Chapter 7

ELECTRIC-FIELD IMPRINTING OF LIQUID CRYSTAL GELS SELF-ASSEMBLED FROM DIBLOCK AND TRIBLOCK COPOLYMERS IN NEMATIC SOLVENT

7.1 Introduction

When a block copolymer having a side-group liquid crystal polymer (SGLCP) block and a random-coil polymer block is dissolved in a small-molecule liquid crystal (LC) solvent, the polymer self-assembles to segregate the random-coil block from the ordered solvent. Self-assembly of a coil-SGLCP diblock copolymer results in the formation of micelles and, at sufficiently high concentration, the osmotic repulsion between neighboring micelles causes the solution to behave rheologically as a gel:[1] the elastic modulus is greater than the storage modulus and is virtually independent of frequency.[2] Self-assembly of a coil-SGLCP-coil triblock copolymer results in the formation of a percolated polymer network because a single polymer chain can participate in up to two different coil-block domains. Triblock copolymer solutions also behave rheologically as gels above a critical concentration.[3, 4]

Although diblock and triblock copolymer gels are rheologically similar, the two are in stark contrast when it comes to their electro-optic performance. Triblock copolymer gels preserve a memory of the LC orientation field present when they self-assemble,[3, 5] but this memory is absent in diblock copolymer gels. These experiments compare the relaxation of diblock and triblock copolymer gels after removal of an orienting electric field as a function of the orienting field's duration.

7.2 Experimental

7.2.1 Materials

Diblock copolymers having a side-group liquid crystal polymer (SGLCP) block and a random coil block (polystyrene, PS) (Figure 7.1) were synthesized according to the methods described in Appendix A from poly[styrene-*b*-1,2-butadiene] prepolymers supplied by David Uhrig (Oak Ridge National Laboratory's Center for Nanophase Materials Sciences). A PS-SGLCP-PS triblock copolymer (Figure 7.1) was synthesized according to the methods described in Appendix A from a poly[styrene-*b*-1,2-butadiene-*b*-styrene] prepolymer purchased from Polymer Source (Montreal, Quebec). The properties of these polymers are summarized in Table 7.1.

Solutions of these polymers in 4-pentyl-4′-cyanobiphenyl (5CB, purchased and used as received from TCI America) were prepared by dissolving the polymer and 5CB together in dichloromethane (DCM) then evaporating the DCM under a stream of air, followed by drying in vacuum overnight. Polymer concentrations were chosen such that the polymers would form gels: 10 wt % for diblocks and 5 wt % for the triblock.

7.2.2 Methods

Solutions of polymer in 5CB were loaded into cells purchased from LC Vision (Boulder, CO) consisting of glass plates with 5 mm x 5 mm transparent indium-tin oxide (ITO) electrodes in their centers and separated by spacers 9 μm thick. Cells were filled with polymer / LC solutions by capillary action: when heated above the gel point (35 °C) the gels transition to liquids and readily flow into the gap. Cooling to the nematic phase produces unaligned, polydomain gels. Cells were mounted in an aluminum block equipped with electrical heaters and a temperature controller stable to within ± 1 °C. Before beginning an experiment, the sample's history was erased by annealing to 50 °C for approximately 15 minutes, then annealing at 25 °C for approximately 15 minutes.

Samples were illuminated through the ITO electrodes with a 10 mW polarized HeNe laser (λ = 633 nm) and the transmitted intensity was measured using a Thorlabs PDA55 photodiode detector. The output of the detector was recorded by a computer using a National Instruments PCI-MIO-16XE-10 data acquisition card. A potential difference was applied to the cell's electrodes using a computer-controlled California Instruments 251TL alternating current power source set to a frequency of 1 kHz.

7.3 Results

Before applying the electric field, diblock and triblock copolymer gels are unaligned and the polydomain orientation of the LC director causes light to be scattered as it passes through the samples. The intensity that reaches the detector in the polydomain state is minimal. When a sufficiently large potential difference is applied across the sample, the LC is uniformly aligned with its optic axis perpendicular to the electrodes, by virtue of the LC's positive dielectric anisotropy. Aligned samples are optically clear and the detected intensity reaches a maximum with the applied field. The transmitted intensity as a function of field strength was recorded for each gel and a representative voltage sweep is presented in Figure 7.2.

