Electronic Supplementary Information

Opto-mechanical effect in photoactive nematic main-chain liquid-crystalline elastomers

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1. Synthesis of main-chain liquid-crystalline elastomers (MCLCEs)

The main-chain mesogen (MCM1 or MCM2), the azobenzene derivative (Azo), 2,4,6,8,10-pentamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (PMPOPS), and 1,1,3,3-tetramethyldisiloxane (TMDSO) were placed in a 5 mL flask. 1 mL of tiophene-free toluene and 30 µL of 1 %-Pt cyclooctadieneplatinum(II) chloride, $Pt(COD)Cl_2$, in dichloromethane were added. The mixture was placed in the spinning Teflon cell form which was heated at 60 °C for 4 h at 5000 rpm.

The reactor was then cooled, and the elastomer was removed from the wall. A load was applied to align the sample during the deswelling process. After this first step the elastomer was not totally crosslinked. In order to fix the orientation, the elastomer was left in the oven under vacuum at 60 °C for 2 days to complete the crosslinking reaction. In order to measure the soluble content (*sc*) of the samples, each elastomer was placed in a liquid-solid extractor for one day, using hexane as a solvent.

MCEAzo-10

DSC (10 K·min^{-1}, N$_2$): T_g -11 (0.2) N 48 (3) I; X-ray: S = 0.73, d_m = 4.4 Å, d_l = 24.1 Å, ξ = 90 Å, ϕ = 30º; Swelling volume ratio (toluene, 25 ºC, 24 h): q = 4.1; λ_{max} = 381 nm; sc = 3.8%; E(30 ºC) = 2.56 ± 0.02 MPa, E(90 ºC) = 1.30 ± 0.01 MPa.

MCEAzo-2.5

DSC (10 K·min^{-1}, N$_2$): T_g -8 (0.3) N 60 (2) I; X-ray: S = 0.73, d_m = 4.7 Å, d_l = 26.1 Å, ξ = 29 Å, ϕ = 30º; Swelling volume ratio (toluene, 25 ºC, 24 h): q = 11.5; λ_{max} = 381 nm; sc = 4.9%; E(30 ºC) = 0.30 ± 0.01 MPa, E(90 ºC) = 0.17 ± 0.01 MPa.
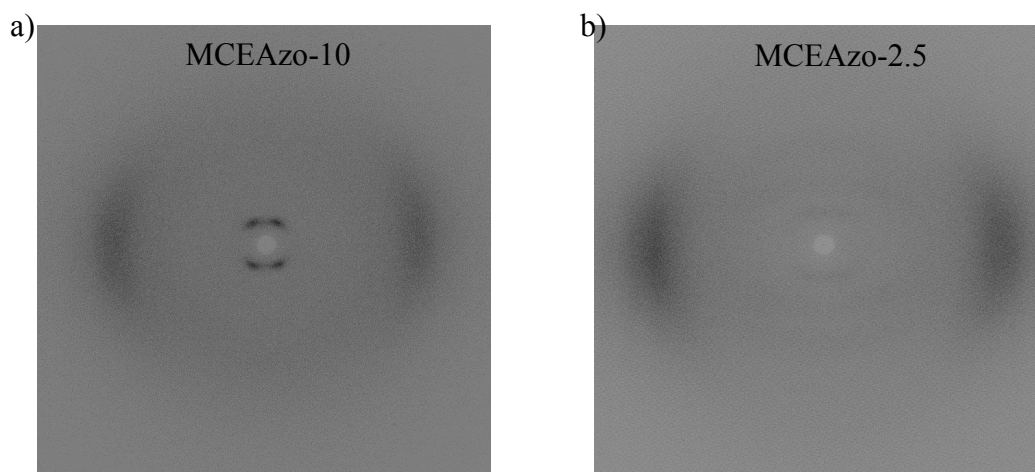

Fig. ESI-1. 2D X-ray pattern for the cybotactic nematic main-chain elastomer (a) MCEAzo-10 and (b) MCEAzo-2.5.

