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Azophenol-Based Liquid−crystalline Elastomers for Light-Driven Actuators

Jaume Garcia-Amorós,[†] Alexandra Piñol,[†] Heino Finkelmann,[‡] and Dolores Velasco*,[†]

Grup de Materials Orgànics, Institut de Nanociència i Nanotecnologia, Departament de Química Orgànica, Universitat de Barcelona, Martí i Franqués 1-11, E-08028, Barcelona, Spain, and Institut für Makromolekulare Chemie, Hermann-Staudinger Haus, Albert-Ludwigs Universität, Stefan-Meier Strasse 31, D-79104 Freiburg im Breisgau, Germany

dvelasco@ub.edu

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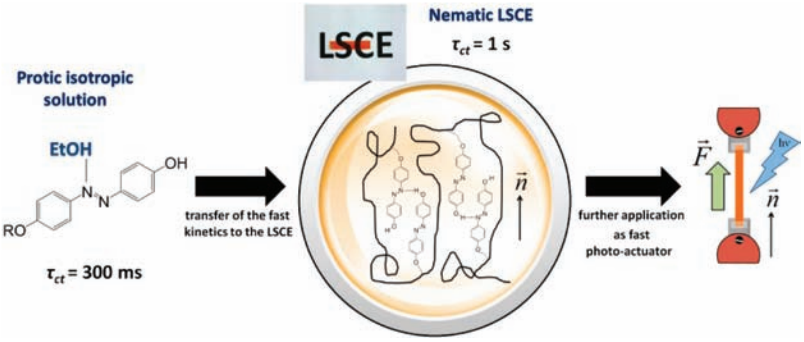
ABSTRACT



Para-substituted azophenols exhibit a fast thermal *cis*-to-*trans* isomerization rate in ethanol, which can be transferred to the solid state by obtaining liquid−crystalline elastomeric systems. The absence of protic solvent is compensated by the establishment of hydrogen bonding between azophenol monomers that are close to each other. Opto-mechanical experiments reveal that azophenol-containing liquid single-crystal elastomers are valuable materials for light-controlled actuators exhibiting relaxation times of 1 s at room temperature.

Liquid single-crystal elastomers (LSCEs) combine both molecular orientational order and rubber elasticity.[1] As a result of this coupling, they undergo large shape changes under appropriate external inputs such as heat or light. The introduction of azobenzenes as chromophores in LSCEs offers a wireless and clean way to modify the macroscopic dimensions of the probe by applying light of the appropriate wavelength. This feature makes azobenzene-based LSCEs valuable materials for light-controlled actuators.[2] To the best of our knowledge, few photoactive LSCEs that are able to thermally relax back quickly have been reported.[3] Thus, obtaining them is currently a challenging point of study.

The proper chemical substitution of the azo-dye allows tuning the response time of photoactuators. Hydroxyazobenzenes exhibit relaxation times for their thermal *cis*-to-*trans* isomerization process ranging from 6 to 300 ms in ethanol at 298 K depending on the placement of the phenol groups.[4] Their good solubility in nematic liquid crystals as well as their easy structural design to be subsequently anchored to a polysiloxane backbone makes them suitable

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[†] Universitat de Barcelona.

[‡] Albert-Ludwigs Universität.

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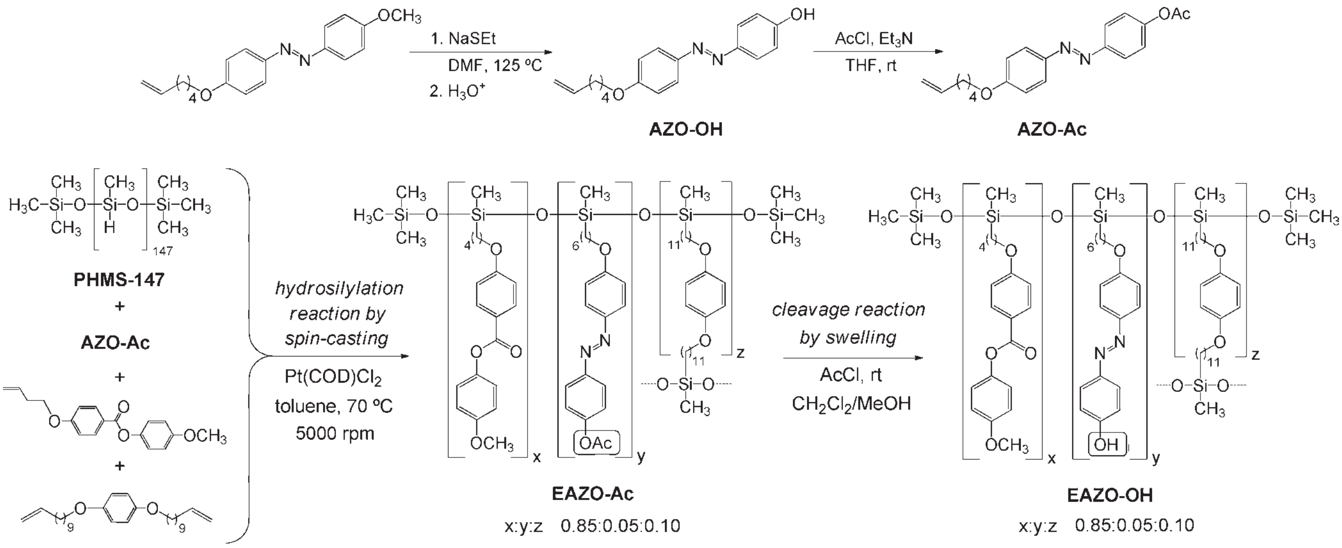
Scheme 1. Synthesis of the Azomonomers **AZO-Ac** and **AZO-OH** and of the Photoactive Nematic LSCEs **EAZO-Ac** and **EAZO-OH**



