

# Using the Photoinduced Reversible Refractive-index Change of an Azobenzene Co-polymer to Reconfigure an Optical Bragg Grating

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# Using the Photoinduced Reversible Refractive-index Change of an Azobenzene Co-polymer to Reconfigure an Optical Bragg Grating

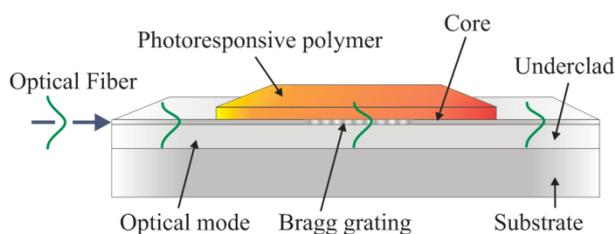
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## Table of Contents Summary and Graphic:

When a photo-switchable material in which azobenzene units are attached to a methacrylate co-polymer, is combined with a direct UV-written silica-on-silicon Bragg grating a novel optical device is produced that undergoes repeated, reversible refractive index changes at telecomm wavelengths.



# Using the Photoinduced Reversible Refractive-index Change of an Azobenzene Co-polymer to Reconfigure an Optical Bragg Grating

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A photoactive material has been synthesised in which azobenzene units are attached to a methyl methacrylate / 2-hydroxyethyl methacrylate co-polymer and shows repeated photoresponsive switching upon irradiation at 365 nm and 254 nm with long term thermal stability. In combination with a direct UV-written silica-on-silicon Bragg grating, this has been used to fabricate a prototype optical device which undergoes reversible refractive index changes at telecom wavelengths. The 63 GHz tuning response demonstrated by this device has potential applicability for reconfigurable dispersion compensation for use in optical networks.

## 1. Introduction

Organic polymers have found many applications in electronic and optical devices. They offer process compatibility, flexibility in design, and the ability for integration of electronic and optoelectronic functions. Numerous polymer systems have been developed for optical applications, with the key requirement imposed for such materials being transparency. Much interest has focused on acrylic polymers because of their well-known optical properties and good film-forming capability<sup>1</sup>. Furthermore, azobenzene-based polymers can act as photosensitive, nonlinear optical, or photorefractive materials with ever increasing fields of application, including: programmable optical interconnects; electro-optic modulation; coherent image amplification; and holographic storage<sup>2</sup>.

The simple azobenzene motif can undergo reversible photoisomerisation allowing the photoactive units to be optically pumped almost exclusively from the *trans* to the *cis* isomeric state upon exposure to ultraviolet light. Upon isomerisation there is a change in the polarisability of the azobenzene molecule, resulting in a change in refractive index. It has been reported<sup>3</sup> that the *trans*-isomer is thermodynamically more stable by 50 kJ mol<sup>-1</sup>, while the barrier to photoisomerisation is approximately 200 kJ mol<sup>-1</sup>. The *cis*-isomer will slowly relax thermally back to the *trans*-isomer in the absence of light, but the activation barrier for this process is 96 kJ mol<sup>-1</sup> in solution or 130 kJ mol<sup>-1</sup> in the solid state. The corresponding half-life of the *cis*-isomer is in the order of a day at room temperature.

Reconfigurable optical devices are of great interest for telecom applications; including dispersion compensation and tunable add-drop multiplexers. Bragg gratings – optical components that reflect at one particular wavelength of light and transmit all others – are important elements in such

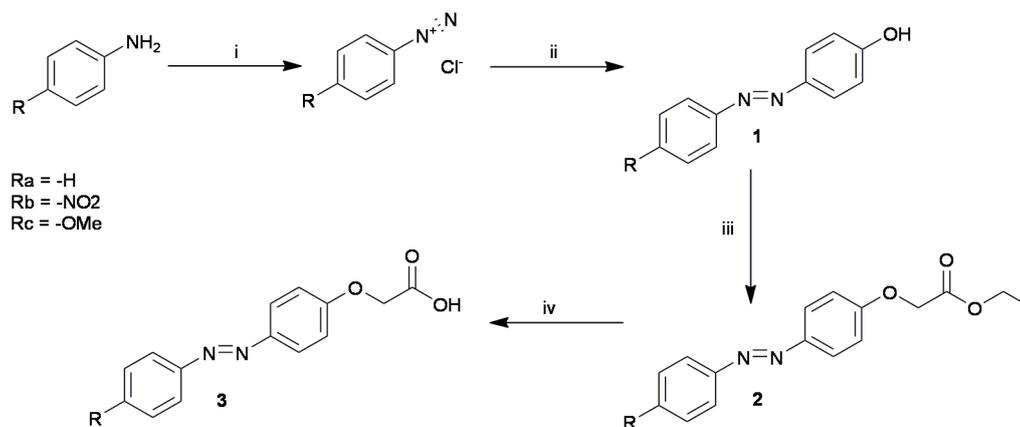
systems. For these applications, optical Bragg grating structures need to be reconfigurable with both fine control and wide tunability of the Bragg wavelength desired. Previous approaches to this problem were to incorporate a degree of reconfigurability into existing Bragg devices through tuning of the refractive index by temperature<sup>4</sup>, piezoelectric<sup>5</sup>, magnetostrictive<sup>6</sup>, or mechanically induced strain<sup>7</sup>. With some exceptions, these all require a continual supply of electrical power to maintain the altered wavelength.

