

Chapter 1

INTRODUCTION

1.1 Background	1
1.2 Motivation	6
1.3 Thesis Organization	8
1.4 Figures	9
1.5 References	17

Portions of this chapter are reproduced from Kempe, Scruggs, Verduzco, Lal, and Kornfield, *Nature Materials* **2004**, 3, 177-182 and from Kempe, Verduzco, Scruggs, and Kornfield, *Soft Matter* **2006**, 2, 422-431.

1.1 Background

Crystals and liquids are familiar condensed matter phases in which the relative positions and orientations of the constituent molecules are either well-defined by a rigid lattice or lacking long-range correlation, respectively. In between the crystal and liquid phases lies a progression of partially ordered phases termed “liquid crystalline mesophases,” the simplest of which is termed the “nematic” phase (Figure 1.1).^[1, 2] Rod-like molecules typically lend themselves to the formation of a nematic phase in a particular range of temperatures, and such materials are termed “calamitic, thermotropic liquid crystals” (LCs). In the nematic phase, the molecules diffuse about one another randomly, but they tend to retain orientation in a preferred direction called the “director,” \mathbf{n} . The director breaks the material’s isotropic symmetry and gives rise to properties such as optical

birefringence, dielectric anisotropy, diamagnetic anisotropy, and orientational elasticity. The coupling of order and fluidity makes LCs particularly intriguing materials because their orientation-dependent properties can be influenced by readily accessible fields.

Nematic LCs are far from perfectly ordered; the LC's molecules have a distribution of orientations with respect to the director. The nematic order parameter, $S = \frac{1}{2} <3 \cos^2 \theta - 1>$, where θ is the angle between a molecule and the director, quantifies the degree of order ranging from $S = 1$ in a perfectly oriented medium to $S = 0$ in an isotropic medium. The intermolecular interactions maintaining the orientational order of a nematic LC are relatively weak: the Maier-Saupe model of nematic ordering estimates their strength to be approximately five times the thermal energy.^[2] For this reason, the local director is in a constant state of flux, and these thermally-induced distortions to the director field are responsible for the turbid, milky appearance of nematic LCs. Distortions to a nematic LC can be expressed as the sum of splay, twist, and bend distortions (Figure 1.2), and the elastic free energy per unit volume, F_V , is given by

$$F_V = \frac{1}{2} \left[K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot (\nabla \times \mathbf{n}))^2 + K_3 |\mathbf{n} \times (\nabla \times \mathbf{n})|^2 \right], \quad (1.1)$$

where K_1 , K_2 , and K_3 are the splay, twist, and bend elastic constants, respectively.^[2] The dynamics of director fluctuations are governed by the LC's elastic constants and anisotropic viscosity coefficients.^[3, 4] One way to express the viscosity of a nematic LC is in reference to the three fundamental orientations of the director in shear flow. The viscosities measured in these geometries, η_a , η_b , and η_c , are known as the Miesowicz viscosities (Figure 1.3).^[1, 2]

Macromolecular LCs can be formed when rod-like molecules are either incorporated directly into a polymer chain to form a main-chain liquid crystal polymer (MCLCP) or laterally attached to a polymer chain via a flexible spacer to form a side-group liquid crystal polymer (SGLCP) (Figure 1.4). Macromolecular LCs are frustrated materials because the defining characteristics of polymers and LCs are directly at odds with one another: polymer chains seek random configurations and LC molecules seek long-range order.^[5] Bonding LC mesogens to a random-coil polymer forces compromise between the opposing

tendencies, compromise that often manifests itself in unique physical phenomena that are not present in either pure LCs or bulk polymers alone.

Nematic order is coupled to the conformation of SGLCPs and MCLCPs in the melt and in solution with small-molecule LCs. The trajectory of an ideal, random-coil polymer is a random walk from one end to the other and the chain's conformation is spherical in solution and in the melt.^[6] The conformation of a liquid crystalline polymer deviates from sphericity in order to accommodate the orientational order of its mesogens.^[5] Neutron scattering experiments on LC polymers in the melt, reviewed by Cotton and Hardouin,^[7] demonstrate that MCLCPs and side-on SGLCPs adopt a highly prolate (aspect ratio > 5) ellipsoidal conformation in the nematic phase.^[8, 9] On the other hand, end-on SGLCPs have mild anisotropy (aspect ratio ≈ 1.5) and can be either prolate^[10] or oblate^[11-15] ellipsoids. Experiments on solutions of liquid crystalline polymers in small-molecule LC solvents, reviewed by Jamieson et al.,^[4] reveal that the orientation of the polymer's attached mesogens is coupled to that of the solvent, and that the polymer adapts to the director field similar to the way it does in the melt: MCLCPs and side-on SGLCPs become strongly prolate^[16-20] while end-on SGLCPs are mildly anisotropic prolate^[21, 22] or oblate^[16, 18, 19, 22-27] ellipsoids. A few experiments on solutions of non-LC polymers in LC solvents have demonstrated that these polymers, too, adopt anisotropic conformations in solution, but the strength of the orientational coupling is not as strong as it is when the polymer itself is mesogenic.^[28]

The coupling between polymer conformation and liquid crystalline order modifies polymer solution thermodynamics and results in novel phase behavior in mixtures of both LC and non-LC polymers with LC solvents. The phase behavior of LC polymers in LC solvents has been treated theoretically by Brochard^[29, 30] and ten Bosch et al.^[31] These theories agree with numerous experimental studies demonstrating the coexistence of two nematic phases in these mixtures,^[27, 32-37] a phenomenon rarely, if ever, observed in binary mixtures of small-molecule LCs.^[36] Nematic-nematic coexistence appears to be a unique consequence of the coupling between LC order and polymer thermodynamics. The phase behavior of non-LC polymers in LC solvents has also been treated theoretically^[38, 39] and

experimentally.^[40-46] In these systems, the solvent's orientational order presents a large entropic penalty to dissolution in the nematic phase, but when the solvent transitions to the isotropic phase the polymer's solubility instantly increases. It is not uncommon to observe a transition from nematic / isotropic coexistence to a single isotropic phase coincident with the solvent's nematic to isotropic phase transition.

When mesogens are grafted to a polymer chain, LC order also becomes coupled to polymer dynamics. Conformational anisotropy of an SGLCP dissolved in small-molecule LC solvent leads to anisotropic modification of the solution's flow properties.^[4, 16, 21, 22, 25, 26, 47-50]

The hydrodynamics of solutions of LC polymers in LC solvents has been treated by Brochard,^[51] whose theory predicts the LC's orientation-dependent viscosity coefficients to be modified differently according to the anisotropy of the dissolved polymer chain: the increase in η_b , for example, is larger when an oblate polymer is dissolved in nematic solvent than when the polymer is prolate. A modification of Brochard's theory^[22] has been used with some success to deduce a dissolved polymer's anisotropy from the solution's rheology.^[21, 25, 26, 50] Polymer anisotropy also leads to anisotropic modification of the director's fluctuation dynamics.^[4, 18, 52, 53] Dynamic light scattering experiments on solutions of SGLCPs in nematic LCs^[4, 18, 52, 53] have demonstrated that prolate polymers preferentially slow the relaxation of splay distortions while oblate polymers more strongly affect the relaxation of bend distortions.

