# Chapter 2

# Liquid Crystalline Gels by Self-Assembly of Triblock Copolymers

The work presented in this chapter represents a collaborative effort with Michael Kempe and Neal Scruggs.

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## 2.1 Abstract

Liquid crystal (LC) gels are of interest for display applications and artificial muscles, but the methods for preparing LC networks are limited. Exploring novel approaches for synthesizing LC gels and elastomers can result in improved material properties and a better-defined network structure. Here, we explore the self-assembly of triblock copolymer to produce LC gels. The LC gels are produced by mixing a small molecule LC with an end-associating side-group liquid crystalline triblock copolymer. The resulting gels are thermoreversible, and they can be easily aligned to form uniform monodomains under shear or under external magnetic or electric fields. Electro-optic measurements demonstrate that the LC gels have potential use in an easily processible scattering-type display device. Additionally, the LC gels have a well-defined structure, making them useful for experimental comparison to theories of liquid crystal gels and networks.

## 2.2 Introduction

Liquid crystals (LCs) combine liquid-like fluidity with crystal-like properties such as birefringence, enabling LCs to be used in a variety of display devices [1]. The fluidity of liquid crystals is a key property that allows them to be quickly and easily reoriented in response to electric fields. On the other hand, the fluidity of liquid crystals poses problems and limitations for device applications. In the case of displays, the substrate surfaces must be coated with a polymer layer and rubbed to uniformly align the nematic director, and this alignment may be unstable to mechanical shock. Liquid crystals are therefore unsuitable for use in applications that require both birefringence and mechanical stability.

The combination of liquid crystals with polymers is an attractive method for fabricating materials with the optical properties and responsiveness of liquid crystals but with the mechanical properties and processing advantages of polymers. Liquid crystalline gels attempt to accomplish this. The potential applications of such materials include easily processible displays [2] but also other functional devices such as artificial muscles that respond to electric fields [3], heat [4], and light [5].

Several approaches have been used to make both chemical and physical LC gels [6, 7, 8]. Polymer stabilized liquid crystals (PSLCs) are made by the in situ uncontrolled radical polymerization of diacrylate LC monomers mixed with a non-reactive LC solvent [2, 8], resulting in a phase-separated polymer matrix encompassing small-molecule LC [9, 10]. In another method [11, 12], both acrylates and diacrylate LC monomers are in situ polymerized, resulting in a more soluble network. Both of these methods produce LC gels with favorable electro-optical properties, but they also have a poorly defined network structure. Another method for preparing LC gels is the addition of small molecule gelators to an LC solvent[13, 14, 15], resulting in a thermoreversible, physical LC gel.

In this study, we investigate a novel method for making LC gels. Our goal is to produce dilute LC gels with a uniform, well-defined structure. We make LC gels by the self-assembly of LC triblock copolymers in a small molecule LC. The copolymers have polystyrene (PS) endblocks and a side-group liquid crystalline (SGLCP) midblock. The midblocks are “nematophilic” and soluble in the LC solvent, but the endblocks are “nematophobic” and physically associate in the nematic phase, producing LC gels with a homogeneous nematic texture (Fig. 2.1). The LC gels have unique thermal, mechano-optic, and electro-optic properties, and they provide several advantages for display applications, such as thermoreversible gelation. In this chapter, we present the synthesis of the LC gels, and we investigate the phase behavior, alignment, and electro-optical properties of the LC gels. We find that the LC gels have a fast electro-optical response, and, because of their homogeneous structure, they are also useful for testing theoretical predictions [16, 17, 18] for liquid crysalline networks.

## 2.3 Experimental

### 2.3.1 Gel permeation chromatography (GPC)

GPC was carried out using three different systems. The first one used two 30 cm long PLgel 5 $\mu$m mixed-C columns from Polymer Laboratories (200 to 2,000,000 g/mol), connected in series with a DAWN 8 EOS multi-angle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer, both from Wyatt Technology. Calculations were performed using the software package ASTRA from Wyatt Technology. The MALLS detector used a 30 mW, 690 nm, linearly polarized gallium-arsenide laser, and the differential refractometer used 690 nm light with a Wollaston prism. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min and a temperature of 35 $^{o}$C. No calibration standards were used and d$n$/d$c$ values were obtained for each injection assuming 100% mass elution from the columns, and assuming dilute conditions where the second virial coefficient is negligible.

The second system used a Waters 410 differential refractometer with two Polymer Laboratories 30 cm long PLgel 10 $\mu$m analytical columns connected in series. These columns were calibrated with monodisperse polystyrene samples. The polydispersity index (PDI) ($M_w/M_n$) of the prepolymers, SGLCP homopolymers, and LC triblock copolymers was measured using THF flowing at a rate of 0.9 mL/min as the mobile phase.

The last column was only used to remove high molecular weight cross-linked polymer byproduct from the ABA LC polymers. The system consisted of a 30 cm long Polymer Laboratories PLgel 10 $\mu$m preparative column connected to the same Waters 410 differential refractometer.

