

Supplementary information

The role of conductivity and molecular mobility on the photoanisotropic response of a new azo-polymer containing sulfonic groups.

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1. Chemical characterisation

Some addition information regarding the preparation of MeOAzB/AMPS/MMA and its intermediates is now shown. The proton Nuclear Magnetic Resonance, $^1\text{H-NMR}$, of 4-(methoxyazobenzene -4'-oxy) methacrylate, **3**, is shown as **Fig. ESI1**. **Fig. ESI2(a)** and **(b)**, on the other hand, show the proton Nuclear Magnetic Resonance, $^1\text{H-NMR}$, and infrared, IR, spectra, respectively, measured at room temperature for MeOAzB/AMPS/MMA. The monomer composition in the terpolymer chain was then estimated in terms of equivalent units, by using the peaks in the 7 – 8 ppm region for the MeOAzB units (aromatic contributions, overall area / 8H), the peak at ~ 2.8 ppm for the AMPS units (s, adjacent to the sulfonic acid groups, CH_2SO_3 , peak area / 2H) and the peak ~3.6 ppm (s, associated with the methyl groups. CO.OCH_3 , peak area / 3H)^{1,2}. The IR spectrum is consistent with the chemical structure in **Fig. 2**, and some characteristic signals are found at 1750 - 1700 cm^{-1} (C=O stretching, st., vibrations from MeOAzB and MMA groups), 3400, 1670 and 1550 cm^{-1} (amide vibrations from AMPS groups), aromatic vibrations (1600, 1500 cm^{-1})³. **Fig. ESI2(c)** shows the Gel Permeation Chromatogram (GPC) of MeOAzB/AMPS/MMA.

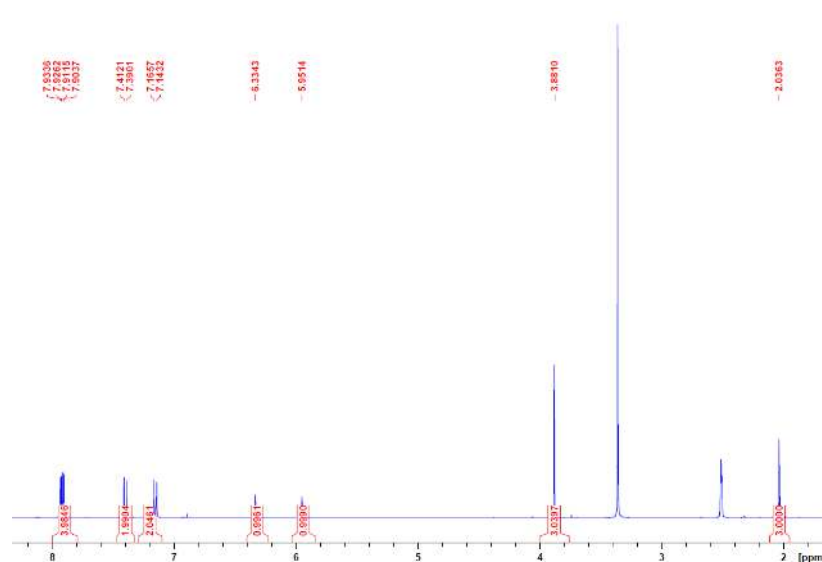


Figure ESI1. $^1\text{H-NMR}$ of 4-(methoxyazobenzene -4'-oxy) methacrylate, **3** (DMSO-d_6)