Direct UV writing can be used to fabricate a wide range of integrated optical devices. This technique is based on the localised refractive index increase of a photosensitive planar glass layer through exposure to a tightly focused UV beam. The translation of this beam relative to a suitable substrate allows for the definition of two-dimensional waveguide structures, without photolithographic or subsequent processing<sup>8,9</sup>. Furthermore, Bragg gratings can be written directly into the substrate by direct grating writing. This is achieved through splitting of the single beam into two interfering beams. Controlled modulation of this interference pattern allows for both the grating and the channel structure to be formed simultaneously using the same photosensitive material response<sup>10</sup>.

Barley<sup>11</sup> has reported an example of a siloxane-based polymer functionalized with an azobenzene derivative. This had a refractive index compatible with that of telecommunication grade devices (~1.46), usefully lower than that seen in other active materials such as liquid crystals. The polymer contained only 5% azobenzene units but still exhibited a change in refractive index of  $3.5 \times 10^{-3}$ . Incorporation of such a polymer into an integrated Bragg grating device would allow for a latched reconfiguration of the Bragg wavelength without the need for continual electrical input by photo-switching between isomeric states.

We present here a proof of concept for a reconfigurable





**Scheme 1** The synthetic pathway towards a family of para substituted azobenzene derivatives; i) NaNO<sub>3</sub>, HCl, <5 °C, ii) phenol, <5 °C, iii) ethyl bromoacetate, K<sub>2</sub>CO<sub>3</sub>, NaI acetone, iv) NaOH, ethanol.

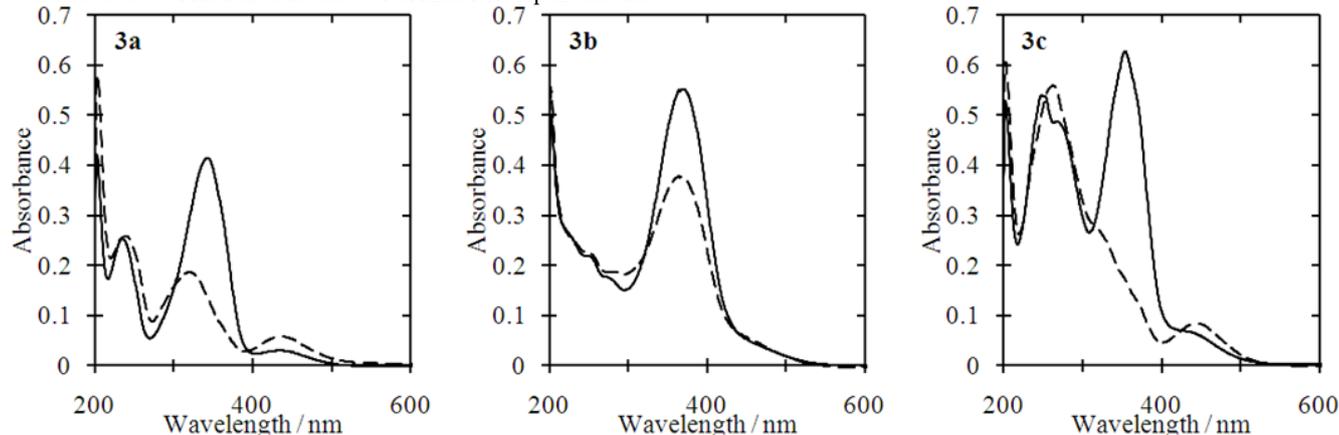
Bragg grating filter using the refractive-index change produced by photo-induced isomerisation of an azobenzene functionalized methacrylate co-polymer. The device may be optically switched between two states and exhibits multi-hour stability.