### 2.3.2 Nuclear magnetic resonance

$^1$H NMR was performed on a Mercury-Vx 300 MHz NMR spectrometer with the software package VNMR Version 6.1B, using 32 scans with a 1 s delay time. Experiments were run at room temperature using $CDCl_3$ as a solvent and a polymer concentration of 10 to 20 mg/mL.

### 2.3.3 Liquid crystal phase identification

The transition temperatures and phases of the LC polymers were determined using both a Zeiss polarized optical microscope (POM) with a Mettler FP82 hot stage and a Perkin Elmer DSC7 differential scanning calorimeter (DSC) using the Pyris software. In the microscope the temperature was slowly raised at between 1 and 5 $^o$C/min, and the phases were identified along with the temperature at which phase transitions began. In the DSC method the samples were heated well into the isotropic phase to remove any thermal history. Then the temperature was raised at a rate of 10 $^o$C/min, and Perkin Elmers Pyris computer software (version 3.04) was used to determine the onset temperature of the various phase transitions. The DSC was calibrated using indium as a standard, at a heating rate of 10 $^o$C/min.

### 2.3.4 Conoscopic imaging

Conoscopic imaging was performed using a Zeiss microscope equipped with an Olympus 1C20 high-numerical-aperture lens, a custom-made translation stage, and a computerized video capture system.

### 2.3.5 Rheometry

Rheometry was performed on a TA Instruments ARES-RFS rheometer equipped with a 25 mm diameter titanium shear cell in a cone-and-plate geometry having a 0.0202 radian cone angle. No surface treatment was applied, and the samples were heated into the isotropic state prior to measurement to erase any thermal history.

### 2.3.6 Electro-optic measurements

The optical properties and electro-optic responses of the gels were measured using a polarized HeNe laser, a beam splitter, two CCD cameras, and a function generator. A beam splitter between the laser and the sample sent half of the incident laser intensity to the sample and half to a CCD camera which was used to normalize the intensity of laser light incident on the sample. A CCD camera 10 cm behind the sample measured the intensity of transmitted light, and this intensity was normalized by the intensity transmitted for the sample in the isotropic state. The function generator was used to apply voltages from 0 V to 270 V at 1000 Hz.

### 2.3.7 Synthesis of SGLCPs: homopolymers and triblocks

All reagents were used as received from Aldrich unless otherwise stated. A "polymer analogous" approach to synthesis allowed high molecular weight polymers to be created. 1,2-polybutadiene (H) was used as the prepolymer for LC homopolymers, and polystyrene-*block*-1,2-polybutadiene-*block*-polystyrene triblock copolymer (ABA) was used as the prepolymer for LC triblock copolymers. H and ABA, synthesized by anionic polymerization, were used as received from Polymer Source (Montreal, Quebec). Hydrosilylation is used to attach LC mesogens to the pendant 1,2-polybuatiene vinyl groups [19, 20, 21, 22]. This method is chosen because it is compatible with a wide range of functionalities and limits the exposure of the polymers to only one reaction. Also, various mesogenic units can be attached to the pendant vinyl groups of 1,2-polybutadiene, so a homologous series of polymers of identical backbone length may be prepared, one of the advantages of a "polymer analogous approach." Here, we describe the attachment of a particular "side-on" type mesogen, 2,5-di(4-butoxybenzoate)-benzaldehyde (BB), to produce LC triblock ABASiBB and LC homopolymer HSiBB (Fig. 2.1).

The synthesis of this mesogenic unit was similar to that used by researchers making polyacrylates [23, 24]. In the first step of the reaction (Fig. 2.2) 4-butoxybenzoic acid (25 g, 0.127 mol) was

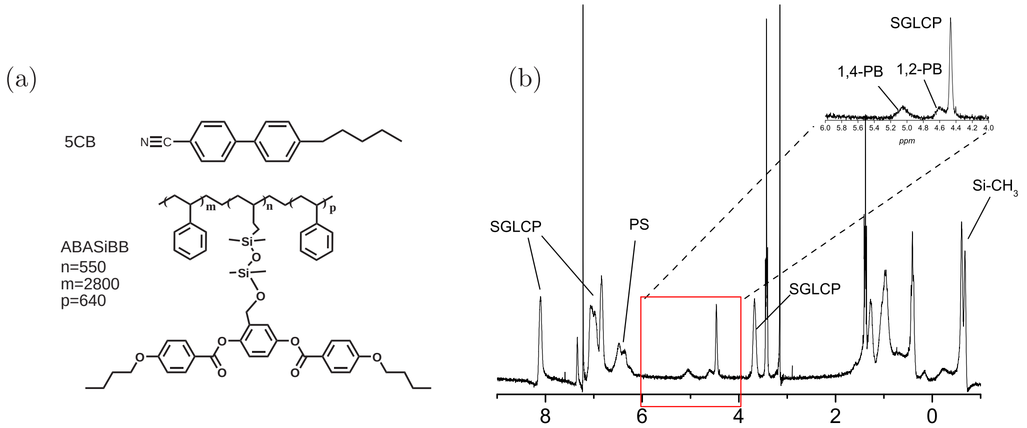

Figure 2.1: (a) Chemical structure of LC 5CB and the end-associating triblock copolymer ABASiBB used in this study and (b) an NMR of ABASiBB.