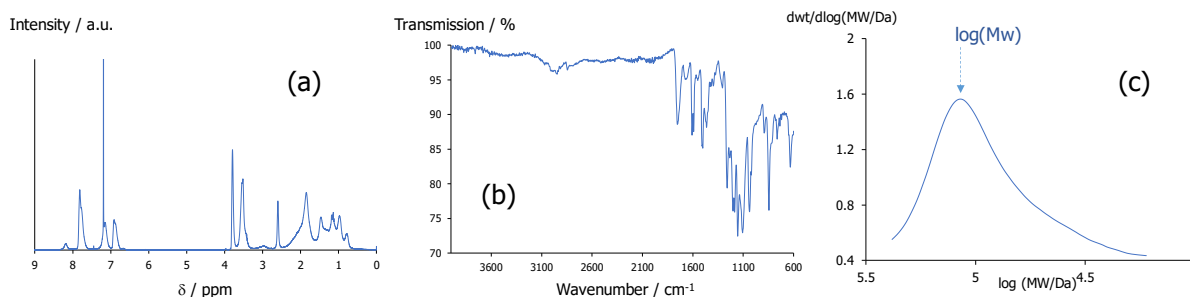


Figure ESI2. Chemical characterisation of MeOAzB/AMPS/MMA (room temperature): (a) $^1\text{H-NMR}$; (b) IR spectra; (c) GPC curve.

2. Results and discussion

In this section we depict some additional figures supplementing the discussion of the experimental results in the main manuscript. **Fig. ESI3** shows a comparison between the kinetics of the thermal back-isomerisation of MeOAzB/AMPS/MMA in the bulk and in THF solution. **Fig. ESI4** displays the UV-Vis absorbance of the chromophores, MY-26 and BiN-GP⁴, whose photoanisotropic responses are compared to MeOAzB/AMPS/AMPS. In **Fig. ESI5**, we have plotted the chemical structures of 10-MeOAzB/AMPS/MMA (a); FIII (b); CFAO (c) and CFMAO (d), which are used to rationalise the dielectric response of the present terpolymer in the main text⁵⁻⁷.

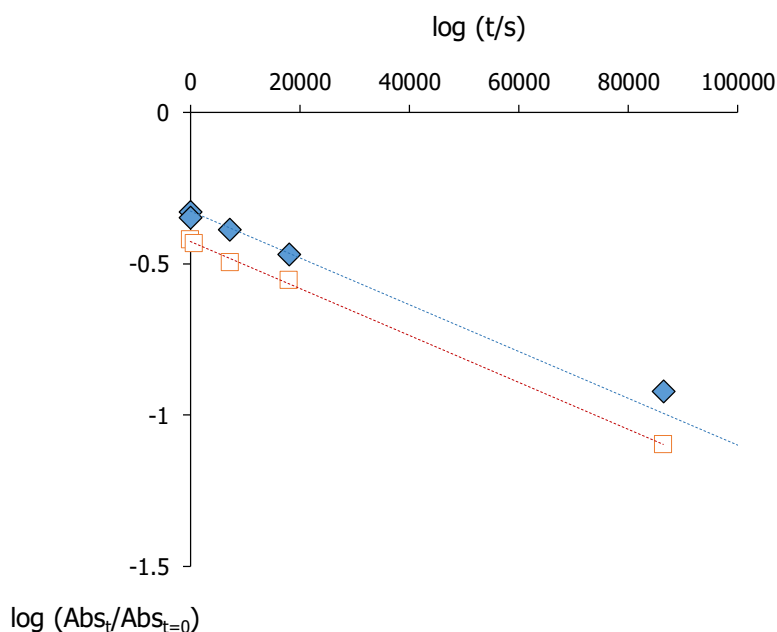


Figure ESI3. Kinetics of thermal back *cis-to-trans* photo-isomerisation of MeOAzB/AMPS/MMA measured in: (◆) bulk; (□) THF solution ($R^2 > 0.99$). t_0 is the time at irradiation.

