C h a p t e r 6

Well-Defined Liquid Crystal Gels from Telechelic Polymers via Ring-Opening Metathesis Polymerization and "Click" Chemistry

Portions of this chapter have been published: Xia, Y.; Verduzco, R.; Grubbs, R. H.; Kornfield, J. A. *J. Am. Chem. Soc.* **2008**, 130, 1735-1740.

Abstract

Well-defined liquid crystal networks with controlled molecular weight between crosslinks and crosslink functionality were prepared by “click” crosslinking of telechelic polymers produced by ring-opening metathesis polymerization (ROMP). The networks readily swell in a small molecule liquid crystal, 5CB, to form LC gels with high swelling ratios. These gels exhibit fast, reversible, and low-threshold optic switching under applied electric fields when they are unconstrained between electrodes. For a given electric field, the LC gels prepared from shorter telechelic polymers showed a reduced degree of switching than their counterparts made from longer polymer strands. The reported approach provides control over important parameters for LC networks, such as the length of the network strands between crosslinks, crosslinker functionality, and mesogen density. Therefore, it allows detailed study of relationships between molecular structure and macroscopic properties of these scientifically and technologically interesting networks.

Introduction

Liquid crystal (LC) elastomers and gels are composed of flexible, liquid crystal polymers crosslinked to form a network. The combination of LC order and rubber elasticity results in an anisotropic polymer network that is responsive to a variety of external influences, including heat, light, electric and magnetic fields. These materials display remarkable changes in shape and optical properties that make them of interest for technological applications.[1-3]

In the context of the theory of LC networks[4-7], key parameters are the rubbery modulus of the network and the strength of orientational coupling between pendant mesogens and the flexible polymer backbone. These are controlled by molecular attributes: the flexibility of the polymer backbone, backbone length between crosslinks, and the choice of mesogen and spacer. Experimental studies of LC elastomers[8-12] and, more recently, gels formed by swelling elastomers with small molecule LC[13-16] show that these molecular parameters strongly influence macroscopic properties. For example, it has been observed qualitatively that decreasing the crosslinker and/or monomer concentrations resulted in lower threshold fields and enhanced electro-optic and electro-mechanical responses of LC gels.[13-15]

Therefore, it is necessary to exert synthetic control of both overall crosslink density and its variability within the network. Widely studied LC elastomers and gels have been prepared either from functionalization and crosslinking of poly(methyl)hydrosiloxane,[10-12,17-19] or from uncontrolled radical polymerization in the presence of crosslinker.[9,13-15,20-23] The preparation methods in these studies all relied on random crosslinking of polysiloxane or on uncontrolled radical reactions, resulting in

poorly defined network structures that make the correlation between network structure and material property difficult. More recent studies have utilized the self-assembly of block copolymers to produce LC elastomers,[24-27] These materials show interesting new properties that arise both from the physical nature of the crosslinks and from the well-defined self-assembled structure; however, they lack the long-term stability that is achieved by covalent crosslinking. Here, we investigate the use of telechelic polymers to create covalent LC elastomers and gels. End-linking of telechelic polymers with polyfunctional crosslinkers is known to give well-defined polymer networks,[28-30] and to our knowledge this strategy has not been extended to the synthesis of LC networks.

We report the preparation of well-defined LC networks by controlled "click" crosslinking of telechelic LC polymers produced by ring-opening metathesis polymerization (ROMP). Copper(I)-catalyzed azide-alkyne "click" cycloaddition[31] has gained increasing attention in polymer and material research due to its extraordinary specificity, quantitative yield, and wide functional group tolerance.[32-34] Crosslinking of telechelic polymers by "click" chemistry has recently been utilized to produce well-defined hydrogels[35] and other networks.[36,37] Furthermore, recent developments in ROMP allow for the preparation of polyalkenamers with a variety of functional groups[38-40] and simultaneous facile control of the end groups can be achieved using a chain transfer agent (CTA).[41-43]

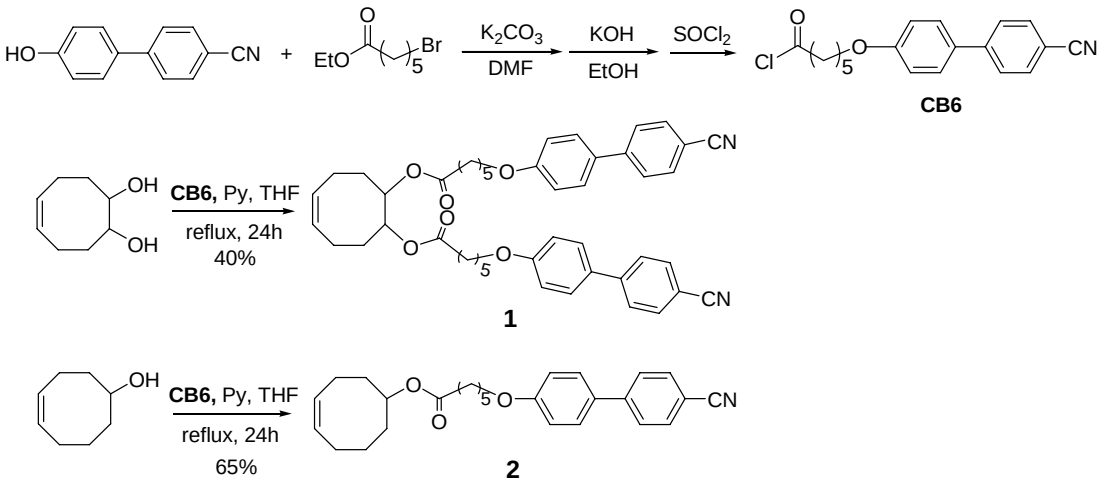
We combine ROMP and "click"-crosslinking to produce LC networks with a regular network architecture, including a controlled molecular weight between crosslinks and crosslink functionality. The resulting LC networks can be swollen in small molecule

LC to produce LC gels, which show fast, reversible, and low-threshold electro-optic switching.

