Chromonic Liquid Crystal Hydrogels as Anisotropic, Active Biomaterials

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Purpose: Liquid crystal polymers have been widely studied as anisotropic soft actuators and are a prominent candidate for the development of artificial muscles. A salient property of these materials is that they can be processed using directed self-assembly, enabling the design of material properties.[1] For example, liquid crystal elastomers can be synthesized by directing the self-assembly of monomers using patterned surfaces and then crosslinking this ordered fluid to trap the molecular order into an elastic solid. This molecular order leads to highly anisotropic mechanical properties and in response to thermal or chemical stimuli, an anisotropic shape change. Liquid crystal elastomers are infrequently used as biomaterials due to their ill-suited intrinsic properties for biological applications. Not only are the monomers commonly hydrophobic, but these materials often require temperatures above ~60 °C to demonstrate significant actuation. Liquid crystalline hydrogels synthesized from water-soluble monomers would enable the use of patterned surfaces to order the molecular structure of biomaterials. In this work, we report on the synthesis and testing of anisotropic, mechanically-active hydrogels using the self-assembly of water-soluble, lyotropic chromonic liquid crystals (LCLC).

Materials & Methods: In this work, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) has been used to synthesize a polymerizable LCLC mesogen, an ionic dimethacrylate derivative of perylene-3,4,9,10-tetracarboxylic diimide (PDI). These monomers self-assemble into stacks that can be aligned using grooved surfaces. Anisotropic hydrogels were generated from photoinduced radical polymerization of these aligned chromonic reactive mesogens (PDI) in the nematic state with a comonomer, n-isopropylacrylamide. Shape change of these materials was quantified as a function of molecular alignment, in water between 20 °C and 50 °C with a thermal stage on a microscope.

Results: Liquid crystalline hydrogels are synthesized in the aligned nematic phase of the LCLC monomer. The swelling and deswelling of aligned hydrogels in water is anisotropic in nature. This anisotropic swelling enables materials to be designed that are capable of a wide variety of shape transformations. By copolymerizing n-isopropylacrylamide with the liquid crystalline monomers, the gels can be rendered thermally responsive. At the lower critical solution temperature of the gel, an anisotropic deswelling is observed. This deswelling is approximately 1.5 times larger along the nematic director than in the orthogonal directions and is reversible in nature (**Figure 1a**). The result is a uniaxially actuating gel. In order to pattern hydrogels that undergo shape transformations from flat to 3D in shape, gels with a twisted molecular orientation were synthesized. On deswelling, these materials exhibit a strain gradient through the thickness of the gel. If this twisted molecular structure is oriented at an angle to the long axis of a rectangular film, shear is induced, and twisting is observed. **Figure 1b** shows the deformation on heating of a flat "X" shape that morphs into two helices with opposite handedness. The suitability of these active materials as substrates for cellular growth and maturation was evaluated using primary embryonic neuronal cell culture. Neurons were found to attach and extend processes on the LCLC gels without surface modification. This neural maturation was found to be consistent with a control static material, polylysine coated polystyrene.

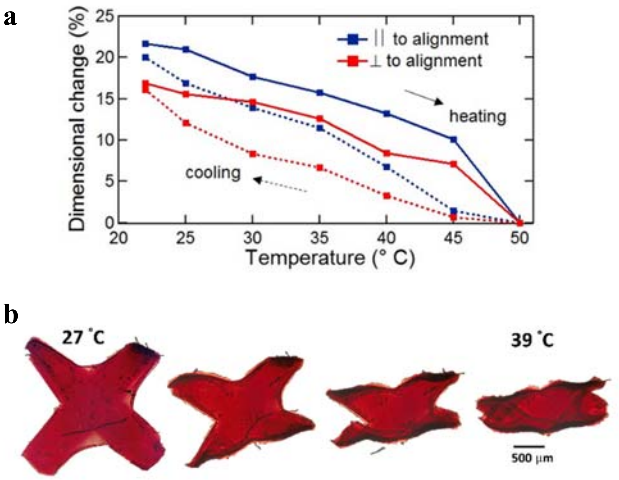

Figure 1. Dynamic shape change in LCLC hydrogels
(a) Dimensional change measured in a uniaxially aligned LCLC hydrogel upon heating and cooling in water (b) Shape change of micron-scale hydrogel actuator at physiologically relevant temperatures with molecular alignment twisted 90° through the thickness of the gel.

Conclusions: In this work, we have demonstrated that a new class of molecularly-ordered hydrogels can be synthesized from lyotropic chromonic liquid crystals. The salient feature of these materials is that the self-assembly of liquid crystals can be used to direct the properties of these biomaterials. Here we use this directed self-assembly to design gels with both uniaxial and twisted molecular alignment. The resulting gels are thermally-responsive and can be designed to undergo shape change from flat to 3D. These active materials may find application as biocompatible actuators for active surfaces or cell encapsulation. Ongoing efforts are exploring the effects of molecular orientation in hydrogels on cellular alignment and the self-assembly of these materials into active microparticles.

References: [1]White TJ. Nat Mat. 2015;14: 1087-1098