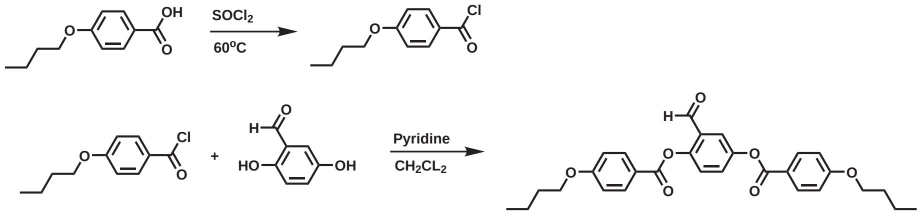

Figure 2.2: Synthesis of LC side-group mesogen

converted into 4-butoxybenzoyl chloride using a large excess of $SOCl_2$ (20 mL, 0.275 mol) as the solvent at 60 $^o$C for one hour. Excess $SOCl_2$ was removed by evaporation under vacuum at 60 $^o$C. 4-butoxy-benzoyl chloride was added at 20% excess to 2,5-dihydroxybenzaldehyde (7 g, 0.056 mol, Lancaster Chemical) in a dichloromethane (DCM) (50 mL) solution with anhydrous pyridine (20 mL), and the reaction was allowed to proceed at room temperature for several hours. The product 2,5-di(4-butoxybenzoate)-benzaldehyde was purified by liquid-liquid extraction using DCM and an aq. 1 N solution of HCl, followed by another extraction using DCM and a saturated aqueous solution of $NaHCO_3$. The product was further purified by recrystallization in ethanol for a yield of 60%.

The spacer was attached to the aldehyde via a hydrosilylation reaction using Wilkinson's catalyst, chlorotris(triphenylphosphine)-rhodium (I) [23] (Fig. 2.3). 3,5-di(4-butoxybenzoate)-benzaldehyde (3 g, 0.0057 mol) was mixed with Wilkinson's catalyst (20 mg) and ten molar equivalents of 1,1,3,3-tetramethyl disiloxane (TMDS) (15 mL, 0.085 mol) in anhydrous toluene (30 mL). The reaction was allowed to progress for 40 min at 60 $^o$C, and then excess TMDS was removed in vacuo at 60 $^o$C. The

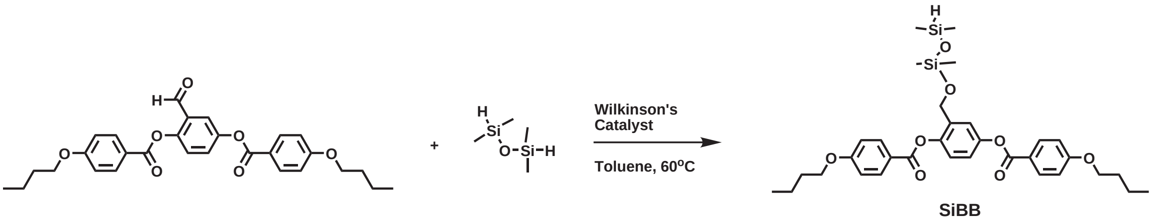

Figure 2.3: Preparation of SiBB by attachment of siloxane spacer to LC side-group mesogen

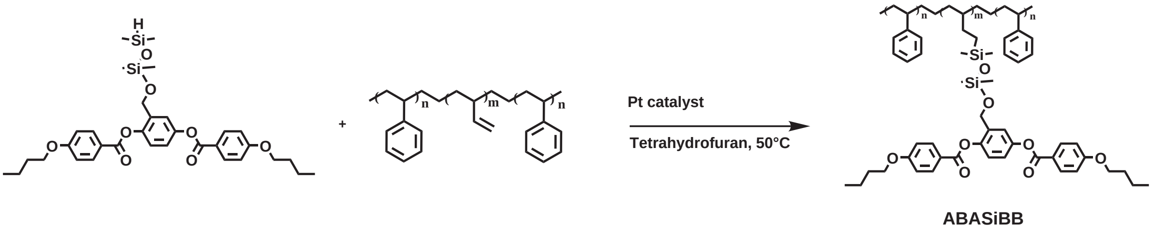

Figure 2.4: Coupling reaction to attach LC side-group mesogen to ABA polymer

product 1,4-bis(4-butoxybenzoate)-2-methyl[(1,1,3,3-tetramethyl-disiloxane)oxy]-benzene (SiBB) was purified on an anhydrous silica gel column. The anhydrous column was prepared by first drying the silica under argon while heating it with a propane torch. Anhydrous hexane was then added to make a slurry and set up the column. The column was sealed with a septum and purged with argon while loading the product. The mesogen was added to the column in an anhydrous solution of toluene, and a solvent mixture of 10% anhydrous ethyl acetate in hexanes was used as the eluent. The yield of SiBB from the hydrosilylation step was 55%.

To attach the LC side group, ABA prepolymer (100 mg, 0.00088 mol vinyl groups) was dissolved in anhydrous THF (40 mL) and combined with three molar equivalents of SiBB (1.7 g, 0.0026 mol). A few drops of platinum catalyst PC085 was added and the mixture was stirred at 50 $^o$C for a period of four days (Fig. 2.4).