A 50 V_{rms} potential difference, far above all three gels' switching thresholds, was applied to initially polydomain gels for increasing durations ranging from one minute to four days. The transmitted intensity was measured at periodic intervals both during the application of the field and for at least six hours after the field was removed, and was converted to percent transmittance by subtracting the initial baseline intensity in the polydomain state (I_0) then dividing by the maximum intensity achieved during application of the field (I_{max}). The transmittance of all three gels changes from 0 to 100% when the field is applied. When the field is removed, the transmittance decreases with time from 100% to value that depends on the duration of the previously applied field (Figure 7.3 - Figure 7.5).

The field-induced orientation is imprinted on diblock copolymer gels: neither 10 wt % 390(60)ABSiCB4 nor 10 wt % 320(120)ABSiCB4 return to 0% transmittance when the field is removed (Figure 7.3 and Figure 7.4). The field-off transmittance increases with the duration of the applied field. When 10 wt % 390(60)ABSiCB4 is exposed to the 50 V_{rms} potential difference for 1 min the transmittance remains above 40% for the entire six-hour window of field-off observation. After exposure for 1 day, the gel's transmittance remains above 85% in the field-off state. 10 wt % 320(120)ABSiCB4 is even more susceptible to imprinting. Applying the field for 1 min causes the field-off transmittance to remain above 50% in the six-hour window of observation, and field durations of 1 hour or more peg the field-off transmittance at greater than 80%.

In contrast to diblock gels, the triblock gel resists imprinting and retains a "memory" of its polydomain field-off orientation. When the 50 V_{rms} potential difference is applied for less than 1 day the transmittance returns to less than 5% within an hour of removing the field. Even when the field-on time is increased to 4 days the triblock gel returns to less than 25% transmittance within the six-hour window of observation.

7.4 Discussion

The presence of an interconnected polymer network in triblock copolymer gels provides a memory of the gel's orientation that is absent in diblock copolymer gels (Figure 7.6). When the orientation of the LC solvent is changed, diblock micelles reorient to align their corona chains with the new director. The required rotation does not change the micelles' positions relative to one another. When the field is removed the micelles return to a random orientation distribution by Brownian diffusion, but the return is slow because the micelles are large and packed relatively close together. In the triblock gel, changing the orientation of the LC solvent causes the conformations of polymer chains spanning between two crosslinks to be significantly distorted and the stresses cannot be relieved without changing the network's connectivity because the positions and orientations of the physical crosslinks are highly correlated with one another.

These electric field imprinting experiments give an order of magnitude estimate of the triblock copolymer network's reorganization time. The network's physical junctions continuously break and reform with a characteristic time scale, t_R, and when a strong bias voltage is used to torque the LC away from its equilibrium orientation it creates a driving force for a broken junction to reform in way that accommodates the new director field. However, network restructuring can only play a role when the field-on time is sufficiently long compared to t_R. The observation that triblock gels retain no memory of field-induced orientation when the field on time is less than or equal to six hours demonstrates that t_R is greater than six hours, in agreement with the order of magnitude ($> 10^3$ s) of the reorganization time scale measured by dynamic light scattering in Chapter 6.

Amongst diblock copolymer gels, the observation that 10 wt % 390(60)ABSiCB4 is less susceptible to imprinting than 10 wt % 320(120)ABSiCB4 may be related to the size of the micelles and the modulus of the gel. SANS from the two gels (Chapter 4) demonstrates that micelles in 10 wt % 320(120)ABSiCB4 are larger than in 10 wt % 390(60)ABSiCB4, and rheology (Appendix E) demonstrates that 10 wt % 320(120)ABSiCB4 is more viscous. Assuming the bias field provides the same degree of orientation in both gels, the relaxation time to return to the polydomain state would be much longer in 10 wt % 320(120)ABSiCB4 because the diffusion of larger micelles in a more viscous medium is slower. Anisotropy of the micelle structure may also play a role. If the aspect ratio of micelles in 10 wt % 320(120)ABSiCB4 is larger than those in 10 wt % 390(60)ABSiCB4, their field-on reorientation may be much faster.[6] At equal field-on times, the micelles in 10 wt % 320(120)ABSiCB4 would be more strongly oriented than those in 10 wt % 390(60)ABSiCB4 and would, therefore, better serve to reinforce the LC's uniform orientation after the field was removed.

