Supplementary information

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

Sakinah Mohd Alauddin[1,2], Nurul Fadhilah Kamalul Aripin[1,2], T.S. Velayutham[2,3] , Irakli Chaganava[4, 5], Alfonso Martinez-Felipe[6, *]

[1] Faculty of Chemical Engineering, University of Technology MARA, 40450 Shah Alam, Selangor Darul Ehsan, Malaysia.

[2]Fundamental and Frontier Sciences in Nanostructure Self-Assembly Center, Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

[3] Low Dimensional Material Research Center, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

[4] Laboratory of Holographic Recording and Processing of Information, Institute of Cybernetics, GTU. 5 Sandro Euli str., 0186 Tbilisi. Georgia.

[5] Georgian State Teaching University of Physical Education and Sport.49, Chavchavadze ave. 0179, Tbilisi. Georgia.

[6] Chemical and Materials Engineering Research Group, School of Engineering, University of Aberdeen, King's College, Old Aberdeen AB24 3UE, UK.

* Corresponding author: a.martinez-felipe@abdn.ac.uk

Keywords: azo-polymers; dielectric spectroscopy; UV-Vis spectrophotometry; photoanisotropy; *trans*-to-*cis* photoisomerisation; conductivity.

Contents

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}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}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.

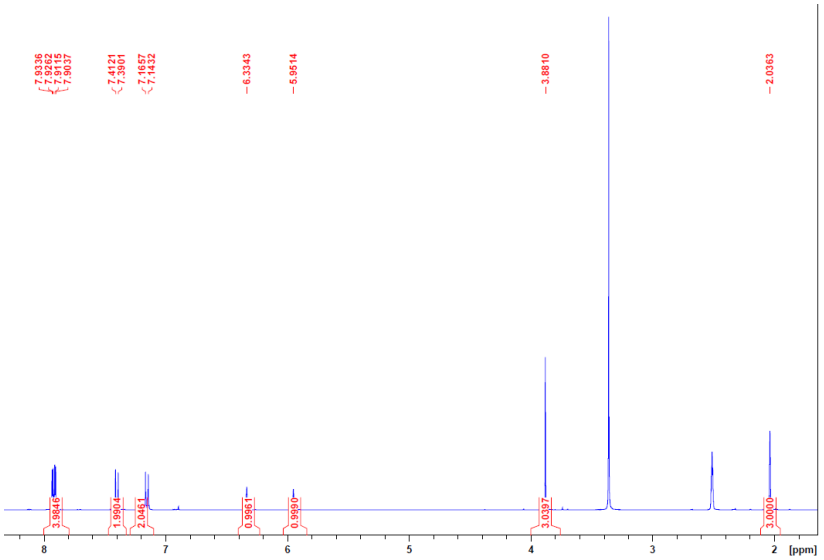

Figure ESI1. ^{1}H-NMR of 4-(methoxyazobenzene -4'-oxy) methacrylate, ***3*** (DMSO-d^{6})

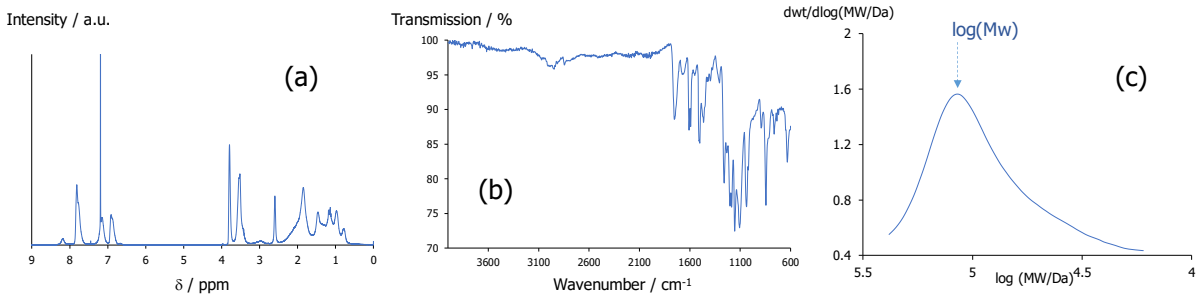

Figure ESI2. Chemical characterisation of MeOAzB/AMPS/MMA (room temperature): (a) ^{1}H-NMR; (b) IR spectra; (c) GPC curve.

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-GP[4], 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 text[5-7].