The discussion of coupling between LC order and polymer conformation has been thus far limited to homopolymers, but introducing LC order also has a profound effect on the structure and dynamics of block copolymers (BCPs).^[54] Two or more different polymers covalently bonded together constitute a BCP, and unfavorable thermodynamic interactions between the blocks usually cause a self-assembled microstructure to form in which the contact between them is minimized. BCPs have been extensively studied in recent decades because they are a versatile system for engineering nanotechnologies, as reviewed by Park, Yoon, and Thomas.^[55] Selection of the length, chemical structure, and connectivity of the component blocks gives access to a wide variety of morphologies, having sizes typically on the order of ~10-100 nm, which can be ordered with respect to one another in grains of one

micrometer or larger.^[55, 56] When one block of a BCP is an LC polymer, the resulting material exhibits order over a variety of length scales from a few nanometers (the cooperative alignment of LC molecules) up to the larger-scale structure of the BCP.^[54, 56] In these systems the orientational order of the mesophase couples strongly to the microphase separated BCP morphology, and the LC director often dictates the orientation of the microdomains. In contrast to the alignment tendency of cylindrical microdomains of a triblock copolymer that normally align in the direction of shear, an orientation perpendicular to the shear plane is observed when one block is a LC polymer because of the anchoring of the mesogens to the cylinder walls.^[57] Another example of this coupling is the observation that changing LC order can either change the morphology of the microphase separated structure (order-order transition),^[58, 59] or trigger the order-disorder transition coincident with the isotropization temperature of the LC block.^[60-62]

BCPs in solution are thermodynamically rich systems because the polymer's self-assembled structure depends not only on pairwise interactions between the different polymer blocks, but also on interactions between the blocks and the solvent.^[63-70] The polymer concentration and the relative enthalpic interactions between the solvent and the polymer blocks (the solvent's "selectivity") determine the morphology of the BCP in solution. In a strongly selective solvent, the solubility of one block, *A*, is distinctly greater than the other block, *B*, and the BCP usually self-assembles into micelles with block *B* segregated to a core surrounded by a solvent-rich corona containing block *A*. In the limit of no selectivity, both blocks are soluble and the BCP will not self-assemble in dilute solution where block-block interactions are screened by polymer-solvent interactions. For a fixed BCP at fixed concentration, the choice of solvent determines whether or not micelles form. If they do, the solvent choice also determines their shape, size, and long-range order relative to one another (e.g., BCC or FCC lattice).

Knowing that orientational order is strongly coupled to the thermodynamics of SGLCP homopolymers in LC solvent and to the morphology of LC BCPs in the bulk suggests an additional layer of complexity might be added to the thermodynamics governing self-assembly of BCPs in solution if one block is an SGLCP and the solvent is nematogenic.

From a practical standpoint, swelling an LC BCP with small-molecule solvent could serve to improve their sluggish and weak responses to electro-magnetic stimuli, making them better candidates for use in devices such as liquid crystal displays. Despite these motivations, only one research group^[71-73] reported experiments on LC solutions of LC BCPs prior to the Kornfield group's studies of liquid crystalline gels self-assembled from triblock copolymers in nematic solvent.^[19, 74, 75] Much of the work described in this thesis was motivated by a desire to better understand the physics of these gels.

1.2 Motivation: Orientational Coupling Phenomena in Self-Assembled Triblock Copolymer Gels

Solutions of coil-SGLCP block copolymers in a nematic solvent combine the thermodynamic phenomena deriving from the coupling of LC order to polymer chains with the rich thermodynamics governing BCP self-assembly in solution. Triblock copolymers were synthesized with polystyrene (PS) endblocks and an SGLCP midblock having mesogens attached either end-on or side-on. Dissolving the triblocks in 4-pentyl-4'-cyanobiphenyl (5CB), a small-molecule nematic LC, causes the random-coil PS endblocks to segregate from the ordered solvent, and a nematic gel is formed when the polymer concentration is 5 wt % or greater (Figure 1.5).^[19, 74] The segregated PS-rich domains form the crosslinks of a polymer network spanned by the LC-soluble SGLCP midblocks. The network structure of 5 wt % polymer gels is thermoreversible because the entropic penalty to dissolution of the PS blocks disappears when the solvent is heated to the isotropic phase ($> 35^\circ\text{C}$), causing the segregated domains to dissolve then re-form when the solution is cooled to the nematic phase again. However, the rheology of gels containing 20 wt % triblock copolymer shows that associations between PS blocks persist beyond the solvent's nematic to isotropic transition,^[74] suggesting that polymer concentration plays a non-trivial role in the self-assembly of LC gels, just as it does in the self-assembly of non-mesogenic BCP solutions.

Director reorientation dynamics in nematic gels self-assembled from coil-SGLCP block copolymers are almost as fast as in 5CB itself and are coupled to the underlying polymeric

network. The gel's director aligns parallel to electric fields of 1.2 V/ μ m or greater, allowing for the creation of an optically clear monodomain from an initially opaque, polydomain gel (Figure 1.6). When the electric field is removed, the coupling of the solvent orientation to the topology of the polymer network provides a memory of the original orientation and the gel returns to the polydomain state on time scales as fast as 15 ms,^[19] comparable to the relaxation time of pure 5CB in a 5 μ m-thick cell (\sim 40 ms).^[76, 77] In stark contrast to small-molecule LCs, the time required to fully return to the original polydomain state depends strongly on the previously applied field: higher applied fields cause the relaxation time to increase (Figure 1.7). Nevertheless, there appears to be a separate, fast relaxation process present that allows the gel's optical response to track the 1 kHz oscillation of the applied voltage (Figure 1.7).

The gels' responses to mechanical strain also demonstrate the coupling of the LC orientation to the polymer network. The LC director becomes uniformly aligned when the gels are subjected to shear and the orientation of the SGLCP mesogens dictates the orientation of the director relative to the velocity gradient: end-on gels align with the director parallel to the velocity gradient, side-on gels align perpendicular (Figure 1.8). These orientations mirror the behavior of SGLCP homopolymers in nematic solvent.^[47] However, in contrast to homopolymer solutions, the gel's network serves to lock in the orientation and the monodomain alignment remains after cessation of shear.

Changing the anisotropy of the SGLCP block by heating or cooling the gel in the nematic phase causes an unusual buckling instability to occur because of the LC director's coupling to the polymer network.^[75] When the network initially forms near the nematic / isotropic phase transition, the order parameter of the solvent is low and the induced conformational anisotropy of the SGLCP midblocks is mild. Upon further cooling into the nematic phase, the conformational anisotropy increases, but the SGLCPs are not free to expand in their preferred direction because their PS endblocks lock them into a network that is constrained by anchoring to the gel's contact surface. The compromise between changing conformational anisotropy and the constraints of the polymer network causes a periodic

distortion to the director field that generates a striking striped texture when the gel is viewed in a microscope between crossed polarizers (Figure 1.9).

