Supplementary Information

All-optical pulsed writing in azobenzene copolymer films in the sub-millisecond regime

Sara Menghetti, Michele Alderighi, Giancarlo Galli*
Dipartimento di Chimica e Chimica Industriale, UdR INSTM Pisa, Università di Pisa, 56126 Pisa, Italy

Francesco Tantussi, Massimo Morandini, Francesco Fuso, Maria Allegrini
Dipartimento di Fisica 'Enrico Fermi' and CNISM, Università di Pisa, 56127 Pisa, Italy

Synthesis of monomer MA4

4-Pentoxy-3'-methyl-4'-hydroxyazobenzene (**2**). A solution of 11.73 g (0.170 mol) of sodium nitrite in 29 mL of water was added dropwise with vigorous stirring to a solution of 25.22 g (0.141 mol) of 4-pwntoxyaniline (**1**) in 146 mL of 3M HCl at 0–5 °C. After 1 h, the excess sodium nitrite was decomposed by addition of urea and the solution was slowly poured in to a solution of 15.21 g (0.141 mol) of *o*-cresol in 150 mL of 2M NaOH. After 10 min, the solution was acidified with HCl. The precipitate was filtered, washed with water, dried and purified by flash chromatography with hexane/ethyl acetate (75/25 vol/vol). Yield 75%; mp 102 °C. ^{1}H NMR ($CDCl_3$): δ(ppm) = 7.9 (2H, aromatic), 7.7 (2H, aromatic), 7.0 (3H, aromatic), 5.2 (1H, OH), 4.0 (2H, CH_2O), 2.3 (3H, aromatic CH_3), 1.8 (2H, $CH_3\underline{CH_2}$), 1.5 (4H, CH_2CH_2), 1.0 (3H, CH_3).

4-Pentoxy-3'-methyl-4'-(6-hydroxyhexyloxy)azobenzene (**3**). A mixture of 10.00 g (0.034 mol) of **2,** 13.93 g (1.008 mol) of anhydrous K_2CO_3 and 10.53 g (0.077 mol) of 6-chloro-1-hexanol in 50 mL of dimethylsulfoxide was stirred for 2 h at 110 °C, then cooled to room temperature, and poured into 200 mL of 1M NaOH. The precipitate was filtered and washed with water. Yield 95%; mp 102 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.9 (2H, aromatic), 7.7 (2H, aromatic), 7.0 (3H, aromatic), 4.1 (4H, CH_2O), 3.7 (2H, $C\underline{H_2}OH$), 2.3 (3H, aromatic CH_3), 1.9–1.4 (14H, aliphatic), 1.0 (3H, CH_3).

4-Pentoxy-3'-methyl-4'-((6-methacryloyloxy)hexyloxy)azobenzene (**MA4**). A solution of 7.84 g (0.075 mol) of methacryloyl chloride in 100 mL of tetrahydrofuran was added dropwise with vigorous stirring to a solution of 10.14g (0.025 mol) of **3**, 12.69 g (0.025 mol) of triethylamine and

100 mg hydroquinone in 20 mL of the same solvent at 0 °C, while nitrogen was bubbled through the reaction mixture. After 2 h, the precipitate was filtered, washed with 5% $NaHCO_3$, 5% HCl and finally water to neutrality. After drying under vacuum, the solid residue was crystallized twice from methanol. Yield 71%; mp 39 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.9 (2H, aromatic), 7.7 (2H, aromatic), 7.0 (3H, aromatic), 6.1 and 5.6 (2H, CH_2=), 4.2 (2H, $COOCH_2$), 4.0 (4H, CH_2O), 2.3 (3H, aromatic CH_3), 2.0–1.3 (17H, aliphatic and CH_3C=), 1.0 (3H, CH_3).

Characterization of the polymer samples

The glass transition and nematic–isotropic transition temperatures of the copolymers were located by DSC (Figure S1). The UV absorption spectra of spin-coated films of the copolymers were all similar to each other; one illustration is shown in Figure S2.

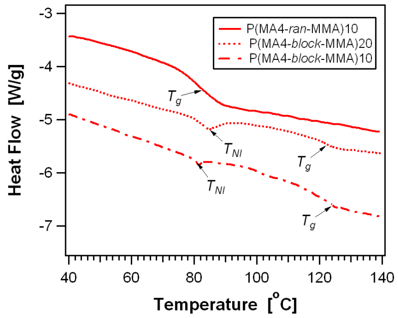

Fig. S1 DSC second-heating curves of copolymers P(MA4-*block*-MMA)10 (·–·–·), P(MA4-*block*-MMA)20 (·····), and P(MA4-*ran*-MMA)10 (——).

