Molecular Engineering of Step-Growth Liquid Crystal Elastomers

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Liquid crystal elastomers (LCEs) are shape-responsive materials that combine the elastic properties of a polymer network with the molecular ordering and responsiveness of liquid crystals. Recent work has relied on step-growth chemistries to produce LCEs with remarkable diversity and functionality. However, the connection between molecular structure and macroscopic properties such as shape responsiveness and phase behavior are poorly understood. Here, we demonstrate general molecular design principles for increasing shape-responsiveness and reducing the glass-transition temperature of LCEs produced through step-growth chemistries. We systematically investigate the phase behavior, liquid crystal ordering, mechanical properties and shape-responsiveness of a series of model polyester LCE networks using a combination of two-dimensional X-ray diffraction and dynamic mechanical analysis. We demonstrate that tailoring the length and composition of the linking group can reduce the glass-transition temperature with little impact on the liquid crystal order parameter, resulting in LCEs with a large shape-response near room temperature. Furthermore, the incorporation of a chain extending unit can significantly increase shape-responsiveness, from 35 up to 78 % reversible strain, and the network crosslink density can be controlled by variation of the network stoichiometry. This work establishes generally applicable molecular design principles applicable to LCEs prepared through step-growth chemistries.

Introduction

Liquid crystal elastomers (LCEs) are shape-responsive materials that combine the elastic properties of a polymer network with the molecular ordering and responsiveness of liquid crystals. Unlike densely crosslinked liquid crystal networks or aligned liquid crystal polymers, LCEs are soft materials that can exhibit large-amplitude, reversible shape changes.¹ Furthermore, functionalities can be incorporated in LCEs to enable remote actuation in response to light and magnetic or electric fields.^{2–7} LCEs therefore have significant potential for biomedical applications, sensors, artificial robots and devices, micro-actuators, responsive surface coatings, as reported in a number of recent reviews^{1,8,9} and a comprehensive textbook¹⁰.

However, despite over three decades of work with LCEs, the preparation of LCEs remains a significant challenge. The most popular approach for producing LCEs involves the use of poly(siloxane) chains and hydrosilylation reactions for functionalizing and crosslinking.^{11–13} The network is aligned mechanically by stretching or de-swelling during crosslinking¹⁴.

While effective, this approach is time consuming and can only produce LCEs with uniaxial alignment of the liquid crystal director.

A number of studies have explored alternative synthetic routes based on step-growth chemistries, as shown schematically in **Figure 1**. Step-growth chemistries have a

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

number of advantages for the preparation of LCEs. The starting materials are small molecules and can be aligned prior to crosslinking through surface alignment layers. Further, the composition and functionality can be systematically tuned through incorporation of different reactive liquid crystal mesogens and flexible linkers. A challenge is that an efficient coupling reaction is needed to achieve high conversion and uniform networks, ideally in solvent free conditions.

Several examples of LCE synthesis have been reported recently. Ware et al. reported step-growth LCE synthesis through Michael addition reactions followed by a photo-induced crosslinking reaction. This chemistry enabled the preparation of voxelated LCEs with complex liquid crystal director patterns imprinted into the network through patterned surface alignment layers.^{15,16} Martella et al. produced LCEs through thiol-yne coupling reactions,¹⁷ which enabled both side-chain and main-chain LCEs aligned using surfaces. Yakacki et al. utilized thiol-acrylate coupling reactions to produce LCEs aligned by stretch,¹⁸ and Ware et al. reported similar LCEs produced through thiol-acrylate coupling and aligned using patterned surfaces.¹⁹ Hong et al. reported the preparation of micron-sized LCE pillars through photo-induced thiol-ene chemistry, and the resulting micro-pillars exhibited greater than 100 % reversible strains.²⁰ Michal et al. also utilized thiol-ene coupling reactions to produce photo-responsive LCEs functionalized with metal-ion binding ligands.²¹ Finally, Pei et al. reported LCEs prepared through reversible trans-esterification reactions, which led to LCEs with reversibly crosslinked networks.²²