1.3 Thesis Organization

Experimental investigations of the physics underlying the novel phenomenology of self-assembled liquid crystalline gels are the subject of this thesis. In Chapter 2, the phase behavior of SGLCP and random-coil homopolymers in 5CB demonstrates the discontinuous change in random-coil polymer solubility that takes place when the LC solvent is heated from the nematic to isotropic phase. The influence of polymer-polymer interactions on the phase behavior of ternary blends of SGLCP, random-coil polymer, and 5CB is used to understand the self-assembly of coil-SGLCP diblock copolymers, whose temperature-dependent structure and rheology is expounded upon in Chapter 3. The consequences of coupling LC order with the polymer's conformational entropy on orientational order and polymer phase behavior is explored in Chapter 4, and in Chapter 5 the influence of polymer architecture (side-on or end-on) and temperature on conformational anisotropy are demonstrated by small-angle neutron scattering. The coupling of director relaxation dynamics to the underlying polymer network is investigated by dynamic light scattering in Chapter 6. Finally, Chapter 7 looks at the effect of the interconnected triblock copolymer network on the gel's orientational memory and demonstrates that memory is absent in gels composed of non-interconnected diblock copolymer micelles.

1.4 Figures

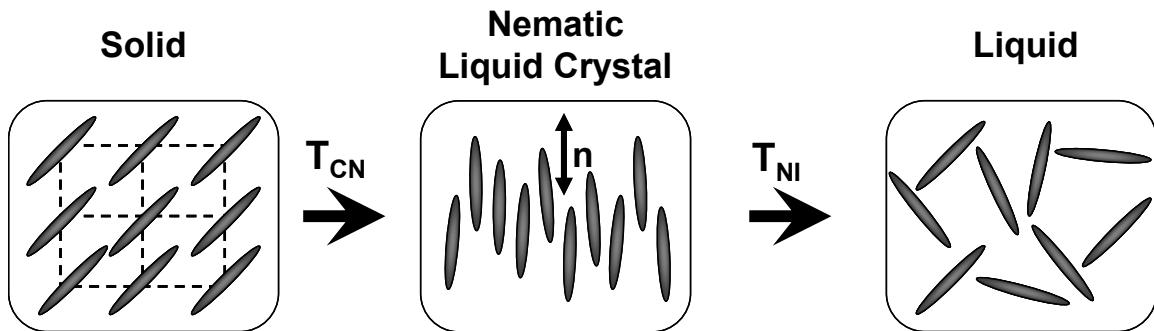


Figure 1.1 Schematic representation of the molecules of a thermotropic liquid crystal, represented by gray ellipses, in the solid, nematic liquid crystal, and liquid phases. In the solid phase, the molecules have regular positions and orientations. When heated above the crystalline to nematic phase transition temperature, T_{CN} , the molecules lose their positional order, but remain oriented in a preferred direction called the “director,” \mathbf{n} . Above the nematic-isotropic transition temperature, T_{NI} , the molecules have no long-range positional or orientational correlations.

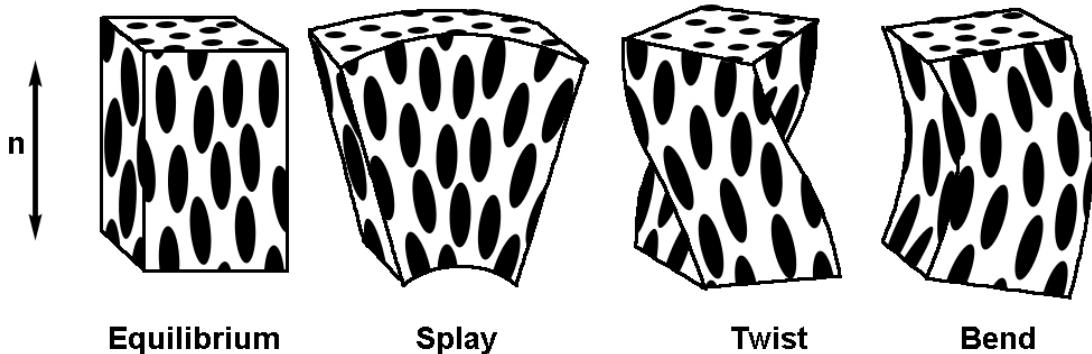


Figure 1.2 Schematic representation of the three fundamental distortions of the nematic LC director. The free energy cost of each distortion is expressed in Equation 1.1 using elastic constants K_1 , K_2 , and K_3 for splay, twist, and bend, respectively. The spatially varying local director orientation is represented by black ellipses and the equilibrium director is denoted \mathbf{n} .

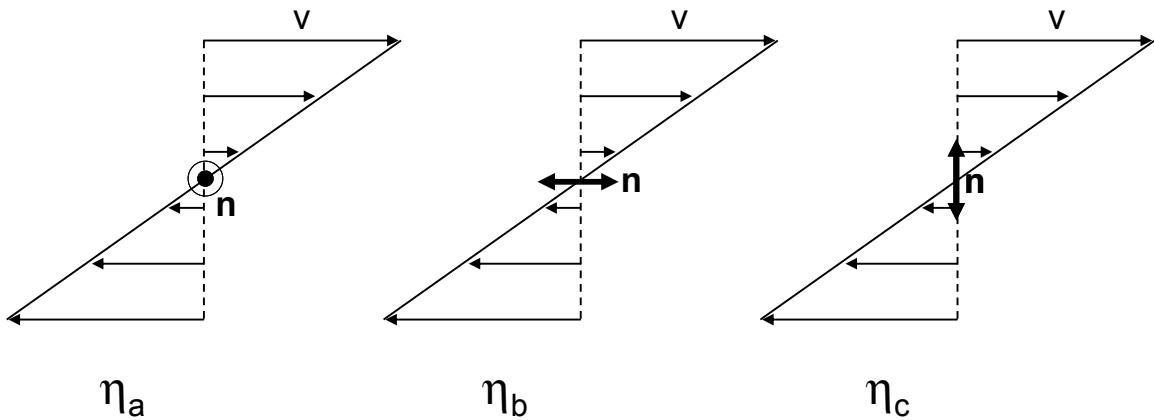


Figure 1.3 Schematic representation of the three fundamental orientations of the nematic director, \mathbf{n} , in relation to the gradient of the velocity, v , in shear flow. The effective viscosities measured in these geometries, η_a , η_b , and η_c , define the Miesowicz viscosities of a nematic LC.