Results and Discussion

Polycyclooctene was chosen for the side-group liquid crystalline polymer (SGLCP) backbone, anticipating that it would give a low T_g and fast segmental dynamics. In LC gels, the director reorientation is coupled to the segmental dynamics of the solvated polymers, so fast electro-optic response is favored by high mobility of the SGLCP. Additionally, control of chain end functionality for cyclooctene is readily achieved via a CTA. However, ROMP of functionalized cyclooctenes with large, pendant substituents have been rarely reported,[44,45] presumably due to the lower ring strain of cyclooctene compared to norbornene.

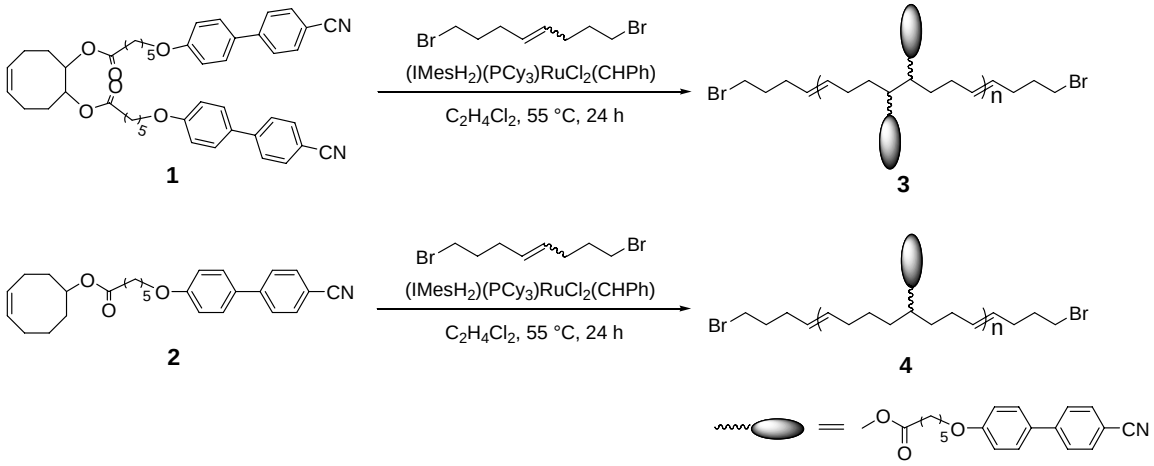
Synthesis of Telechelic LC Polymers. Cyclooctene monomers were functionalized with either one or two mesogenic groups as outlined in Scheme 1: cyano-biphenyl mesogens were coupled via a six-carbon spacer to either dihydroxy-cyclooctene to yield monomer **1** or hydroxy-cyclooctene to give monomer **2**. This monomer pair allows us to vary the mesogen density on the final polymer backbone. Both monomers were crystalline solids exhibiting a single phase transition to the isotropic state.



Scheme 1. Synthesis of monomers **1** and **2**.

To prepare telechelic SGLCPs, the monomers were polymerized by the highly active ruthenium catalyst, $(IMesH_2)(PCy_3)RuCl_2(CHPh)$, in dichloroethane at 55 °C for 24 h in the presence of a CTA (Scheme 2). Since the ruthenium catalyst is known to be incompatible with azide groups, 1,8-dibromo-4-octene was utilized as the CTA to give telechelic polymers with primary bromide end groups which can subsequently be converted to azide groups quantitatively. Monomer concentrations were chosen to be the maximum concentration possible while maintaining a low enough viscosity to permit efficient chain transfer: 1M for **1** and 1.5M for **2**. A monomer-to-catalyst ratio, [M]/[C], of 1000 was used for all polymerizations. Complete monomer conversion was achieved at this catalyst loading, as indicated by the complete shift of the monomer olefin resonance at 5.65 ppm to the polymer olefin resonance at 5.3 ppm in the ^{1}H-NMR spectrum. The polymer molecular weights were regulated by the ratio of monomer to CTA, [M]/[CTA] (Table 1). Good agreement between the absolute molecular weight obtained from GPC equipped with light scattering detector and the molecular weight determined by ^{1}H-NMR end group analysis indicates that the polymers are telechelic.

The bromide end groups of telechelic polymers **3** and **4** were transformed into azide groups by nucleophilic substitution with sodium azide in DMF. This substitution was carried out to quantitative yields as indicated by the complete shift of the terminal methylene signals from 3.4 to 3.2 ppm in the ^{1}H-NMR spectrum and the appearance of characteristic alkyl azide absorbance at 2099 cm^{-1} in the IR spectrum.



Scheme 2. ROMP of functionalized cyclooctene monomers.

Table 1. Synthesis and characterization of functionalized polycyclooctenes[a]

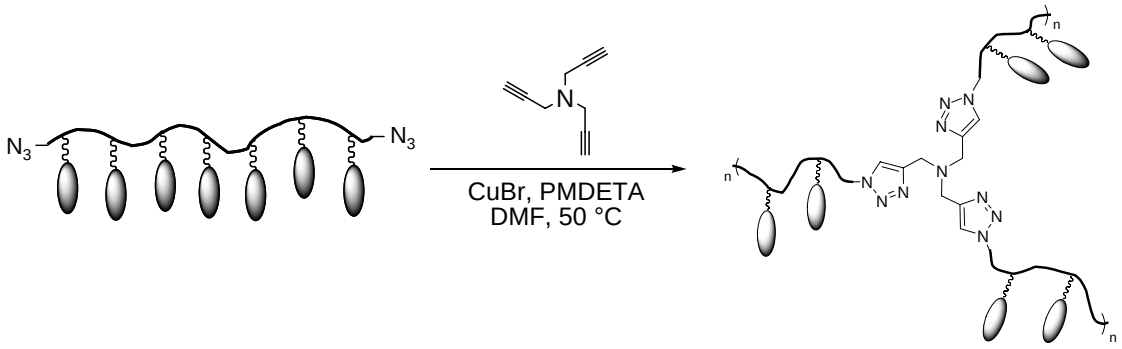
Polymer	$[M]_0/[CTA]_0$	% yield[b]	$M_{n,GPC}$[c]	$M_{n,NMR}$[d]	PDI	T_g / °C[e]	T_{NI} / °C[e]
3a	10	97	11 300	11 100	1.79	23.8	51.4
3b	20	99	24 800	26 200	1.84	27.1	58.5
4	20	95	13 700	16 600	1.43	8.5	N/A

[a]Polymerization conditions: $[M]_0$=1M for **1** and 1.5M for **2** in $C_2H_4Cl_2$; $[M]_0/[cat]$=1000; 55 °C, 24 h. [b]Isolated polymer yield. [c]Determined by THF GPC coupled with 18-way light scattering detector. [d]Determined by end group analysis from ^{1}H-NMR in $CDCl_3$ assuming F_n=2. [e]Measured by DSC, heating rate=10 °C/min.