## 2. Results and Discussion

### 2.1. Investigation of the effect of para substituents on the absorption spectrum upon isomerisation.

The absorption spectrum of the azobenzene unit contains an intense absorption peak corresponding to the  $\pi$ - $\pi^*$  electronic transition of the *trans*-isomer and a weak peak that originates from the weak  $n$ - $\pi^*$  electronic transition of the *cis*-isomer<sup>12</sup>. The change in absorption upon photoisomerisation is directly related to the change in refractive-index. This is defined by the Kramers–Kronig relationship, whereby a larger change in absorption implies a greater change in refractive-index. This allows for the change in refractive-index to be predicted from the magnitude of the change in the absorbance spectrum. To investigate the change in refractive-index upon photoisomerisation, a family of para-substituted 4-phenylazophenoxyacetic acid derivatives was synthesized, as shown in Scheme 1.

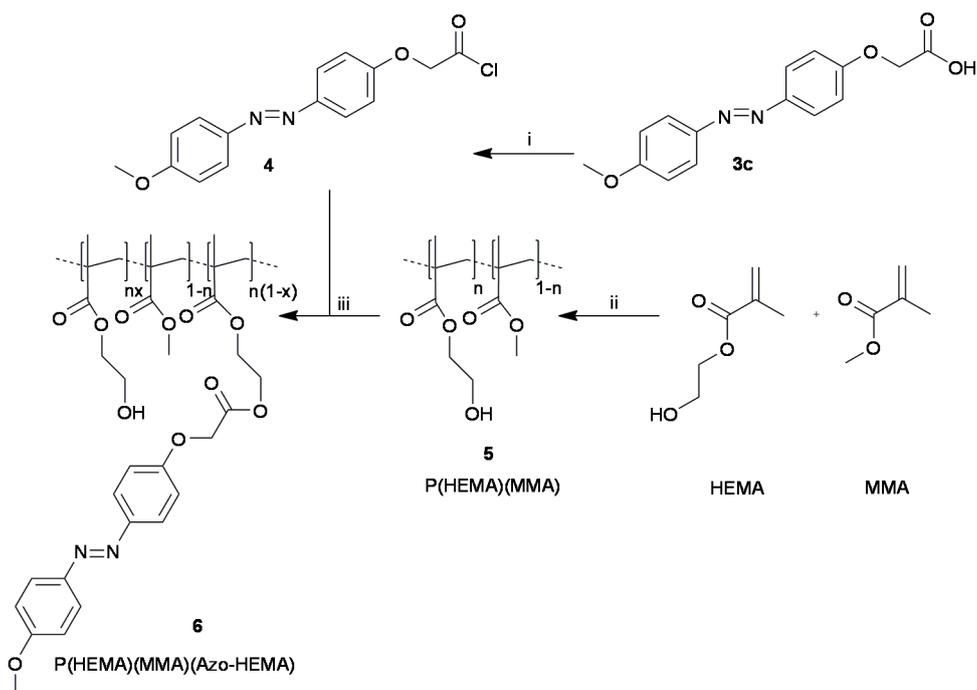
The relative absorbance of the two isomers is dependent on



**Fig. 1** The absorption spectra for *cis* (dashed) and *trans* (solid) para substituted azobenzene derivatives: *cis*-**3a** ( $\lambda_{\max}$  = 320.5, 450.5 nm) and *trans*-**3a** ( $\lambda_{\max}$  = 342.0 nm), *cis*-**3b** ( $\lambda_{\max}$  = 367.5 nm) and *trans*-**3b** ( $\lambda_{\max}$  = 370.0 nm), *cis*-**3c** ( $\lambda_{\max}$  = 444.0 nm) and *trans*-**3c** ( $\lambda_{\max}$  = 356.0 nm).

the electron density within the conjugated azobenzene motif. Upon photoisomerisation, the azobenzene passes from the planar *trans*-isomer to the twisted *cis*-isomer in which the phenyl rings are rotated out of alignment to avoid steric interference. This results in reduced conjugation in the *cis*-isomer. Increasing electron density within the conjugated system exaggerates this difference in orbital alignment between the fully conjugated and partially conjugated states. This results in significant changes in the UV-visible spectrum of the electron rich *p*-methoxy derivative, **3c**, and the electron deficient *p*-nitro derivative, **3b** (Fig.1).

