

Supporting Information

Exploring optical mechanotransduction in fluorescent liquid crystal elastomers

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Preparation of the monomers. 4-methoxyphenyl-4-(3-butenyloxy)benzoate (**M4OMe**), 1,4-di-(10-undecenyl)benzene (**CL**), 9-(2-propenyl)-9*H*-carbazole (**CBZ-3**) 9-(5-hexenyl)-9*H*-carbazole (**CBZ-6**) and 9-(10-undecenyl)-9*H*-carbazole (**CBZ-11**) were prepared as reported elsewhere.^[1-2] *N*-vinylcarbazole (**CBZ-2**) was purchased from Aldrich and used as received without further purification.

Preparation of the liquid single crystal elastomers ECBZ-2 – ECBZ-11. **M4OMe** (80 % mol), **CL** (5 % mol), **CBZ-X** (10 % mol) and polyhydrogenomethylsiloxane (~147 Si-H groups per chain) were dissolved in dry thiophene-free toluene (2 mL). Then, a solution of cyclooctadieneplatinum (II) chloride in dry dichloromethane (1 %, 20 μ L) was added. The reaction mixture was placed in a spinning Teflon mould and heated up to 70 °C for 2 hours at 5000 rpm. Afterwards, the mould was cooled to room temperature and the elastomer (not totally cross-linked) was carefully removed from the wall. After that, a uniaxial stress along the polymer chains was applied to align the mesogenic molecules during the deswelling process. In order to fix this orientation, the cross-linking reaction was completed by leaving the sample under load in the oven at 70 °C for 2 days. The non-reacted monomers were removed from the network by a swelling-deswelling process using toluene and hexane, respectively.

Characterization of the elastomers. Phase transformation temperatures (T_g and T_{N-I}) as well as the associated thermodynamic parameters (ΔC_p and ΔH_{N-I}) were determined by means of Differential Scanning Calorimetry (DSC). DSC measurements were performed in a Mettler Toledo DSC-822e/400 apparatus under a nitrogen atmosphere at a scan rate of 5 K min⁻¹. The qualitative analysis of the macroscopic orientation of the nematic director, \mathbf{n} , along the elastomeric sample was realized by means of polarized optical microscopy (POM). POM was carried out at room temperature using a Nikon Eclipse polarizing microscope. POM experiments were run by rotation of the analyzer of the microscope with respect to the longest axis of the elastomeric sample. The macroscopic orientation of the nematic director, \mathbf{n} , along the elastomeric sample was analysed by means of X-Ray diffractometry (XRD). XRD measurements were carried out with the monochromatic Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), using a two-dimensional image plate system as detector. The incident beam was normal to the surface of the elastomer. XRD experiments were realized at room temperature. The effective cross-linking density of the networks was estimated by means of swelling experiments. The dimensions of the

network in the deswollen and swollen state in toluene were measured at room temperature with a graduated magnifying glass. The swelling ratio was calculated as $q = \alpha_{//} \times \alpha_{\perp}$ (where $\alpha_{//}$ and α_{\perp} are the ratios between the dimensions in the deswollen liquid-crystalline state and in the swollen isotropic state in the different directions with respect to the nematic director, \mathbf{n}). In the stress–strain measurements, a monodomain elastomer was stretched along its optical axis at a constant temperature ($T = 298$ K). Stress-strain measurements were performed using a Zwick/Roell Z100Allround instrument with a 10 N load cell. Young's moduli (E) were determined from the initial slope of the stress–strain curves at small stress values.

Fluorescence spectroscopy and mechanofluorescent experiments. Fluorescence spectroscopy and all mechanofluorescent experiments were performed in a PTI 810 fluorimeter at 298 K. Excitation and emission spectra were collected by fixing the emission and excitation wavelength at $\lambda_{Em} = 350$ nm and $\lambda_{Ex} = 290$ nm, respectively. All mechanofluorescent experiments were carried out by fixing the elastomeric sample by both ends to a homemade measurement cell and further applying a uniaxial deformation along the director direction of the elastomeric material stepwise. After deformation, the elastomeric sample was left to equilibrate for 10 minutes prior to the spectrum collection. In all instances, carbazole fluorophores were excited at a λ_{Ex} of 290 nm, with light polarized parallel to the longest axis of the elastomeric material placing a Glan Thompson polarizer between the light source and the sample; the resulting luminescence was collected at $\lambda_{Em} = 350$ nm. Time-resolved mechanofluorescent experiments were performed by applying a constant force of $F = 75$ mN to a previously-equilibrated elastomeric material and collecting its fluorescence intensity at $\lambda_{Em} = 350$ nm over time.

[1] Gray, G. W.; Jones, B. *J. Chem. Soc.* **1953**, 4179–4180.

[2] Taraneekar, P.; Baba, A.; Park, J. Y.; Fulghum, T. M.; Advincula, R. *Adv. Funct. Mater.* **2006**, *16*, 2000–2007.