Polymers **3a** and **3b** (Table 1) made from the disubstituted monomer **1** were nematic at room temperature, as confirmed by polarized optical microscopy (POM) and X-ray scattering. The polymer had a nematic to isotropic transition temperature (T_{NI}) between 50 and 60 °C, as measured by differential scanning calorimetry (DSC) and POM. On the other hand, polymer **4** prepared from the monosubstituted monomer **2** was not

liquid crystalline and did not show any phase transitions in the range of 20-100 °C under DSC or POM. Both polymers were soluble in a small molecule liquid crystal, 5CB, up to the highest concentration tested of 10 wt %.

Synthesis of LC Networks. Controlled "click" crosslinking of these telechelic polymers was achieved by reacting a triacetylene species, tripropargylamine, with the polymer azide end groups in the presence of CuBr as catalyst and PMDETA as a ligand in DMF at 50 °C (Scheme 3). The solution was allowed to react for 2 more days after gelation had occurred to ensure complete reaction. The resulting gels were extracted in DMF and THF repeatedly to remove copper catalyst and uncrosslinked fraction, and elastomers were obtained after drying under vacuum.



Scheme 3. Cross-linking of telechelic polymers by "click" chemistry.

Polymer **3a** was used to study the effect of crosslinking conditions on the gel fraction. Polymer concentration had minimal effect on the gel fraction (Table 2, entry 1-3). When high polymer concentrations (50 wt % and 33 wt %) were used, a gel was instantly formed as tripropargylamine was added, precluding preparation of thin films for electro-optic study. Therefore, 25 wt % polymer concentration was chosen to evaluate the effect of the ratio of acetylene (from crosslinker) and azide (from polymer end groups) groups (Table 2, entry 3-6). It was found that ratios deviating in either direction (more or

less acetylene groups) from a 1:1 ratio resulted in decreased gel fractions. The effect of acetylene:azide ratio is asymmetric: using less crosslinker than needed decreased gel fraction more strongly than using excess crosslinker. The effect of acetylene:azide ratio on gel fraction is consistent with the observed time for gelation to occur: only in the case of a 1:1 ratio did gelation occur instantaneously. In all other cases, an insoluble gel formed only after stirring for several hours up to 2 days.

Table 2. Effect of polymer precursor concentrations and stoichiometry of acetylene and azide groups on the gel fraction.

Polymer precursor	Polymer precursor concentration (wt %)	Acetylene:azide[a]	Gel fraction[b]
3a	50	1:1	92%
3a	33	1:1	91%
3a	25	1:1	89%
3a	25	0.75:1	71%
3a	25	1.25:1	85%
3a	25	1.5:1	78%
3b	25	1:1	93%
4	25	1:1	92%

[a]Molar ratio of acetylene functional groups (3 per crosslinker) to azide end group (2 per polymer chain); [b]gel fraction = (mass of polymer precursor-mass of extractable polymer) / mass of polymer precursor.

A polymer concentration of 25 wt% and a stoichiometric amount of crosslinker that allows the azide/acetylene ratio to be 1:1 were used to crosslink all the telechelic polymers for further characterization. Gelation typically occurred within 5 min and the gels were cured at 50 °C for 2 days to give high gel fractions. IR spectrometry of the

resulting crosslinked polymers showed complete disappearance of the azide absorbance, indicating that most of the azide end groups have reacted in the crosslinking. Films for electro-optic studies were made by crosslinking in glass cells with predetermined gaps.

All the elastomers readily swelled in 5CB to form LC gels with high swelling ratios, including the one derived from the non-LC polymer **4**. The swelling ratios exhibited the expected dependence on the molecular weight of the strands: larger network strands resulted in LC gels with higher swelling ratios (Table 3).

Table 3. T_{NI} and swelling ratio of liquid crystalline gels prepared from telechelic polymers

	Precursor polymer and its M_n	T_{NI} (gel)[a]	swelling ratio in 5CB[b]
LCG 1	Polymer **3a**, 11 k	37.5	10 ± 1
LCG 2	Polymer **3b**, 25 k	37.3	19 ± 2
LCG 3	Polymer **4**, 14 k	35.0	15 ± 1

[a]Measured by POM, heating rate=1 °C/min; [b]the ratio of absorbed 5CB and dried polymer network, W_{5CB}/W_p.

Electro-optic properties of LC gels. We are interested in understanding how the network structure affects the electro-optic switching of the LC gels between a scattering polydomain state and a transmissive monodomain state. We focused on the disubstituted gels LCG1 and LCG2 with the same polymer structure but different network strand lengths. The length of the network strands, the swelling ratio, and the degree of side-group substitution may all play a role in the electro-optic characteristics.

Previous studies of the electromechanical properties of LC gels have observed a significant difference for “constrained” LC gels that are physically pressed between electrodes and “unconstrained” LC gels that are freely floating in an LC solvent that fills

the gap between electrodes.[15,22,23,46] It was found that a mechanical constraint suppressed the electric field response of nematic gels. We investigated the electro-optic behavior of both constrained and unconstrained gels.

Constrained samples were prepared by pressing a LC gel sample between ITO-coated glass plates separated by spacers. The initial thickness of the LC gel was approximately twice the final gap. The threshold for the constrained gel was high, approximately 10 V/μm, and only partial alignment was achieved for fields as high as 19 V/μm (Figure 1). Notably, the constrained gel exhibited fast director oscillations that follow the AC signal. The director oscillates at twice the frequency of the applied field due to the uniaxial symmetry of the nematic director. The response time of the constrained gel was within 1 ms.