These recent studies have established the effectiveness and versatility of step-growth chemistries for LCE synthesis. However, for each of these cases, it is desirable to tailor the phase behavior, mechanical properties, and shape-responsiveness for a specific application. For example, room-temperature applications of LCEs require a T_g below room temperature to trigger a shape-response at ambient conditions. Lower transition temperatures are also desirable to produce large shape changes near ambient temperatures. Further, spontaneous strain in many of the LCEs reported was limited to 20 – 30 %, and higher reversible strains are desirable. As a specific example, the polyester networks reported by Pei et al. had a glass-transition temperature above room temperature (55 °C) and a maximum thermoreversible shape-responsiveness (under no external load) of 35 %.²² In a subsequent study, Li et al. reported that the T_g of this material could be reduced to near room temperature by modifying network stoichiometry, but at a significant loss in liquid crystal ordering and thermoreversible strain.²³ It would be desirable to choose the proper composition of linker and mesogen to both decrease the T_g and increase shape-responsiveness and/or liquid crystal ordering. However, such molecular engineering approaches for LCEs are limited.

Herein, we systematically investigate the phase behavior, liquid crystal ordering, mechanical properties and shape-responsiveness of a series of LCE networks prepared through step-growth, reversible trans-esterification coupling reactions. These networks are excellent model systems for establishing

the connection between molecular structure and macroscopic properties due to their simplicity; only one linker and mesogen are needed to produce LCEs in a one-step reaction. We demonstrate general molecular design principles for increasing shape-responsiveness and reducing the glass-transition temperature of LCEs produced through step-growth chemistries. Specifically, we find that tailoring the length and composition of the linking group can reduce the glass-transition temperature with little impact on the liquid crystal order parameter, resulting in an LCE with shape-responsiveness near room temperature. Furthermore, reduction of network branching through the incorporation of a chain extending unit can significantly increase shape-responsiveness, from 35 up to 78 % reversible strain. This work establishes generally applicable molecular design principles applicable to LCEs synthesized through step-growth chemistries.

Experimental

Materials

4,4'-dihydroxybiphenyl and hexadecanedioic acid (**C16**) were obtained from TCI America and used as received. Benzyltrimethylammonium bromide, sebacic acid (**C10**), 1,5,7-triazabicyclo[4.4.0]dec-5-ene, epichlorohydrin, and chloroform were purchased from Sigma-Aldrich and used as received. Carboxydecyl terminated polydimethylsiloxane (**10CPDMS**) was purchased from Gelest and used as received. Di-epoxy mesogen 4, 4'-diglycidyloxybiphenyl (**BP4OH**) and di-hydroxyl mesogen 2'-([1,1'-biphenyl]-4,4'-diylbis(oxy))diethanol (**BP2OH**), were synthesized as previously reported.²⁴

LCE Network Synthesis. LCEs were prepared in a one-step coupling reaction between linkers and mesogens, resulting in the formation of a crosslinked liquid crystal network. In a representative example, 293.1 mg (0.950 mmol) of **BP4OH** and 192.0 mg (0.950 mol) of sebacic acid (**C10**) were added to a rectangular PTFE mold (3 cm x 2 cm x 1 cm). The samples were blended by heating to 180 °C and mixing manually. Next, 1,5,7-triazabicyclo[4.4.0]dec-5-ene catalyst (13.2 mg, 10 mol %) was added while the mixture was stirred manually with a spatula to ensure uniform mixing. The reaction was allowed to proceed at 180 °C for 10 minutes, after which the sample was cooled to room temperature. The elastomer was removed from the mold and placed in a melt press at 180 °C. Samples were held at 180 °C in the melt press for 4 hours to ensure completion of the reaction, and the final thickness the samples was 0.4 mm. The resulting polydomain LCE was then cooled to room temperature and cut to a rectangular shape before alignment, as described below.

