

# Liquid crystal networks and self-organizing hydrogels: nanotechnology towards soft actuators and nanoporous systems

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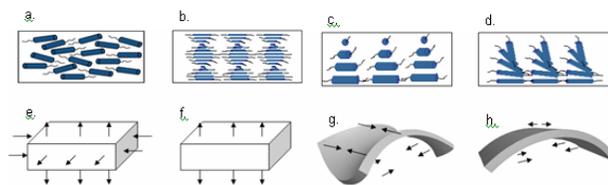
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## Introduction

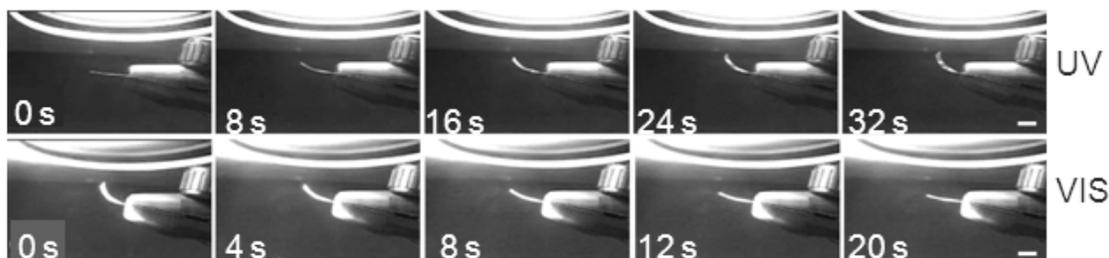
In-situ photopolymerization of polyfunctional liquid crystalline monomers has proven to be a valuable technique for the formation of highly ordered polymer networks.<sup>1</sup> Their anisotropic properties have lead to a variety of applications in optics<sup>2,3</sup>, electronics<sup>4</sup> and mechanics<sup>5</sup>. The use of light to initiate the polymerization process enables lithographic approaches to structure the polymers<sup>6</sup>. The liquid crystalline behavior of the monomers enables the formation of complex morphologies on a molecular level, especially if combined with special surface boundary conditions, surfactants, chirality and polymerization-induced diffusion processes.<sup>7</sup> This combination of photolithography (top-down) with self-organizing structuring (bottom-up) accommodates a wealth of applications that even are not fully explored yet. By adding additional functional moieties to the reactive mesogens, such as light-responsive azo moieties or reversibly-breakable hydrogen bridges, the application field can even be extended. Some of these new potential applications, i.e. the soft actuators responding to heat, light of chemical changes and the nano-sculptured porous membranes, will be discussed in this paper.

## Results and Discussion

Liquid crystal networks may undergo mechanical deformation, expansion or contraction, under the action of an external stimulus where the directionality and the extent of the deformation depends on their average (local) molecular orientation. For densely crosslinked networks the mechanical deformation in general originates from small reversible changes of the order parameter. Examples of molecular orientation profiles and their responses as caused by a change of the order parameter are shown in Figure 1. Especially the twisted or splayed director configurations, tied up in the network configuration, are useful actuation modes resulting in mechanical bending deformation [5]. This can for instance lead to expansion at one side and shrinkage at the opposite side of the thin film. 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 which affects the order in neighboring rod-like crosslinks [7]. An example is shown of a splayed LC network containing azo groups which is subsequently exposed by a UV lamp (365 nm) and a visible light source.

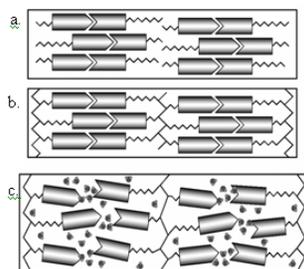


**Figure 1.** Schematic representation of various molecular orderings, planar uniaxial (a.), cholesteric (b.), twisted nematic (TN) (c.) and splay (d.), with their corresponding deformations (e. – h.) upon a decrease of molecular order.