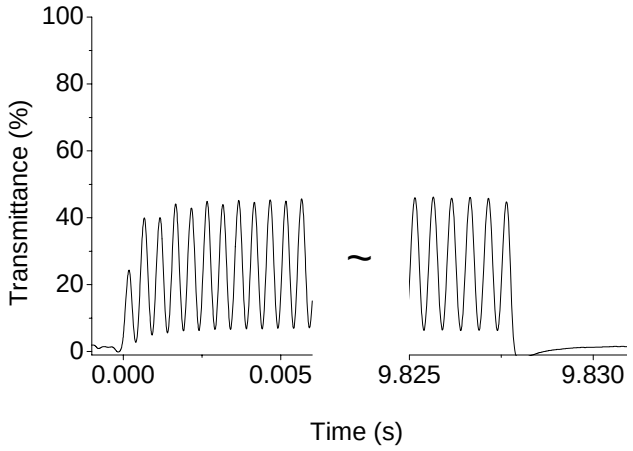


Figure 1. Dynamic electro-optic response of a constrained LC gel (LCG2, Table 3) under 19 V/μm, 1000 Hz AC signal. The signal is applied at 0 s and removed at 9.826 s approximately. Note that the transmitted intensity (recorded at 6000 Hz) quickly reaches its long-time value, and the oscillation of the optical intensity is 2000 Hz (2 cycles per 0.001 seconds). The data was smoothed using a spline interpolation.

Unconstrained samples were prepared by placing a thin (~40 μm) LC gel sample (LCG2, Table 3, same as for the constrained case described above) in a 100 μm thick gap between indium-tin-oxide (ITO) and lecithin coated glass plates filled with 5CB. The

lecithin layer aligns surrounding small molecule LC homeotropically at each substrate, so that it does not scatter light in orthoscopic imaging, ensuring that the observed change in transmission is due primarily to the response of the LC gel. In contrast to the constrained gel, the unconstrained LCG2 responds to the electric field at much lower fields (Figure 2). The transmission increases at fields as low as 0.1 V/μm; however, further experiments are required to exclude the possibility that this response may be due to the reorientation of the LC solvent at the gel interface. Nevertheless, a significant increase was observed below 1.0 V/μm, demonstrating the low threshold switching in these materials that has been confirmed for some LC gels.[13,22] Also, the transmitted intensities while ramping voltage up were almost superimposable with those recorded while ramping voltage down (Figure 3), demonstrating the excellent reversibility of the electro-optic response.

The dynamics of the electro-optic response for unconstrained LCG2 are fast and, in constrast to physically self-assmbled gels we have previously reported,[24] insensitive to the applied field. The transmittance reaches 90% of its maximum value after application of the AC field and drops down to 10% of its maximum after removal of the field in <50 ms (Figure 2). Interestingly, an oscillation in the transmitted intensity was also observed for unconstrained gels. The width of these oscillations strongly depends on the AC field frequency and amplitude. At the same electric field amplitude, the oscillation band is about 5 times wider at 100 Hz than at 1000 Hz. This reflects that the director oscillates fast enough to follow the AC field at 100 Hz, which roughly corresponds to a response time of 10 ms.

The electro-optic switching behavior of the LC gel was also captured by POM. An initially polydomain LCG2 gel shows strong birefringence in the absence of an

electric field (Figure 4A), but almost uniform alignment of the gel is obtained under an AC field of 2.0 V/μm (Figure 4B).

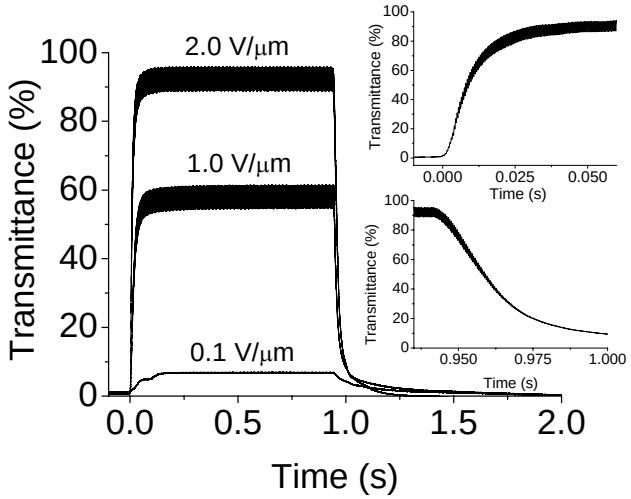


Figure 2. Transient electro-optic response of an unconstrained LC gel (LCG2) under various AC electric fields at 1000 Hz. The insets show the electro-optic response around the time the signal is applied (top inset) and removed (bottom inset).

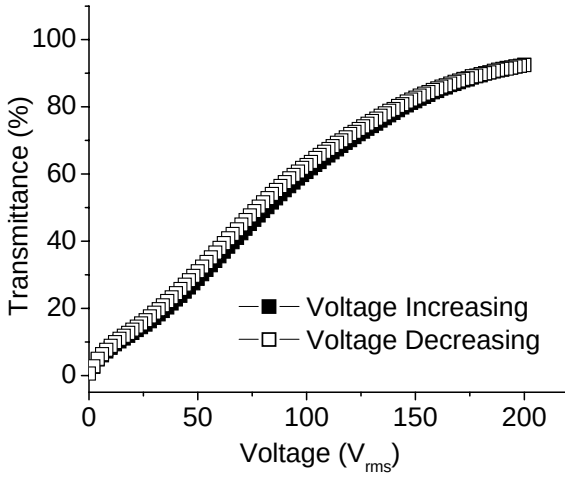


Figure 3. Transmittance as a function of voltage applied for an unconstrained LC gel (LCG2) in a 100 μm thick gap. The applied AC voltage (rms) sweeps from 0 to 200 V at 0.5 V interval and 1000 Hz. The measured intensity is the average of the oscillation; the software measures the intensity several times for each data point and averages them together. The transmittance when increasing the voltage (closed square) is almost superimposable with that when decreasing the voltage (open square).