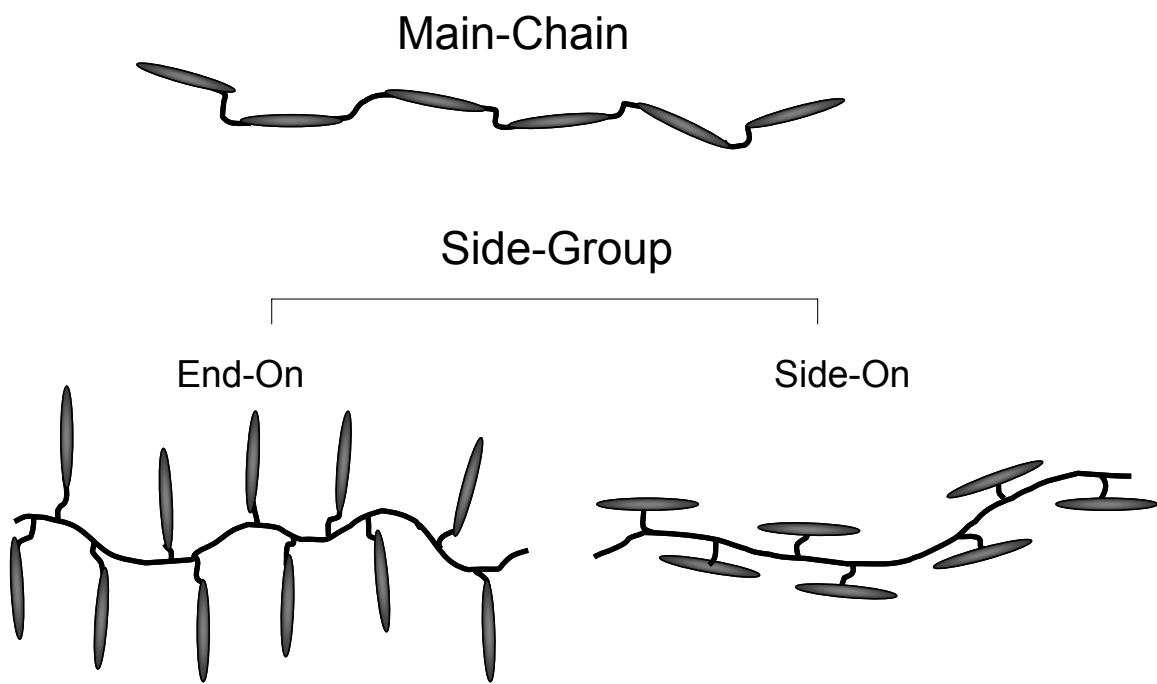


Figure 1.4 Schematic representation of liquid crystalline polymers. Main-chain liquid crystal polymers incorporate the mesogens into the polymer chain, and side-group liquid crystal polymers have mesogens laterally attached to the backbone via a flexible spacer. End-on polymers have the mesogens attached with their long axes perpendicular to the polymer, while side-on polymers have the mesogens attached with their long axes parallel.

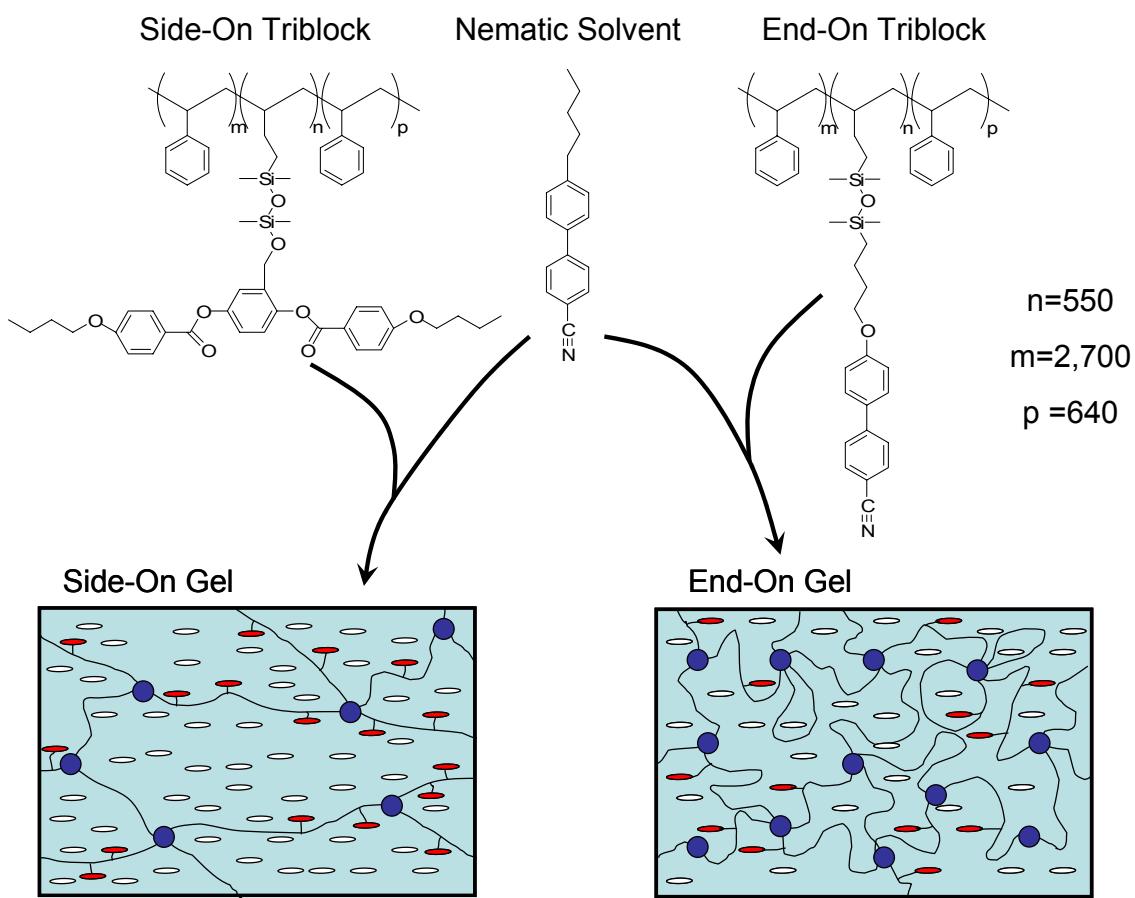


Figure 1.5 Chemical structures of the side-on and end-on triblock copolymers that self-assemble in the nematic solvent (4-pentyl-4'-cyanobiphenyl, 5CB) to form liquid crystalline gels. Schematics of the gels illustrate the segregation of the polystyrene blocks (blue circles) to form physical crosslinks spanned by the LC-soluble SGLCP midblocks (black lines to represent the polymer backbone with red ellipses to represent the attached mesogens). The solvent is represented in the schematics by white ellipses. The relative sizes of the segregated domains, SGLCP midblocks, and solvent molecules are not drawn to scale.