To monitor the reaction progress, a small sample was taken periodically and proton NMR was performed to observe the disappearance of the vinyl peak near $\Delta = 4.9$ ppm. When the size of the vinyl peak did not change significantly over two consecutive readings, the reaction was quenched by adding 5 mL of styrene followed by stirring for one more day at 50 $^o$C. The reaction solution was then concentrated under a stream of air, and the product was precipitated by the addition of a solution of 50 ppm 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) in methanol (5 mL). The product was purified by dissolving in THF and precipitating out in methanol five times. The polymer was then stored in the bulk at 0 $^{o}$C.

The conversion was found by comparing the integrated area for the peaks corresponding to both the 1,2-polybutadiene and mesogen at 4.7-4.9, with the peak corresponding to the alkyl chain on the mesogen (Fig. 2.1b). Comparison of the areas of the peaks allowed determination of the degree of attachment of the side-group. The fraction of 1,4-polybutadiene groups in the prepolymer was determined from an NMR of the ABA prepolymer by comparing the peaks at 5.3 and 5.0 ppm.

### 2.3.8 Mixing of nematic gels

To create nematic gels, the copolymers were dissolved together with 4-pentyl-4′-cyanobiphenyl (5CB) (Fig. 2.1a) in dichloromethane, and the solvent was subsequently removed by blowing air over the mixture until it became milky white. It was then placed in a vacuum at room temperature for two days. To ensure that the gel was completely dry, the gel was periodically heated well into the isotropic phase (approximately 45 $^{o}$C) and stirred periodically during the drying process.

## 2.4 Results

### 2.4.1 Polymer characteristics

The SGLCP copolymer ABASiBB and homopolymer HSiBB are rubbery, LC polymers at room temperature (Tab. 2.1). The low $T_g$ of HSiBB can be attributed to the presence of tetramethyldisiloxane in the mesogenic group. Similar polymers without siloxane typically have higher $T_{NI}$s [25, 26]. No $T_g$ was observed for the ABASiBB midblock down to -30 $^{o}$C, which may be due to the significant content of unconverted butadiene groups in the backbone. A $T_g$ was also not observed for the polystyrene endblocks. The PDIs of the SGLCPs are higher than those of the prepolymers due to minute crosslinking of the polymers.

The type of LC order was inferred from the textures they exhibited when observed under POM.

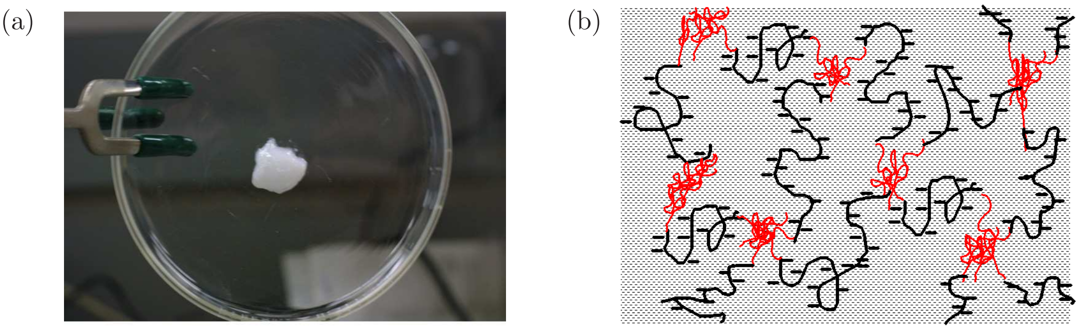

Figure 2.5: (a) A sample of LC physical gel, and (b) a schematic of the LC triblock gel. In the schematic, the speckled background represents the LC solvent 5CB, the dark black lines represent the SGLCP midblock, and the red chains represent the polystyrene endblocks.

Table 2.1: Polymer characteristics. "H" is the 1,2-polybutadiene prepolymer and "ABA" the polystyrene-*block*-1,2-polybutadiene-*block*-polystyrene triblock prepolymer. "HSiBB" and "ABASiBB" are the homopolymer and triblock SGLCPs, respectively. The number average molar mass ($M_n$) of the SGLCPs were determined by combining two measurements: GPC, to determine the size of the prepolymer, and $^1$H NMR, to determine the fractional conversion to mesogenic side groups. The $M_n$ of the different blocks of the ABA prepolymer were determined by Polymer Source using a MALLS system. DSC down to -30 $^o$C did not detect a $T_g$ for ABASiBB.

| | | | | LC BLock Composition | | | | |
|---|---|---|---|---|---|---|---|---|
| Polymer | Total $M_n$ $(\frac{\text{kg}}{\text{mol}})$ | PDI | LC Block $M_n$ $(\frac{\text{kg}}{\text{mol}})$ | 1,2 PB (mol %) | 1,4 PB (mol %) | Mesogen (mol %) | $T_{NI}$ ($^o$C) | $T_g$ ($^o$C) |
| H | 63 | 1.04 | 0 | 97 | 3 | 0 | N/A | |
| HSiBB | 713 | 1.08 | 713 | 8 | 3 | 89 | 120 | 7.7 |
| ABA | 270 | 1.26 | N/A | 86 | 14 | N/A | N/A | -15.8,105.9 |
| ABASiBB | 1445 | 1.40 | 1321 | 16 | 14 | 70 | 74 | <-30 |

Both ABASiBB and HSiBB had textures characteristic of nematic LCs. This is consistent with previous studies of side-on LC polymers [27]. The reduced isotropization temperature in the triblock as compared to the homopolymer is consistent for a variety of polymers with the same backbone and different side groups [22]. This is attributed both to the reduced number of LC side groups in the triblock relative to the homopolymer and to the presence of PS endblocks.

