Electronic Supplementary information

Photoactuation and thermal isomerisation mechanism of cyanoazobenzene-based liquid crystal elastomers

Jaume Garcia-Amorós[1], Manuel Martínez[2], Heino Finkelmann[3] and Dolores Velasco[1,*]

[1]*Grup de Materials Orgànics, Institut de Nanociència i Nanotecnologia (IN²UB), Departament de Química Orgànica, Universitat de Barcelona, Martí i Franquès 1, E-08028, Barcelona, Spain.*

[2]*Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès, 1-11, E-08028, Barcelona, Spain.*

[3]*Albert-Ludwigs-Universität Freiburg, Institut für Makromolekulare Chemie, Hermann-Staudinger-Haus, Stefan-Meier-Straße 31, D-79104 Freiburg, Germany*

Materials and general instrumentation

All reagents for synthesis were used as received without further purification. DMF (Fluka) was stored over activated 4Å molecular sieves under inert atmosphere. Flash chromatography was carried out over silica gel (SDS, 230-240 mesh). Melting points were determined by polarized optical microscopy (POM) using a Nikon Eclipse polarizing microscope equipped with a Linkam THMS 600 hot stage and a Linkam CI 93 programmable temperature controller at a scan rate of 5 ºC·min^{-1}. FT-IR spectra were registered in a Nicolet 510 FT-IR spectrophotometer from Thermo Scientific. Electronic spectra were recorded in a Varian Cary 500E UV-Vis-NIR spectrophotometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were collected on a Varian Gemini spectrophotometer. NMR spectra have been processed with the MestRec commercially available software. HRMS was performed in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray (ESI-MS) technique.

Synthesis of the azo monomer AZO-CN

4-cyanoazophenol (500 mg) and NaH (197 mg, 60 % dispersion in mineral oil) were dissolved in anhydrous DMF (15 cm^3) under inert atmosphere. The reaction mixture was heated up to 150 ºC and then, a solution of 6-bromo-1-hexene (365 mg) in anhydrous DMF (2 cm^3) was added. The reaction was stirred at 150 ºC for 24 hours. After, the reaction was cooled to room temperature and diluted with water. The product was extracted with CH_2Cl_2. The combined organic extract was washed several times with water, dried over anhydrous sodium suphate, filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using CH_2Cl_2 as eluent. **AZO-CN** was obtained as a yellow solid

(Yield = 52 %). **m.p.** (POM): 102-103 ºC. **IR** (KBr) *v* 3081 (C^{sp2}-H st); 2939 (C^{sp3}-H st); 2220 (CN st); 1597 (ar C-C st); 1250 (C-O-C st); 844 (C-O-C st) cm^{-1}. **UV-vis** (ethanol): λ_{max} = 364 nm (ε = 28 530 M^{-1} cm^{-1}). **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.62 (2H, m), 1.84 (2H, m), 2.15 (2H, m), 4.07 (2H, t, J = 6.3 Hz), 4.90-5.00 (2H, m), 5.84 (1H, m), 7.02 (2H, d, J = 8.8 Hz), 7.78 (2H, d, J = 8.8 Hz), 7.94 (4H, 2 × d, J = 8.8 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 25.3, 28.6, 33.4, 68.2, 113.1, 114.8 (3C), 118.6, 123.0 (2C), 125.4 (2C), 133.1 (2C), 138.3, 146.6, 154.7, 162.6 ppm. **HRMS** (ESI-MS): *m*/*z* calcd. for $C_{19}H_{20}N_3O$ [MH^+] 306.1606; found 306.1602 [MH^+].

X-Ray diffractometry

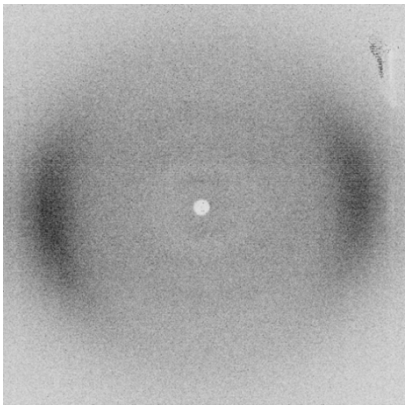

Figure S1. X-Ray scattering pattern for the nematic liquid single crystal elastomer **EAZO-CN**.

Kinetic rate constants for AZO-CN and EAZO-CN

Table S1. Values of the observed rate constants for all the reactions studied as a function of solvent, temperature and pressure for azoderivative **AZO-CN**.

Azocompound	Solvent	*P* /atm	*T* /ºC	$10^5 \times k^{th}$ /s^{-1}
AZO-CN	*ethanol*	1	25	4.6
		1	35	15
		500		15
		1500		15
		1	45	43
	toluene	1	25	3.2
		1	35	11
		500		13
		1500		12
		1	50	65
		1	55	110
	acetonitrile	1	25	2.6
		1	45	30
		1	55	90
		1	60	160
	hexane	1	25	3.5
		1	35	12
		1	50	68
		1	55	120

Table S2. Rate constants (k^{irrad} and k^{th}), respective characteristic times (τ^{irrad} and τ^{th}) for the UV-irradiation and thermal relaxation process, respectively, and *cis* isomer population at the photostationary state at different temperatures for the nematic liquid single crystal elastomer **EAZO-CN**.

T /K	k^{irrad} /s^{-1}	τ^{irrad} /min	k^{th} /s^{-1}	τ^{th} /min	ϕ_{cis} /%
298	0.00093	17.9	0.00018	92.6	81
303	0.0012	13.9	0.00028	59.5	77
308	0.0015	11.1	0.00040	41.7	73
313	0.0018	9.26	0.00060	27.8	67
318	0.0022	7.58	0.00090	18.5	59
323	0.0028	5.95	0.0013	12.8	54
328	0.0035	4.76	0.0018	9.25	49
333	0.0044	3.79	0.0025	6.67	43