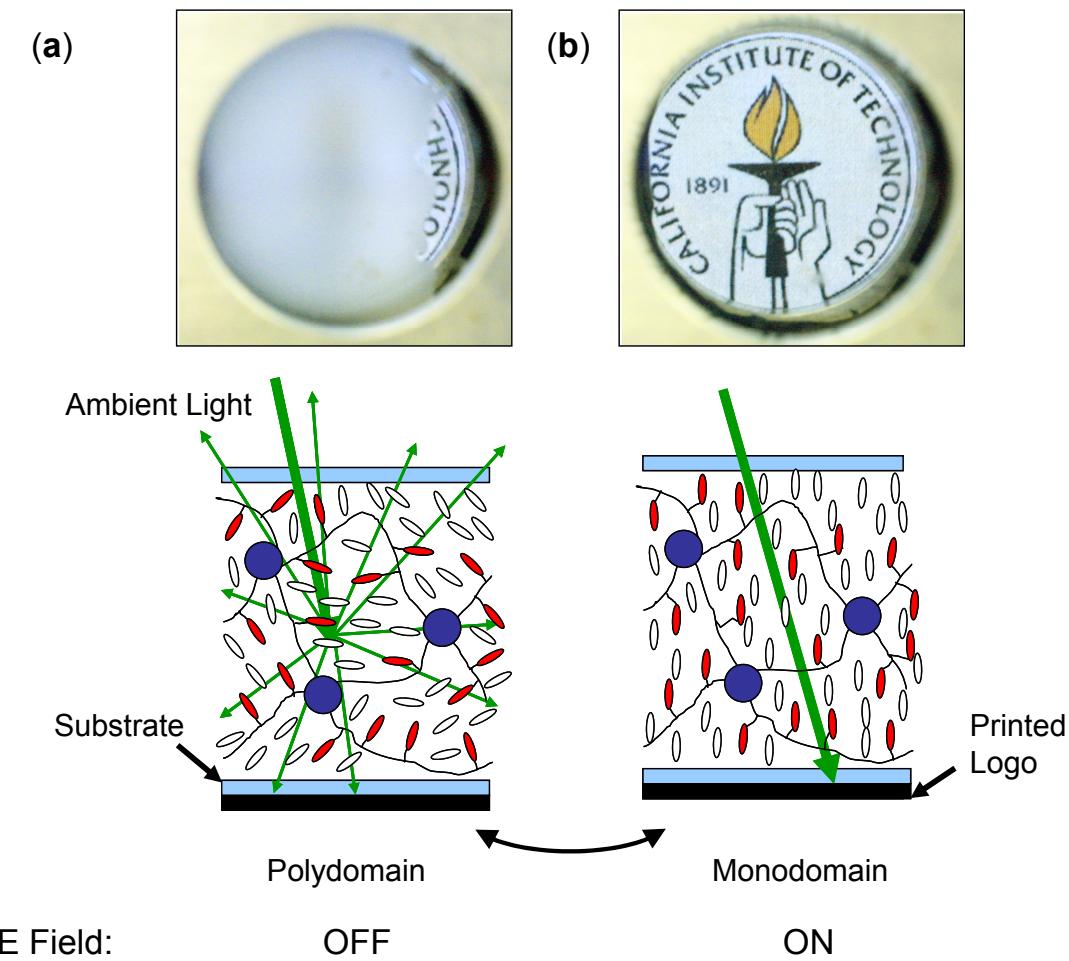


Figure 1.6 (a) A 5 wt % end-on triblock copolymer gel is sandwiched between two transparent indium-tin-oxide electrodes spaced 25 μm apart. The gel is loaded into the cell by capillary action: when heated above 35 $^{\circ}\text{C}$ it transitions to a liquid and flows into the gap, cooling to the nematic phase triggers the polymer's self-assembly. In this case, the gel is only partially filling the field of view, and the printed logo placed behind the cell is clearly visible in the empty portion. (b) Applying an electric field of 1.6 V/ μm reoriented the LC director and creates an optically clear monodomain; the empty portion of the cell cannot be distinguished from the portion containing aligned gel and the printed logo behind the cell is clearly visible. The opaque, polydomain state (a) is recovered when the field is removed. The gel's structure is represented schematically according to the same conventions as in Figure 1.5.

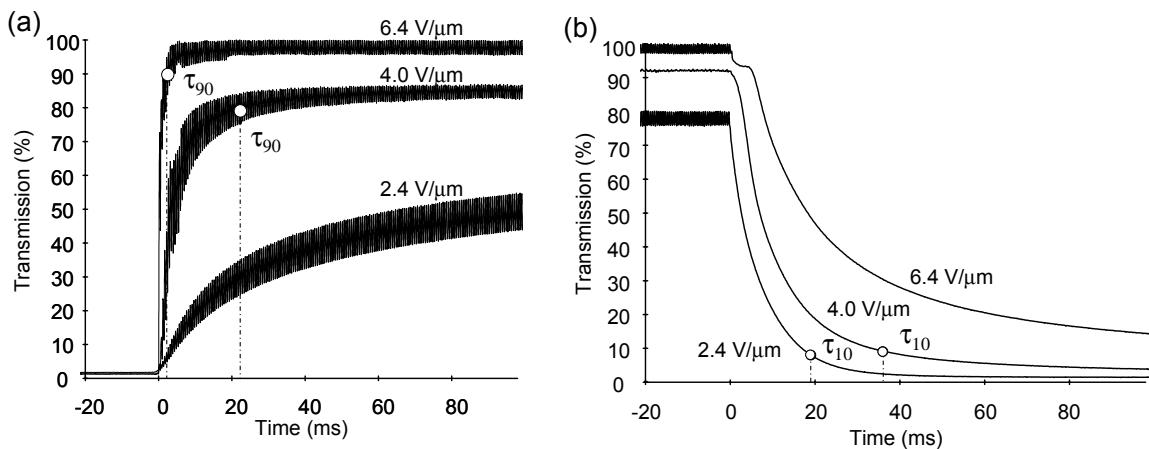
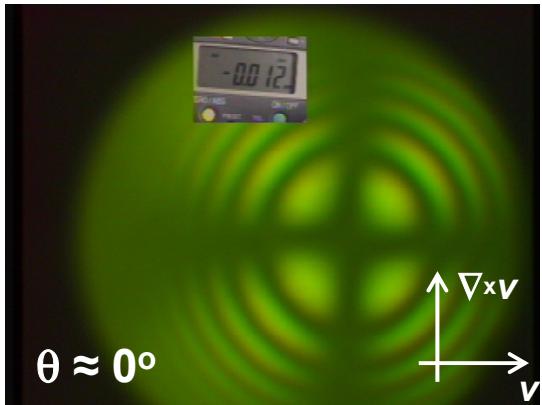


Figure 1.7 Transient electro-optic response of a 5 wt % side-on triblock copolymer gel under application of alternating current electric fields of 2.4, 4.0, and 6.4 V/ μ m oscillating at 1 kHz. The gel is contained between transparent indium-tin-oxide electrodes and the transmission of a 10 mW, 633 nm laser beam is measured during application of the field. (a) The time required for the transmitted intensity to reach 90% of its maximum when the field is switched on is denoted τ_{90} . (b) The time required for the transmitted intensity to reach 10% of its maximum when the field is switched off is denoted τ_{10} . When not shown, τ_{90} and τ_{10} are beyond the graphs' scales.

