Article

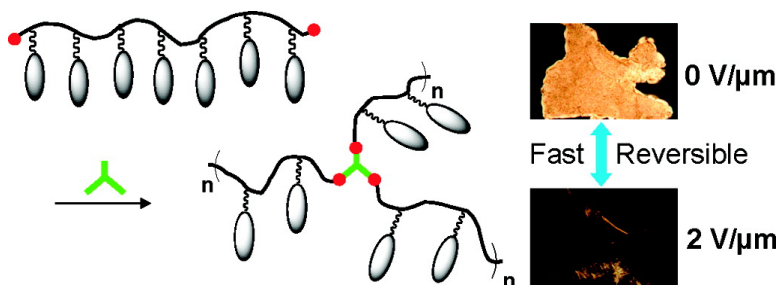# Well-Defined Liquid Crystal Gels from Telechelic Polymers

Yan Xia, Rafael Verduzco, Robert H. Grubbs, and Julia A. Kornfield

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Well-Defined Liquid Crystal Gels from Telechelic Polymers

Yan Xia, Rafael Verduzco, Robert H. Grubbs,* and Julia A. Kornfield*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received September 17, 2007; E-mail: rhg@caltech.edu; jak@cheme.caltech.edu

Abstract: Well-defined liquid crystal networks with controlled molecular weight between cross-links and cross-link functionality were prepared by "click" cross-linking 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 cross-links, cross-linker functionality, and mesogen density. Therefore, it allows a 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 cross-linked 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, and 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 cross-links, 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 LCs[13-16] show that these molecular parameters strongly influence macroscopic properties. For example, it has been observed qualitatively that decreasing the cross-linker and/ or monomer concentrations resulted in lower threshold fields and enhanced electro-optic and electromechanical responses of LC gels.[13-15]

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

(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. *Eur. 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. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 317–322.
(18) Küpfer, J.; Finkelmann, H. *Makromol. 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. *Nat. 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. Funct. Mater.* **2006**, *16*, 556–560.

Scheme 1. Synthesis of Monomers **1** and **2**
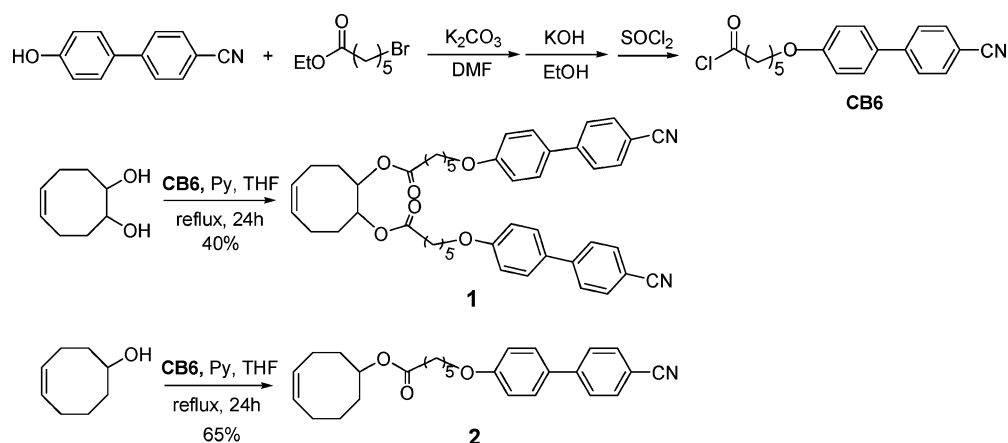
nature of the cross-links and from the well-defined self-assembled structure; however, they lack the long-term stability that is achieved by covalent cross-linking. Here, we investigate the use of telechelic polymers to create covalent LC elastomers and gels. End-linking of telechelic polymers with polyfunctional cross-linkers 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" cross-linking 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] Cross-linking 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"-cross-linking to produce LC networks with a regular network architecture, including a

controlled molecular weight between cross-links and cross-link 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 a 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.