Table ESI-1a. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime (τ_{photo}), kinetic constant (k_{photo}), exponential factor (β_{photo}) and correlation factor (R) during the photo-isomerization process for the sample MCEAzo-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	τ_{photo}	k_{photo}	β_{photo}	R
°C	Pa	Pa	s	s^{-1}		
30.0	107354 ± 63	16983	3474 ± 7	$2.88\times10^{-4} \pm 1\times10^{-6}$	0.530 ± 0.001	0.9996
35.0	110940 ± 58	15417	2275 ± 4	$4.40\times10^{-4} \pm 1\times10^{-6}$	0.538 ± 0.001	0.9997
40.0	97386 ± 125	17198	1707 ± 8	$5.86\times10^{-4} \pm 3\times10^{-6}$	0.526 ± 0.002	0.9991
45.0	80905 ± 83	15510	1087 ± 4	$9.20\times10^{-4} \pm 4\times10^{-6}$	0.534 ± 0.001	0.9995
50.0	55878 ± 43	15314	693 ± 2	$1.44\times10^{-3} \pm 1\times10^{-5}$	0.587 ± 0.002	0.9994
55.0	38088 ± 101	11779	642 ± 6	$1.56\times10^{-3} \pm 2\times10^{-5}$	0.541 ± 0.004	0.9992
60.0	25732 ± 149	11252	476 ± 9	$2.10\times10^{-3} \pm 4\times10^{-5}$	0.54 ± 0.01	0.995
65.0	11902 ± 35	9901	283 ± 4	$3.54\times10^{-3} \pm 4\times10^{-5}$	0.61 ± 0.01	0.992
70.0	5646 ± 13	9380	168 ± 4	$5.94\times10^{-3} \pm 4\times10^{-5}$	0.68 ± 0.02	0.991

Table ESI-1b. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime (τ_{photo}), kinetic constant (k_{photo}), exponential factor (β_{photo}) and correlation factor (R) during the photo-isomerization process for the sample MCEAzo-2.5 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	τ_{photo}	k_{photo}	β_{photo}	R
°C	Pa	Pa	s	s^{-1}		
30.0	13700 ± 18	20202	2080 ± 9	$4.81\times10^{-4} \pm 3\times10^{-6}$	0.575 ± 0.003	0.995
35.0	12826 ± 9	18946	1843 ± 7	$5.42\times10^{-4} \pm 2\times10^{-6}$	0.570 ± 0.002	0.996
40.0	12246 ± 13	18087	1550 ± 9	$6.45\times10^{-4} \pm 4\times10^{-6}$	0.582 ± 0.002	0.997
45.0	12088 ± 11	18519	1284 ± 6	$7.79\times10^{-4} \pm 3\times10^{-6}$	0.555 ± 0.002	0.997
50.0	10624 ± 5	17402	1127 ± 4	$8.88\times10^{-4} \pm 3\times10^{-6}$	0.580 ± 0.002	0.997
55.0	8307 ± 12	14980	722 ± 4	$1.39\times10^{-3} \pm 1\times10^{-5}$	0.618 ± 0.004	0.998
60.0	5694 ± 7	10622	449 ± 3	$2.23\times10^{-3} \pm 1\times10^{-5}$	0.72 ± 0.01	0.997
65.0	6951 ± 8	10021	393 ± 3	$2.54\times10^{-3} \pm 2\times10^{-5}$	0.61 ± 0.01	0.992
70.0	7228 ± 3	10329	291 ± 2	$3.44\times10^{-3} \pm 2\times10^{-5}$	0.77 ± 0.01	0.995
75.0	6148 ± 18	10285	250 ± 5	$4.00\times10^{-3} \pm 4\times10^{-5}$	0.64 ± 0.01	0.98

Table ESI-2a. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime ($\tau_{thermal}$), kinetic constant ($k_{thermal}$), exponential factor ($\beta_{thermal}$) and correlation factor (R) during the thermal-isomerization process for the sample MCEAzo-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	$\tau_{thermal}$	$k_{thermal}$	$\beta_{thermal}$	R
°C	Pa	Pa	s	s^{-1}		
30.0	110167 ± 65	14170	19160 ± 7	$5.22\times10^{-5} \pm 2\times10^{-8}$	1.000 ± 0.001	0.9998
35.0	112187 ± 59	14170	11746 ± 9	$8.51\times10^{-5} \pm 1\times10^{-7}$	1.000 ± 0.001	0.9994
40.0	102635 ± 131	11950	8228 ± 7	$1.22\times10^{-4} \pm 1\times10^{-7}$	0.972 ± 0.001	0.9996
45.0	81374 ± 84	15042	5424 ± 9	$1.84\times10^{-4} \pm 1\times10^{-6}$	1.000 ± 0.002	0.9991
50.0	59301 ± 46	11891	3552 ± 8	$2.82\times10^{-4} \pm 1\times10^{-6}$	1.000 ± 0.001	0.9990
55.0	41029 ± 109	8837	2349 ± 9	$4.26\times10^{-4} \pm 2\times10^{-6}$	0.938 ± 0.003	0.9990
60.0	25539 ± 148	11445	1621 ± 9	$6.17\times10^{-4} \pm 4\times10^{-5}$	1.000 ± 0.01	0.990
65.0	13015 ± 38	8788	1085 ± 9	$9.22\times10^{-4} \pm 4\times10^{-5}$	0.86 ± 0.01	0.993
70.0	5628 ± 13	9397	887 ± 9	$1.13\times10^{-3} \pm 2\times10^{-5}$	0.71 ± 0.01	0.990