End-On Gel



Side-On Gel

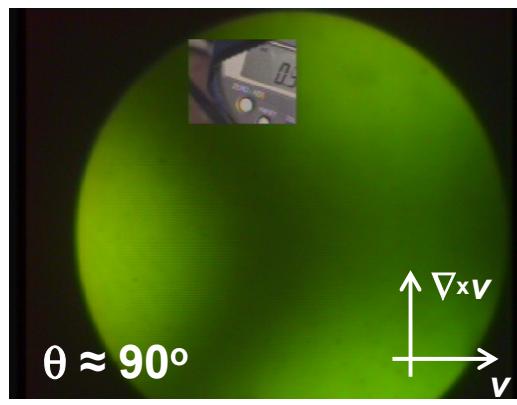


Figure 1.8 Conoscopic figures demonstrating monodomain alignment of end-on and side-on LC gels induced by shear flow. The angle θ is the angle between the optic axis and the velocity gradient direction deduced from the type of conoscopic figure observed.^[78, 79] The cross pattern observed for end-on gels is characteristic of alignment of the director parallel to the velocity gradient, and the hyperbolic pattern observed for side-on gels is characteristic of alignment perpendicular.

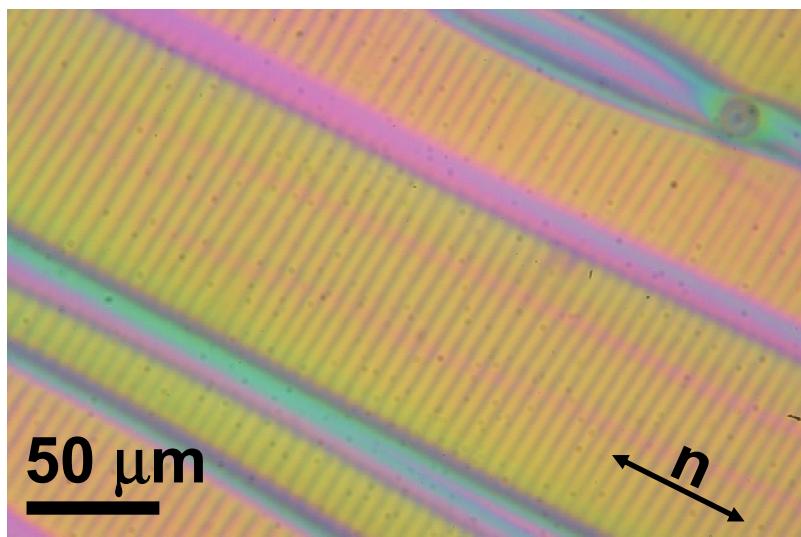


Figure 1.9 Optical micrograph of a 5 wt % end-on LC gel observed at room temperature between crossed polarizers. A periodic stripe pattern is observed because of a buckling instability induced by changes in conformational anisotropy of the gel's SGLCP midblock. The orientation of the director is denoted “*n*”.

1.5 References

- [1] Collings, P. J.; Hird, M. *Introduction to Liquid Crystals: Chemistry and Physics*, Taylor and Francis: Bristol, PA, 1997.
- [2] de Gennes, P.-G. *The Physics of Liquid Crystals*, 2nd ed; Clarendon Press: Oxford, 1993.
- [3] Ho, J. T. Light scattering and quasielastic spectroscopy. In *Liquid Crystals*; S. Kumar, Editor; Cambridge University Press: Cambridge, 2001.
- [4] Jamieson, A. M.; Gu, D. F.; Chen, F. L.; Smith, S. Viscoelastic behavior of nematic monodomains containing liquid crystal polymers. *Prog. Polym. Sci.* **1996**, *21*, 981-1033.
- [5] Wang, X. J.; Warner, M. Theory of nematic comb-like polymers. *J. Phys. A: Math. Gen.* **1987**, *20*, 713-731.
- [6] Rubinstein, M.; Colby, R. H. *Polymer Physics*, 1st ed; Oxford University Press: New York, 2003.
- [7] Cotton, J. P.; Hardouin, F. Chain Conformation of Liquid-Crystalline Polymers Studied by Small-Angle Neutron Scattering. *Prog. Polym. Sci.* **1997**, *22*, 795-828.
- [8] Lecommandoux, S.; Achard, M. F.; Hardouin, F.; Brulet, A.; Cotton, J. P. Are nematic side-on polymers totally extended? A SANS study. *Liq. Cryst.* **1997**, *22*, 549-555.
- [9] Leroux, N.; Keller, P.; Achard, M. F.; Noirez, L.; Hardouin, F. Small Angle Neutron Scattering experiments on "side-on fixed" liquid crystal polyacrylates. *J. Phys. II France* **1993**, *3*, 1289-1296.
- [10] Davidson, P.; Noirez, L.; Cotton, J. P.; Keller, P. Neutron scattering study and discussion of the backbone conformation in the nematic phase of a side chain polymer. *Liq. Cryst.* **1991**, *10*, 111-118.
- [11] Pepy, G.; Cotton, J. P.; Hardouin, F.; Keller, P.; Lambert, M.; Moussa, F.; Noirez, L.; Lapp, A.; Strazielle, C. Liquid Crystal Polymers: Studies of Labelled Parts by Neutron Scattering. *Makromol. Chem. - M. Symp.* **1988**, *15*, 251-258.
- [12] Keller, P.; Carvalho, B.; Cotton, J. P.; Lambert, M.; Moussa, F.; Pepy, G. Side chain mesomorphic polymers: studies of labelled backbones by neutron scattering. *J. Physique Lett.* **1985**, *46*, L-1065 - L-1071.
- [13] Hardouin, F.; Noirez, L.; Keller, P.; Lambert, M.; Moussa, F.; Pepy, G.; Richard, H. Liquid Crystal Polymers: A Small Angle Neutron Scattering Study. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 389-397.
- [14] Kirste, R. G.; Ohm, H. G. The conformation of liquid-crystalline polymers as revealed by neutron scattering. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 179-185.
- [15] Richardson, R. M.; Gray, G. W.; Tajbakhsh, A. R. Neutron scattering studies of terminally attached side chain liquid crystal polymers. *Liq. Cryst.* **1993**, *14*, 871-879.
- [16] Gu, D. F.; Jamieson, A. M. Rheological Characterization of Director Dynamics in a Nematic Monodomain Containing Mesogenic Polymers of Differing Architectures. *Macromolecules* **1994**, *27*, 337-347.

