Chapter 6

Covalent Liquid Crystal Networks via “Click” Chemistry

The work in this chapter was done jointly with Yan Xia, under the mentorship of Professor Robert H. Grubbs.

6.1 Introduction

Liquid crystal elastomers are composed of flexible, liquid crystal polymers crosslinked to form a network. The combination of LC order and rubber elasticity results in a polymer network that is responsive to a variety of external influences, including heat, light, and electric and magnetic fields. These materials display remarkable shape-changing and optical properties which make them of interest for technological applications [1].

The first method for preparing an LC elastomer was devised by Finkelmann et al. [2, 3] and involved the functionalization and crosslinking of poly(methyl)hydrosiloxane. Subsequent studies have produced a number of different types of LC elastomers and investigated the significance of various molecular parameters to the macroscopic behavior, including the size, type, and concentration of crosslinker [4, 5, 6]; the use of polyacrylates or polymethacrylates [7, 8]; the incorporation of mesogens into the polymer backbone [9]; and the effect of the side-group [10]. While these materials have shown interesting and useful properties, the preparation methods rely on uncontrolled radical reactions or random crosslinking of polysiloxane, resulting in poorly defined materials. There is a need for materials with better defined molecular properties. More recent endeavors have been aimed at achieving these goals, and recent studies have utilized the self-assembly of block copolymers to produce LC elastomers [11, 12, 13, 14]. These materials show promising new properties that emphasize the need for a well-defined network structure. Here, we report the preparation of a covalent LC network by controlled "click" crosslinking of telechelic LC polymers. Specifically, we used copper(I)-catalyzed azide-alkyne cycloaddition of azide-terminated LC polymers and triacetylene crosslinker. This reaction has gained increasing attention in polymer and material research [15, 16, 17, 18, 19], due to its extraordinary specificity, quantitative yield, and wide functional group tolerance. Recently, it has been utilized to produce well-defined hydrogels [20] and model networks [21] through controlled crosslinking of telechelic polymers. The LC polymers are prepared via ring-opening metathesis polymerization (ROMP), which, in the presence of a chain transfer agent (CTA), allows for the preparation of polyalkenamers with high functionalities [22, 23, 24, 25] and simultaneous facile control of the end group functionality [26, 27, 28].

We produce a covalent LC network with a regular network architecture, including a controlled molecular weight between crosslinks and crosslink functionality. The resulting LC elastomer can be swollen in small molecule LC to produce LC gels. We first present the preparation and characterization of the LC network, and then we present results on the temperature-dependent swelling and electro-optic response of the gel.

6.2 Experimental

All reagents were purchased from Aldrich unless otherwise stated. Refer to Chapter 2 for details on differential scanning calorimetry, polarized optical microscopy, and electro-optical measurements. NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. All NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. For end group analysis, a Varian Mercury 500 MHz ^{1}H NMR was used.

Gel permeation chromatography (GPC) was carried out in tetrahydrofuran (THF) on two PLgel 5 m mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser

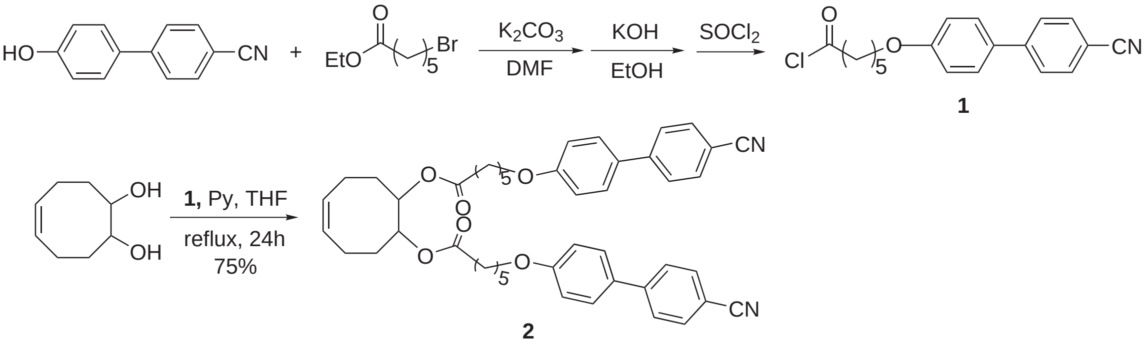

Figure 6.1: Synthesis of substituted octene monomer

light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection by assuming 100% mass elution from the columns.

Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet Nexus 470 spectrometer with a DTGS detector, a KBr beam splitter, and a 1 mW He-Ne laser (633 nm). The chamber was purged using dry N_2 gas and a background was taken using a blank card (3M type 2 IR cards, poly(tetrafluoroethylene) substrate). The samples were prepared by dissolving the material in a volatile solvent, placing a few drops of the solution on the card, and allowing the solvent to evaporate.

6.2.1 Synthesis of 5,6-disubstituted cyclooctene-based mesogen 2

The ester ethyl 6-bromohexanoate (99% pure) (19.8 mL, 111 mmol) was attached to the mesogen 4-cyano-4′-hydroxybiphenyl (95% pure from TCI) (15.4g, 78.9 mmol) by a Williamson's ether synthesis (Fig. 6.1 in anhydrous N,N-dimethylformamide ($>$ 99.8% pure under nitrogen in Sure/Seal bottles) (100 mL) with anhydrous K_2CO_3 ($>$ 99% pure) (10.8 g, 78.1 mmol) at 90 ^{o}C for 6 h and monitored by TLC. The product was recrystallized in ethanol (95% pure denatured from EMD) for an 89% yield.

The ethyl ester was deprotected by reacting with anhydrous KOH (6 g, 150 mmol) in anhydrous ethanol (95% denatured ethanol from EMD, dried over CaH) (200 mL) at 90 ^{o}C for 6 h. 1 M

HCl (from JT Baker) (50 mL) was added to precipitate the acid product which was collected by filtration, washed with H_2O, and dried in vacuo at 60 ^oC for a 95% yield.

The acid chloride was produced by reacting the acid (13.3 g, 45 mmol) in $SOCl_2$ ($>$ 99% pure) (60 mL, 766 mmol) at 70 ^oC for five hours. Excess $SOCl_2$ was removed under reduced pressure to yield the acid chloride.

5-Cyclooctene-1,2-diol was synthesized according to previously published procedures [29].

To attach the mesogen to the octene diol, the acid chloride (5.3 g, 16.2 mmol) was added dropwise to a solution of octene diol (0.77 g, 5.4 mmol) in anhydrous pyridine ($>$ 99% pure)(5 mL, 63.2 mmol) and anhydrous tetrahydrofuran ($>$ 99% pure) (50 mL). The mixture was refluxed for 24 h and the product was purified by extraction with 1 N HCl (20 mL, repeat 3 times), followed by extraction with a saturated solution of aqueous $NaHCO_3$ (50 mL) and with a saturated aqueous solution of KCl (50 mL). The product was dried over $MgSO_4$ and purified by fractionation on a silica gel column with 30% ethyl acetate in hexanes (75% yield).

6.2.2 Polymerization via ROMP and end-group functionalization

In a typical experiment, 0.725 g (1.0 mmol) of monomer and a stir bar were added to a small vial. Under an argon atmosphere, 1.0 ml of degassed dichloroethane (DCE) was then added via syringe. The vial was then degassed through three freeze-pump-thaw cycles. Next, the desired amount of CTA was injected from its stock solution in degassed DCE. 84 μl of a 10.0 mg/ml catalyst **4** solution in degassed DCE was injected to initiate the polymerization. The reaction vial was stirred at 55 C under argon for 24 h. The reaction mixture was quenched with 0.1 ml of ethyl vinyl ether and then dissolved in 2 ml CH_2Cl_2 and precipitated into 200 ml stirring methanol (MeOH). The light yellow precipitate was washed with fresh MeOH and dried in vacuo overnight to yield 0.7 g polymer.

