-handed and right-handed spirals are approximately same. This is expected, as the energies of spiral patterns with different c values are identical according to Frank's

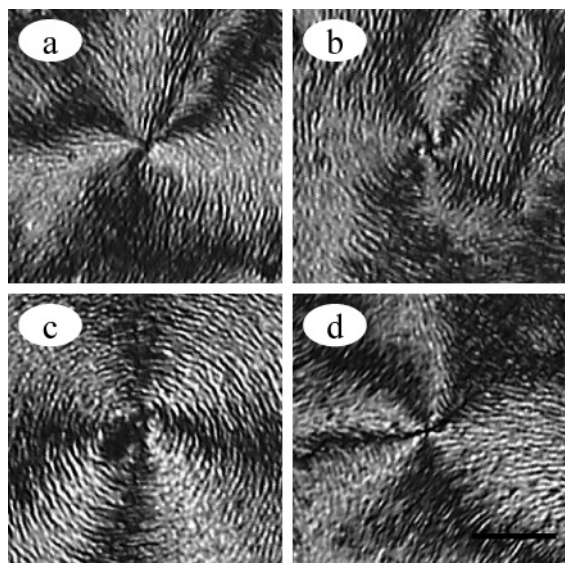


Figure 3. A set of polarizing optical micrographs of different types of integer disclinations: (a) radial pattern (R), $s = +1$, $c = 0$; (b) spiral pattern (S), $s = +1$, $-\pi/2 < c < 0$; (c) circular pattern (C), $s = +1$, $c = \pi/2$; (d) hyperbolic pattern (H), $s = -1$. The scale bar is $20 \mu\text{m}$.

continuum theory.⁵ For any given material, only radial or circular patterns of a positive disclination should be stable, according to whether the bend or splay elastic constant is larger.⁵ That all the different configurations of disclinations with strengths of $s = \pm 1$ were observed in this work indicates that the splay and bend elastic constants in our side-chain liquid crystalline polymer must be of the same order of magnitude. This result is in agreement with previous measurements for elastic constants of side-chain liquid crystalline polymers.^{11,12,14}

An isolated disclination like a charged particle is not stable energetically and therefore must interact with neighbors in order to reduce the systemic energy. Interactions between several disclinations are very complex. Studies on simple pair interaction can help us understand such a complex system.^{21–25} As mentioned above, with an increase in annealing time, defect densities decrease. As a result, the distance between two adjacent disclinations becomes large enough to study their interactions. We found that specific configurations of $(+1, -1)$ pairs of disclinations dominate the clusters after long annealing time, as shown in Figure 4. We define the parameter δ as the angle between the line joining the two defect cores and one of hyperbolic symmetric axes for which the director is radial. For a pair of radial (R) and hyperbolic (H) disclinations, denoted as (R, H), the R core lies on one of hyperbolic symmetric axes. The angle δ is therefore 0. For a pair of circular (C) and hyperbolic (H) disclinations, denoted as (C, H), the angle δ is $\pi/4$. For a pair of spiral (S) and hyperbolic (H) disclinations, denoted as (S, H), the angle δ lies between 0 and $\pi/4$. Recalling that c is a variable for spiral (S) disclinations, reflecting the balance between the splay and bend distortions, it is clear that the value of δ will also depend on the particular value of c . The larger the ratio of splay to bend, the larger the angle δ is. The energy of all these configurations is the same in the one-constant approximation of Frank elasticity. Special geometrical shapes of positive disclinations determine the different configurations, indicating that only translation motion occurs once these specific configurations form. These experimental results agree well with the theoretical prediction.²⁶

In addition to disclinations of integer strength, an isolated inversion wall can also be observed in the thin films, as shown in Figure 5. Inversion walls have mirror symmetry and lead to