- [17] Chiang, Y.-C.; Jamieson, A. M. Electrorheological determination of the Leslie viscosity coefficient (a_2) of a main-chain liquid crystal polymer in a nematic solvent. *Rheol. Acta* **1999**, *38*, 268-273.
- [18] Gu, D. F.; Jamieson, A. M.; Kawasumi, M.; Lee, M.; Percec, V. Dynamic Light Scattering from Nematic Monodomains Containing Mesogenic Polymers of Differing Architectures. *Macromolecules* **1992**, *25*, 2151-2155.
- [19] Kempe, M. D.; Scruggs, N. R.; Verduzco, R.; Lal, J.; Kornfield, J. A. Self-assembled liquid-crystalline gels designed from the bottom up. *Nat. Mater.* **2004**, *3*, 177-182.
- [20] Matoussi, H.; Ober, R.; Veyssie, M.; Finkelmann, H. Conformation of Side Chain Nematic Polymers in Nematic Solutions: a Small-Angle X-Ray Scattering Study: SAXS. *Europhys. Lett.* **1986**, *2*, 233-240.
- [21] Chiang, Y.-C.; Jamieson, A. M.; Zhou, Y.; Kasko, A. M.; Pugh, C. Effect of molecular weight on the elctrorheological behavior of side-chain liquid crystal polymers in nematic solvents. *Polymer* **2002**, *43*, 4887-4894.
- [22] Yao, N.; Jamieson, A. M. Transient shear flow behavior of dilute solutions of side-chain liquid-crystalline polysiloxanes in 4,4'-(n-pentyloxy)cyanobiphenyl. *Macromolecules* **1998**, *31*, 5399-5406.
- [23] Kempe, M. D.; Kornfield, J. A.; Lal, J. Chain Anisotropy Side-Group Liquid Crystalline Polymers in Nematic Solvents. *Macromolecules* **2004**, *37*, 8730-8738.
- [24] Matoussi, H.; Ober, R. Conformation of Comblike Liquid-Crystalline Macromolecules. *Macromolecules* **1990**, *23*, 1809-1816.
- [25] Liu, P.-Y.; Jamieson, A. M.; Yao, N. Twist Viscosity of a Side-Chain Liquid-Crystalline Polysiloxane Dissolved in a Tumbling Nematic Solvent. *Macromolecules* **2000**, *33*, 1692-1697.
- [26] Yao, N.; Jamieson, A. M. Rheological behavior of dilute solutions of a side-chain liquid-crystalline polysiloxane in 4,4'-n-octylcyanobiphenyl. *Rheol. Acta* **2000**, *39*, 338-345.
- [27] Pereira, F. V.; Borsali, R.; Merlo, A. A.; Pesco da Silveira, N. Small angle X-ray scattering study of chiral side chain liquid crystalline polymers in 5CB and 8CB solvents. *Liq. Cryst.* **2004**, *31*, 655-661.
- [28] Dubault, A.; Ober, R.; Veyssie, M.; Cabane, B. Anisotropy of a flexible polymeric chain in a nematic field: neutron scattering versus magnetic resonance. *J. Physique* **1985**, *46*, 1227-1232.
- [29] Brochard, F.; Jouffroy, J.; Levinson, P. Phase diagrams of mesomorphic mixtures. *J. Physique* **1984**, *45*, 1125-1136.
- [30] Chiu, H.-W.; Kyu, T. Equilibrium phase behavior of nematic mixtures. *J. Chem. Phys.* **1995**, *103*, 7471-7481.
- [31] ten Bosch, A.; Maissa, P.; Sixou, P. Molecular model for nematic polymer in liquid crystal solvents. *J. Chem. Phys.* **1983**, *79*, 3462-3466.
- [32] Chiu, H.-W.; Zhou, Z. L.; Kyu, T.; Cada, L. G.; Chien, L.-C. Phase Diagrams and Phase Separation Dynamics in Mixtures of Side-Chain Liquid Crystalline Polymers and Low Molar Mass Liquid Crystals. *Macromolecules* **1996**, *29*, 1051-1058.
- [33] Kihara, H.; Kishi, R.; Miura, T.; Kato, T.; Ichijo, H. Phase behavior of liquid-crystalline copolymer/ liquid crystal blends. *Polymer* **2001**, *42*, 1177-1182.

- [34] Sigaud, G.; Achard, M. F.; Hardouin, F.; Coulon, C.; Richard, H.; Mauzac, M. Flory's Parameters in Solutions of Liquid Crystalline Side-Chain Polymers in Low Molecular Weight Liquid Crystals. *Macromolecules* **1990**, *23*, 5020-5024.
- [35] Sigaud, G.; Achard, M. F.; Hardouin, F.; Mauzac, M.; Richard, H.; Gasparoux, H. Relationships between Molecular Structure and Immiscibility of Liquid Crystalline Side-Chain Polymers in Low Molecular Weight Nematic Solvents. *Macromolecules* **1987**, *20*, 578-585.
- [36] Casagrande, C.; Veyssie, M.; Finkelmann, H. Phase separations in the mixtures of a mesomorphic polymer with a low molecular mass liquid crystal. *J. Physique* **1982**, *43*, L671 - L675.
- [37] Benthack-Thoms, H.; Finkelmann, H. Phase separations in binary mixtures of nematic liquid crystal side chain polymers and low-molar-mass liquid crystals, 1 Influence of the chemical constitution of the low-molar-mass component. *Makromol. Chem.* **1985**, *186*, 1895-1903.
- [38] Brochard, F. Solutions of flexible polymers in a nematic liquid. *C. R. Acad. Sc. Paris* **1979**, *289*, 229-232.
- [39] Matsuyama, A.; Kato, T. Phase separations and orientational ordering of polymers in liquid crystal solvents. *Phys. Rev. E* **1999**, *59*, 763-770.
- [40] Ahn, W.; Kim, C. Y.; Kim, H.; Kim, S. C. Phase Behavior of Polymer/Liquid Crystal Blends. *Macromolecules* **1992**, *25*, 5002-5007.
- [41] Hori, H.; Urakawa, O.; Adachi, K. Dielectric Relaxation in Phase-Segregated Mixtures of Polystyrene and Liquid Crystal 5CB. *Macromolecules* **2004**, *37*, 1583-1590.
- [42] Benmouna, F.; Daoudi, A.; Roussel, F.; Buisine, J.-M.; Coqueret, X.; Maschke, U. Equilibrium Phase Diagram of Polystyrene and 8CB. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1841-1848.
- [43] Benmouna, F.; Daoudi, A.; Roussel, F.; Leclercq, L.; Buisine, J.-M.; Coqueret, X.; Benmouna, M.; Ewen, B.; Maschke, U. Effect of Molecular Weight on the Phase Diagram and Thermal Properties of Poly(styrene)/8CB Mixtures. *Macromolecules* **2000**, *33*, 960-967.
- [44] Gogibus, N.; Maschke, U.; Benmouna, F.; Ewen, B.; Coqueret, X.; Benmouna, M. Phase Diagrams of Poly(dimethylsiloxane) and 5CB Blends. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 581-588.
- [45] Kim, W.-K.; Kyu, T. Phase Separation Dynamics in a Mixture of Polystyrene and Liquid Crystal. *Mol. Cryst. Liq. Cryst.* **1994**, *250*, 131-141.
- [46] Kronberg, B.; Bassignana, I.; Patterson, D. Phase Diagrams of Liquid Crystal + Polymer Systems. *J. Phys. Chem.* **1978**, *82*, 1714-1719.
- [47] Kempe, M. D.; Kornfield, J. A. Shear alignment behavior of nematic solutions induced by ultralong side-group liquid crystal polymers. *Phys. Rev. Lett.* **2003**, *90*, 115501.
- [48] Quijada-Garrido, I.; Siebert, H.; Friedrich, C.; Schmidt, C. Flow Behavior of Two Side-Chain Liquid Crystal Polymers Studied by Transient Rheology. *Macromolecules* **2000**, *33*, 3844-3854.
- [49] Yao, N.; Jamieson, A. M. Electrorheological creep response of tumbling nematics. *J. Rheol. (Melville, NY, U. S.)* **1998**, *42*, 603-619.