To prepare telechelic SGLCPs, the monomers were polymerized by the highly active ruthenium catalyst, (IMesH₂)-(PCy₃)RuCl₂(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: 1 M for **1** and 1.5 M 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 ¹H NMR spectrum. The polymer molecular weights

(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.
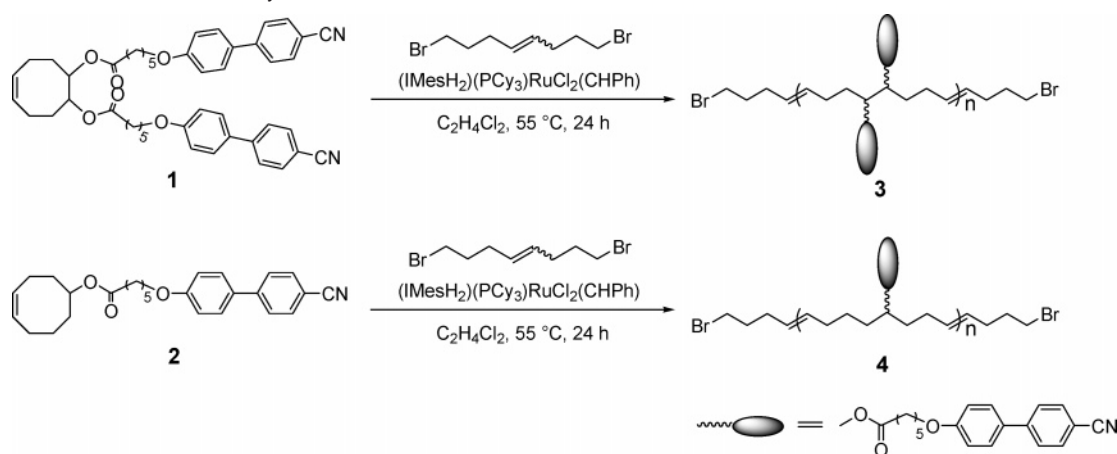(40) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.
(41) Bielawski, C. W.; Morita, T.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 678−680.
(42) Morita, T.; Maughon, B. R.; Bielawski, C. W.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6621−6623.
(43) Scherman, O. A.; Ligthart, G. B. W. L.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **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.

Scheme 2. ROMP of Functionalized Cyclooctene Monomers

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: $[M]_0 = 1$ M for **1** and 1.5 M 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 an 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.

were regulated by the ratio of monomer to CTA, [M]/[CTA] (Table 1). Good agreement between the absolute molecular weight obtained from GPC utilizing a 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 (see the Supporting Information Figure 1S).

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 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" cross-linking 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

uncross-linked fraction, and elastomers were obtained after drying under vacuum.

Polymer **3a** was used to study the effect of cross-linking conditions on the gel fraction. Polymer concentration had minimal effect on the gel fraction (Table 2, entry 1−3). When high polymer concentrations (50 and 33 wt %) were used, a gel was instantly formed as tripropargylamine was added, precluding preparation of thin films for electro-optic study. Therefore, a 25 wt % polymer concentration was chosen to evaluate the effect of the ratio of acetylene (from cross-linkers) 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 the acetylene/azide ratio is asymmetric: using less cross-linkers than needed decreased the gel fraction more strongly than using excess cross-linker. The effect of the acetylene/azide ratio on the 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.

A polymer concentration of 25 wt % and a stoichiometric amount of cross-linker that allows the azide/acetylene ratio to be 1:1 were used to cross-link 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 cross-linked polymers showed the complete disappearance of the azide absorbance, indicating that most of the azide end groups have reacted in the cross-linking (see the Supporting Information Figure 2S). Films for electro-optic studies were made by cross-linking 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).