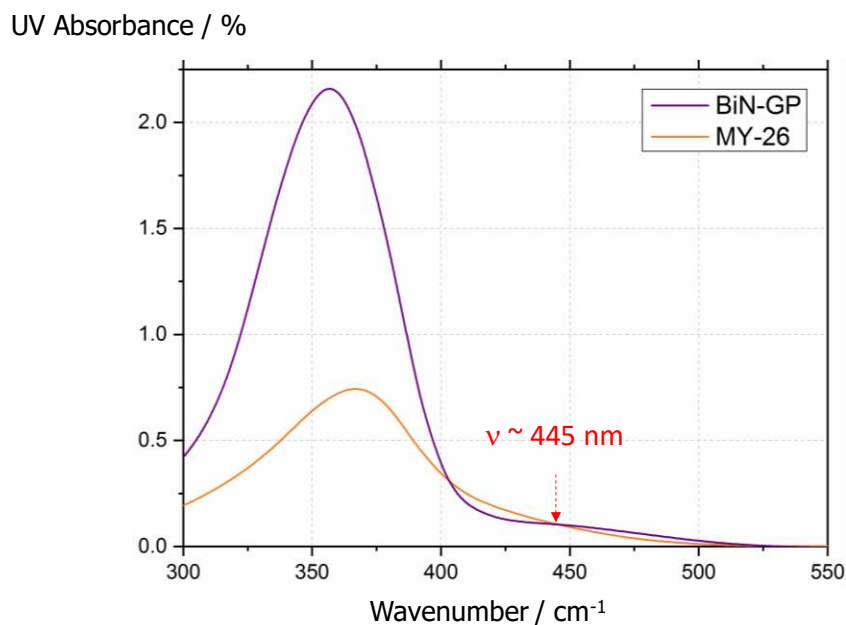


Figure ESI4. UV-Vis spectra of MY-26 and BiN-GP, obtained at room temperature on thin films cast on quartz.

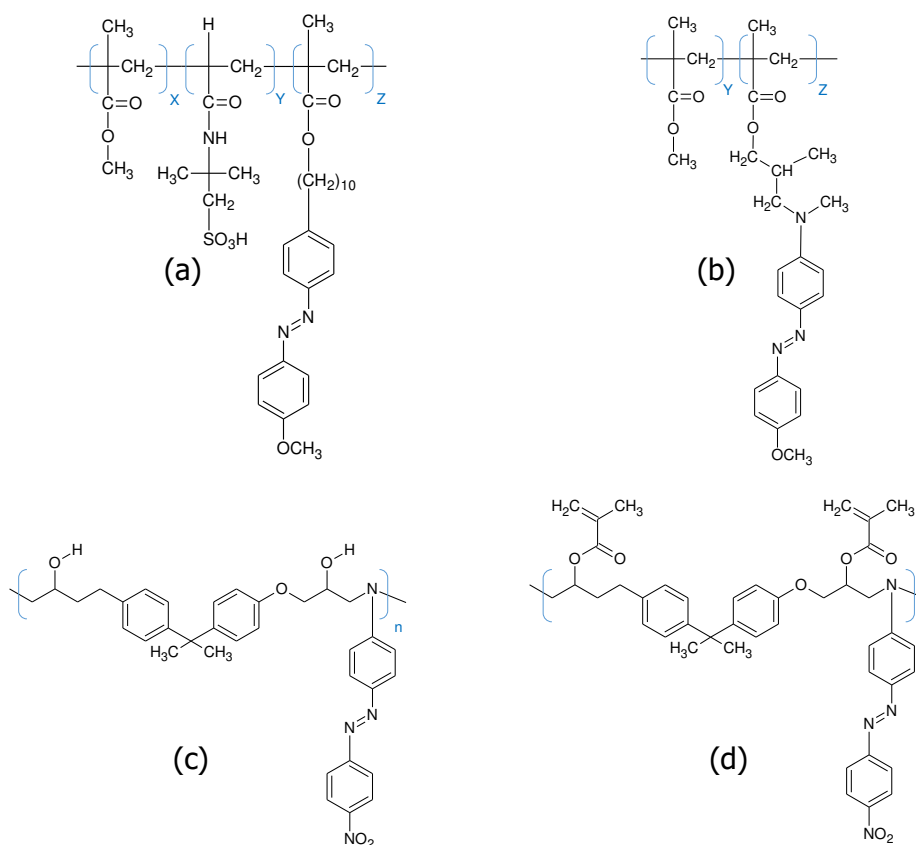


Figure ESI5. Chemical structures of: (a) 10-MeOAzB/AMPS/MMA; (b) FIII; (c) CFAO and (d) CFMAO, in [Table 1](#).

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