The substitution of the bromide endgroups was carried out by first dissolving 0.7 g (0.1 mmol -Br) dibromo-terminated polymer and 13 mg (0.2 mmol) NaN_3 in 15 ml DMF. The resulting solution was stirred at 25 ^oC overnight. The solution was then concentrated and precipitated into 200 ml MeOH three times and dried in vacuo overnight to yield 0.65 g white polymer.

6.2.3 Crosslinking of telechelic polymers by "click" chemistry

The desired diazido-terminated polymer and CuBr (3 eq. to alkyne) were added to a small vial. The vial was evacuated and backfilled with argon three times. Degassed DMF (3 ml/g of polymer) and pentamethyl diethylene triamine (PMDETA) were injected, and the vial was stirred for 5 min. The correct amount of crosslinker was then injected from its stock solution. The mixture was stirred at 50 ^oC, and within 5 min an insoluble material was evident. The resulting gels were repeatedly washed with DMF and then THF to remove copper catalyst, and were dried in vacuo to yield light yellow elastomers.

6.3 Results

6.3.1 Synthesis of covalent LC network

Cyclooctene based monomer **2** was used to make the telechelic LC polymers. While ROMP has been widely used to synthesize LCP from norbornene-based monomers, ROMP of cyclooctene-based monomers with large, pendant substituents has been rarely reported [30, 31], presumably due to the lower ring strain of cyclooctene compared to norbornene. However, in contrast to norbornene-based monomers, polymerization of a functionalized cyclooctene monomer results in a polymer with a flexible backbone, which is required for the present application. Additionally, control of chain end via a CTA during ROMP is readily achieved for cyclooctene.

The monomer was polymerized by the highly active ruthenium catalyst **4** $(IMesH_2)(PCy_3)RuCl_2(CHPh)$ in dichloroethane at 55 ^oC for 24 h in the presence of a CTA, as depicted in Fig. 6.2. Since the ruthenium catalyst is known to be incompatible with azide groups, 1,8-dibromo-4-octene is utilized as the CTA to give the resulting telechelic polymers primary bromide end groups which can then be converted to azide groups in quantitative yield. In general, the polymer yield for ROMP reactions is improved with increasing monomer concentration, especially for substituted cyclooctenes, but at very high polymer concentrations the increased solution viscosity can retard the chain transfer and decrease the functionality of the chain ends. We used a concentration of 1.5 M, which we found to

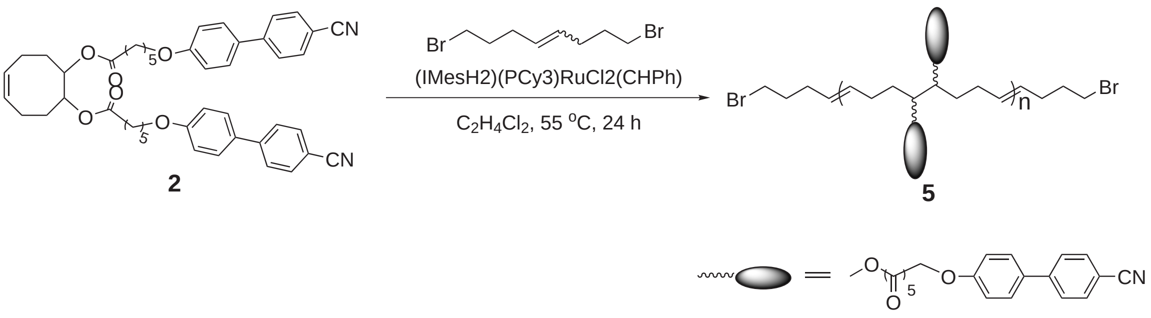

Figure 6.2: Reaction scheme for ROMP of substituted cyclo-octene

be the highest monomer concentration possible without making the solution so viscous as to impede good mixing. A monomer-to-catalyst ratio of 1000 was used. Complete monomer conversion was achieved at this catalyst loading, as indicated by the disappearance of the monomer olefin peaks in ^{1}H-NMR, while a catalyst loading ratio of 2000 resulted in incomplete conversion.

