

Photoresponsive Liquid Crystalline Elastomers

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Literature Seminar

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Liquid crystals (LCs) are a special class of materials that exhibit liquid-like behavior as well as long-range crystalline order of the solute molecules.¹ Incorporating rigid, shape-anisotropic molecules, also known as mesogens, into polymeric systems results in macromolecular compounds that couple physical properties of polymers to unique optical properties of LCs. These liquid crystalline polymers (LCPs) show interesting optical properties that depend on the average orientation of the anisotropic or chiral mesogens. The three main types of LCPs describe the location of their mesogen relative to the polymer. They include main chain, side chain and elastomers.² Of particular interest are elastomers that are crosslinked to enhance rubber elasticity, enabling a “memory” effect in the resulting polymer.^{1,3,4}

The application of internal stresses by either physical or thermal means results in a change of orientation of the mesogens. This ultimately changes the optical and/or physical properties of the material. It was discovered that these internal stresses could also be induced by optical means.⁵ Photochromic molecules such as spiroopyrans,⁶ azobenzenes,^{7,8} fulgides,⁹ and diarylethylenes¹⁰ change structure when irradiated with a particular wavelength of light. The change in molecular structure of these compounds results in applied stresses whether they are incorporated into the polymer backbone or simply dissolved in the polymer matrix. Hence, these molecules are well suited for practical application in photoresponsive polymer systems.

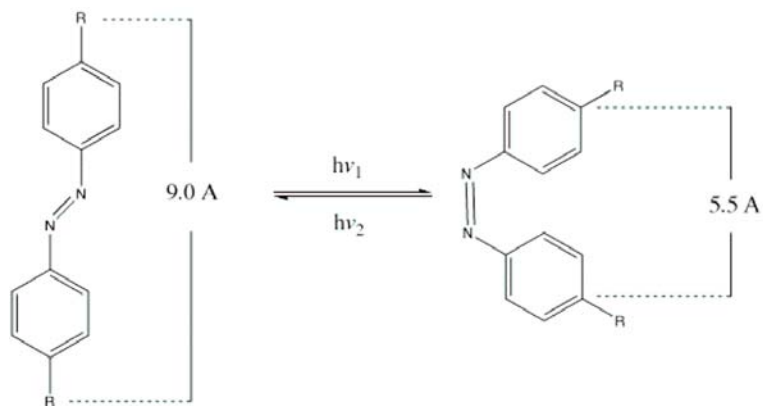


Figure 1: Isomerization of azobenzenes induces mechanical strain. $h\nu_1$ and $h\nu_2$ are typically 350-380 nm and 450 nm respectively.⁵

Early reports of photoresponsive polymers used azobenzene moieties. This was due to its large mechanic response from the cis-trans isomerization of the N=N bond (Figure 1), the large quantum yield for this isomerization (ca. 0.2-0.3) as well as its high thermal stability. First, Agolini and Gay⁷ reported a polyimide-azobenzene film. After exposure to polarized UV light and 200°C, the 500 nm thick films were reversibly deformed by 0.23%. Eisenbach⁵ reported application of azobenzenes in isotropic

elastomeric networks using both a main chain azobenzene monomer and varying concentrations of an azo-aromatic crosslinker. Rubbed films ranging from 0.15-0.5 mm thick were irradiated at 372 nm yielding reversible deformations up to 0.25%.

Azobenzene moieties are particularly useful due to their dual function as a mesogen and photochromic functionality. However, their ability to induce large (>5%) changes in bulk material seems strongly dependent on the LC phase incorporation in the polymer matrix. Work by Finkelmann and Nishikawa was the first to show that a mesogenic side chain from a poly[oxy(methylsilylene)] backbone can exhibit optically induced reversible contractions on the order of 20%.¹¹ This single domain nematic elastomer is formed using a two stage cross-linking in which the second cross-linking step incorporates the photoresponsive azobenzene.

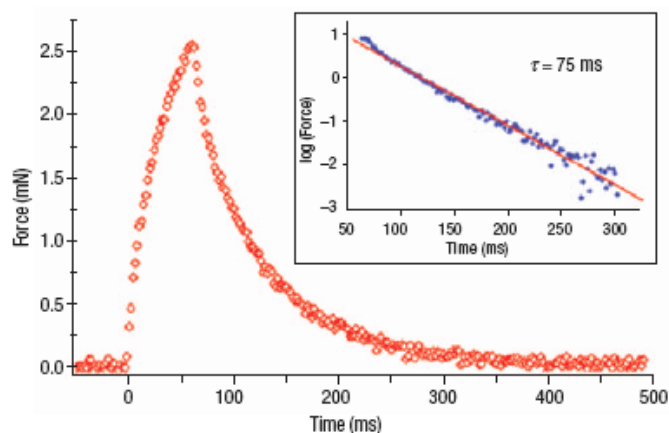


Figure 2: Force plot of LCE before and after 60ms illumination. Inset is logarithm of force measured during relaxation to resting state.¹²

Although large macroscopic contractions have been successfully demonstrated, previously reported networks do so only over long time scales (ca. 60 min). For most applications (ie: optical actuators, artificial muscles, optical data storage) much faster responses are required. Recent work focuses on networks with response times less than 20 s. For example, the polysiloxane LCE formed with a tri-functional cross-linking agent reported by Palffy-Muhoray et al.¹² uses Disperse Orange azo dye dissolved in the network. The resulting 0.32 mm thick films exhibited remarkable response times (20 ms at 600 mW) when irradiated with 512 nm light from an Ar ion laser. Another example of comparatively fast response times is the all azobenzene networks developed by Ikeda et al.¹³ Assuming that only the surface azobenzene moieties are isomerizing, 10 μ m thick films were irradiated at 360 nm (3 mW cm⁻²) and reached a maximum response in 20 s.

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