Table ESI-2b. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime ($\tau_{thermal}$), kinetic constant ($k_{thermal}$), exponential factor ($\beta_{thermal}$) and correlation factor (R) during the thermal-isomerization process for the sample MCEAzo-2.5 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	$\tau_{thermal}$	$k_{thermal}$	$\beta_{thermal}$	R
°C	Pa	Pa	s	s^{-1}		
30.0	14008 ± 18	19893	18612 ± 20	$5.37\times10^{-5} \pm 1\times10^{-7}$	1.000 ± 0.001	0.9994
35.0	14343 ± 10	17428	12400 ± 16	$8.06\times10^{-5} \pm 1\times10^{-7}$	0.994 ± 0.001	0.9994
40.0	11761 ± 12	18572	8241 ± 5	$1.21\times10^{-4} \pm 1\times10^{-7}$	0.984 ± 0.001	0.9998
45.0	11993 ± 10	18614	5281 ± 8	$1.89\times10^{-4} \pm 3\times10^{-7}$	1.000 ± 0.002	0.9990
50.0	10589 ± 5	17436	3363 ± 13	$2.97\times10^{-4} \pm 1\times10^{-6}$	0.955 ± 0.004	0.995
55.0	8313 ± 12	14974	1960 ± 6	$5.10\times10^{-4} \pm 2\times10^{-6}$	0.941 ± 0.003	0.9990
60.0	5790 ± 7	10525	1286 ± 3	$7.78\times10^{-4} \pm 2\times10^{-6}$	0.938 ± 0.002	0.9995
65.0	6878 ± 7	10094	841 ± 3	$1.19\times10^{-3} \pm 1\times10^{-5}$	0.957 ± 0.005	0.998
70.0	7378 ± 3	10179	641 ± 15	$1.56\times10^{-3} \pm 4\times10^{-5}$	0.96 ± 0.02	0.97
75.0	5604 ± 13	10829	567 ± 13	$1.76\times10^{-3} \pm 4\times10^{-5}$	1.00 ± 0.04	0.991

Table ESI-3a. Lifetimes (τ_{photo} and $\tau_{thermal}$), kinetic constants (k_1 and k_2), half lifetimes ($t_{1/2,photo}$ and $t_{1/2,thermal}$) and cis-isomer population (ϕ_{cis}) for the sample MCEAzo-10 at different inverse temperatures.

$1/T$	τ_{photo}	$\tau_{thermal}$	k_1	k_2	$t_{1/2,photo}$	$t_{1/2,thermal}$	ϕ_{cis}
K^{-1}	s	s	s^{-1}	s^{-1}	min	min	
0.00329	3474	19160	0.00024	0.00005	40.1	221	0.82
0.00324	2275	11746	0.00035	0.00009	26.3	136	0.81
0.00319	1707	8228	0.00046	0.00012	19.7	95.1	0.79
0.00314	1087	5424	0.00074	0.00018	12.6	62.7	0.80
0.00310	693	3552	0.00116	0.00028	8.0	41.0	0.80
0.00305	642	2349	0.00113	0.00043	7.4	27.1	0.73
0.00301	476	1621	0.00148	0.00062	5.5	18.7	0.71
0.00297	283	1085	0.00261	0.00092	3.3	12.5	0.74
0.00292	168	887	0.00482	0.00113	1.9	10.3	0.81

Table ESI-3b. Lifetimes (τ_{photo} and $\tau_{thermal}$), kinetic constants (k_1 and k_2), half lifetimes ($t_{1/2,photo}$ and $t_{1/2,thermal}$) and cis-isomer population (ϕ_{cis}) for the sample MCEAzo-2.5 at different inverse temperatures.