ROMP of **2** reached full monomer conversions under the optimized conditions. The molecular weight determined by GPC was 24.8 kg/mol, and this agrees well with the value determined by ^{1}H-NMR end group analysis of 26.2 kg/mol. Good agreement between the two measurements indicates that the polymer is telechelic. The polydispersity index (PDI) of the polymer was 1.84, as measured by GPC. Polymer **3** was nematic at room temperature, as confirmed by polarized optical microscopy (POM). The polymer had a nematic to isotropic transition temperature (T_{NI}) between 50 and 60 ^{o}C, as measured by differential scanning calorimetry (DSC) and polarized optical microscopy.

Controlled "click" crosslinking of these telechelic polymers was achieved by reacting a tri-acetylene species, tripropargylamine, with the polymer azide end groups in the presence of CuBr as catalyst and PMDETA as a ligand in DMF at 50 ^{o}C (Fig. 6.3). Gelation occured within 5 min of addition of a stochiometric amount of crosslinker.

To remove excess Cu, we washed the gels in DMF and THF several times before drying the LC elastomer in vacuo. IR spectrometry shows complete disappearance of the azide absorbance, indicating that most of the azide end groups had reacted in the crosslinking.

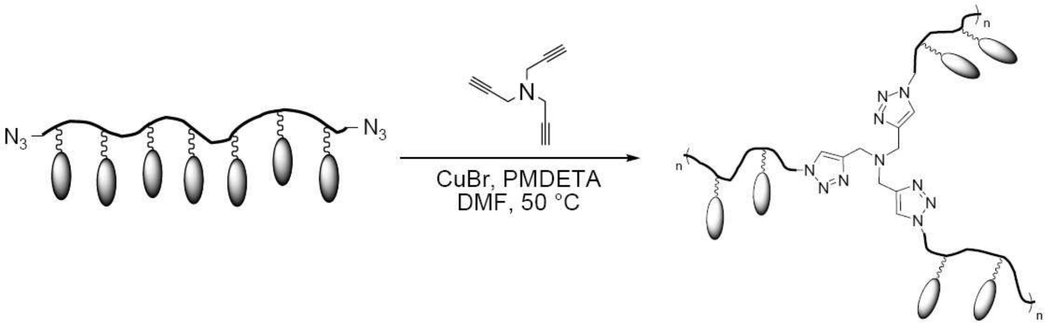

Figure 6.3: Crosslinking of telechelic LC polymers by “click” chemistry

6.3.2 Temperature-dependent swelling of covalent LC networks in liquid crystal

To create an LC gel, the dried elastomer was first swollen in THF and 4-pentyl-4′-cyanobiphenyl (5CB) for one day. The THF was then removed in vacuo, resulting in an LC covalent network swollen with 5CB. The LC gel had a degree of swelling, defined as the ratio of the mass of the gel to the mass of the dried polymer, of 17.5.

At 35.0 ^{o}C, 5CB transitions to the isotropic phase, but the gel remains nematic up to 36.0 ^{o}C. Heating the gel to temperatures above 35 ^{o}C but below 36 ^{o}C causes the gel to deswell (Figs. 6.4 and 6.5). The gel deswells due to the changing order parameter of the LC solvent, which in its pure state is isotropic above 35.0 ^{o}C. Heating the LC gel to temperatures above 36.0 ^{o}C causes the gel to phase transition to the isotropic phase, and it reswells with isotropic 5CB. This swelling and deswelling with temperature has been observed in previous LC gels, and the behavior is captured by a mean field theory that incorporates the free energy of isotropic mixing, the free energy of nematic ordering, and the elastic free energy of the network [32, 33].