7.5 Conclusions

The network structure in an LC gel self-assembled from a triblock copolymer serves to reinforce the alignment state present when the gel is formed. When an orienting electric field is removed from an initially polydomain gel, the network causes the alignment to return to the polydomain state. When the field is left on for very long times, the network can restructure to accommodate the new director field. In contrast, gels formed from diblock copolymers, in which the micelles are not interconnected, do not return to their polydomain alignment state when the electric field is removed. Instead, the slow diffusion of the micelles back to a random orientation distribution serves to preserve the field-on orientation.

7.6 Tables

Table 7.1 Molecular weight, conversion, and polydispersity of the side-group liquid crystal block copolymers. Details of their characterization may be found in Appendix A.

Name	PS Block	SGLCP Block				PDI[a]
	M_n [kg/mol]	M_n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB	Mole Fraction LC	
390(60)ABSiCB4	59	388	0.15	0.03	0.85	1.11
320(120)ABSiCB4	121	323	0.22	0.01	0.77	1.05
1100ABASiCB4	57,67	1,012	0.02	0.14	0.84	1.16

[a] PDI = Polydispersity Index (M_w/M_n)

7.7 Figures

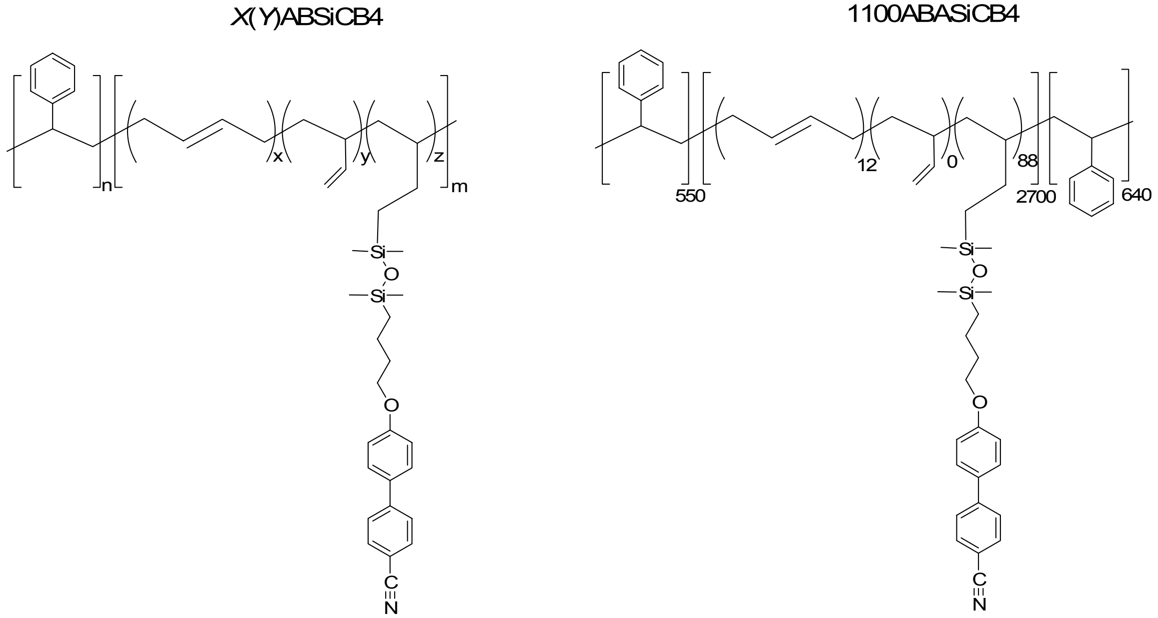

Figure 7.1 Chemical structures of side-group liquid crystal diblock (*X*(*Y*)ABSiCB4) and triblock (1100ABASiCB4) copolymers. The diblocks' names are derived from the molecular weights of the SGLCP block (*X*) and the PS block (*Y*) in units of kg/mol, the letters "AB" to indicate a diblock copolymer, and "SiCB4" to indicate end-on mesogens. The triblock's name derives from its total molecular weight (1100 kg/mol) and the letters "ABA" to indicate a triblock copolymer. In addition to monomers having an attached mesogen, the polymers also contain some residual 1,2- and 1,4-butadiene monomers. Compositions, expressed as the mole fractions *x*,*y*, and *z*, are given in Table 7.1. Details of polymer characterization are presented in Appendix A.