The solution phase UV-visible absorption spectra for compounds **3a**, **3b** and **3c** are shown in Figure 1, for a concentration of  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup> in methanol. For all three compounds, exposing the *trans*-isomer to ultraviolet light, at 365 nm, induces photoisomerisation to the *cis*-isomer with a reduction of the peak at 340-370 nm. For **3c**, the strong peak at 356 nm undergoes complete loss while simultaneously a second peak, corresponding to the *cis*-isomer, is observed to form at 444 nm. A similar transition is observed for **3a**, albeit to a lesser extent, with only a decrease in the absorption peak at 342 nm. In contrast, the *p*-nitro-functionalized derivative **3b** shows a much less marked spectral change, with the formation of the new peak at



**Scheme 2** The synthetic pathway towards an azobenzene functionalised methacrylate co-polymer; i) thionyl chloride, reflux, ii) AIBN, methanol, iii) triethylamine, 2-butanone.

higher wavelength not being observed.

While **3b** is the most polar of the three compounds, it has the lowest electron density within the conjugated system and this is seen with the smallest transition in the absorption spectrum upon photoisomerisation. In contrast **3c** has two electron-donating groups on the periphery of the azobenzene core and this correlates to the most marked change in the UV-visible absorption spectrum.

## 2.2. Preparation and characterization of an azobenzene functionalized methacrylate co-polymer.

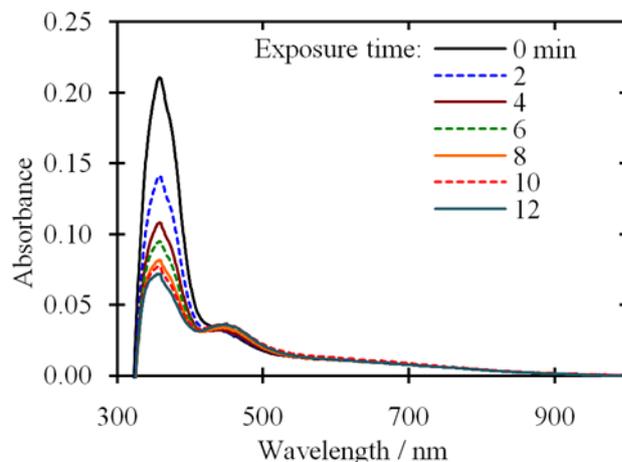
Methyl methacrylate derived co-polymers, such as poly(methyl methacrylate / 2-hydroxyethyl methacrylate), P(MMA)(HEMA), have suitable refractive-indices for use in waveguide systems (refractive-index of P(MMA)(HEMA) = 1.497 – 1.516, depending on the MMA:HEMA composition<sup>12</sup>), while the pendant hydroxyl groups in the latter component allow further functionalisation. The present work describes the radical copolymerization of methyl methacrylate and 2-hydroxyethyl methacrylate to form a 51:49 P(MMA)(HEMA) co-polymer, **5**, into which 4.8% paramethoxy azobenzene units, **4**, were incorporated along the polymer backbone, **6** (Scheme 2). The molecular weight ( $M_w$ , expressed as ‘PMMA equivalent’ molecular weight) of **5** was determined to be ca. 190,500 by GPC (gel permeation chromatography), increasing to 301,500 after attachment of the pendant azobenzene arms, **6**.

The UV-visible absorption spectrum for the co-polymer film, **6**, spun onto a silica substrate, shows that there is an intense absorption peak at 361 nm (Fig. 2) corresponding to the *trans*-isomer and a weak peak at 451 nm which originates from the *cis*-isomer. When the film is irradiated by ultraviolet light at 365 nm, the azobenzene units within the co-polymer

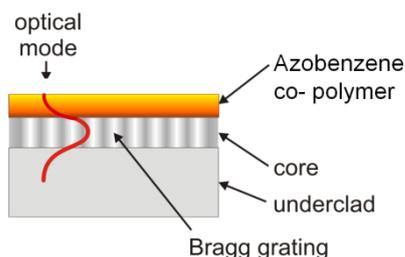
undergo *trans-cis* isomerisation; indicated by the decline of the strong *trans* and increase of the weak *cis* absorption band. After twelve minutes, no further change was detected in the adsorption spectrum, while the reverse isomerisation from *cis* to *trans* took fifteen minutes.