At temperatures below the $T_{NI}$ of 5CB, 35 $^o$C, HSiBB and ABASiBB were fully soluble in 5CB at all concentrations tested (0 - 20 wt %). From 35 $^o$C up to 45 $^o$C, solutions of HSiBB in 5CB exhibited a broad nematic-isotropic biphasic region at the concentrations tested. On the other hand, mixtures of ABASiBB in 5CB had a sharp nematic-isotropic transition, with a biphasic region narrower than 1 $^oC$ starting at 35 $^oC$.

### 2.4.2 Monodomain alignment of LC gels

With only 5 wt % ABASiBB added to 5CB, the mixture forms a gel that does not flow (Fig. 2.5). When heated above its $T_{NI}$ of 35 $^oC$, however, the gel becomes clear and flows like a liquid. Furthermore, the gel has a homogeneous nematic texture under the optical microscope. Micron-sized thread-like aggregates have previously been observed for block copolymers in LC solvents [28], but these aggregates were only found for block copolymers with LC block weight fractions less than 90%. The present polymers have an LC block weight fraction of approximately 90%.

Unaligned LCs strongly scatter light, due to a spatially varying director orientation [29]. This is also true for the LC gels, as can be seen in the photograph of the bulk gel sample (Fig. 2.5). However, the LC gels can be uniformly aligned into a clear state by shear, electric fields, or magnetic fields. Such alignment is useful for characterizing the anisotropic properties of the LC gel and for utilizing the gel in a practical device.

Shear-induced alignment is demonstrated for a 5 wt % ABASiBB gel under conoscopic imaging (Fig. 2.6). In conoscopic imaging, convergent polarized light is passed through a sample viewed under an optical microscope. A resulting interference pattern indicates monodomain alignment and also provides information about the director orientation in uniform LC monodomains [30]. The gel was placed in a shear cell that allows for conoscopic imaging and heated above its $T_{NI}$. While cooling below the $T_{NI}$, a strain of 500% was applied at a rate of 1.2 $s^{-1}$. This resulted in uniform alignment of the gel as indicated by the appearance of an interference figure (Fig. 2.6). The interference figure indicates that the nematic director is oriented slightly off-axis in the plane of the sample.

The preferred direction of alignment under shear results from the coupling of the director field to the polymer conformation. The pendant mesogens of HSiBB tend to orient parallel to the backbone, and shear causes the backbone to preferentially orient at an angle between $45^o$ and $90^o$ relative to the velocity gradient direction. The direction of alignment induced by shear varies with molecular structure of the SGLCP. In contrast to the present sample, polymers with transverse attachment of

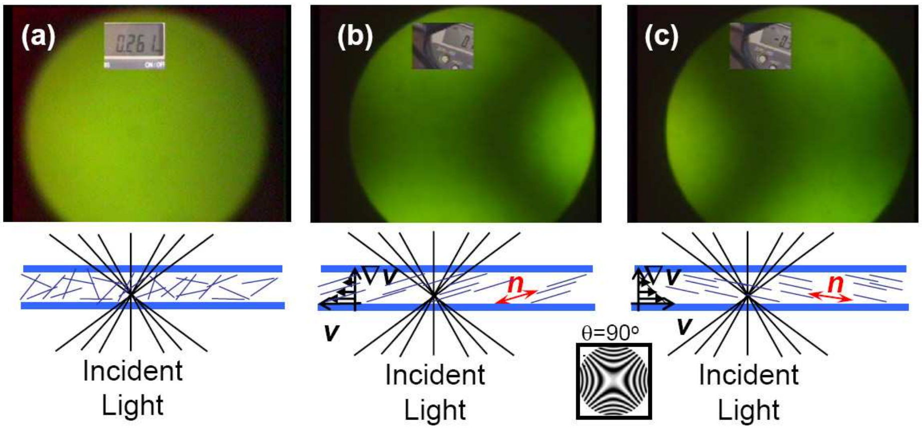

Figure 2.6: Conoscopic images of gel during shear. The sample under study is a 150 $\mu$m thick 5 wt % ABASiBB gel at 25 $^o$C. (a) The gel before shear and (b),(c) during shear. The cross-section schematics under each image illustrate how light interacts with the corresponding polydomain (a) and single-crystal-like (b),(c) orientation of the director. The axes of (b) and (c) indicate the direction of shear $v$ and define the angle $\theta$ of the director ($\boldsymbol{n}$). The interference figure (taken from Van Horn and Winter, *Appl. Opt.*, 40(13):2089-2094, 2001) below (b) and (c) is what is expected for the director aligned perfectly in the plane of the sample.

the LC side group exhibit homeotropic director alignment under shear, or alignment perpendicular to the cell substrates [31].