6.3.3 Electro-optical properties of LC gels

LC elastomers and gels can respond to electric fields by quickly changing texture and shape. The dynamics of the response depends on the polymer content, with a lower content correlated with a faster response, and therefore LC gels are generally more responsive than elastomers to electric fields

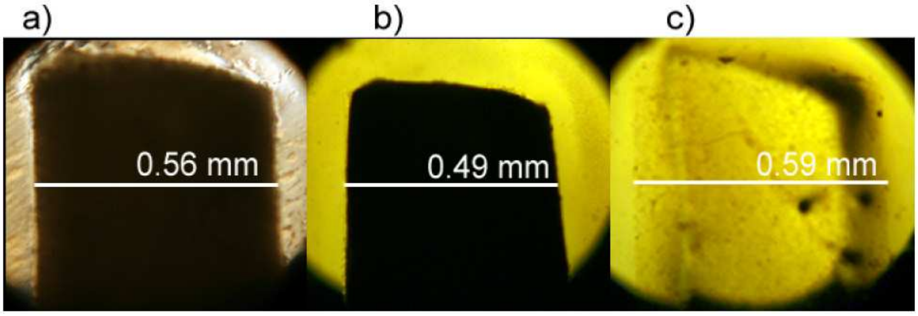

Figure 6.4: LC gels at a) 34.5 ^{o}C, b) 35.5 ^{o}C, and c) 37.0 ^{o}C. Image **a** was taken with crossed polarizers, and images **c** and **d**were taken with uncrossed polarizers. The gel scatters light and appears dark when nematic (**a** and **b**) because it is not uniformly aligned.

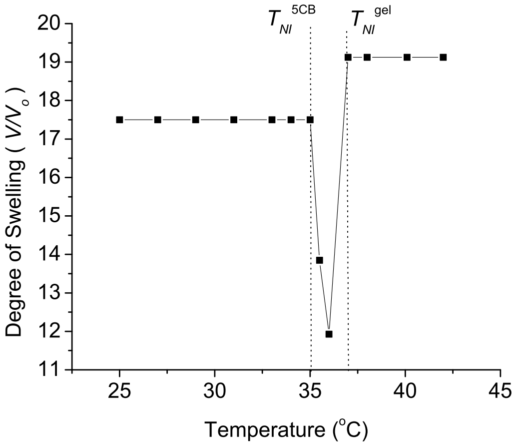

Figure 6.5: Degree of swelling V/V_o of covalent LC network, where V is the volume of the gel, and V_o is the volume of the dry elastomer

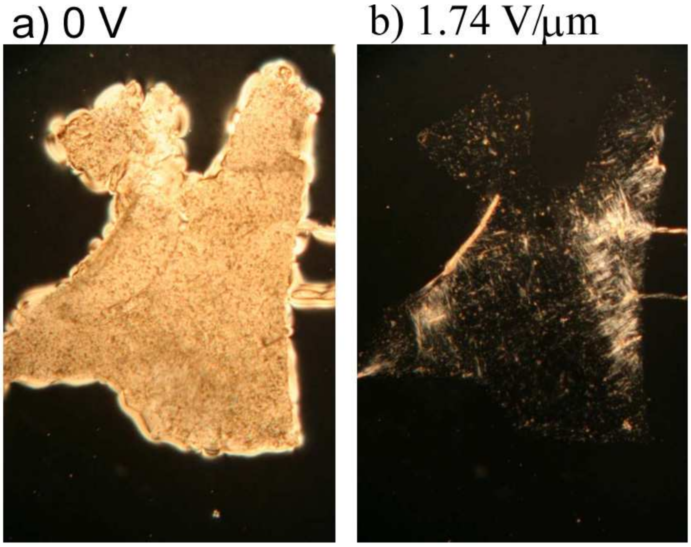

Figure 6.6: Polarized optical micrograph of unconstrained covalent LC gel under an AC field of a) 0 V/μ, and b) 1.74 V/μm. The gap between electrodes is 100 μm, and the gel is approximately 18 μm thick.