The gel fraction of all samples was determined using two methods. First, following the procedure reported by Pei et al.²² we soaked elastomers in trichlorobenzene at room temperature for 24 hours. Samples were then dried under vacuum (30 in. Hg) at 100°C until the day-to-day change in

weight of the LCE under vacuum was less than 0.1 %. The final gel fraction was determined by dividing the LCE mass by its pre-swollen weight. Most samples had a gel fraction above 98 %, and all were above 96 % using this approach. In a second, more stringent approach, samples were subjected to Soxhlet extraction with acetone for 2 days. The resulting samples were similarly dried under vacuum and weighed daily until the weight-change was less than 0.5 %. Samples exhibited much greater mass loss using this approach, between 65 and 94 %. Gel fractions for samples with a 1:1 stoichiometry of linker:mesogen are shown in the Supporting Information **Table S1**.

LCE Alignment. Polydomain LCEs were aligned through mechanical loading at 165 °C. In a representative example, a polydomain LCE produced using the procedure described above was suspended vertically, and a load was applied by attaching weights on one end of the sample (50 – 150 kPa). Next, the samples were heated under vacuum to 165 °C, and the sample was maintained at 165 °C until the sample length reached 200 % of its initial length. The sample was then removed from the heating oven, cooled to room temperature, and the load was removed.

Instrumentation

Differential scanning calorimetry (DSC). Phase behavior of LCE samples including glass-transition temperature T_g and smectic-to-isotropic transition temperatures T_{SI} were determined by a TA instruments Q20 DSC. Samples were heated and cooled at a rate of 5 °C/min. Phase transition temperatures were determined from second heating cycles.

Dynamic Mechanical Analysis (DMA). Storage modulus and shape-responsiveness were determined through temperature-controlled dynamic mechanical analysis (DMA) measurements using a TA Instruments Q800 DMA. Storage modulus was measured under a dynamic force ramp from 0.01 N at 1.5 N/min at low strains (< 1%). For reversible shape-change analysis, a small (0.001 N) force was maintained along the sample to ensure the sample was taut between the plates, and the sample was heated and cooled at 10 °C/min over several cycles. The maximum and minimum temperatures analyzed for each sample corresponded approximately to 10 °C above the T_{SI} and T_g , respectively.

Two-dimensional X-ray diffraction measurements (2D-XRD). Liquid crystal orientation, phase, and order parameter was measured using a Rigaku Diffractometer consisting of a RUH3R Copper Target Rotating Anode (X-ray wavelength 1.54 Å), Osmic Blue Confocal Optics with 0.3 or 0.5 mm collimator, a single, phi axis goniometer with vertical orientation, and a Rigaku R-Axis IV++ Image Plate Area Detector. The detector imaging area is approximately 380 mm x 380 mm, and the distance from sample to detector is set to 300 mm. The orientational order parameter is determined by fitting the azimuthal 2-D X-ray intensity corresponding to the smectic

Scheme 1. Reaction scheme for the coupling and trans-esterification chemistry used in this work. Reaction between bis-epoxy mesogen **BP4OH** and di-acid linker **C10** results in the formation of an LCE network. **R** groups represent ester linkages or unreacted hydroxyl functional groups.

layer spacing ($d \approx 14.7$ Å) to the Maier-Saupe probability distribution.²⁵

Results

The LCEs studied here are prepared through the coupling of a reactive mesogen and linking group, as shown in **Scheme 1** and in **Figure 1**. This particular LCE system was chosen for its simplicity and versatility. The reaction requires a minimum of only two components, a reactive mesogen and linker, along with a base to catalyze ring opening and trans-esterification reactions. The reactive mesogen acts as both a chain extender and a branching unit, and each mesogen can react with up to four **C10** linking groups. As shown in **Scheme 1**, the reaction proceeds initially through a ring-opening reaction between **BP** and **C10**, which produces an ester linkage and a hydroxyl group. The hydroxyl and ester functional groups can continue to react in trans-esterification reactions, and the number of branch points or crosslinks in the final network will be determined by the reaction stoichiometry. This is quantified through functional group ratio $r = [-\text{COOH}]/[-\text{OH}]$, where r is the molar ratio of carboxylic acid to hydroxyl functionalities. At a 1:1 ratio of **BP4OH**:**C10**, $r = 0.5$ indicating that half of the hydroxyl groups are unreacted in the final network. For clarity, an example intra-molecular trans-esterification reaction is shown in the Supporting Information Scheme S1.