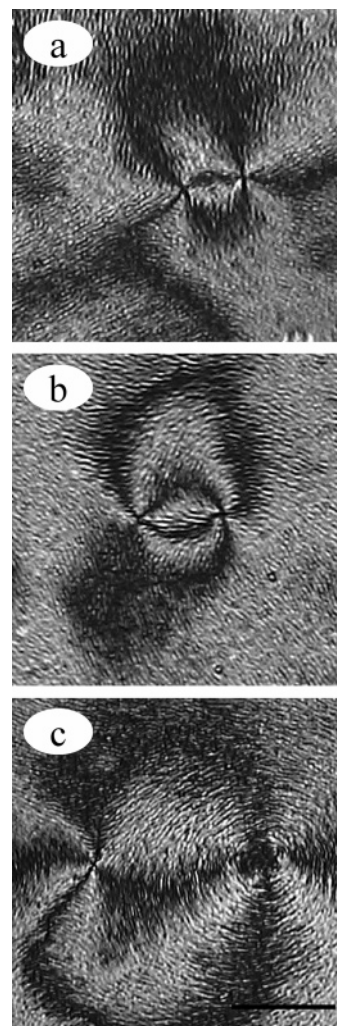


Figure 4. A set of optical micrographs of three typical configurations of $(+1, -1)$ disclinations: (a) radial-hyperbolic (R, H); (b) spiral-hyperbolic (S, H); (c) circular-hyperbolic (C, H). One can see that the director rotates continuously in space. The scale bar is $30 \mu\text{m}$.

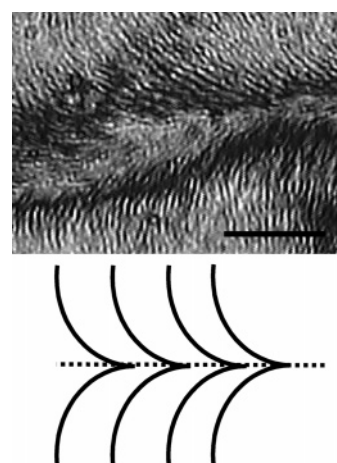


Figure 5. Optical micrograph of a splay inversion wall and the corresponding director field. The scale bar is $30 \mu\text{m}$.

a discontinuous change in the molecular director across wall. The director undergoes a rotation of π from one side of the wall to the other. These results show that the deformation of the director across the inversion wall is approximately two-dimensional.

Disclination Instability. With increase of the film thickness, the integer disclinations became unstable and were divided to

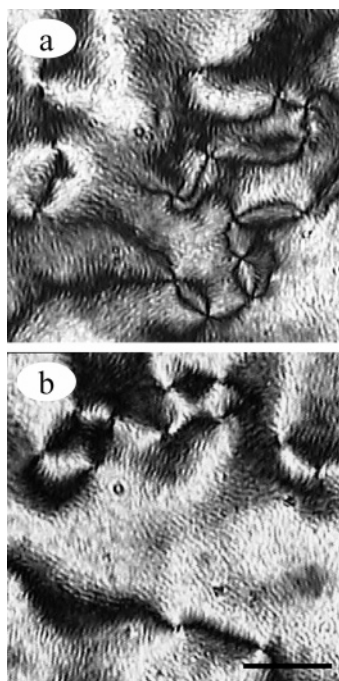


Figure 6. Polarizing optical micrographs of typical Schlieren textures of thick films with different thickness: (a) 5 μm (b) 20 μm . The scale bar is 30 μm .

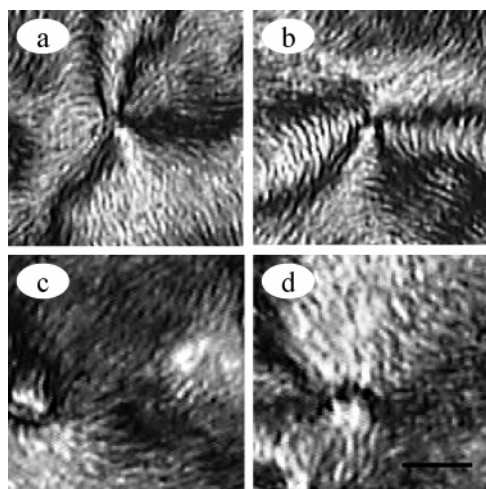


Figure 7. A set of polarizing optical micrographs of the different types of half-integer disclinations: (a) two $s = +1/2$ and (b) two $s = -1/2$ in the thick film of 5 μm ; (c) $s = +1/2$ and (d) $s = -1/2$ in the thick film of 20 μm . The scale bar is 20 μm .