[34, 35]. Here, we investigate the electro-optic response of the covalent LC gels. We are interested in the threshold for obtaining a response, the dynamics of the response, and the texture and shape changes associated with the electro-optic response.

Previous experiments on the electro-optic behavior have observed a significant difference in the electro-optic properties for LC gels constrained between cell electrodes and unconstrained LC gels that are freely floating in a solvent between the electrodes [36, 37]. We examine the electro-optical response for both constrained and unconstrained samples. Constrained samples were prepared by pressing a LC gel sample between ITO-coated quartz plates separated by spacers. The initial thickness of the LC gel was larger than the final gap. Unconstrained samples were prepared by carefully cutting away a thin ($\sim$ 7 μm) piece of the LC elastomer and placing it in a 100 μm-thick gap between ITO coated plates filled with 5CB. The sample was allowed to swell for several days; equilibrium swelling was confirmed by measuring the T_{NI}, which matched the previously measured value of the swollen gel described in the previous section.

For the unconstrained gel, the electric-field threshold for a response is approximately 0.5 V/μm, and the gel is uniformly aligned above 1.7 V/μm (Fig. 6.6). In the case of the constrained gel, the

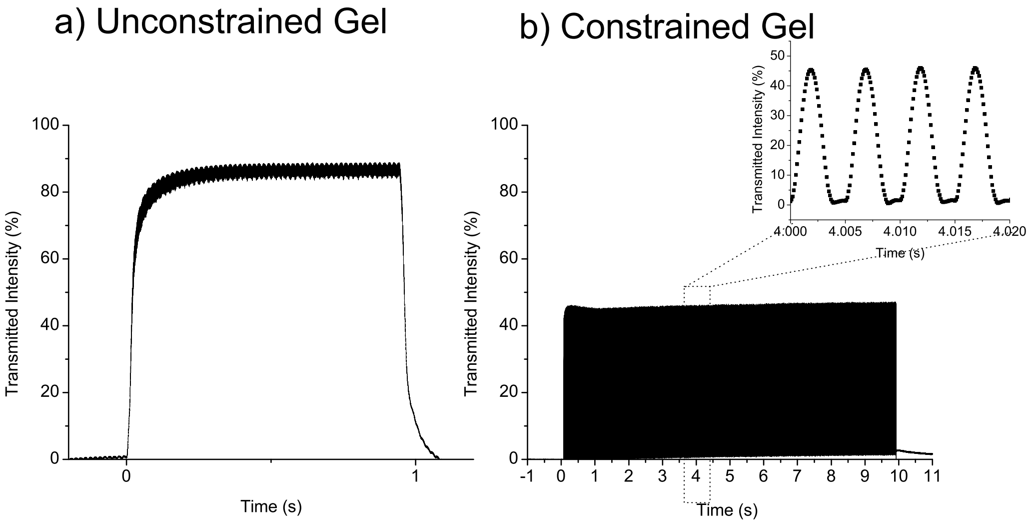

Figure 6.7: Dynamic electro-optic behavior of a) unconstrained gel under a 1.9 V/μm, 1000 Hz AC signal, and b) constrained gel under a 19 V/μm, 100 Hz AC signal. The transmittance is measured at a rate of 10,000 counts/s. A lower frequency is used for the constrained gel in order to accurately measure the time-dependent transmittance, which oscillates rapidly with the applied AC field.

threshold is approximately 10 V/μm, and uniform alignment is not achieved for fields as high as 20 V/μm. No significant shape change is observed for either constrained or unconstrained gels.