The samples are aligned by applying a mechanical load at 165 °C. At this temperature, the sample undergoes reversible trans-esterification reactions, which serve to re-organize the crosslinked network.²² Alignment is reflected in an anisotropic 2-D X-ray diffraction pattern and through reversible shape response with changes in temperature. As shown in **Figure 2**, after alignment a clear anisotropy is observed in the X-ray diffraction pattern for the sample, which reflects a low-angle and wide-angle diffraction peak characteristic of smectic order. The low-angle peak ($d = 14.7$ Å) corresponds to the smectic layer spacing while the wide-angle peak ($d = 4.3$ Å)

Figure 2. Molecular structure of LCE with **C10:BP4OH** at a 1:1 ratio, 2-D X-ray diffraction analysis of polydomain and monodomain LCEs, and temperature-dependent strain of aligned LCE samples under no load and with temperature ramping.

corresponds to lateral spacing between mesogens. The degree of ordering is quantified through calculation of a liquid crystal order parameter S , which can be determined through analysis of either the low- or wide-angle peak. The numbers reported here are based on the low-angle peak for consistency with previous analysis of similar materials.²²

As shown in **Figure 2**, aligned LCEs exhibit spontaneous and reversible actuation with changes in temperature. Aligned LCEs contract on heating and reversibly elongate on cooling due to temperature-dependent changes in the liquid crystal order parameter S which is directly coupled to the network anisotropy.^{10,26} Large and reversible shape changes are unique to LCEs and distinct from other materials such as shape-memory polymers, which exhibit shape-memory only under the application of an external load,²⁷ with some exceptions.^{28–31} The reversible strain in the **C10:BP4OH** elastomers is approximately 25 %, and some loss of reversible strain is observed with cycling.

Before investigating the effect of the linker and mesogen composition, we wanted to understand the impact of stoichiometry by studying the **C10:BP4OH** system. A study of the effect of stoichiometry of similar networks was reported recently,²³ but this prior study did not investigate the reversible shape-response (no-load) of aligned LCEs. To

investigate the effect of stoichiometry, a series of samples was aligned and characterized with respect to phase behavior, reversible strain, and liquid crystal order parameter (see **Table 1**). As shown in **Table 1**, the LCE storage modulus trends approximately with the functional group ratio r . This is expected due to increased branching and crosslink density for r values near one, and is predicted from statistical models for branching and crosslinking in step growth reactions.³² Only samples with a 1:1 and 1:0.9 ratio of linker:mesogen deviate from this trend, and this might be due to large changes in both T_g and T_{SI} between these samples.

An increase in the molar ratio of **C10:BP4OH** results in a decrease of both T_g and T_{SI} . At the same time, a substantial loss of liquid crystal ordering and network anisotropy is observed on reducing the content of liquid crystal mesogen. This is reflected in the decreased ΔH but more dramatically in the low liquid crystal order parameters and reversible strain values. All samples were cycled between the temperatures of 10 °C above T_g and 10 °C above T_{SI} . Very little shape-change is observed outside of this temperature range for all samples. The reversible strain decreases rapidly below **C10:BP4OH** ratios of 1:0.9, with only a 15 and 5 % reversible strain for stoichiometric ratios of 1:0.8 and 1:0.7. Order parameter measurements also reveal a significant loss of alignment at lower stoichiometric ratios, as expected due to a lower mesogen content. 2-D X-ray diffraction measurements show that the d -spacings are not affected by the network stoichiometry. 2-D X-ray measurements and temperature-dependent strain measurements for all samples are provided in the ESI for all samples (**Table S2** and **Figures S1 – S4**). Finally, the storage modulus generally increases with a lower content of **BP4OH** (as expected due to a higher crosslink density) but a drop in modulus is observed in going from a 1:1 to a 1:0.9 ratio. This may be due to large changes in T_g and T_{SI} between these samples.