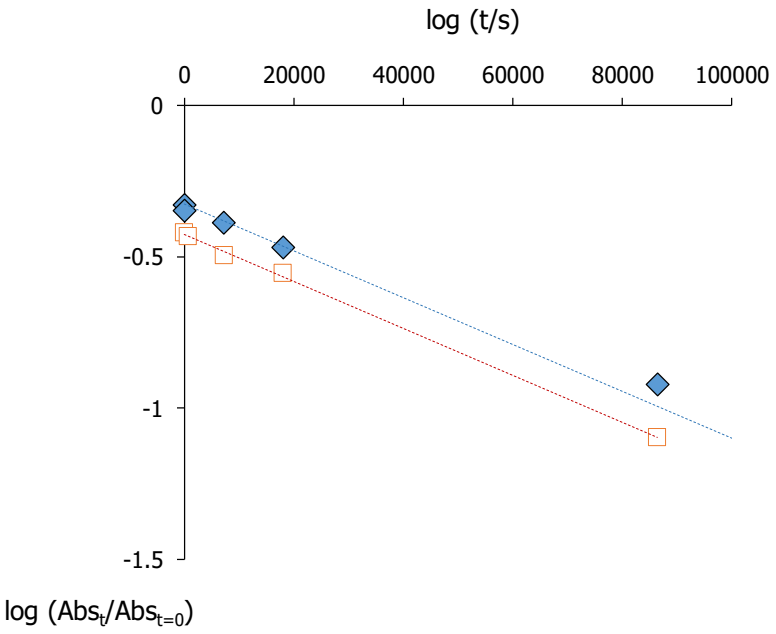

Figure ESI3. Kinetics of thermal back *cis*-to-*trans* photo-isomerisation of MeOAzB/AMPS/MMA measured in: (◆) bulk; (□) THF solution (R^2> 0.99). t_0 is the time at irradiation.

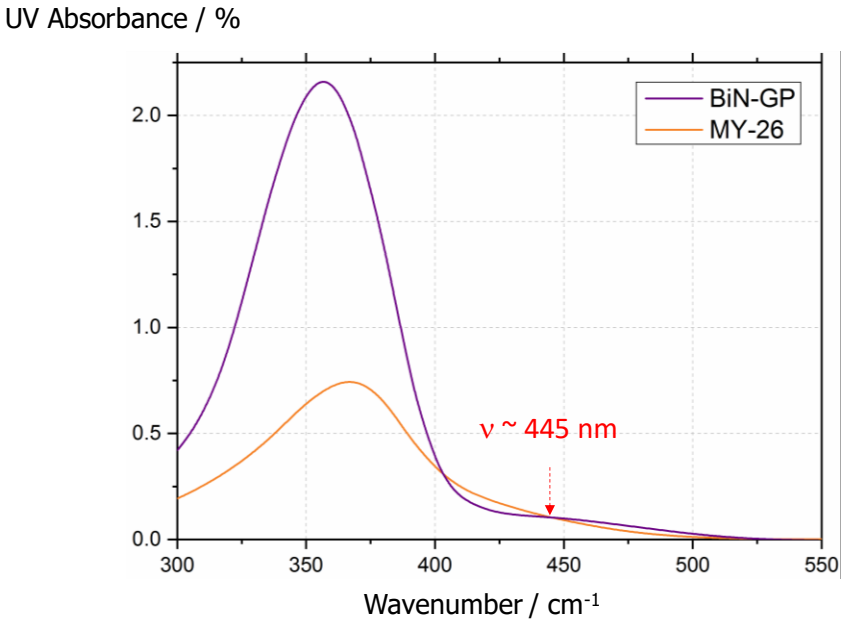

Figure ESI4. UV-Vis spectra of MY-26 and BiN-GP, obtained at room temperature on thin films cast on quartz.

