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Microstructure and Shape Memory of Main-Chain Liquid Crystalline Elastomers

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Main-chain liquid crystalline elastomers incorporate mesogens directly into the backbone of the network, and thus offer the potential for greater coupling between mesogen order and the network's macroscopic behavior than is possible with side-chain architectures. Polydomain main-chain liquid crystalline elastomers exhibiting a smectic-C phase were prepared by hydrosilylation chemistry in which diene mesogens were polymerized with hydride terminated poly(dimethylsiloxane) and crosslinked with a tetravinyl silane. Mechanical and calorimetric analyses showed that the networks have a glass transition and an isotropization temperature that are each controlled by the mesogen composition. In particular, changing the mesogenic composition in copolymer networks allowed the merging or separation of these transitions. Owing to the use of poly(dimethylsiloxane) spacers, the networks are "soft" and feature a tensile elastic modulus less than 10 MPa for temperatures as low as -70°C. Interestingly, the smectic-C LCEs revealed reversible contraction/elongation when thermally cycled around the clearing point, but excellent *one-way* shape memory response when thermally cycled around the constituent mesogen Tg. A combination of these effects occurs when clearing and vitrification are merged for particular compositions. The evolution of underlying microstructure during one-way shape memory fixing and recovery were studied in LCEs featuring merged transitions using ex-situ wide angle x-ray scattering. Not surprisingly, we found that the orientation of mesogens, siloxane chains, and smectic layers increased with increasing strain. Examination of the low-angle peaks, however, revealed a surprising result: the chevron arrangement of smectic layers transforms from a shallow pitch of 30° to a sharper, asymptotic pitch of 45° as strain increases. The reverse is observed during strain recovery, though with significant microstructural hysteresis. We exploit the unique combination of one-way shape memory behavior and softness by demonstrating reversible imprinting/erasure of micro-scale topographies on the elastomer's surface, yielding a new type of smart substrate with broad applicability.