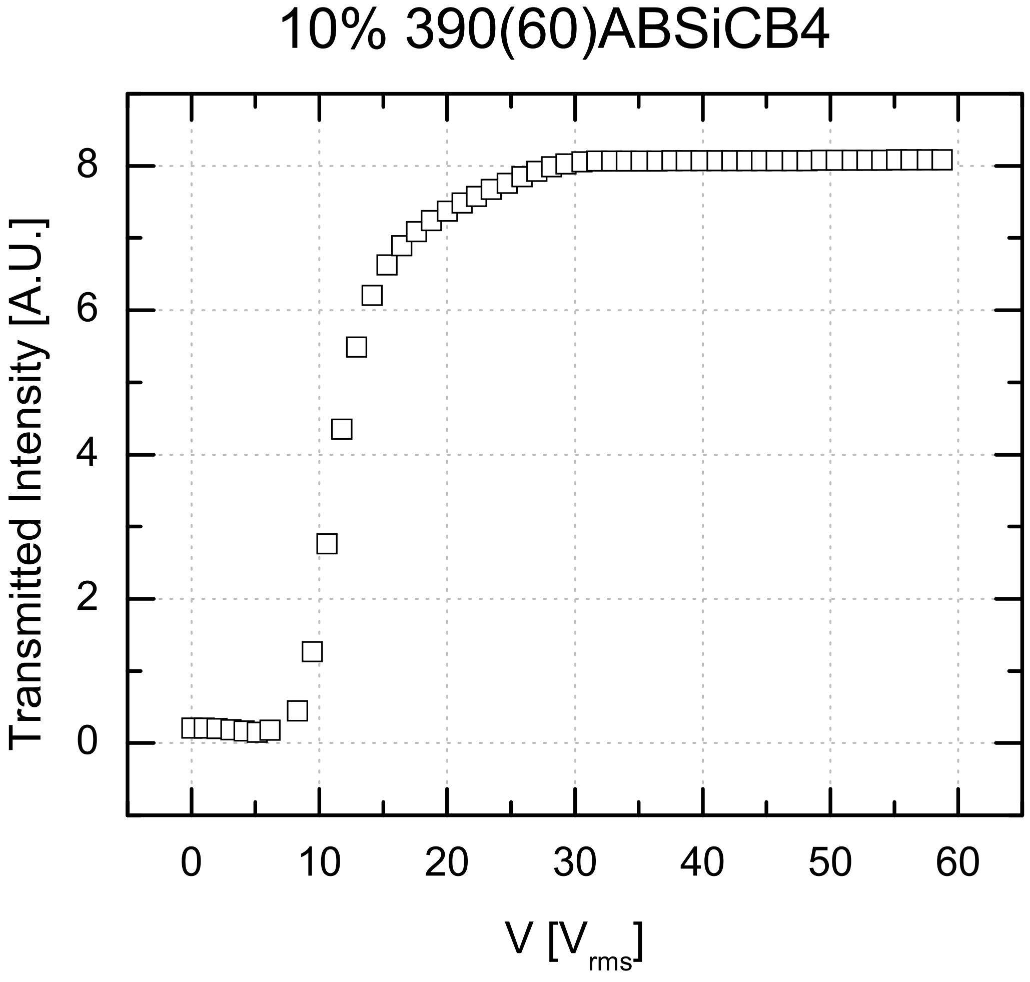

Figure 7.2 Representative voltage sweep performed on a 10 wt % 390(60)ABSiCB4 gel. A potential difference of 50 V_{rms} is well above the threshold field for switching. Voltage sweeps from 10 wt % 320(120)ABSiCB4 and 5 wt % 1100ABASiCB4 gels were similar.

