

Micro- and nano-structured LC networks towards responsive materials and nanoporous membranes

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In-situ photopolymerization of liquid crystalline (LC) monomers has proven to be a valuable technique for the formation of well-ordered polymer networks. Their anisotropic properties led to a variety of applications in optics, electronics and mechanics. The use of light to initiate polymerization enables lithographic approaches for patterning. The LC behaviour enables formation of complex morphologies on molecular level, especially when combined with surface boundary conditions, chirality and polymerization-induced diffusion. The combination of top-down lithography with bottom-up self-organization accommodates a wealth of applications that even are not fully explored yet. Polymerization initiated by means of a dichroic photoinitiator provides an additional degree of freedom in controlling the structure of the LC network. The photoinitiator adapts the director profile of the LC monomer. As a result planar oriented areas aligned orthogonal to the light beam polymerize faster than the parallel ones. Similarly, planar aligned areas with their orientation parallel to the electrical field vector of the light polymerize faster than the planar aligned areas oriented perpendicular to that. Based on this principle complex lithographic structures are built, not only forming structures in the plane of the polymerizing film but also in the third dimension along its cross-section. Controlling the director profile of a liquid crystal network film in transversal direction gives a mechanical bending deformation upon minor changes in order parameter. Examples of suited profiles of molecular orientation are twisted or splayed director configurations tied up in the network configuration. Reversible order parameter changes can be induced by a variety of means. It can be simply induced by temperature changes resulting in gradients in thermal expansion over the cross-section of the film. But more sophisticated and of interest for applications is a light induced change as a result of the E-Z isomerization of a built-in azo group.

Agent-responsive actuators can be made by H-bridged crosslinks. Rather than composing the monomers of covalent bonds alone, one can choose to replace some bonds by secondary interactions such as hydrogen bridges. We have chosen to apply the H-bridge based dimerization of benzoic acid to form nematic liquid crystal acrylate monomers. After the formation of the polymer network the H-bridges are broken when brought in contact with alkaline solutions. In order to give the structure shape memory and mechanical integrity we have copolymerized the hydrogen bridged monomers with fully covalent diacrylate monomers. In the paper we will demonstrate that by a controlled and reversible rupture of the hydrogen bridges mechanical responses can be initiated. This becomes of especial interest if this is combined with special director profiles such as twist or splay. These well-ordered polyelectrolyte network exhibit a repeated bending motion activated by pH changes or by water uptake. Localized photopolymerization of smectic LC monomers lock in structures of different length scales. The first length scale is the resolution of lithography, and goes down to a few micrometers. The second length scale is set by the spacing of smectic layers and is typically a few nanometers. The third length scale is the intermolecular distance in the layers, usually around 0.4 nm. By modifying the smectic molecules also with H-bridges the smectic periodicity can break-up into separated layers with a well-defined spacing, often also in the nanometer range. The nanopores form by breaking the H-bridges at elevated temperatures or by contact with an alkaline solution. Also here the integrity of the film is maintained by copolymerizing with fully covalent smectic crosslinkers.