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Molecular engineering of step-growth liquid crystal elastomers

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ABSTRACT

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.

1. 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 textbook [10].

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 crosslinking [14]. 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 Fig. 1. Step-growth chemistries have a 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

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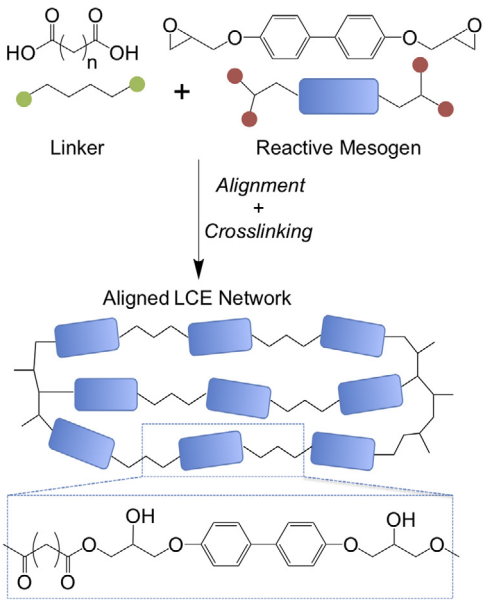

Fig. 1. Schematic for LCE synthesis through reactive, step-growth coupling of liquid crystal mesogens and flexible linkers. Alternative chemistries can include multi-functional linking groups, additional reactive crosslinkers and branching units, or other variations.

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.

2. Experimental

2.1. 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].

2.2. 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 × 2 cm × 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 min, 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 h 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 h. 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 that 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.