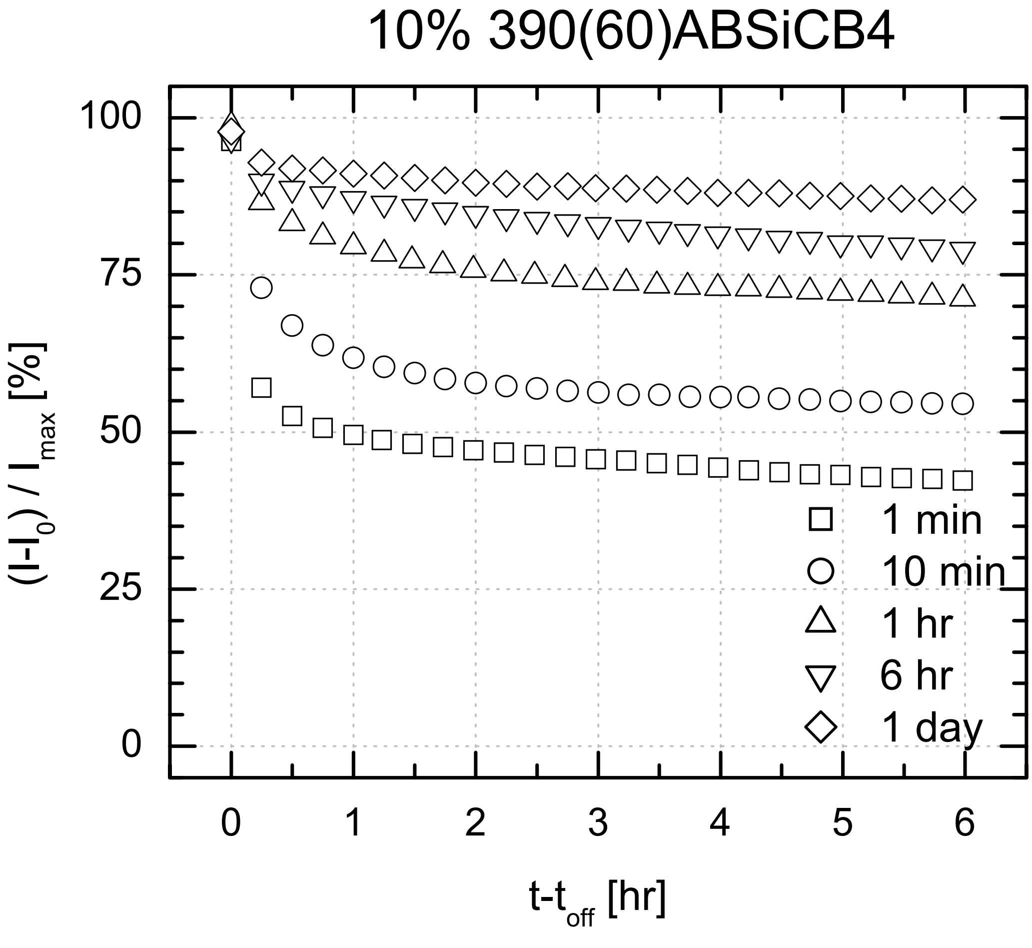

Figure 7.3 Time-dependence of the percent transmittance of light ($(I-I_0)/I_{max}$) through a gel composed of 10 wt % 390(60)ABSiCB4 in 5CB after applying a 50 V_{rms} potential difference for 1 min, 10 min, 1 hr, 6, hr, or 1 day then removing it at time $t = t_{off}$.