Table 1. Thermal properties, phase behavior, and mechanical properties of liquid crystal elastomers with varying stoichiometry

C10:BP4OH	r^a	E'^b (MPa)	T_g^c (°C)	T_{SI}^c (°C)	ΔH^d (J/g)	reversible strain (%)	S^e
1:1.2	0.42	3.63	62.9	109.2	17.1	30	0.85
1:1	0.50	7.71	55.8	107.8	17.0	25	0.82
1:0.9	0.56	5.91	47.9	99.6	15.3	25	0.81
1:0.8	0.63	13.2	46.8	91.7	15.0	14	0.78
1:0.7	0.71	27.7	42.4	89.2	13.7	4	0.62

^a molar ratio of carboxylic acid to hydroxyl functional groups, $[-COOH]/[-OH]$ ^b storage modulus measured at 80 °C for all samples ^c measured by DSC. ^d enthalpy of smectic-to-isotropic phase transition measured by DSC. ^e liquid crystal order parameter from analysis of smectic layering peak.

The series of samples studied demonstrates that varying stoichiometry influences phase behavior but can also come with a substantial loss in liquid crystal ordering and reversible shape response. Furthermore, the lowest T_g observed was 42.5 °C, a value still well above room temperature and with a significant loss in reversible strain. Thus, alternative strategies

beyond varying stoichiometry are needed to achieve room temperature shape-change with large, reversible actuation.

Next, we investigated the impact of incorporating different linkers and mesogens into the LCE. A series of linkers varying in length and composition was chosen to understand the impact on phase behavior and, in particular, glass-transition temperature T_g . We hypothesized that the incorporation of longer, more flexible linkers (**C16** and **PDMS**) could depress T_g , but this could also potentially come with a loss in liquid crystal ordering and shape responsiveness. For these studies, the ratio of linker:mesogen was kept at 1:1.

First, we investigated substitution of the shorter **C10** linker with the longer **C16** unit. By mixing **C10** and **C16** linking groups, we were able to achieve a reduction of both T_g and T_{SI} (Table 2). This is likely due to mismatch in the lengths of the linking groups, which de-stabilizes the smectic phase and reduces the transition temperature to the isotropic phase.³³ The smectic-layer d -spacing was sensitive to the linker composition. The largest d -spacing (17.9 Å) was measured in the sample with **C16** linker, while the smallest value (15.0 Å) was measured in the LCE with **C10** linker. LCEs with mixtures of **C10** and **C16** have smectic layer d -spacings between these two extremes (see ESI Table S3 and Figures S5 – S9). Similar effects have been reported in studies of liquid crystal copolyesters.³³

Linking Groups:

Reactive Mesogens:

Scheme 2. Structures of linking groups and reactive mesogens investigated.

Table 2. Thermal properties, phase behavior, and mechanical properties of liquid crystal elastomers with **BP4OH** mesogen and varying linker composition. All samples are synthesized with an equimolar ratio of mesogen:linker.

Linker Composition (mol fraction)			T_g^a (°C)	T_{SI}^a (°C)	ΔH^b (J/g)	S^c	Reversible Strain (%)
C10	C16	PDMS					
1	0	0	55.8	107.8	17.0	0.82	25
0	1	0	43.1	110.0	15.0	0.84	8
0.5	0.5	0	42.8	91.9	11.2	0.86	35
0.66	0.34	0	43.2	83.0	11.2	0.88	40
0.83	0.17	0	44.6	95.9	12.8	0.87	28
0.63	0.32	0.05	33.3	78.3	10.9	0.88	36
0.6	0.3	0.1	16.3	67.4	10.2	0.88	40

^a measured by DSC. ^b enthalpy of smectic-to-isotropic phase transition measured by DSC. ^c liquid crystal order parameter from analysis of smectic layering peak.

The lowest values of T_g and T_{SI} were found with a 2:1 ratio of **C10** and **C16** linking groups. However, the T_g for all samples with **C10** and **C16** linkers was above room temperature. Interestingly, we observed a substantial loss of thermoreversible strain when replacing the **C10** linker with **C16**. However, mixtures of **C16** and **C10** exhibited thermoreversible strains in the range of 28 % to 40 %. The largest thermoreversible strain (40 %) was observed for a 2:1 ratio of **C10** and **C16** linkers.