target molecules for obtaining fast photosensitive actuators.

The main drawback of using azophenols is that they exhibit rapid isomerization rates when dissolved in alcoholic solutions. Otherwise, their relaxation time increases to the time scale of minutes in nonprotic solvents, such as toluene.[4] But, how to introduce protons in a thin solid network without destroying the nematic order? The strategy reported herein consists in the preparation of a coelastomer where hydrogen bonding between the azophenolic monomers can be established without modifying the liquid-crystalline properties of the network. As a result of this interaction, the resulting photoactuator, which contains the free hydroxyl group on its structure, exhibits a thermal isomerization rate almost as fast as that of the azomonomer dissolved in ethanol making it one of the fastest reported actuators so far.

4-(5-Hexenyloxy)-4′-hydroxyazobenzene (**AZO-OH**) was synthesized from 4-(5-hexenyloxy)-4′-methoxyazobenzene by cleaving its methyl ether with NaSEt in DMF at 125 °C.[5] **AZO-OH** was further acetylated with AcCl in THF at room temperature in the presence of Et_3N furnishing 4-acetyl-4′-(5-hexenyloxy)azobenzene (**AZO-Ac**, Scheme 1).

Two different liquid single-crystal elastomers, **EAZO-Ac** and **EAZO-OH**, were prepared in order to compare the influence of phenolic group in the opto-mechanical properties of the final photoactuator.

The uniaxially oriented acetylated elastomer **EAZO-Ac** was prepared following the well-known spin-casting technique in two steps developed by Küpfer et al.[6] The preparation of **EAZO-Ac** was carried out by means of the well-known $Pt(COD)Cl_2$-catalyzed hydrosilylation reaction between the different monomers, which contain a terminal reactive alkene, and the polyhydromethylsiloxane (**PHMS-147**) (Scheme 1).[7] **EAZO-Ac** contained only a small proportion of the azo moiety (5% mol) in order to not overly disrupt the nematic order of the elastomer.

For preparing elastomer **EAZO-OH**, the acetylated elastomer **EAZO-Ac** was swollen in a mixture of CH_2Cl_2 and MeOH (2:1 v/v) with one drop of AcCl at room temperature.[8] Acetyl chloride presumably enters the network by diffusion producing a mild and chemoselective cleavage of the ester group of the acetylated pendant group, **AZO-Ac**. The evolution of the cleavage reaction was nicely followed by ATR FT-IR spectroscopy (Figure 1). The disappearance of the C=O stretching signal at 1765 cm^{-1} and the appearance of a small band corresponding to the O−H stretching at 3425 cm^{-1} was observed. No hydrolysis

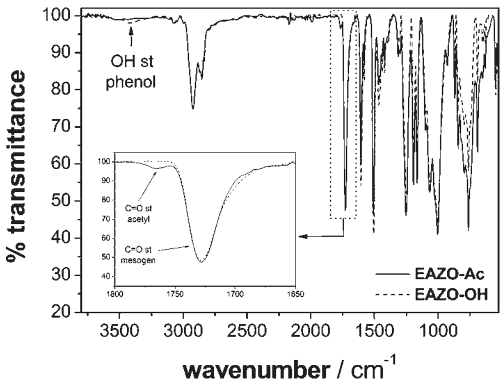


Figure 1. ATR FT-IR spectra for the LSCEs **EAZO-Ac** and **EAZO-OH**. Inset: evolution of the C=O stretching bands during the cleavage reaction.

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of the other ester group placed in the mesogen was observed (C═O stretching band at 1730 cm^{-1}, Figure 1). The elastomer was kept swollen in acetone to remove the catalyst, and next, *n*-hexane was dropped in the acetone solution in order to deswell the elastomer. Finally, the sample was carefully removed from the solution and hung in an oven with a residual load in order to dry it without modifying the induced anisotropy during the first step of the synthesis.

