

Shape Memory Effect Exhibited by Smectic-C Liquid Crystalline Elastomers

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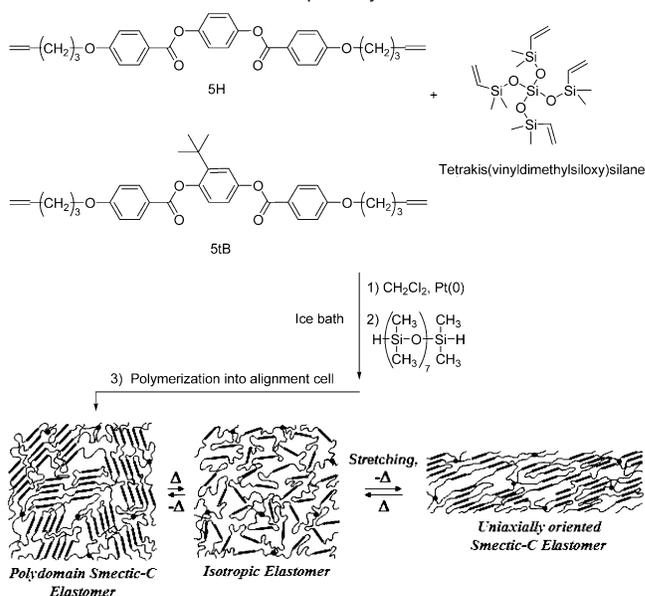
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Side-chain liquid crystalline elastomers (LCEs) have been widely studied over the past two decades because of their thermomechanical properties that include large strain reversible actuation and soft elasticity.^{1,2} The thermally stimulated actuation behavior is explained by a coupling between liquid crystalline order and rubber elasticity resulting from the underlying cross-linked structure. Yet, higher actuator performance has been long expected³ and recently shown for main-chain liquid crystalline elastomers (MC-LCEs) due to an enhanced coupling between their intrinsically high, yet labile, ordering and network strain as compared to their side-chain analogues.⁴ Challenges exist, however, for main-chain liquid crystalline polymers due to high transition temperatures and processing difficulties so that to date they have not received adequate attention. Network architectures have been varied, but only limited attention has been given to the influence of varying mesophases structure – from nematic to cholesteric to smectic – on thermomechanical behavior.⁵ We therefore sought in this study to synthesize and investigate the behavior of new smectic-C LCEs as candidates for shape memory purposes. Here, shape memory refers to a thermomechanical phenomenon in which large distortions may be “fixed” and later relaxed to an equilibrium shape under an environmental trigger.⁶

Shape memory materials require not only tailored transition temperatures (including, for LCEs, isotropization), but also specific mechanical properties. Such characteristics can be readily achieved using liquid crystalline elastomers with varying composition, thereby enabling specific transition temperatures for facile actuation. Herein, we present the thermomechanical characterization of newly synthesized main-chain smectic-C LCEs that reveals the exceptional capabilities of such materials as shape memory elastomers possessing low transition temperatures.

We have designed and prepared MC-LCEs incorporating two distinct benzoate-based mesogenic groups, 1,4-bis[4-(4-pentenyl-oxy)benzoyl]hydroquinone and 2-*tert*-butyl-1,4-bis[4-(4-pentenyl-oxy)benzoyl]hydroquinone, symbolized 5H and 5tB, respectively, coupled with hydride-terminated poly(dimethylsiloxane) spacers (DP = 8). Both mesogens, varying in their pendant group, were synthesized in our laboratory following well-known synthetic routes.^{4,7} While 5H has been previously synthesized (although incompletely characterized^{8,9}), the preparation of the 5tB structure has not yet been reported. Despite their similar structure, the thermal, physical, and optical behaviors of these LC dienes differ considerably: while 5H melts to a nematic phase at 136.6 °C and clears to an isotropic phase at 229.5 °C, 5tB exhibits similar transitions at much lower temperatures of 80.6 and 91.4 °C, respectively. Therefore, we expected that, via copolymerization of these two mesogens, properties of the final material could be specifically targeted, although we could not predict the observed smecticity from these nematogens. The overall scheme for the synthesis of our new siloxane-based MC-LCEs is given in Scheme 1.

Scheme 1. Schematic Representation of the Synthesis Route Followed to Obtain Smectic Liquid Crystalline Elastomers^a



^a The resulting polydomain smectic-C elastomer undergoes isotropization upon heating through the clearing transition, allowing for subsequent stretching and fixing of a secondary uniaxially oriented smectic-C elastomer.

Elastomers resulting from the synthesis described in Scheme 1 exhibit a profound shape memory effect. Specifically, upon heating of the films above the smectic-C-to-isotropic transition, the relaxed state of the elastomer (whose shape was acquired during cross-linking) can be easily deformed to tensile strains of about 300%. Subsequent “fixing” of this secondary shape is possible by cooling to the smectic-C phase. From X-ray diffraction studies of both the primary and the secondary shapes, we were able to determine the smectic-C nature of our new LCEs (Figure 1), revealing characteristic mesogenic tilt angles varying slightly with the elastomer composition from 41.5° to 45.0°. On the other hand, the layer spacing (~33.7 ± 0.5 Å), as shown in Figure 1, does not appear to vary significantly upon changing the mesogenic composition of the elastomer. The measured layer spacing values agree well with calculated values that assume a fully extended configuration of a mesogenic unit linked to half a flexible spacer unit, about 31 Å. From the inset of Figure 1, we notice the orientation of the siloxane backbone and the long-range smectic order (second order reflections) achieved upon stretching and fixing of the secondary shape. Interlayer mesogen correlations as indicated by the external arcs at high angle are also clearly present.