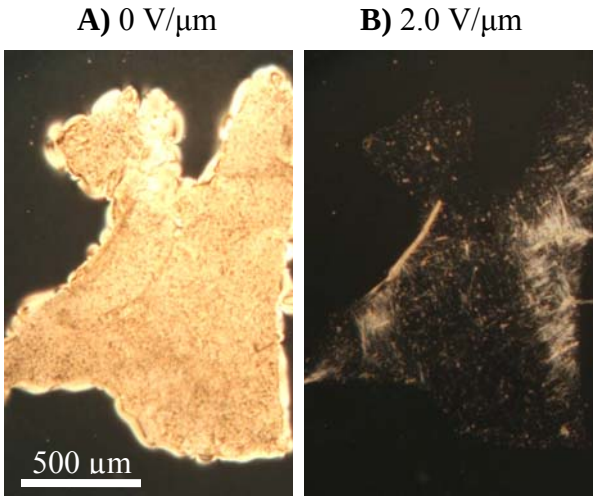


Figure 4. Polarized optical micrograph of unconstrained LC gel (LCG2) between ITO and lecithin coated glass plate under A) no AC field and B) an AC field of 2.0 V/μm.

The effects of molecular variables on electro-optic response are evident in comparisons between LCG2 (above), LCG1 (higher crosslink density, Figure 5), and LCG3 (greater space between mesogens, Figure 6), The main effects of increasing crosslink density are to reduce the transmittance at a given electric field but to speed switching: LCG1 reaches only ~50% transmittance at 2.0 V/μm (compared to ~90% for LCG2) but switches "on" and "off" in ~20 ms (compared to ~50 ms for LCG2). A gel having similar crosslink density to LCG2, but with only half the number of mesogens per repeat unit (LCG3), exhibits similar behavior to LCG2 with 75% transmittance at 2.0 V/μm, a fully reversible electro-optic response, low threshold switching, and fast dynamics.

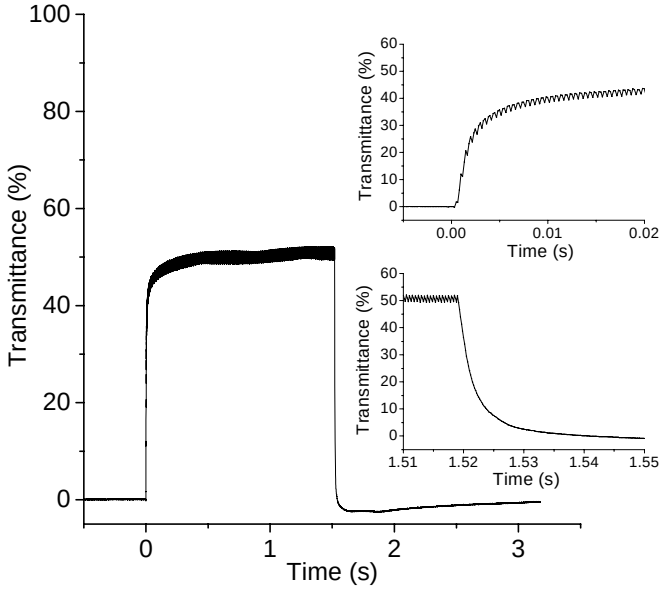


Figure 5. Transient electro-optic response of an unconstrained LC gel (LCG1) under an AC electric field of 2.0 V/μm at 1000 Hz. The insets show the electro-optic response near the time the signal is applied (top inset) and removed (bottom inset).

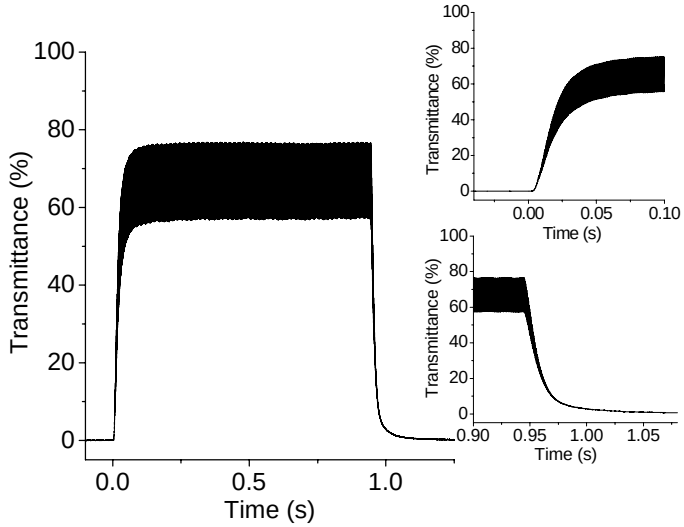


Figure 6. Transient electro-optic response of an unconstrained LC gel (monosubstituted LCG3) under an AC electric field of 2.0 V/μm at 1000 Hz. The insets show the electro-optic response near the time the signal is applied (top inset) and removed (bottom inset).

These electro-optic studies demonstrate important features of the electro-optic response of LC gels made by crosslinking telechelic polymers and of LC gels in general. First, mechanical constraints significantly affect the electro-optic response, even for low

concentration gels (5 wt% polymer). It is well known that mechanical deformation is strongly coupled to director orientation in LC elastomers,[1,47-49] and we found that this holds true for dilute gels as well. This can clearly be seen by comparing the response of constrained and unconstrained LCG2. Mechanically constrained gels have a greater threshold for a response and do not reach uniform alignment even for fields as high as 19 V/μm. Samples that were only slightly constrained had a significantly reduced electro-optic response, and much care had to be taken to prepare unconstrained samples. Mechanical constraints frustrate sample alignment, preventing the comparatively easy reorientation of the director observed for unconstrained gels. This hypothesis is supported by previous studies of monodomain LC gels that change shape in response to electric fields.[15,23]

Our gels with a controlled network strand length reveal how the network structure affects the electro-optic switching behavior. Unconstrained LCG2, which has longer network strands and a greater degree of swelling, has a stronger response to external fields. We expect that the electro-optic behavior depends on both the crosslink density and the degree of swelling, which are not independently varied in these experiments. The observed trends accord with previous studies of LC gels prepared by uncontrolled radical polymerization, which found that decreasing the crosslinker and/or monomer concentrations (expected to give the network longer strands overall), results in lower threshold fields and enhanced electro-optic and electro-mechanical responses of LC gels.[13-15]

The very low threshold observed here for LC gels prepared by end-linking telechelic polymers might be a result of a relatively uniform network structure. Regions

of high crosslink density are difficult to avoid in systems prepared by uncontrolled radical polymerizations. Trifunctional crosslinking of already formed polymers gives very few closely spaced crosslinks (random selection of three chains from the overall distribution gives a narrower distribution of the molar mass linked to a crosslink than that of the telechelic chains themselves). Therefore, the present strategy for making LC gels might find use in devices that require a low-threshold optical or mechanical response.