## 2.3. A reconfigurable Optical Bragg grating.

A silica-on-silicon sample was fabricated, where the core layer was doped with germanium to provide photosensitivity. On exposure to a pair of interferometric UV laser beams ( $\lambda = 244$  nm) the refractive-index of the germanium-doped glass locally increased, forming an optical waveguide, furthermore modulation of the beam intensity allowed for four Bragg gratings of different periods to be simultaneously written



**Fig. 2** Time-lapse UV-vis spectra showing the *trans-cis* transition of a 191 nm thick *p*-methoxy azobenzene containing methacrylate co-polymer film, on exposure to ultraviolet light (354 nm) over 12 minutes.



**Fig. 3** A schematic of the evanescent field of the optical waveguide penetrating into the photo-responsive azobenzene co-polymer film.

along the channel waveguide. The reflectance spectrum in the visible and near-infrared regions were analysed remotely by commercial telecoms test and measurement equipment via a fibre pigtail, allowing for the sub-picometer resolution of the peak Bragg wavelengths<sup>10</sup>.

Unlike an optical fibre, no overclad layer was present allowing the evanescent optical field to penetrate up from the waveguide surface. The exposed evanescent field caused the optical mode to be sensitive to the refractive-index of its surroundings and the corresponding shift in peak wavelength of the Bragg spectrum was used to interrogate changes in this environment. Onto this surface a  $413 \pm 27$  nm thick film of the azobenzene-functionalized co-polymer, **6**, was spun (Fig. 3). The presence of the film and its ability to undergo photoisomerisation was confirmed by diffuse-reflectance UV-visible spectroscopy.

Analysis initially focused on the interrogation of the Bragg responses around 780 nm, spectrally near to the absorption feature. At this wavelength, the co-polymer induced high optical loss into the waveguide device, with almost total loss of the optical mode after travelling only 20 mm along the polymer-coated waveguide. Despite the loss, we were able to interrogate the reflectance spectrum of two Bragg gratings within the waveguide. The sample was alternately exposed to ultraviolet light at 365 and 254 nm, thermal changes being monitored by a thermocouple in thermal contact with the optical device. The Bragg response demonstrated reproducible wavelength tuning between the two isomeric states, separated by 35 pm – a well-resolved transition that corresponds to 17 GHz of spectral tuning at 780 nm.

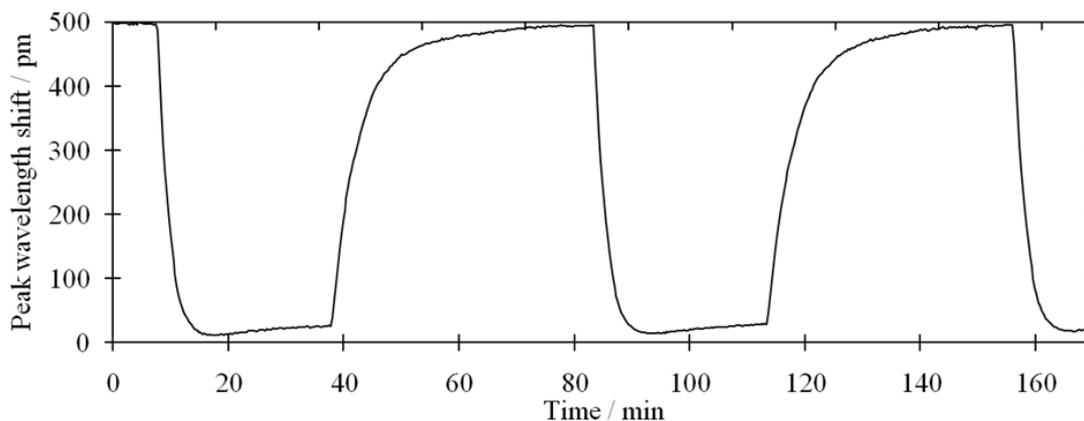
Switching the interrogation to telecom wavelengths (C

band, 1530-1560 nm) resulted in a reduced transition upon isomerisation – consistent with being much further from the absorption feature. However at this wavelength the co-polymer demonstrated greater transparency to the evanescent mode resulting in full guidance along the waveguide with little optical loss. The higher transmitted power along the waveguide resulted in the reflected peak intensity of the Bragg gratings increasing from 6 dB to 22 dB above the noise floor, improving the signal-to-noise ratio. The lower loss at  $\sim 1550$  nm allowed for the deposition of a thicker film ( $719 \pm 23$  nm), resulting in a greater evanescent interaction between the waveguide and **6**, increasing the Bragg shift upon photoisomerisation by over an order of magnitude to 486 pm (Fig. 4). The maximum Bragg shift corresponds to 63 GHz tuning at telecom wavelengths, sufficiently broad for practical optical tuning within a telecom channel.