In order to further reduce the T_g we incorporated siloxane based linker **PDMS**. This linker has a central poly(dimethylsiloxane) unit flanked by two aliphatic carbon chains, as shown in **Scheme 2**. This linker was incorporated into the LCE while maintaining a 2:1 ratio of **C10**:**C16** and a 1:1 overall ratio of linker:mesogen. Incorporation of **PDMS** linker produced a significant reduction in T_g , down to 33.3 and 16.3 °C for 5 and 10 mol % **PDMS**, respectively. These linkers also substantially reduced T_{SI} , down to 78.3 and 67.4 °C for 5 and 10 mol % **PDMS** linker incorporated, respectively, while the smectic layer d -spacing was not significantly affected by the **PDMS** linker (see ESI Table S3.) Incorporation of larger amounts of **PDMS** linker beyond 10 mol % of the overall linker composition was not possible due to poor compatibility which led to macroscopic phase separation (see micrograph in the ESI Figure S10). We also measured a significant reduction in the gel fraction for elastomers that incorporated the **PDMS** linker, depending on the method used to measure gel fraction (Supporting Information Table S1). This indicates that the **PDMS** linker is a less effective crosslinker, but nevertheless is beneficial for reducing T_g while maintaining high reversible strains as discussed below.

Relative to the LCEs with only **C10** and **C16** linkers incorporated at a 2:1 ratio, we measure a small decrease in thermoreversible strain with 5 mol % **PDMS** linker added and an increase in thermoreversible strain with 10 mol % **PDMS** linker. The latter sample with a blend of three linkers **C10**, **C16**, and **PDMS** at a molar ratio of 6:3:1 exhibited a T_g well below room temperature (16.7 °C) and a thermoreversible strain in excess of 40 %. The 2-D XRD and DMA analysis of this particular sample is shown in **Figure 2**, which demonstrates a

large, thermoreversible strain over moderate temperatures. The temperature is cycled between 30 and 90 °C with a reversible strain of approximately 40 – 45 %. By comparison, the starting two-component **C10:BP4OH** LCE was cycled between 70 and 120 °C (due to its much higher T_g and T_{SI}) to produce a maximum shape change of only 25 %.

This series of samples demonstrates that a substantial reduction in both T_g and T_{SI} is possible by selecting a mixture of linkers with different composition and maintaining an overall linker:mesogen stoichiometry of 1:1. The impact of linker composition is primarily through influencing the T_g , T_{SI} , and the smectic layer spacing. On the other hand, this series of samples highlight surprising and non-intuitive trends with changes in linker composition. The reversible strain varies over a wide range (20 – 45 %) in the samples with mixed linkers even though we measure a very similar order parameter S in this series of aligned LCEs. This suggests that changes in storage modulus, crosslink density, d -spacing, and liquid crystal ordering can govern shape-responsiveness in non-trivial

ways that are not fully understood.

Next, we investigated monomer functionality and its impact on network anisotropy. Networks based on **BP4OH** mesogen have a high branching density since each **BP4OH** mesogen can react with up to 4 linking groups. A statistical model for step-growth reactions can provide an estimate of the number of branch points depending on the monomer and linker functionality and stoichiometry.³² Based on the network stoichiometry of 1:1 and assuming equal reactivity of all hydroxyl groups, on average a branch point forms after every three **BP4OH** mesogens (the expected probability for a mesogen to react with 3 or 4 [-COOH] groups is 31%). This is shown schematically in **Figure 4**, where a series of three mesogens is terminated by a branch point, which can decrease network chain anisotropy. Incorporating bifunctional mesogen **BP2OH** reduces the number of branch points and increases the average length of network chains between branch points since **BP2OH** can only act as a chain extender rather than a branching unit. With incorporation of 10 and 20 mol% **BP2OH** relative to the overall mesogen content, the branching probability decreases to 30 and 28 mol %, respectively. While modest, this can have a direct impact on network anisotropy.

To test the impact of bifunctional mesogen on shape-responsiveness, LCEs with **C10** linker and a mixture of **BP2OH** and **BP4OH** monomers were synthesized using the same general approach. The overall stoichiometric ratio of linker:mesogen was kept at 1:1, as shown in **Figure 4**. Incorporation of **BP2OH** increases the functional group ratio $r = [-COOH]/[-OH]$ since each **BP2OH** monomer only contributes two reactive hydroxyl groups. A molar concentration up to 20 mol % **BP2OH** was tested; at higher contents samples were macroscopically phase separated. This is likely due to water formed as a byproduct of the condensation reaction between **C10** and **BP2OH**, shown in **Figure 4**.