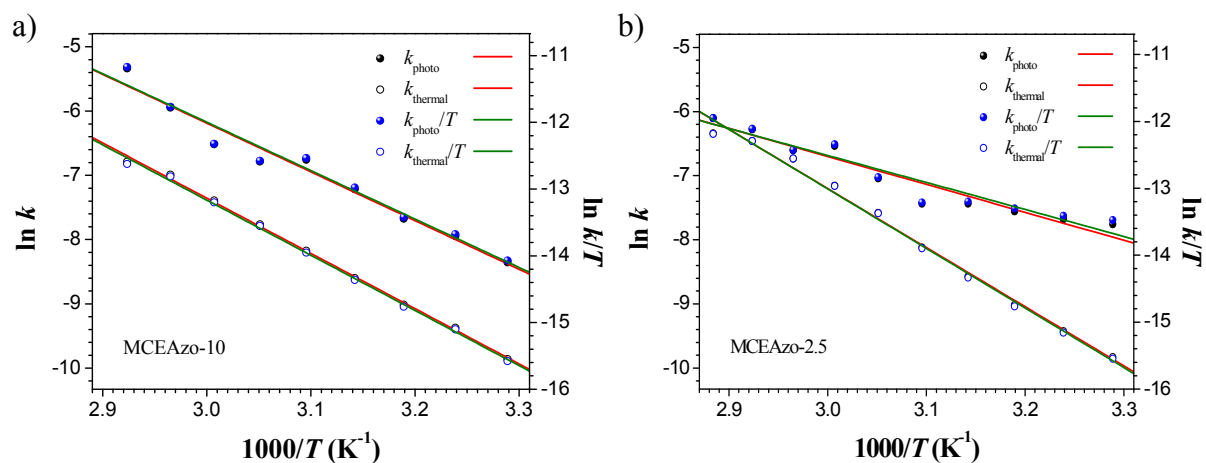| $1/T$	τ_{photo}	$\tau_{thermal}$	k_1	k_2	$t_{1/2,photo}$	$t_{1/2,thermal}$	ϕ_{cis}
K^{-1}	s	s	s^{-1}	s^{-1}	min	min	
0.00329	2080	18612	0.00043	0.00005	24.0	215	0.89
0.00324	1843	12400	0.00046	0.00008	21.3	143	0.85
0.00319	1550	8241	0.00052	0.00012	17.9	95.2	0.81
0.00314	1284	5281	0.00059	0.00019	14.8	61.0	0.76
0.00310	1127	3363	0.00059	0.00030	13.0	38.9	0.66
0.00305	722	1959	0.00087	0.00051	8.3	22.6	0.63
0.00301	449	1285	0.00145	0.00078	5.2	14.9	0.65
0.00297	393	841	0.00135	0.00119	4.5	9.7	0.53
0.00292	291	641	0.00188	0.00156	3.4	7.4	0.55
0.00288	250	567	0.00224	0.00176	2.9	6.6	0.56

Figure ESI-2. Arrhenius (black symbols and red fitting curves) and Eyring (blue symbols and green fitting curves) plots for the photo- (k_{photo}) and thermal-isomerization ($k_{thermal}$) processes of the two elastomeric samples: a) MCEAzo-10, and b) MCEAzo-2.5.

Table ESI-4a. Activation energy (E_a), pre-exponential factor (A), activation enthalpy ($\Delta H^{\ddagger}$), activation entropy ($\Delta S^{\ddagger}$), and free activation enthalpy ($\Delta G^{\ddagger}$) of the photo-isomerization process for the two samples from the Arrhenius and Eyring plots.

Sample	E_a $\overline{\text{kJ·mol}^{-1}}$	A $\overline{\text{s}^{-1}}$	$\Delta H^{\ddagger}$ $\overline{\text{kJ·mol}^{-1}}$	$\Delta S^{\ddagger}$ $\overline{\text{J·mol}^{-1}\text{·K}^{-1}}$	$\Delta G^{\ddagger}$ $\overline{\text{kJ·mol}^{-1}}$
MCEAzo-10	63 ± 4	$1.57\times10^7 \pm 2\times10^5$	60 ± 4	-116 ± 13	98 ± 4
MCEAzo-2.5	36 ± 3	$5.86\times10^2 \pm 4\times10^0$	34 ± 3	-201 ± 11	99 ± 3

Table ESI-4b. Activation energy (E_a), pre-exponential factor (A), activation enthalpy ($\Delta H^{\ddagger}$), activation entropy ($\Delta S^{\ddagger}$), and free activation enthalpy ($\Delta G^{\ddagger}$) of the thermal-isomerization process for the two samples from the Arrhenius and Eyring plots.

Sample	E_a $\overline{\text{kJ·mol}^{-1}}$	A $\overline{\text{s}^{-1}}$	$\Delta H^{\ddagger}$ $\overline{\text{kJ·mol}^{-1}}$	$\Delta S^{\ddagger}$ $\overline{\text{J·mol}^{-1}\text{·K}^{-1}}$	$\Delta G^{\ddagger}$ $\overline{\text{kJ·mol}^{-1}}$
MCEAzo-10	71 ± 1	$1.01\times10^8 \pm 1\times10^6$	69 ± 1	-101 ± 4	102 ± 1
MCEAzo-2.5	77 ± 2	$7.67\times10^8 \pm 2\times10^6$	74 ± 2	-84 ± 7	101 ± 2