Finally, it is worth noting that the handling of the gels is rather delicate: the cell in which crosslinking is performed must be opened so that the copper catalyst may be fully extracted prior to introducing the small molecule LC. Ongoing attention is being given to making these procedures more robust. Significant sample-to-sample variability of the electro-optic response (maximum transmitted intensities varied from 95% to 75% for LCG2 and from 50% to 20% for LCG1) was observed, which is very likely due to variations in gel thickness (hence optical path length) and irregularities introduced when the gel is removed from the mold (partial adhesion to both glass plates) and when it is loaded in the electro-optic cell (as noted, the boundary conditions have strong effects and partial contact of the gel with the substrate may be responsible for some of the variability observed).

The demonstrated approach allows for the control of LC network structure, including the length of the network strands between crosslinks and crosslinker functionality. We believe that LC networks from telechelic prepolymers, like the ones described here, will enable quantitative tests of molecular theories of nematic elastomers and gels, an active area of current research. The first molecular description of LC nematic elasticity,[1] developed by Terentjev and Warner, described a variety of novel

effects, most notably “soft elasticity”, arising from the coupling of rubber elasticity and nematic order. This theory assumes an ideal, Gaussian network. More recent theoretical work has investigated the implications of this molecular theory to the dynamics[5] of LC networks and also extended the original theory to describe more realistic networks (i.e., with excluded volume interactions[50]). However, to experimentally validate predicted relationships between molecular structure and macroscopic properties, network details such as crosslink density and length between crosslinks must be known and systematically varied. Indeed, there is still controversy concerning the validity of the previous molecular theories proposed, and many scientists in the field[51,52] remain unconvinced that the molecular theories of Terentjev, Warner, and others are applicable to real LC networks. Synthetic routes to well-defined networks provide the molecular tools required to study these fundamental questions.

Conclusions

Azide-terminated telechelic side-group LC polymers were produced by ROMP and crosslinked with a triacetylene species to prepare covalent LC networks in high yields. These well-defined networks were highly swollen in 5CB, resulting in nematic gels with low polymer content. In accord with Urayama’s findings,[15,23] these LC gels are sensitive to mechanical constraint, which suppressed the electro-optic response of the gels. Unconstrained LC gels exhibited fast and completely reversible switching at low electric fields. For a given electric field, the LC gels prepared from longer telechelic polymers (hence, lower polymer concentration at equilibrium swelling) showed a higher degree of switching than their counterparts made from shorter polymer strands. Thus, the present approach for preparing LC elastomers and gel materials with well-defined

structures will be valuable in establishing the relationship between the LC network structure and material properties, which may guide rational design of LC materials in the future. We are currently investigating methods for making monodomain LC gels through crosslinking in the nematic state[15,23] and producing telechelic LC polymers with a higher degree of anisotropy.[25]

Experimental Section

General procedures. NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. All NMR spectra were recorded in $CDCl_3$ or DMSO-d_6, and referenced to residual proteo species. For end group analysis, a Varian Mercury 500 MHz ^{1}H NMR was used. FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/d*c* values were obtained for each injection by assuming 100% mass elution from the columns.

Materials. Dichloroethane (DCE) was dried over CaH_2 and distilled prior to use. *trans*-5,6-dihydroxy-cyclooctene[53] and 5-hydroxy-cyclooctene[38] were synthesized according to literature procedures. All other materials were used as received.

Synthesis of functionalized cyclooctene-based monomers. Ethyl 6-bromohexanoate (19.8 mL, 111 mmol) was attached to 4-cyano-4′-hydroxybiphenyl (15.4g, 78.9 mmol) in anhydrous DMF (100 mL) with anhydrous K_2CO_3 (10.8 g, 78.1 mmol) at 90 °C for 6 h. The product was recrystallized in ethanol (89% yield), and was then deprotected by reacting with KOH (6 g, 150 mmol) in anhydrous ethanol (200 mL) at 90 °C for 6 h. 1 M

HCl (50 mL) was added to precipitate the acid product which was collected by filtration, washed with water and cold acetone, and dried in vacuo at 60 °C (95% yield).

The acid (5.2 g, 16.2 mmol) was reacted in $SOCl_2$ (60 mL, 766 mmol) at 70 °C for five hours to convert into the acid chloride. Excess $SOCl_2$ was removed under reduced pressure. The acid chloride was then dissolved in 20 mL anhydrous THF and was added dropwise to a solution of *trans*-5,6-dihydroxy-cyclooctene (0.77 g, 5.4 mmol) in anhydrous pyridine (5 mL, 63.2 mmol) and anhydrous THF (50 mL). The mixture was refluxed for 24 h and the product was purified by extraction with 1 N HCl (20 mL, 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 MgSO4 and purified on a silica gel column (ethyl acetate/hexanes, 3:7 v/v) to give 1.6 g disubstituted cyclooctene **1** as a white crystal (40% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.60 (m, 8H), 7.52-7.49 (m, 4H), 6.97-6.94 (m, 4H), 5.64 (t, J = 4.2 Hz, 2H), 5.18 (t, J = 3.3 Hz, 2H), 3.98 (t, J = 6.3 Hz, 4H), 2.52-2.00 (m, 12H), 1.85-1.45 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 159.6, 145.2, 132.6, 131.4, 128.7, 128.3, 127.0, 119.5, 115.0, 109.5, 73.7, 67.7, 34.3, 29.9, 28.9, 25.7, 24.7, 23.0. HRMS (FAB) *m/z* calc. for $C_{46}H_{48}O_6N_2$: 724.3522, found 724.3512.