half-integer disclinations. Figure 6 shows two typical optical micrographs of the thick films with thickness of 5 μm and 20 μm . Compared to the thin films as shown in Figure 2, the thick films in Figure 6 exhibited strong birefringence. We found that the black four-brushes and two-brushes coexisted in the thick film of 5 μm , whereas only black two-brushes appeared in the thick film of 20 μm . This result indicates that integer disclinations are not stable in the thick films. One can still see the stripes in the thick films, although they become ambiguous due to the weak effect of equilibrium instability as discussed in our previous work.¹³

Figure 7 shows the typical patterns of contrasting stripes around the half-integer disclinations with strengths of $s = \pm 1/2$ in the thick films. Again, the stripes follow the director pattern around each disclination, as predicted by Frank theory.⁵ For the thick film of 5 μm , we observed the starting for change from integer disclinations to half-integer disclinations, as shown

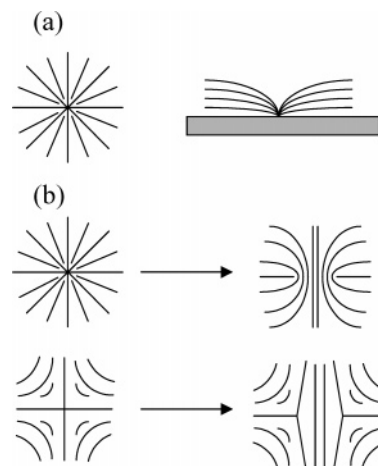


Figure 8. Schematic diagram of (a) a stabilized integer disclination in a thin film; (b) changes from integer disclinations to half-integer disclinations in a thick film.

in Figure 7 a,b. Each integer disclination splits into two-half-integer disclinations with the same sign as their parent. Therefore, the overall topological charge of the system is conserved. For the thick film of 20 μm , the stripes revealed isolated half-integer disclinations with strength of $s = \pm 1/2$, as shown in Figure 7 c,d.

Obviously, the film thickness plays a crucial role in disclination instability. This is expected since the precise nature of defects observed in the planar films will depend on the detailed balancing of distortion of defects in the bulk elastic energy, and surface anchoring energy.^{1,2} For a thin film, the surface anchoring energy due to confined environments, and the strong interaction between LC molecules and substrate, dominates over the bulk elastic energy. In our previous work, we employed TEM and AFM to prove that the center of the integer disclination is lower than the surrounding material and the mesogenic groups are tilting out of the film plane.^{13–15} In such a geometric confined environment, the integer disclinations may be stabilized by “escaping core”, as shown in Figure 8a. Increasing the film thickness makes the bulk elastic energy become dominant. As the bulk free energy of a disclination is proportional to s^2 , the most energetically stable planar rotation disclinations are of low strength.^{1,2} As a result, the integer disclinations become unstable in the thick films, and each one will split into two-half-integer disclinations which will then repel each other. Each of newly born half-integer disclinations has the same sign as their parent so that the total topological charge in the systems is conserved, as shown in Figure 8b.

Conclusions

In summary, black brushes together with two-dimensional stripes have been observed in side-chain liquid crystalline polymer films under polarizing optical microscopy. The stripes are parallel to the local director and serve to decorate the underlying molecular alignment, yielding a map of director fields around disclinations. Three patterns (radial, spiral and circular) of $s = +1$ disclinations and one hyperbolic pattern of $s = -1$ disclination are observed in the thin films. At the late stage of annihilation, specific configurations of pairs of $(+1, -1)$ disclinations are observed, indicating only translation motion occurs. Increasing the film thickness leads to disclination instability. Black four-brushes of disclinations with $s = \pm 1$ are decomposed into black two-brushes, where two types of director patterns of disclinations with half-integer strengths of $s = \pm 1/2$ produce.