Figure 3. Molecular structure of LCE with C10:C16:PDMS:BP4OH at a 0.6:0.3:0.1:1 molar ratio, 2-D X-ray diffraction analysis of polydomain and monodomain LCEs, and temperature-dependent strain of aligned LCE samples under no load and with temperature ramping.

Table 3. Thermal properties, phase behavior, and mechanical properties of liquid crystal elastomers with **C10** linker and varying mesogen composition. All samples are synthesized with an equimolar ratio of mesogen:linker.

Mesogen Composition (mol fraction)		r^a	T_g^b (°C)	T_{SI}^b (°C)	E'^c (MPa)	S^d	reversible strain (%)
BP4OH	BP2OH						
1	0	0.50	55.8	107.8	7.7	0.82	27
0.9	0.1	0.53	48.2	105.5	12.7	0.86	78
0.8	0.2	0.56	47.6	103.8	8.4	0.86	54

^amolar ratio of hydroxyl functional groups to carboxylic acid, $[-COOH]/[-OH]$ ^b measured by DSC. ^c storage modulus measured at 80 °C for all samples ^dliquid crystal order parameter from analysis of smectic layering peak

Incorporation of the **BP2OH** mesogen led to a significant increase in the reversible strain of aligned LCEs. As shown in **Table 3** and **Figure 5**, incorporation of 10 mol % **BP2OH** mesogen more than doubled the reversible strain in LCEs. This particular sample also showed virtually no loss in reversible strain over 10 heat/cool cycles. Incorporation of a greater amount of **BP2OH** mesogen, 20 mol %, resulted in a smaller reversible strain, but a value still larger than the **C10:BP4OH**

LCE. The decrease in reversible strain in going from 10 to 20 mol % **BP2OH** may be due to a decrease in crosslink density or a significant drop in sample storage modulus.

The order parameter increases from 0.82 to 0.86 with incorporation of the **BP2OH** mesogen at 10 and 20 mol %. The network chain orientation is directly coupled to the average mesogen orientation, and thus this increase in S also represents an increase in network chain anisotropy. This is likely responsible for the increased reversible strain observed upon incorporation of **BP2OH**. Incorporation of the **BP2OH** mesogen only has a modest impact on T_g and T_{Si} , resulting in a slight decrease for both.

Interestingly, the LCE storage modulus increases with 10 mol % **BP2OH** and then decreases on incorporation of 20 mol % **BP2OH**. The reasons for this are unclear, but may be due to both a decrease in the crosslink density and an increase in network chain anisotropy with increasing **BP2OH**. Other possibilities are that the lower degree of branching can also decrease the number of topological "loop" defects,^{34,35} which reduce the storage modulus, or the lower content of hydroxyl functionalities has an impact on the network storage modulus.

Figure 4. Schematic for changing network anisotropy through incorporation of bifunctional mesogen. Incorporation of a bifunctional mesogen reduces the network crosslink density. Water is a byproduct of the condensation reaction between **C10** and **BP2OH**. 1 molar equivalent of H_2O is formed for **BP2OH** hydroxyl group that reacts.

Finally, we aimed to find an optimal LCE system with both a low T_g and enhanced shape change through incorporation of the optimized linker reactive mixture and bi-functional mesogen. The experiments above suggest that an elastomer with an overall 1:1 mesogen linker ratio with a 6:3:1 ratio of **C10**:**C16**:**PDMS** linkers and a 9:1 ratio of **BP4OH**:**BP2OH** mesogens. Unfortunately, this composition of linkers and mesogens produced samples that were heterogeneous and macroscopically phase-separated, likely due to the strong incompatibility between the **PDMS** linker and **BP2OH** mesogens. Reaction of **BP2OH** with the linkers produces water as a byproduct, which can also be detrimental sample uniformity. A similar test of a system with **C10** and **C16** linkers at a 2:1 ratio and a mixture of **BP4OH** and **BP2OH** mesogens at a 9:1 ratio produced a sample with similar shape responsiveness as the starting **C10**:**BP4OH** system. Thus, while the molecular engineering approaches demonstrated were