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

Scheme 3. Cross-linking of Telechelic Polymers by "Click" Chemistry
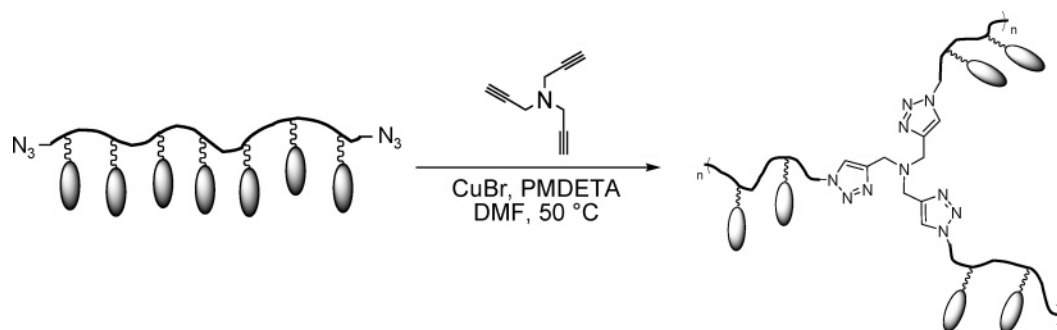
Table 2. Effect of Polymer Precursor Concentrations and Stoichiometry of Acetylene and Azide Groups on the Gel Fraction

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.

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.

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 an 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

(46) Zentel, R. *Liq. Cryst.* **1986**, *1*, 589−592.

the applied field due to the uniaxial symmetry of the nematic director. The response time of the constrained gel was within 1 ms.

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 LCs 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
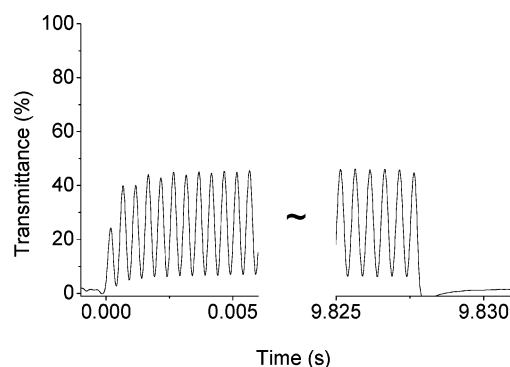

Figure 1. Dynamic electro-optic response of a constrained LC gel (LCG2, Table 3) under 19 V/μm, 1000 Hz AC signal. The signal is applied at 0 s and removed at 9.826 s approximately. Note that the transmitted intensity (recorded at 6000 Hz) quickly reaches its long-time value, and the oscillation of the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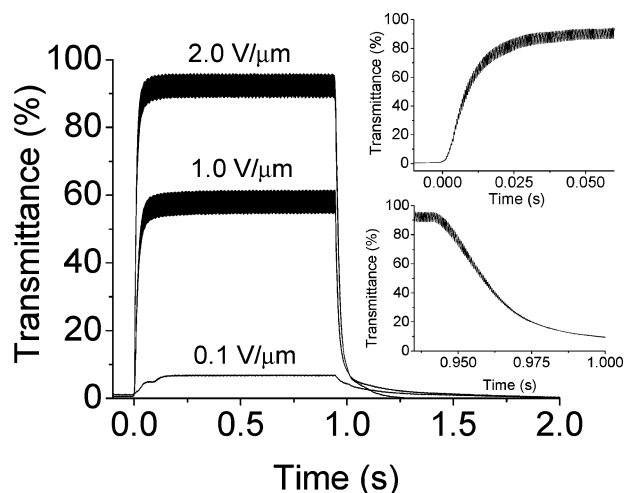
Figure 2. Transient electro-optic response of an unconstrained LC gel (LCG2) under various AC electric fields at 1000 Hz. The insets show the electro-optic response around the time the signal is applied (top inset) and removed (bottom inset).
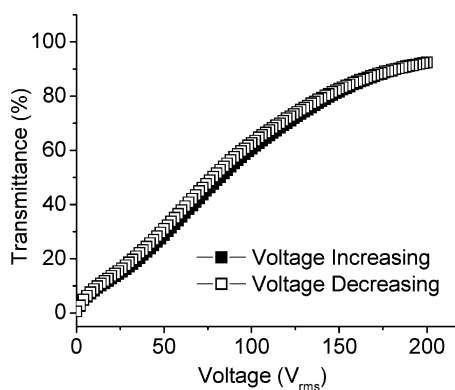