Gels can also be aligned by cooling from the isotropic to the nematic phase in a magnetic or electric field. In the case of magnetic field alignment, gels up to a concentration of 50 wt % polymer were amenable to alignment in approximately one hour under a field of 8.8 T. Similarly, gels can be aligned by cooling from the isotropic to the nematic phase while applying an electric field greater than 4 V/$\mu$m. The variety of methods available for alignment makes it possible to align LC gels with the director oriented either in the plane of the cell (using a magnetic field or shear) or perpendicular to the substrates (using an electric field).

### 2.4.3 Dynamic mechanical analysis

Rheometry was performed on single-phase solutions of the triblock copolymers in 5CB at various concentrations. As is often the case for block copolymer solutions, the viscoelastic relaxation spectrum changes shape with temperature rather than simply shifting to faster timescales with increasing temperature. This is particularly evident at temperatures near the isotropic-nematic transition temperature (Fig. 2.7). A dramatic change in $G'$ and $G''$ is observed between $T_{NI}$ and $T_{NI} + 2\ ^{o}$C. This abrupt change cannot be attributed to a change in the overall mobility of the solvent; the dominant viscosity of 5CB in the nematic phase is only approximately 3 to 6 times higher than its isotropic viscosity [32].

The enhancement of the modulus in the nematic phase correlates with strong aggregation of the PS endblocks evident in small-angle neutron scattering (SANS) (see Chapter 5). Therefore, the increase in $G'$ and $G''$ below $T_{NI}$ can be attributed to microphase separation of the PS endblocks and the formation of a physical network in the nematic phase.

The gelation threshold in concentration is approximately 3 wt %. At 1 wt % (Fig. 2.7a) the gel is a viscoelastic liquid ($G'' > G'$), and the relaxation spectrum resembles power law behavior with an exponent of 2/3, i.e. ($G' = 3^{1/2} \cdot G'' \sim \omega^{2/3}$). With increasing polymer concentration, a plateau in $G'$ emerges in the nematic phase: It is not present at 1 wt % but is clearly evident at 3 and 5 wt %, indicating gelation (Fig. 2.7). The gel displays solid-like ($G' >> G''$) rheological behavior in the nematic phase.

As the temperature increases toward the isotropization temperature ($T_I$), the plateau modulus decreases (Fig. 2.7 b,c), and in the isotropic phase, terminal behavior is observed. On cooling, the gel recovers its initial modulus, and therefore the gel thermoreversibly transitions between a liquid-like state above the $T_{NI}$ and a solid-like state in the nematic phase below the $T_{NI}$.

At all concentrations there is a dense spectrum of relaxation times: There is no minimum in $G''$ for any of the concentrations examined, even when there is a broad plateau in $G'$. This is in contrast to the single relaxation time "Maxwell model" that describes some telechelic associative polymer gels [33].

### 2.4.4 Reversible electro-optic response

LC physical gels have a reversible electro-optic response and can be utilized as display layers. In typical twisted-nematic or super twisted-nematic displays, the director is uniformly aligned between substrates. Here, we are interested in a scattering-type device that can be reversibly switched