The dynamic electro-optic behavior is fast for both constrained and unconstrained gels (Fig. 6.7). In the case of the unconstrained gel, the transmittance reaches 90% of its maximum value in $\sim$ 70 ms after application of the AC field, and the transmittance drops down to 10% of its maximum within 100 ms of removing the field. These response times are much faster than bulk LC elastomer and are comparable to those found in previous studies of elastomers swollen with an LC solvent [38, 36]. Other LC gel systems, on the other hand, such as polymer-stabilized liquid crystals [39], triblock LC gels [11], LC gels formed by small-molecule gelators [40], and polymer-dispersed LCs [41] show a faster response than the present gels.

The unconstrained gel has extremely fast director oscillations that follow the AC signal (Fig. 6.7b). The director oscillates at twice the frequency of the applied field, due to the uniaxial symmetry of the nematic director. These large amplitude oscillations reflect the extremely fast director dynamics in contrained gels. Nevertheless, the large threshold for an electro-optic response precludes the use of constrained gels in electro-optic applications.

6.4 Discussion

The preparation of covalent LC elastomers and gels via “click” crosslinking is a significant achievement. They represent the first examples of LC networks with precise control of network structure, including crosslink density and functionality. The present gels capture the fast and low threshold electro-optic response and swelling/deswelling across the T_{NI} that have been reported in LC gels produced by uncontrolled radical reactions [33, 34]. Therefore, the covalent LC gels can be used to pursue careful studies of the relationship between network structure and material properties. These materials will prove useful in testing existing theories [42, 43], as discussed below, and investigating structure-property relationships of LC networks.

The synthetic method of ROMP combined with the azide-tri-acetylene “click” crosslinking provides the opportunity to vary several network parameters: The molecular weight of the network strands can be tuned by the concentration of CTA during ROMP, the degree of substitution can be halved by starting with a monosubstituted cyclooctene monomer, and the crosslinker functionality can be changed. Modifying the spacer length or the mesogenic side-group can result in a stronger coupling between the backbone conformation and LC order, resulting in gels and elastomers that display large spontaneous shape changes [10] and significant shape changes in response to electric fields [44, 45].

Several questions pertaining to the equilibrium and dynamical properties of LC networks remain unanswered [43, 46, 47]. For example, theoretical work by Oyerokun et al., which accounts for excluded volume interactions in nematic rubbers, predicts that increasing the crosslink density will decrease the spontaneous distortion of LC elastomers when heating through the T_{NI} [43]. The theory furthermore predicts a strain-induced softening of the modulus, especially near the T_{NI}. The system presented here provides a systematic way to vary the crosslink density to test this prediction, which has not been experimentally investigated. Another area of debate pertains to the dynamic mechanical properties of LC elastomers [42, 46, 47], which are predicted to have distinct, widely separated relaxation modes of the network and the nematic director. This has not been observed in previous experimental investigations [47, 48, 46, 49], but it is possible that the disparity between theory and experiment arises from the non-uniform structure of prior materials. The present system with a controlled network structure and proper choice of LC side group is a promising candidate to elucidate the dynamic behavior of LC elastomers.

One of the unresolved challenges of these materials is achieving a uniformity of alignment and control of the specimen size, and this represents the next major hurdle to utilizing the covalent LC networks for careful physical studies. The popular "two-step" crosslinking method [3] for obtaining aligned elastomers is not applicable to the present LC networks. However, a promising idea to accomplish uniform alignment is to perform the crosslinking step in an LC solvent, which can be uniformly aligned with coated cell substrates.

6.5 Conclusions

Covalent LC networks were prepared by "click" chemistry, specifically by the copper(I)-catalyzed cycloaddition of an azides and alkynes. Azide-terminated LC polymers were produced by ROMP and crosslinked with a tri-acetyline species to produce covalent LC networks. The resulting networks provide model systems that capture the fascinating properties of LC gels, specifically swelling/deswelling across the T_{NI} and fast and low-threshold electro-optic behavior. The covalent networks open the door for structure-property studies of LC elastomers and gels. Future work includes developing a method for producing aligned LC elastomers and gels of a controlled size and shape.

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