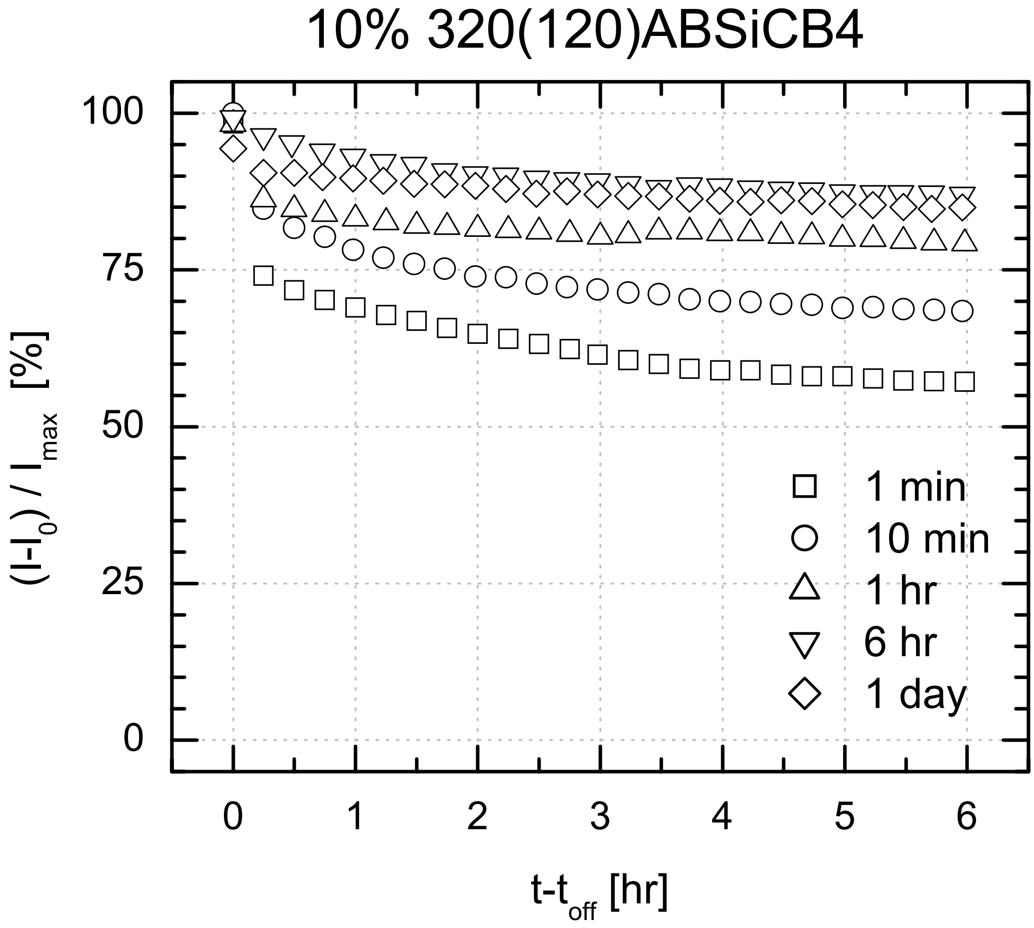

Figure 7.4 Time-dependence of the percent transmittance of light ($(I\text{-}I_0)/I_{max}$) through a gel composed of 10 wt % 320(120)ABSiCB4 in 5CB after applying a 50 V_{rms} potential difference for 1 min, 10 min, 1 hr, 6, hr, or 1 day then removing it at time $t = t_{off}$.