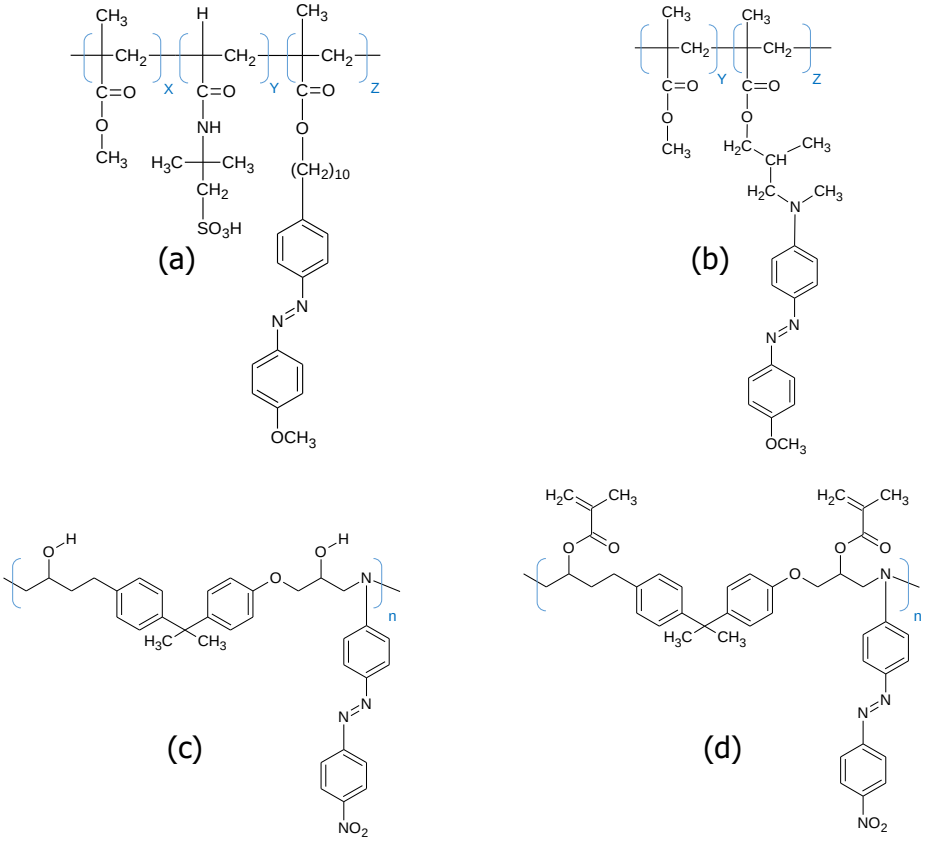

Figure ESI5. Chemical structures of: (a) 10-MeOAzB/AMPS/MMA; (b) FIII; (c) CFAO and (d) CFMAO, in **Table 1**.

References

1 Martinez-Felipe A, Lu Z, Henderson PA, Picken SJ, Norder B, Imrie CT, Ribes-Greus A. Synthesis and characterisation of side chain liquid crystal copolymers containing sulfonic acid groups. Polymer 2012; 53; 2604-12.

2 Vanti L, Mohd Alauddin S, Zaton D, Aripin NFK, Giacinti-Baschetti M, Imrie CT, Ribes-Greus A, Martinez-Felipe A. Ionically conducting and photoresponsive liquid crystalline terpolymers: Towards multifunctional polymer electrolytes. Eur. Polym. J. 2018; 109; 124-32.

3 Martinez-Felipe A, Imrie CT, Ribes-Greus A. Study of structure formation in side-chain liquid crystal copolymers by variable temperature fourier transform infrared spectroscopy. Ind. Eng. Chem. Res. 2013; 52; 8714-21.

4 Chaganava I, Kilosanidze B, Kakauridze G, Oriol L, Pinol M, Martinez-Felipe A. Induction of the vector polyphotochromism in side-chain azopolymers. J. Photochem. Photobiol. A 2018; 354; 70-7.

5 Martinez-Felipe A, Santonja-Blasco L, Badia JD, Imrie CT, Ribes-Greus A. Characterization of functionalized side-chain liquid crystal methacrylates containing nonmesogenic units by dielectric spectroscopy. Ind. Eng. Chem. Res. 2013; 52; 8722-31.

6 Nikonorova NA, Balakina MY, Fominykh OD, Sharipova AV, Vakhonina TA, Nazmieva GN, Castro RA, Yakimansky AV. Dielectric spectroscopy and molecular modeling of branched methacrylic (co)polymers containing nonlinear optical chromophores. Mater. Chem. Phys. 2016; 181; 217-26.

7 Nikonorova NA, Balakina MY, Fominykh OD, Pudovkin MS, Vakhonina TA, Diaz-Calleja R, Yakimansky AV. Dielectric spectroscopy and molecular dynamics of epoxy oligomers with covalently bonded nonlinear optical chromophores. Chem. Phys. Lett. 2012; 552; 114-21.