DSC experiments showed that both elastomers exhibited a broad nematic phase between their glass transition temperature at T_g = 277−278 K and their nematic-to-isotropic phase transition temperature at T_{N-I} = 335−336 K. XRD pattern of both elastomers showed two equatorial maxima placed in the wide-angle regime (Figure 2, inset), indicating that the networks obtained were uniaxially oriented along the director, ***n***. From the azimuthal integration of the wide-angle reflexes, the orientational order parameter of the mesogenic units, *S*, was calculated to be 0.71 and 0.69 for **EAZO-Ac** and **EAZO-OH**, respectively. The effective cross-linking density of both LSCEs was analyzed by means of swelling experiments. The swelling ratio, *q*, was calcultated as $q = \alpha_{\|}\alpha_{\perp}^2$, where $\alpha_{\|}$ and $\alpha_{\perp}$ are the ratios between the dimensions in the deswollen liquid-crystalline state and in the swollen isotropic state in toluene in the different directions with respect to the nematic director. The swelling ratio was determined to be 5.0 and 3.3 for **EAZO-Ac** and **EAZO-OH**, respectively. The lower *q* value found for **EAZO-OH** evidences the hydrogen bonding established between the phenol groups of the azo-dyes, which act as additional cross-linking units. Thermo-mechanical experiments provide information about the coupling between the nematic order and the macroscopic dimensions of the sample. The uniaxial thermal expansion in both directions parallel ($\lambda_{\|} = L/L_{iso}$) and perpendicular ($\lambda_{\perp} = 1/\lambda_{\|}^{1/2}$) to the nematic director were determined for both networks (Figure 2).[9] The two networks increased their length up to 59% along the director at T_{red} = 0.90 ($T_{red} = T/T_{N-I}$), which was accompanied with a contraction up to 21% in the direction perpendicular to ***n*** on cooling from the isotropic state to the nematic one. Both thermo-mechanical and X-ray scattering experiments clearly indicate that no change in the degree of order of the LSCE occurred during the cleavage reaction.

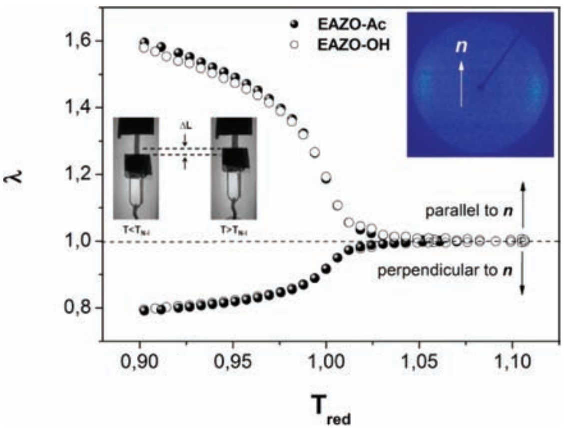

Figure 2. Thermo-mechanical experiments: uniaxial thermal expansion, λ, in both directions parallel and perpendicular to the director for **EAZO-Ac** and **EAZO-OH**. Inset: X-ray diffraction pattern for **EAZO-OH** at 298 K.

The thermal *cis*-to-*trans* isomerization process for both azomonomers, **AZO-Ac** and **AZO-OH**, was studied in ethanol and toluene isotropic solutions. *cis*-**AZO-Ac** exhibited a very slow thermal isomerization kinetics, presenting relaxation times, τ, of more than a day in both solvents at 298 K (Table 1). A dramatic acceleration of the thermal isomerization kinetics was observed for *cis*-**AZO-OH** in ethanol up to 311 ms because of a change in the isomerization mechanism from inversion to rotation. In ethanol, the reaction proceeds by a first solvent-assisted tautomerisation to a phenylhydrazone-type intermediate with a subsequent rotation around the N−N bond.[4] Otherwise, the thermal relaxation time of **AZO-OH** increased more than 3 orders of magnitude up to 23 min when it was dissolved in toluene; **AZO-OH** isomerizes through the inversional mechanism in this solvent.

Table 1. Relaxation Time, τ (τ = 1/*k*), of the Thermal *Cis*-to-*Trans* Isomerization Process for the Azomonomers **AZO-Ac** and **AZO−OH** and for the LSCEs **EAZO-Ac** and **EAZO-OH** at 298 K

	solvent	τ/h		solvent	τ/ms
AZO-Ac	ethanol	49	**AZO-OH**	ethanol	311
	toluene	35		toluene	1.4×10^6
EAZO-Ac	nematic	21	**EAZO-OH**	nematic	1000

The mechanical response generated by both elastomers under UV-illumination as well as their response time were tested by means of opto-mechanical experiments. Both LSCEs, **EAZO-Ac** and **EAZO-OH**, can act as light-controlled actuators when they are irradiated with UV light (λ = 380 nm). The azo-dye isomerizes changing its geometry from linear to bent producing a decrease in the local order parameter.[10] This feature causes a shortening of the LSCE in the director direction. If the network is fixed at both ends, the system cannot shrink and the appearance of a retractive force in the elastomer is observed.