Monosubstituted cyclooctene **2** was synthesized in analogy to **1** by coupling the acid chloride with 5-hydroxy-cyclooctene (65% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.62 (m, 4H), 7.55-7.50 (m, 2H), 7.00-6.95 (m, 2H), 5.73-5.57 (m, 2H), 4.88-4.80 (m, 1H), 4.00 (t, J = 8.1 Hz, 2H), 2.38-2.07 (m, 6H), 1.92-1.50 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 159.7, 145.3, 132.6, 131.3, 129.8, 129.6, 128.3, 127.1, 119.1,

115.0, 110.0, 75.5, 67.8, 34.6, 33.8, 33.7, 28.9, 25.6, 25.5, 24.8, 24.7, 22.3. HRMS (FAB) *m/z* calc. for $C_{27}H_{31}O_3N$: 417.2304, found 417.2294.

Synthesis of 1,8-dibromo-4-octene. 5-Bromo-1-pentene (1.0 g, 6.7 mmol) was added to a solution of Grubbs 1st generation catalyst (30 mg, 0.036 mmol) in 5 mL degassed CH_2Cl_2, and the reaction stirred at room temperature overnight. The solvent was evaporated and the remaining residual was purified on a silica gel column (ethyl ether/hexanes, 1:20 v/v) to give 0.80 g 1,8-dibromo-4-octene (89% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45-5.37 (m, 2H), 3.43-3.38 (m, 4H), 2.24-2.12 (m, 4H), 1.96-1.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.8, 129.3, 33.3, 32.5, 32.2, 30.8, 25.7. HRMS (FAB) *m/z* calc. for $C_8H_{14}Br_2$: 269.9442, found 269.9455.

General procedure for polymerization and end group functionalization. In a typical experiment, an oven-dried small vial was charged with 0.725 g (1.0 mmol) of monomer **1** and a stir bar. Under an argon atmosphere, 1.0 mL of degassed DCE was 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 Grubbs 2nd generation catalyst 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 MeOH. The pale yellow precipitate was washed with fresh MeOH and dried in vacuo overnight to yield 0.70 g of white polymer (97% yield).

0.7 g (0.1 mmol -Br) dibromo-terminated polymer and 13 mg (0.2 mmol) NaN_3 were dissolved in 15 ml DMF. The resulting solution was stirred at 25 °C overnight and

then concentrated and precipitated into 200 ml MeOH three times and dried in vacuo overnight to yield 0.65 g light yellow polymer (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7-7.6 (m, 8H), 7.6-7.5 (m, 4H), 7.0-6.9 (m, 4H), 5.4-5.3 (br, 2H), 5.1-5.0 (br, 2H), 4.05-3.9 (br, 4H), 3.3-3.2 (m, end group -C*H*$_2$-N_3), 2.4-2.3 (m, 4H), 2.2-1.45 (br m, 20H).

Diazido-terminated polymer **4** was synthesized from monomer **2** using a similar procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.6-7.5 (m, 2H), 7.0-6.9 (m, 2H), 5.4-5.3 (br, 2H), 4.95-4.8 (br, 1H), 4.05-3.95 (br, 2H), 3.3-3.2 (m, end group -C*H*$_2$-N_3), 2.4-2.3 (m, 2H), 2.2-1.2 (br m, 16H).

General procedure for crosslinking. The desired diazido-terminated polymer and CuBr (2 eq. to alkyne) were added to a small vial with a Teflon-lined cap. The vial was evacuated and backfilled with argon three times. The desired amount of degassed, anhydrous DMF (resulting in a 25 wt% polymer solution) and pentamethyl diethylene triamine (PMDETA) (1 eq. to CuBr) were injected and the vial was stirred for 5 min. The correct amount of tripropargylamine (1/3 eq. to polymer azide end group) was then injected from its stock solution. The mixture was stirred at room temperature for 20 seconds. The vial was then placed in an oven preset to 50 °C and allowed to react for 2 days. The resulting gels were repeatedly extracted with DMF and then THF (2 h for each extraction and for 1-2 days until the solution was visually colorless) to remove copper catalyst and soluble polymer fraction. Upon drying in vacuo, the material returns to the light yellow color of the prepolymer. The elastomer films for electro-optic studies were prepared by injecting the reaction mixture into rectangular glass cells with predetermined gaps. This was required for preparing samples of a uniform thickness. A cell was sealed in a degassed vial with a Teflon-lined cap. After injecting the reaction mixture into the

rectangular cell, the vial was placed in a heating oven at 50 ^{o}C. After 2 days at 50 °C, the glass cell was soaked in DMF for several hours and opened carefully to remove the gel. The catalyst and soluble polymer fraction was extracted as described above. The gel was then dried in vacuo and the resulting film was reswelled with 5CB for 24 h to give the LC gel film.

Electro-optic measurements of the gels. The electro-optic properties of the gels were measured under oscillating applied voltage using a polarized He-Ne laser, a beam splitter, and a CCD detector as previously described.[24] Constrained samples were prepared by pressing a LC gel sample between indium-tin-oxide (ITO)-coated quartz plates separated by 10 μm spacers. Unconstrained samples were prepared by placing a thin (ca. 40 μm, measured using an outside micrometer by gently placing the gel between the anvil and the spindle) piece of the LC gel in a 100 μm thick gap between ITO and lecithin coated glass plates filled with 5CB, and the samples were allowed to stand overnight to allow full alignment of 5CB before measurements.

References

(1) Warner, M.; Terentjev, E. M. *Liquid Crystal Elastomers*; Oxford University Press: Oxford, 2003.

(2) Yu, Y.; Ikeda, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 5416-5418.

(3) Ikeda, T.; Mamiya, J.; Yu, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 506-528.

(4) Olmsted, P. D. *J. Phys II France* **1994**, *4*, 2215-2230.

(5) Stenull, O.; Lubensky, T. C. *Phys. Rev. E* **2004**, *69*, 051801.

(6) Warner, M.; Terentjev, E. M. *Prog. Polym. Sci.* **1996**, *21*, 853-891.

(7) Terentjev, E. M.; Warner, M. *Euro. Phys. J. E* **2001**, *4*, 343-353.

(8) Clarke, S. M.; Hotta, A.; Tajbakhsh, A. R.; Terentjev, E. M. *Phys. Rev E* **2001**, *6406*.