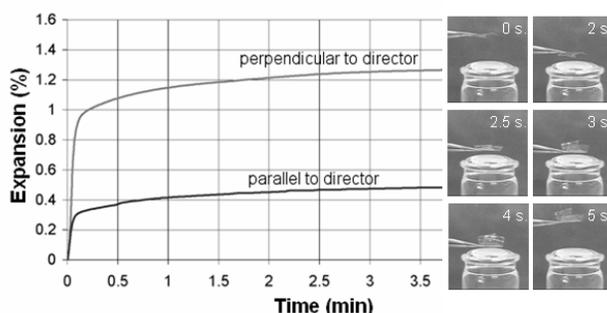


**Figure 2.** Deformation of a beam made of a splayed nematic network containing 5 wt-% of an azo crosslinker while being exposed by a UV and a visible light source respectively.

Agent-responsive actuators can be made by hydrogen-bridged crosslinks in the LC network such that an ordered hydrogel is formed. Rather than composing the monomers, that form an LC network, of covalent bonds alone, one can choose to replace some bonds by secondary interactions such as hydrogen bridges. In fact early work of Strzelecki [8] was already based on hydrogen bridge nematogens, although at that time not further explored towards applications. Later the Kato group elaborated further on this [9]. We have chosen to apply the hydrogen-bridge based dimerization of benzoic acid to form nematic liquid crystal acrylate monomers. They can be in-situ polymerized as described above, during which the nematic order is maintained. But after the formation of the polymer network the hydrogen bridges can be broken when brought in contact with alkaline materials. The principle is schematically shown in Figure 3. In order to give the structure shape memory and mechanical integrity we have copolymerized the hydrogen bridge monomers with fully covalent diacrylate monomers. Here we 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 as created by the above described bottom-up technologies. These well-ordered polyelectrolyte network exhibit a repeated bending motion activated by pH changes or by water uptake (Figure 4).<sup>10,11</sup>



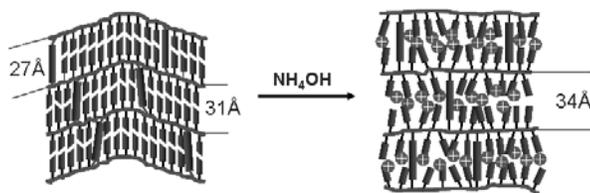
**Figure 3.** Formation of hydrogen-bridged liquid crystal network from monomer dimers (a). Dimers are based on benzoic acid provided with acrylate groups for polymerization. The hydrogen bridges in the network (b) can be broken at  $\text{pH} > \text{pK}_a$  of the benzoic acid in the network. This reduces the order of the network and causing macroscopic anisotropic swelling (c).



**Figure 4.** Degree of swelling of a network of acryloyloxy alkyloxy benzoic acid crosslinked with 12 wt% nematic diacrylate after been activated by a KOH dip (left) and the film with a twisted nematic director configuration being brought towards the meniscus of a water surface (right).

A completely new class of LC networks is formed when the hydrogen bridged benzoic acid monomers are polymerized in their smectic state. In the smectic networks the hydrogen bridges are organized in planes in between the layers of the two-dimensional acrylate networks. Also here the hydrogen bridge layers can be broken up by rupture of the hydrogen bonds by high-pH treatment as shown by X-ray diffraction. The pores that are formed can be controlled in size by the amount and size of copolymerized fully-covalent liquid crystal diacrylate.

Figure 5 shows schematically the network that is formed during polymerization of acryloyloxy hexyloxy benzoic acid in its smectic state in the presence of 5 wt% of a smectic diacrylate. It appeared from X-ray diffraction that the average molecular orientation is tilted to the layer planes and that the layer periodicity of the smectic network is equal to the average molecular length before polymerization but becomes smaller during polymerization. The tilted structure is frozen in by polymerization but converted to a more planar configuration when the hydrogen bonds are broken by a dip in ammonia. The periodicity increases with 0.3 nm giving a small degree of swelling parallel to the director but a large degree of swelling perpendicular to that.



**Figure 5.** Schematic representation of the rupture of a hydrogen bonded smectic network under high pH condition leading to sub-nanometer porous channels.

Experiments with the uptake of pH sensitive dyes demonstrated the still somewhat acidic environment inside the sub-nanometer porous channels that are formed during the formation of the ammonia salts. It is of further interest that the pore size can be enlarged by complexing the carboxylic acid group of benzoic acid monomers with di-pyridine compounds. Also these complexes can be polymerized in their smectic states providing networks of which the di-pyridine segments can be removed by solvent treatment or evaporation.

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