Figure 5. 2-D X-ray diffraction analysis of polydomain and monodomain LCEs (top) and temperature-dependent strain of aligned LCE samples under no load and with temperature ramping. The elastomers are comprised of **C10**:**BP4OH**:**BP2OH** at a 1:0.9:0.1 ratio.

successful in reducing the T_g and enhancing shape-responsiveness separately, optimization of step-growth LCEs is a non-trivial, multi-variable problem. Shape-responsiveness is governed by several molecular parameters, which at a minimum include network chain anisotropy, storage modulus, crosslink density, liquid crystal ordering and domain size, network stoichiometry, and defects in the network.

The shape-responsiveness of LCEs with mixed linkers (10 % **PDMS**) was compared to that of the LCE with the **10C** linker. Both samples were first fixed into a coiled shape below T_g . The sample with mixed linkers could be unwound by heating to 35 °C, while the LCE with the **10C** linker required heating to 60 °C. Further, the LCE with mixed linkers exhibited reversible thermo-mechanical strain when heated from room temperature up to 35 °C (17 % reversible strain), while the LCE with the **10C** linker required heating up to 80 °C to achieve a 10% reversible strain. Both samples were wound into a spiral and cooled below T_g . The sample with mixed linkers could be unwound by heating to 35 °C. Thus, the use of mixed linkers enables actuation and shape responsiveness near room

temperature. Videos of this particular sample demonstrating the shape-change as the sample is heated above room temperature are provided in the Supporting Information.

Conclusions

In this work, we explored molecular engineering approaches for tailoring the phase behavior and shape responsiveness of liquid crystal elastomers. Focusing on a model step-growth LCE system, we show that incorporation of a mixture of linkers, if properly chosen, can substantially decrease the network T_g without loss of liquid crystal ordering or shape-responsiveness. Furthermore, tailoring the functionality of the mesogen led to a substantial enhancement in shape-responsiveness, more than double the starting networks.

While this work focused on a particular LCE system, these approaches are generally applicable to LCEs prepared through step-growth chemistries. However, a number of questions remain unanswered regarding the optimization of both shape-responsiveness and phase behavior in step-growth LCEs. While we demonstrated simple approaches for tailoring LCE properties, more generally it would be of interest to know how

to balance various network properties that change simultaneously with composition, including network storage modulus, network anisotropy, branching and crosslink density, and functional group stoichiometric ratio. A quantitative, predictive tool that accounts for these various molecular parameters and can predict macroscopic properties is lacking. Further, a number of alternatives beyond what was demonstrated here are possible. For example, the overall mesogen content of the system could be increased through incorporation of a mesogen with reactive carboxylic acid groups. The branching density could be substantially reduced beyond what was explored here, and the functional group ratio could be kept close to 1:1 while tailoring network branching and crosslinking. Future work will focus on these and other studies of LCEs with different crosslink histories, and modeling can likely play an important role in predicting optimal network compositions to enhance desirable physical properties.

Acknowledgments

This work was supported by the American Heart Association (14BGIA18750004), the John S. Dunn Foundation, the Welch Foundation for Chemical Research (C-1888), and the National Science Foundation (CBET-1336073). We acknowledge support from the Texas Center for Superconductivity at the University of Houston.

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LCE: 10C:16C:PDMS = 0.6:0.3:0.1

LCE: 10C linker only

Figure 6. Representative shape-responsiveness in LCE with mixed linker composition (top) and with 10C linker (bottom). Each sample is initially fixed into a semi-permanent coiled shape below T_g . Samples recover an unwound shape after heating above T_g . LCEs with a mixture of linkers exhibit reversible shape changes near room temperature, while LCEs with only the **10C** linker must be heated to 80 °C to exhibit significant change in length. The images show 17 % strain for LCEs with mixed linkers compared with 10 % strain over a wider temperature for LCEs with **10C** linker.

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