Figure 3. Transmittance as a function of voltage applied for an unconstrained LC gel (LCG2) in a 100-μm-thick gap. The applied AC voltage (rms) sweeps from 0 to 200 V at a 0.5 V interval and 1000 Hz. The measured intensity is the average of the oscillation; the software measures the intensity several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

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 that at 1000 Hz (see the Supporting Information Figure 3S). 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).

The effects of molecular variables on electro-optic response are evident in comparisons between LCG2 (above), LCG1 (greater cross-link density, Figure 4S), and LCG3 (greater space between mesogens, Figure 6S). The main effects of increasing the cross-link density are to reduce the transmittance at a given electric field and 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 a similar cross-link density to that of
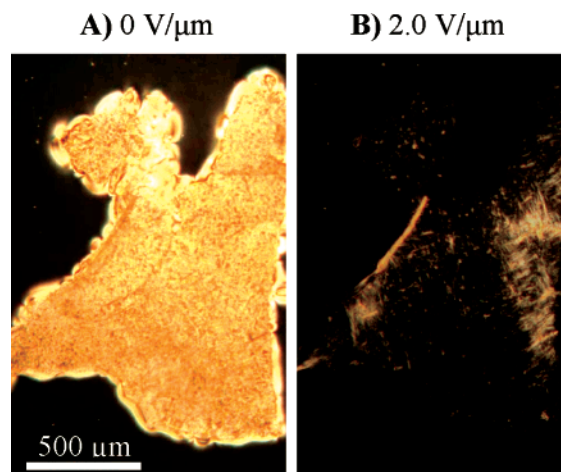

Figure 4. Polarized optical micrograph of unconstrained LC gel (LCG2) between ITO and lecithin coated glass plate under (A) no AC field and (B) an AC field of 2.0 V/μm.

LCG2, but with only half the number of mesogens per repeat unit (LCG3), exhibits similar behavior to that of LCG2 with 75% transmittance at 2.0 V/μm, a fully reversible electro-optic response, low threshold switching, and fast dynamics (see the Supporting Information Figure 6S and 7S).

These electro-optic studies demonstrate important features of the electro-optic response of LC gels made by cross-linking 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 cross-link 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 cross-linker and/or monomer concentrations (expected to give the network longer strands overall) results in lower threshold fields and enhanced electro-optic and electromechanical responses of LC gels.[13−15]

(47) Camacho-Lopez, M.; Finkelmann, H.; Palffy-Muhoray, P.; Shelley, M. *Nat. Mater.* **2004**, *3*, 307−310.
(48) Kundler, I.; Finkelmann, H. *Macromol. Rapid Commun.* **1995**, *16*, 679−686.
(49) Yu, Y. L.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145.

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 cross-link density are difficult to avoid in systems prepared by uncontrolled radical polymerizations. Trifunctional cross-linking of already formed polymers gives very few closely spaced cross-links (random selection of three chains from the overall distribution gives a narrower distribution of the molar mass linked to a cross-link 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 cross-linking 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 the LC network structure, including the length of the network strands between cross-links and cross-linker 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 cross-link density and length between cross-links 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 cross-linked 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 cross-linking in the nematic state[15,23] and producing telechelic LC polymers with a higher degree of anisotropy.[25]

Supporting Information Available: Experimental section, NMR and IR spectra, transient electro-optic response of LCG2 at electric fields of different frequencies, transient electro-optic response and voltage sweep of LCG1 and LCG3. This material is available free of charge via the Internet at http://pubs.acs.org.

JA077192J

(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.