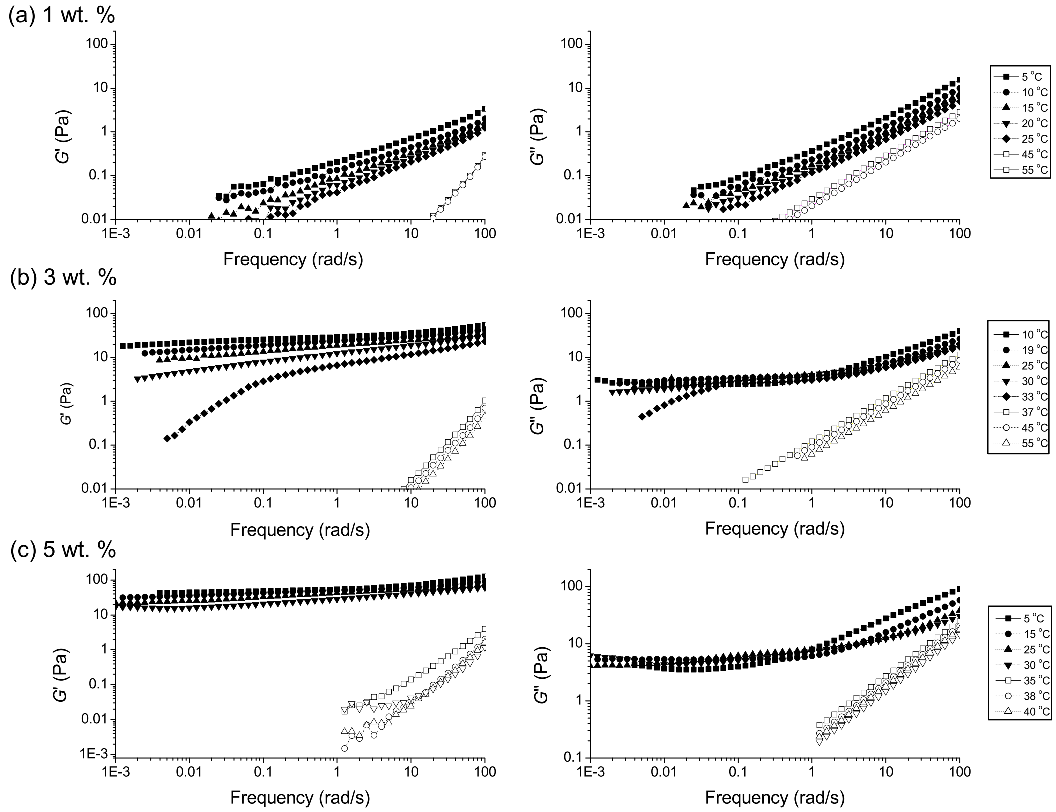

Figure 2.7: Dynamic storage modulus ($G'$) and loss modulus ($G''$) of a mixture of (a) 1 wt %, (b) 3 wt %, and (c) 5 wt % of the side-on nematic triblock ABASiBB in 5CB. The mixture is isotropic for all $T \geq 35$ $^o$C (open symbols) and nematic for $T \leq 35$ $^o$C.

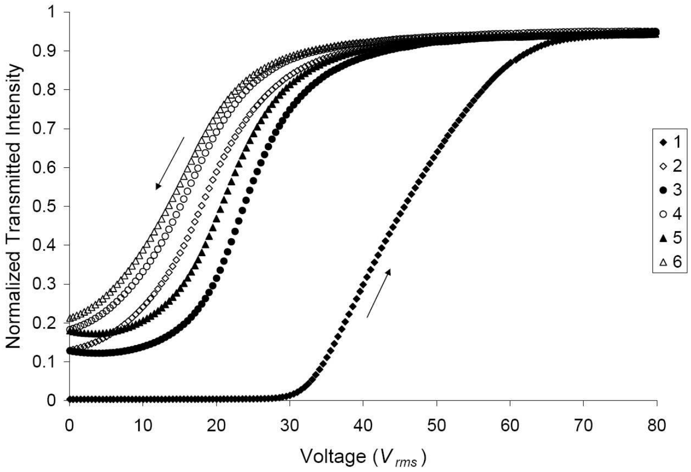

Figure 2.8: Transmitted intensity as a function of voltage $V_{rms}$ for a 5 wt % gel in a 15 $\mu$m thick gap. The transmitted intensity when increasing the voltage (filled symbols) does not overlap with that when decreasing the voltage (empty symbols).

between a scattering polydomain state and a transmissive monodomain state [8, 14, 34]. These displays require a low ($< 2.0$ V/$\mu$m) threshold and a fast ($\sim$ 50 ms) response time.

In order to investigate the threshold for switching and for monodomain alignment, the transmitted intensity of a 15 $\mu$m thick gel layer was recorded as a function of applied voltage (Fig. 2.8). The transmitted intensity is normalized by the transmitted intensity of the gel in the isotropic state. The transmittance was initially linear, with voltage above a threshold field of 2.3 V/$\mu$m. With increasing voltage, the transmittance saturated to a maximum that was more than 90% that of the isotropic cell. Saturation was reached at approximately 4.5 V/$\mu m$ for 5 wt % ABASiBB. Hysteresis is observed, meaning that the transmitted intensities while ramping voltage up are not superimposable on those recorded while ramping voltage down. After one full sweep, the threshold decreases, and the transmitted intensity at a voltage below the saturation voltage increases. If the gel is heated to the isotropic state and cooled, the gel recovers its initial electro-optic response.

The threshold field for switching was insensitive to gap thickness (Fig. 2.9). This is also true for PSLCs [11, 35] and for polymer-dispersed liquid crystals (PDLCs) [36] and originates from the elastic restoring force of the polymeric network throughout the volume of the gel rather than only at the surface alignment layers. In contrast, pure liquid crystals exhibit a threshold *voltage* for

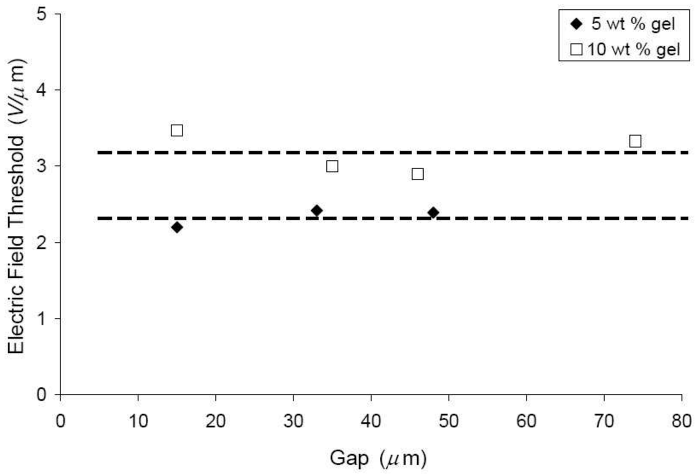

Figure 2.9: Electric field threshold for an electro-optic response in 5 and 10 wt % gels

switching, or a threshold field $E_{th}$ that varies linearly with the gap thickness $d$, $E_{th} \sim d$ [36].