Investigation of LCE phase behavior and structural ordering reached through stretching and fixing of a secondary shape suggested the possibility of a shape memory cycle by sequential and repeated shape fixing and recovery. Thus, after being heated above the clearing transition of the initial polydomain smectic-C

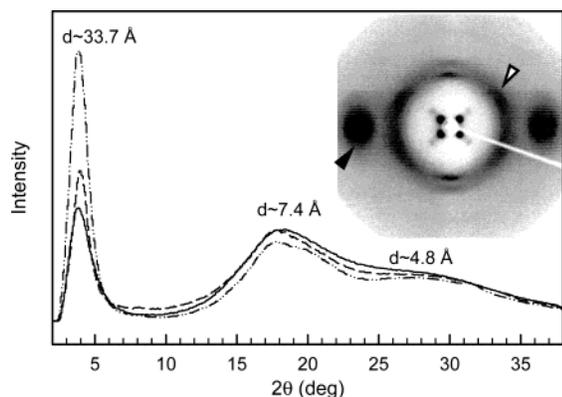


Figure 1. Averaged wide-angle X-ray diffraction patterns from three siloxane-based liquid crystalline elastomers with varying mesogenic composition: 50% 5H/50% 5tB (solid line), 70% 5H/30% 5tB (dashed-dotted line) thick film, and 90% 5H/10% 5tB (dashed line). The inset represents the 2D X-ray diffraction pattern obtained from a stretched (stretching direction vertical) and fixed 90% 5H/10% 5tB elastomer, typical of all other stretched and fixed elastomers of varying composition, where the orientations both of the mesogens (▲) as well as of the siloxane backbone (△) are noticeable.

primary shape, the network loses its smectic ordering and becomes highly deformable. A secondary shape can then be adopted by the network, upon stretching or twisting, and subsequently fixed by cooling below the clearing transition (I-SmC). The latter secondary state is characterized by a highly ordered smectic-C structure apparently energetically stable and allowing shape retention over long times. The primary shape can, however, be recovered on demand by a second heating above the clearing transition, which allows for “melting” of the smectic-C phase and release of the deformed network toward its equilibrium configuration. Because the shape fixing and recovery are triggered by the clearing transition, control of this temperature via mixed-mesogen composition would allow tuning of properties for end-use applications. In the present case, for instance, a greater 5tB percentage within the network formulation systematically decreases T_{SI} , therefore making the corresponding elastomer suitable for new and subambient applications. Indeed, $T_{SI} \approx 37$ °C for body temperature triggering is possible.

To precisely characterize both shape fixing and shape recovery, dynamic mechanical analysis was used. The typical response of our smectic-C elastomers is given in Figure 2, where one can see the complete characterization of the shape memory cycle for the film composed of 70% 5H/30% 5tB in comparison to the response of a natural rubber that does not exhibit shape memory. Upon releasing of the force (“shape fixing step”), the smectic LCE retains its deformed shape (83.6%), while the natural rubber directly recovers its original, undeformed shape. The LCE recovers its original shape quite completely (99.1%) only as commanded by additional heating through the clearing transition. In comparison with classic SMPs under comparable strains, both shape fixing and recovery values attained by our LCEs are competitive. The main difference between classic SMPs¹⁰ and new shape memory smectic-C elastomers resides in their varying physical properties; indeed, while classic SMPs, such as polycyclooctene (PCO), exhibit relatively high modulus below the critical temperature, greater than 100 MPa,¹¹ our new shape memory LCEs (SMLCEs) still possess a rubbery structure even down to -120 °C with a modulus less than 20 MPa (Supporting Information).

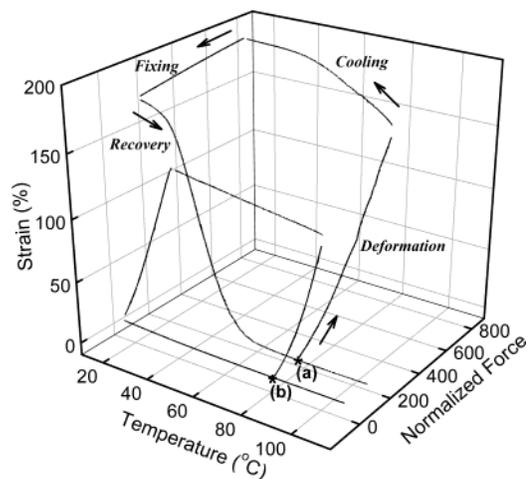


Figure 2. Shape memory cycle as measured by dynamic mechanical analysis for (a) a smectic-C elastomer (70% 5H–30% 5tB-HPDMS₇) and (b) natural rubber. The star indicates the start of the experiment (initial sample dimensions, temperature, and load), when both the LCE and the rubber are deformed under constant load at constant temperature. The deformation step is followed by a cooling step (2 °C/min) under constant load. At low temperature, the load is removed and the shape fixing is observed. Shape recovery of the primary equilibrium shape is obtained by heating (2 °C/min) through the clearing transition.

To our knowledge, the observed shape memory effect has never been reported before for any known liquid crystalline elastomer, whether side-chain, main-chain, nematic, smectic, or cholesteric. We expect numerous applications for such soft actuation, especially in the biomedical area where low modulus and low temperature shape memory materials are required.

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Supporting Information Available: A real time movie picturing the shape memory effect exhibited by our films as well as the dynamic mechanical analysis of one of our elastomers in conjunction with its thermal behavior; a more detailed description of the elastomer synthesis (PDF and MPG). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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