(9) Hirschmann, H.; Roberts, P. M. S.; Davis, F. J.; Guo, W.; Hasson, C. D.; Mitchell, G. R. *Polymer* **2001**, *42*, 7063-7071.

(10) Zanna, J. J.; Stein, P.; Marty, J. D.; Mauzac, M.; Martinoty, P. *Macromolecules* **2002**, *35*, 5459-5465.

(11) Cho, D. U.; Yusuf, Y.; Cladis, P. E.; Brand, H. R.; Finkelmann, H.; Kai, S. *Chem. Phys. Lett.* **2006**, *418*, 217-222.

(12) Cho, D. U.; Yusuf, Y.; Cladis, P. E.; Brand, H. R.; Finkelmann, H.; Kai, S. *Jpn. J. Appl. Phys.* **2007**, *46*, 1106-1113.

(13) Ren, H.; Wu, S.-T. *Appl. Phys. Lett.* **2002**, *81*, 1432-1434.

(14) Urayama, K.; Kondo, H.; Arai, Y. O.; Takigawa, T. *Phys. Rev. E* **2005**, *71*, 051713.

(15) Urayama, K.; Honda, S.; Takigawa, T. *Macromolecules* **2006**, *39*, 1943-1949.

(16) Urayama, K.; Honda, S.; Takigawa, T. *Phys. Rev. E* **2006**, *74*, 041709.

(17) Finkelmann, H.; Kock, H.-J.; Rehage, G. *Makromole. Chem. Rapid Commun.* **1981**, *2*, 317-322.

(18) Küpfer, J.; Finkelmann, H. *Makromole. Chem. Rapid Commun.* **1991**, *12*, 717-726.

(19) Lacey, D.; Beattie, H. N.; Mitchell, G. R.; Pople, J. A. *J. Mater. Chem.* **1998**, *8*, 53-60.

(20) Chang, C.-C.; Chien, L.-C.; Meyer, R. B. *Phys. Rev. E* **1997**, *56*, 595-599.

(21) Thomsen, D. L.; Keller, P.; Naciri, J.; Pink, R.; Jeon, H.; Shenoy, D.; Ratna, B. R. *Macromolecules* **2001**, *34*, 5868-5875.

(22) Yusuf, Y.; Huh, J. H.; Cladis, P. E.; Brand, H. R.; Finkelmann, H.; Kai, S. *Phys. Rev. E* **2005**, *71*, 061702.

(23) Urayama, K.; Honda, S.; Takigawa, T. *Macromolecules* **2005**, *38*, 3574-3576.

(24) Kempe, M. D.; Scruggs, N. R.; Verduzco, R.; Lal, J.; Kornfield, J. A. *Nature Mater.* **2004**, *3*, 177-182.

(25) Li, M.-H.; Keller, P.; Yang, J.; Albuoy, P.-A. *Adv. Mater.* **2004**, *16*, 1922-1925.

(26) Gabert, A. J.; Verploegen, E.; Hammond, P. T.; Schrock, R. R. *Macromolecules* **2006**, *39*, 3993-4000.

(27) Ahir, S. V.; Tajbakhsh, A. R.; Terentjev, E. M. *Adv. Func. Mater.***2006**, *16*, 556-560.

(28) Hild, G. *Prog. Polym. Sci.* **1998**, *23*, 1019-1149.

(29) Patel, S. K.; Malone, S.; Cohen, C.; Gillmor, J. R.; Colby, R. H. *Macromolecules* **1992**, *25*, 5241-5251.

(30) Hedden, R. C.; Saxena, H.; Cohen, C. *Macromolecules* **2000**, *33*, 8676-8684.

(31) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.

(32) Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020-15021.

(33) Hawker, C. J.; Wooley, K. L. *Science* **2005**, *309*, 1200-1205.

(34) Malkoch, M.; Thibault, R. J.; Drockenmuller, E.; Messerschmidt, M.; Voit, B.; Russell, T. P.; Hawker, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 14942-14949.

(35) Malkoch, M. V., R.; Gupta, N.; Mespouille, L.; Dubois, P.; Mason, A. F.; Hedrick, J. L.; Liao, Q.; Frank, C. W.; Kingsbury, K.; Hawker, C. J. *Chem. Commun.* **2006**, 2774-2776.

(36) Johnson, J. A.; Lewis, D. R.; Diaz, D. D.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *J. Am. Chem. Soc.* **2006**, *128*, 6564-6565.

(37) Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *Macromolecules* **2007**, *40*, 3589-3598.

(38) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311-6316.

(39) Maughon, B. R.; Weck, M.; Mohr, B.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 257-265.

(40) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903-2906.

(41) Bielawski, C. W.; Morita, T.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 678-680.

(42) Morita, T.; Maughon, B. R.; Bielawski, C. W.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6621-6623.

(43) Scherman, O. A.; Ligthart, G. B. W. L.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 11850-11855.

(44) Winkler, B.; Rehab, A.; Ungerank, M.; Stelzer, F. *Macromol. Chem. Phys.* **1997**, *198*, 1417-1425.

(45) Breitenkamp, K.; Simeone, J.; Jin, E.; Emrick, T. *Macromolecules* **2002**, *35*, 9249-9252.

(46) Zentel, R. *Liquid Crystals* **1986**, *1*, 589-592.

(47) Camacho-Lopez, M.; Finkelmann, H.; Palffy-Muhoray, P.; Shelley, M. *Nature Mater.* **2004**, *3*, 307-310.

(48) Kundler, I.; Finkelmann, H. *Macromole. Rapid Commun.* **1995**, *16*, 679-686.

(49) Yu, Y. L.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145.

(50) Oyerokun, F. T.; Schweizer, K. S. *J. Phys. Chem. B* **2005**, *109*, 6595-6603.

(51) Fried, E.; Sellers, S. *J. Mech. Phys. Solids* **2004**, *52*, 1671-1689.

(52) Brand, H. R.; Pleiner, H. M., P. *Soft Matter* **2006**, *2*, 182-289.

(53) Jernow, J. L.; Gray, D.; Closson, W. D. *J. Org. Chem.* **1971**, *36*, 3511-3515.