- [50] Weill, C.; Casagrande, C.; Veyssie, M.; Finkelmann, H. Nematic solutions of nematic side chain polymers: twist viscosity effect in the dilute regime. *J. Physique* **1986**, *47*, 887-892.
- [51] Brochard, F. Viscosities of Dilute Polymer Solutions in Nematic Liquids. *J. Polym. Sci. Pt. B-Polym. Phys.* **1979**, *17*, 1367-1374.
- [52] Gu, D. F.; Jamieson, A. M. Dynamic Light Scattering from a Side-Chain Liquid Crystal in a Nematic Solvent. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 147-153.
- [53] Gu, D. F.; Jamieson, A. M.; Rosenblatt, C.; Tomazos, D.; Lee, M.; Percec, V. Dynamic Light Scattering from a Nematic Monodomain Containing a Side-Chain Liquid Crystal Polymer in a Nematic Solvent. *Macromolecules* **1991**, *24*, 2385-2390.
- [54] Mao, G.; Ober, C. K. Block copolymers containing liquid crystalline segments. *Acta Polym.* **1997**, *48*, 405-422.
- [55] Park, C.; Yoon, J.; Thomas, E. L. Enabling nanotechnology with self assembled block copolymer patterns. *Polymer* **2003**, *44*, 6725-6760.
- [56] Muthukumar, M.; Ober, C. K.; Thomas, E. L. Competing Interactions and Levels of Ordering in Self-Organizing Polymeric Materials. *Science* **1997**, *277*, 1225-1232.
- [57] Sanger, J.; Gronski, W.; Leist, H.; Wiesner, U. Preparation of a liquid single-crystal triblock copolymer by shear. *Macromolecules* **1997**, *30*, 7621-7623.
- [58] Anthamatten, M.; Wu, J.-S.; Hammond, P. T. Direct Observation of a Smectic Bilayer Microstructure in Side-Chain Liquid Crystalline Diblock Copolymers. *Macromolecules* **2001**, *34*, 8574-8579.
- [59] Sanger, J.; Gronski, W.; Maas, S.; Stuhn, B.; Heck, B. Structural transition in a nematic LC block copolymer induced by the transition to the LC phase. *Macromolecules* **1997**, *30*, 6783-6787.
- [60] Anthamatten, M.; Zheng, W. Y.; Hammond, P. T. A Morphological Study of Well-Defined Smectic Side-Chain LC Block Copolymers. *Macromolecules* **1999**, *32*, 4838-4848.
- [61] Hamley, I. W.; Castelletto, V.; Lu, Z. B.; Imrie, C. T.; Itoh, T.; Al-Hussein, M. Interplay between Smectic Ordering and Microphase Separation in a Series of Side-Group Liquid-Crystal Block Copolymers. *Macromolecules* **2004**, *37*, 4798-4807.
- [62] Zheng, W. Y.; Hammond, P. T. Phase Behavior of New Side Chain Smectic C* Liquid Crystalline Block Copolymers. *Macromolecules* **1998**, *31*, 711-721.
- [63] Hamley, I. W.; Fairclough, J. P. A.; Ryan, A. J.; Ryu, C. Y.; Lodge, T. P.; Gleeson, A. J.; Pedersen, J. S. Micellar Ordering in Concentrated Solutions of Di- and Triblock Copolymers in a Slightly Selective Solvent. *Macromolecules* **1998**, *31*, 1188-1196.
- [64] Hanley, K. J.; Lodge, T. P.; Huang, C.-I. Phase Behavior of a Block Copolymer in Solvents of Varying Selectivity. *Macromolecules* **2000**, *33*, 5918-5931.
- [65] Lai, C.; Russel, W. B.; Register, R. A. Phase Behavior of Styrene-Isoprene Diblock Copolymers in Strongly Selective Solvents. *Macromolecules* **2002**, *35*, 841-849.
- [66] Lodge, T. P.; Hanley, K. J.; Pudil, B.; Alahapperuma, V. Phase Behavior of Block Copolymers in a Neutral Solvent. *Macromolecules* **2003**, *36*, 816-822.

- [67] Lodge, T. P.; Pudil, B.; Hanley, K. J. The Full Phase Behavior for Block Copolymers in Solvents of Varying Selectivity. *Macromolecules* **2002**, *35*, 4707-4717.
- [68] Lodge, T. P.; Xu, X.; Ryu, C. Y.; Hamley, I. W.; Fairclough, J. P. A.; Ryan, A. J.; Pedersen, J. S. Structure and Dynamics of Concentrated Solutions of Asymmetric Block Copolymers in Slightly Selective Solvents. *Macromolecules* **1996**, *29*, 5955-5964.
- [69] McConnell, G. A.; Gast, A. P. Melting of Ordered Arrays and Shape Transitions in Highly Concentrated Diblock Copolymers Solutions. *Macromolecules* **1997**, *30*, 435-444.
- [70] Lodge, T. P.; Blazey, M. A.; Liu, Z. Asymmetric block copolymers in neutral good solvents: self-diffusion through the ordering transition. *Macromol. Chem. Phys.* **1997**, *198*, 983-995.
- [71] Walther, M.; Bohnert, R.; Derow, S.; Finkelmann, H. Structure formation of liquid-crystalline isotropic AB block copolymers in nematic solvents. *Macromol. Rapid Commun.* **1995**, *16*, 621-629.
- [72] Walther, M.; Faulhammer, H.; Finkelmann, H. On the thread-like morphology of LC/I block copolymers in nematic solvents. *Macromol. Chem. Phys.* **1998**, *199*, 223-237.
- [73] Walther, M.; Finkelmann, H. Formation of a transient periodic stripe domain pattern in nematic AB block copolymer solution during photo-induced director reorientation. *Macromol. Rapid Commun.* **1998**, *19*, 145-148.
- [74] Kempe, M. D.; Verduzco, R.; Scruggs, N. R.; Kornfield, J. A. Rheological study of structural transitions in triblock copolymers in a liquid crystal solvent. *Soft Matter* **2006**, *2*, 422-431.
- [75] Verduzco, R.; Meng, G.; Kornfield, J. A.; Meyer, R. B. Buckling instability in liquid crystalline physical gels. *Phys. Rev. Lett.* **2006**, *96*, 147802.
- [76] Khoo, I.-C.; Wu, S. T. *Optics and Nonlinear Optics of Liquid Crystals*, World Scientific: Singapore, 1993.
- [77] Skarp, K.; Lagerwall, S. T.; Stebler, B. Measurements of hydrodynamic parameters for nematic 5CB. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 215-236.
- [78] Van Horn, B. L.; Winter, H. H. Analysis of the conoscopic measurement for uniaxial liquid-crystal tilt angles. *Appl. Opt.* **2001**, *40*, 2089-2094.
- [79] Bloss, F. D. *Optical Crystallography*, Mineralogical Society of America: Washington, D.C., 1999.