The transmittance of the LC gels were recorded transiently while an electric field was applied and removed. The time required for the transmitted intensity ($I$) to reach 90% of its maximum is defined as the orientation time, $\tau_{90}$. On removal of the field, the time required for $I/I_{max}$ to fall to 10% is defined as the relaxation time, $\tau_{10}$. The response times were insensitive to gap thickness but highly dependent on the applied field (Fig. 2.10). For a 5 wt % gel, $\tau_{90}$ decreases strongly (from 10,000 ms to 100 ms) as the applied field increases from 2 V/$\mu$m to 6 V/$\mu$m. For the same gel, $\tau_{10}$ increases significantly (from 19 ms to 170 ms) with applied field (Fig. 2.10). The dynamic electro-optic response of the LC gels also depends on the polymer concentration and the sample history (Appendix A). For reference, the decay times are approximately 10 ms for PSLCs [35], 1 ms for small molecule gelators mixed with LC [37], 5 ms for PDLCs, and 5 ms for reverse-mode PDLCs [36].

## 2.5 Discussion

Physically associated triblock gels are LC systems with a fast electro-optic response and exceptional uniformity. The use of a triblock copolymer to form the self-assembled gels affords both flexibility in the molecular structure and control in the polydispersity. The resulting self-assembled gels are

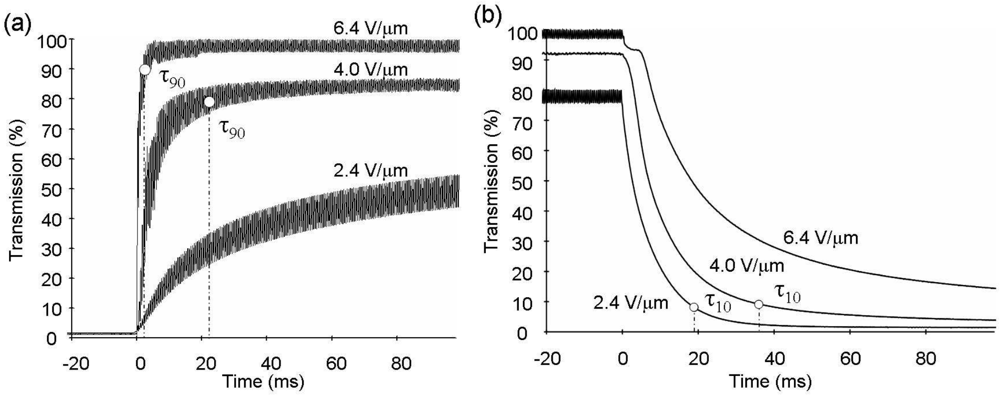

Figure 2.10: Transient electro-optic properties of a 5 wt % ABASiBB, 25 $\mu$m thick layer, under application of a.c. fields at 1000 Hz. (a) Switching the electric field on. The time required to reach 90% of the maximum transmittance is denoted $\tau_{90}$. At the lowest field of 2.4 V/$\mu$m, the $\tau_{90}$ of 1000 ms is beyond the scale of the graph. (b) Switching the electric field off. The time required to return to 10% of the maximum transmittance is denoted $\tau_{10}$. At the highest field of 6.4 V/$\mu$m, the $\tau_{10}$ of 170 ms is beyond the scale of the graph.

heterogenous at the scale of the microphase separated endblocks but homogenous at length scales much smaller optical wavelengths, making the gels potentially viable for display devices. Unlike the commonly studied PSLCs [38, 2, 8], the polymer strands are solvated by the host LC solvent 5CB, resulting in a higher degree of homogeneity and a potential for new effects in LC gels arising from the coupling of polymer conformation to LC order.

The electro-optic experiments suggest that an ABA nematic gel could be effectively used in a reflective electro-optic display by placing a layer of the LC gel in front of a uniform black background [39, 40]. Without an applied field, ambient light is scattered to produce a bright state analogous to the blank areas on a sheet of paper. Application of an electric field induces a transparent state that allows incident light to be transmitted and absorbed on the back surface, yielding a dark appearance, like ink on a printed page. At intermediate voltages, the ratio of absorbed to scattered light can be modulated to provide grayscale images. The most significant advantage of the present LC gels over PSLCs or PDLCs in a reflective display is the facile loading enabled by the self-assembled gels. However, several technical problems would have to be overcome before implementation of the gel in a commercially viable device, in particular the increased driving voltage and hysteresis. A potential solution to the latter problem would be to chemically crosslink the network after self-assembly.

Self-assembled LC gels also represent a significant step towards gaining a better understanding of LC networks. The unique properties of the self-assembled gel – namely its thermoreversible gel structure, optical clarity, and well-defined molecular architecture – make the gels useful tools for studying the coupling of LC order to a polymer network. Chapters 3 and 4 present experimental studies of novel equilibrium and dynamic properties that arise due to this coupling.

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