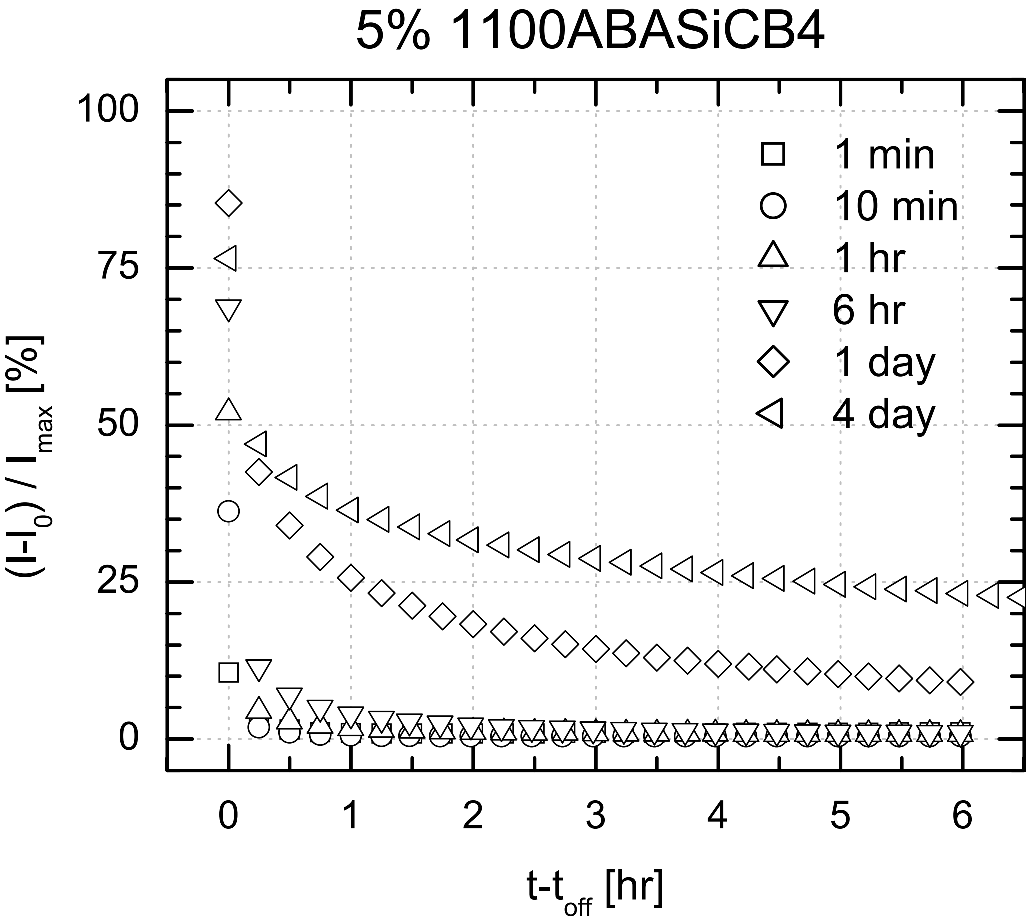

Figure 7.5 Time-dependence of the percent transmittance of light ($(I\text{-}I_0)/I_{max}$) through a gel composed of 5 wt % 1100ABSiCB4 in 5CB after applying a 50 V$_{rms}$ potential difference for 1 min, 10 min, 1 hr, 6, hr, 1 day, or 4 days then removing it at time $t = t_{off}$.

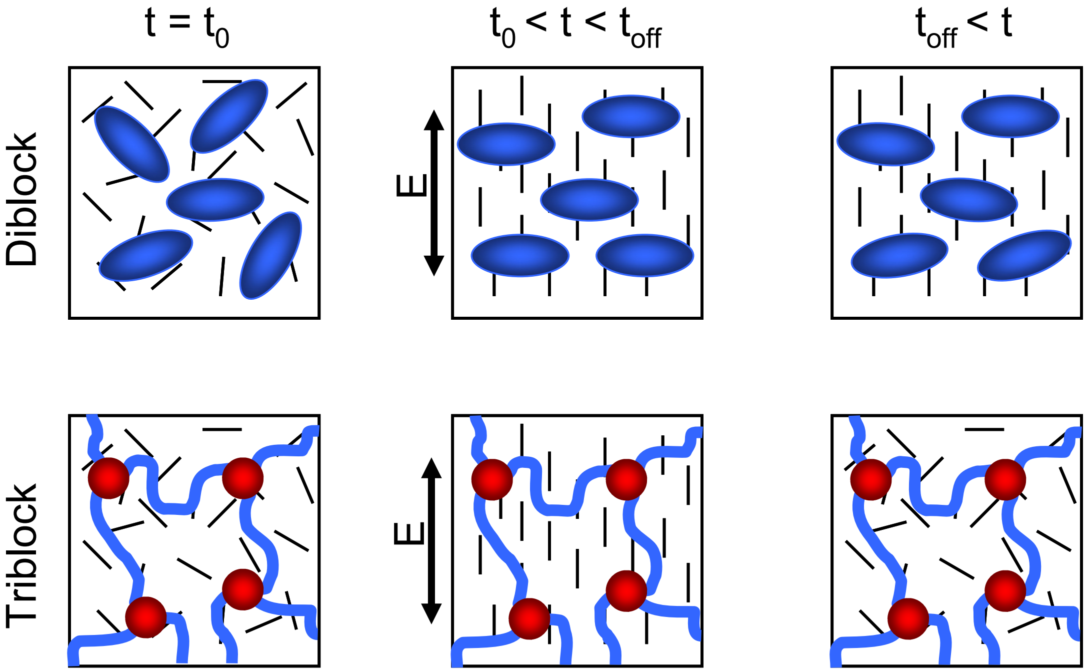

Figure 7.6 Schematic illustrating the reorientation of liquid crystalline gels before applying an electric field ($t = t_0$), during field application ($t_0 < t < t_{off}$), and after removing the electric field ($t_{off} < t$). The micelles in the diblock copolymer gel can rotate to align with the field, then diffuse slowly back to a random distribution when the field is removed. The network structure in the triblock copolymer gel provides memory of the initial polydomain alignment state, unless the field is applied long enough to allow the network to restructure.

7.8 References

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