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References and Notes

- (1) De Gennes, P. G.; Prost, P. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, 1993.
- (2) Kleman, M. *Points, Lines and Walls: in Liquid Crystals, Magnetic Systems and Various Ordered Media*; Wiley: Chichester, U.K., 1983.
- (3) Song, W. H.; Kinlock, I. A.; Windle, A. H. *Science* **2003**, 302, 1363.
- (4) Cladis, P. E.; Van Saarloos, W.; Finn, P. L.; Kortan, A. R. *Phys. Rev. Lett.* **1987**, 58, 222.
- (5) Frank, F. C. *Discuss. Faraday Soc.* **1958**, 25, 19.
- (6) Nehring, J.; Saupe, A. *J. Chem. Soc., Faraday Trans. 2* **1972**, 68, 1.
- (7) Hu, Z.; Chen, S.; Zhang, S.; Qian, R. *Macromol. Rapid Commun.* **2000**, 21, 1028.
- (8) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, 1992.
- (9) Shibaev, V. P.; Lam, L. *Liquid Crystalline and Mesomorphic Polymers*; Springer: New York, 1994.
- (10) Kleman, M. *Faraday Discuss. Chem. Soc.* **1985**, 79, 215.
- (11) Schmidtke, J.; Stille, W.; Strobl, G. *Macromolecules* **2000**, 33, 2922.
- (12) Fabre, P.; Casagrande, C.; Veyssie, M.; Finkelman, H. *Phys. Rev. Lett.* **1984**, 53, 993.
- (13) Zhang, S. J.; Terentjev, E. M.; Donald, A. M. *Eur. Phys. J. E* **2003**, 11, 367.
- (14) Zhang, S. J.; Terentjev, E. M.; Donald, A. M. *Macromolecules* **2004**, 37, 390.
- (15) Zhang, S. J.; Terentjev, E. M.; Donald, A. M. *Langmuir* **2005**, 21, 3539.
- (16) O'Rourke, M. J. E.; Ding, D. K.; Thomas, E. L. *Macromolecules* **2001**, 34, 6658.
- (17) Ding, D. K.; Thomas, E. L. *Macromolecules* **1993**, 26, 6531.
- (18) Wood, B. A.; Thomas, E. L. *Nature (London)* **1986**, 324, 656.
- (19) Hundon, S. D.; Thomas, E. L. *Phys. Rev. Lett.* **1989**, 62, 1993.
- (20) Finkelmann, H.; Rehage, G. *Adv. Polym. Sci.* **1984**, 60, 97.
- (21) Harrison, C.; Cheng, Z. D.; Sethuraman, S.; Huse, D. A.; Chaikin, P. M.; Vega, D. A.; Sebastian, J. M.; Register, R. A.; Adamson, D. H. *Phys. Rev. E* **2002**, 66, 011706.
- (22) Wang, W.; Leiser, G.; Wegner, G. *Liq. Cryst.* **1993**, 15, 1.
- (23) Hudson, S. D.; Thomas, E. L. *Phys. Rev. A* **1991**, 44, 8128.
- (24) Xie, F.; Hu, Z.; Liu, J.; Yan, D.; He, T.; Wang, B.; Zheng, R.; Cheng, S. Z. D.; Percec, V. *Macromol. Rapid Commun.* **2001**, 22, 396.
- (25) Chen, S.; Song, W.; Jin, Y.; Qian, R. *Liq. Cryst.* **1993**, 15, 247.
- (26) Ranganath, G. S. *Mol. Cryst. Liq. Cryst.* **1983**, 97, 77.