Figure 3 shows the evolution of the internal stress generated inside both LSCEs, **EAZO-Ac** and **EAZO-OH**, with time at 323 and 298 K, respectively. On turning on the UV light, the internal stress, σ, grows until the photostationary state is reached. The curve describes a *plateau* which corresponds to the maximum response produced by the photoactuator, $\Delta\sigma_{max} = \sigma_{max} - \sigma_0$.

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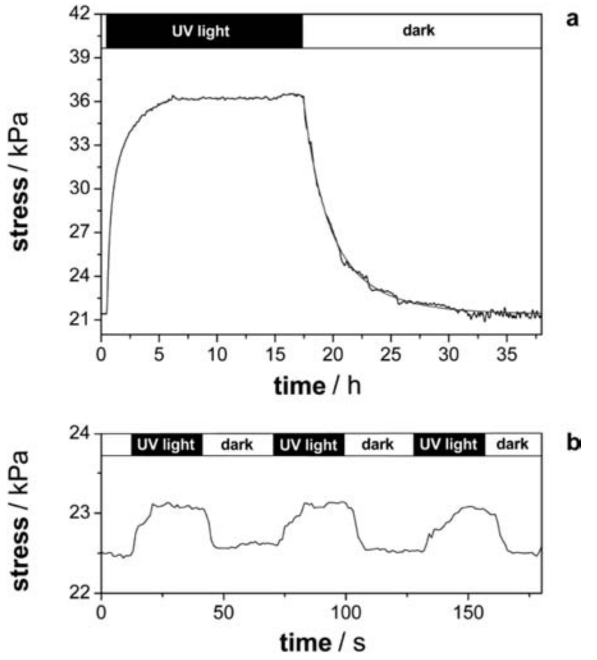

Figure 3. Opto-mechanical experiment for **EAZO-Ac** at 323 K (a) and for **EAZO-OH** at 298 K (b) with UV light of 212 mW·cm^{-2}.

EAZO-Ac produced a maximum opto-mechanical response of $\Delta\sigma_{max}$ = 15 kPa at 323 K (Figure 3a), which can be increased by lowering the temperature. In addition, when the same experiment was carried out at 298 K for the elastomer **EAZO-OH**, a maximum opto-mechanical response of $\Delta\sigma_{\max}$ = 0.6 kPa was obtained (Figure 3b).

The thermal *cis*-to-*trans* relaxation of the network in the dark is described by a first-order monoexponential decay (eq 1).[2a,9]

$$\sigma_t - \sigma_0 = \Delta\sigma_{\max} e^{-t/\tau} \tag{1}$$

Due to the very slow thermal relaxation of elastomer **EAZO-Ac**, its opto-mechanical experiments were carried out at high temperatures. **EAZO-Ac** exhibited a relaxation time for its thermal back reaction of τ = 21.3 h at room temperature, which was determined by extrapollation of the corresponding Eyring plot (see the Supporting Information). Opto-mechanical experiments also revealed a completely different kinetic behavior between both photoactuators. While **EAZO-Ac** presented a relaxation time of almost 1 day, **EAZO-OH** gave a value of only 1 s at room temperature (Table 1). The fast thermal relaxation exhibited by **EAZO-OH** evidence again the establishment of hydrogen bonding between the different phenol groups. This interaction indicates that the azo-dye isomerization takes place through the rotational mechanism.

The low mechanical response registered for the free-phenol-containing elastomer **EAZO-OH** in comparison with that of **EAZO-Ac** is associated to the low proportion of *cis* isomer present when **EAZO-OH** reaches the photoequilibrium state at 298 K due to the fast thermal relaxation of the *cis*-**AZO-OH** moiety. Moreover, higher mechanical responses are expected for **EAZO-OH** when working with a more powerful light source.

In summary, when azophenol monomers are bonded as pendant groups to liquid-crystalline siloxane-based polymers, they can interact efficiently with each other through intermolecular hydrogen bonding even without the presence of any protic solvent. This feature produces the fast thermal isomerization of the azo-dye in the LSCE. Thus, the fast isomerization observed in the azo monomers in alcoholic solutions can be easily transferred to the solid rubber state. The introduction of *p*-hydroxyazobenzenes as photoactive side-on comonomers in LSCEs reveals a relaxation time for the thermal *cis*-to-*trans* isomerization of the network of 1 s at room temperature. Accordingly, the introduction of azophenols in nematic liquid-crystalline elastomers leads to obtaining stable photoactuators with low response times.

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Supporting Information Available. Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.