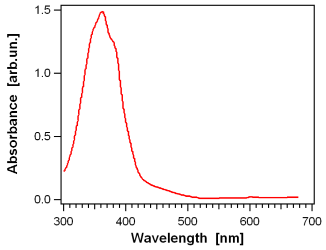

Fig. S2 UV-Vis absorption spectrum of a spin-coated film (from toluene solution) of copolymer P(MA4-*block*-MMA)20.

Data treatment for the optical analysis

Core of the birefringence measurement is a photoelastic modulator (Hinds-Instruments PEM 100) operating at the fixed frequency of 50 kHz. When mounted with one of its axes at 45° with respect to the x-axis (parallel to the incoming laser polarization direction), the time-dependent polarization of the output light can be expressed by the following vector:

$$V = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{i\Delta(t)} \\ 1 \end{pmatrix}, \qquad \text{Eq. 1}$$

with $\Delta(t) = A\sin(2\pi ft+\delta)$; here, f = 50 kHz denotes the PEM modulation frequency, A is the maximum retardation produced by the PEM, typically set to $A = \pi$, and δ represents a constant phase factor depending on internal delays.

According to the Jones' formalism, the optical behavior of any component crossed by the so-polarized radiation can be expressed by a 2×2 matrix. A generic birefringent component, with its optical axes rotated by a generic angle θ with respect to the reference system, can for instance be represented by the matrix product M:

$$M = \frac{1}{\sqrt{2}}\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} e^{-i\Delta\phi} & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}, \qquad \text{Eq. 2}$$

where $\Delta\phi$ is the optical retardation produced by the component.

Due to the presence of an optical analyzer (a linear polarizer) in front of the detector, whose behavior can be represented by the matrix P

$$P = \begin{pmatrix} \cos\theta' & -\sin\theta' \\ \sin\theta' & \cos\theta' \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} \cos\theta' & \sin\theta' \\ -\sin\theta' & \cos\theta' \end{pmatrix}, \qquad \text{Eq. 3}$$

θ' being the angle between the polarizer axis and the x direction, the electromagnetic field D collected by the detector is given by the product:

$$D = P \otimes M \otimes V, \qquad \text{Eq. 4}$$

which is time-modulated due to the modulation of the PEM at frequency f. Demodulation of the signal by the lock-in (at frequency f or $2f$, depending on the experimental configuration), providing with the AC signal, can be numerically calculated. Similarly, the DC signal, time averaged over an interval much longer than $1/f$, can be numerically evaluated. In this way, the radiation read by the detector, hence the AC/DC ratio, can be found corresponding to a certain value of the optical retardation $\Delta\phi$ and of the angles θ and θ' entering matrix M and P, respectively.

However, the above picture must be modified in order to properly describe our experimental setup. Due to the presence of several optical components between the PEM and the sample, in particular of a beam-splitter cube used to superpose the reading and the writing laser beams and of dielectric mirrors needed to properly align the beams with the objective, a residual optical activity is present, leading to a non-negligible instrumental pedestal in the AC/DC ratio. Such a residual birefringence, which can be simulated by introducing additional Jones' matrices of the M form described above, has been carefully evaluated by analyzing the temporal behavior of the detector signal, which has then been compared with the simulations in order to derive the relevant values needed to simulate the optical activity due to the optical chain.

The relationship between the optical retardation $\Delta\phi$ and the AC/DC ratio, as measured in the typical conditions of the experiment, is plotted in Figure S3. Note that the analysis is restricted here to positive values of the optical retardation. By using a polarization direction rotated by 90°, negative values of both AC/DC ratio and $\Delta\phi$ are obtained, which follow the same behavior plotted in the figure but for a negative sign.

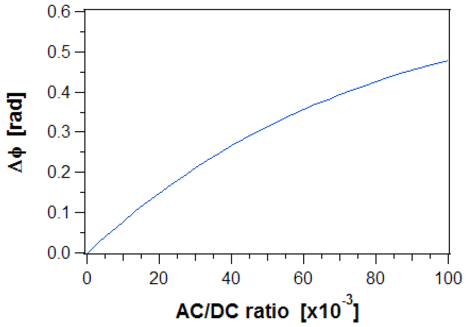

Fig. S3 Optical retardation as a function of the AC/DC ratio measured in the experiment. For the sake of clarity, the instrumental pedestal in AC/DC signal, accounting for the residual birefringence of the optical chain, has been removed.