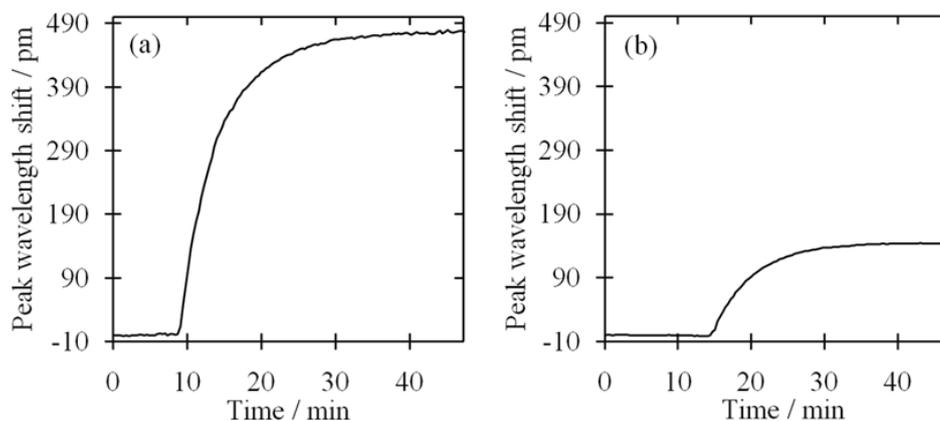
By limiting the duration of the UV exposure the *cis:trans* ratio within the co-polymer can be regulated, allowing fine control of the Bragg wavelength to any value within this half nanometer tuning band. The index change showed the *trans-cis* transition is faster than the reverse process, consistent with observations in the time-lapse UV-visible absorption measurements (Fig. 2).

There has been no evidence of degradation of the index change response upon repeated switching of the device during evaluation. However, whilst the *cis* isomer has long-term instability at room temperature, with Barley<sup>6</sup> reporting  $\sim 20$  h for a 50% reversion, the methacrylate polymer reported here shows a significantly slower linear reversion over 5 days, with a 50% reversion taking  $\sim 60$  h at 21 °C.

Investigation into the modal overlap of the transverse electric (TE) and transverse magnetic (TM) orthogonal optical modes in the presence of the co-polymer overlayer revealed the existence of birefringence. The TE mode penetrates much further from the surface than the TM mode, resulting in a higher sensitivity to changes at the surface. In the presence of the azobenzene-functionalized co-polymer overlayer, this manifested itself as a greater range of tuning than that of the TM mode (Fig. 5). The relative insensitivity of the TM mode could be used for *in situ* temperature referencing through differential studies of the two modes allowing for the fabrication of an athermal optical device<sup>13</sup>.



**Fig. 4** Reversible photo-switching between the two isomeric states results in a detectable optical Bragg shift of 486 nm when interrogated at  $\sim 1550$  nm.



**Fig. 5** The transverse electric mode (a) shows a much larger response to the refractive-index change upon photoisomerisation than the transverse magnetic mode (b).

### 3. Conclusions

A *p*-methoxy azobenzene-functionalised methacrylate copolymer has been synthesised. This has been shown to undergo reversible photoisomerisation when exposed to UV light, producing a corresponding change in refractive-index. This co-polymer demonstrated high thermal stability to isomerisation, giving rise to applications in passively latched devices. When deposited upon an optical surface a reconfigurable Bragg grating was formed that has the potential for a range of optical applications. In this prototype device the maximum observed tuning was 489 pm, corresponding to 63 GHz at telecom wavelengths. This level of tuning is sufficient for future devices that could find application for wavelength trimming of lasers or for reconfigurable dispersion compensation.

## 4. Experimental

### 4.1. General Method.

Melting points were measured using an Electrothermal melting point apparatus and are uncorrected. Electrospray mass spectra were recorded using a Micromass Platform II single quadrupole mass spectrometer. Nuclear magnetic resonance spectra were collected using either a Bruker AV300 spectrometer, or a Bruker DPX400 spectrometer; operating at 400 MHz respectively for  $^1\text{H}$  NMR experiments and 100 MHz for  $^{13}\text{C}$  and Dept-135 NMR experiments.  $^{13}\text{C}$  spectra were collected fully decoupled. Infrared spectra were collected on a Nicolet 380 FT-IR spectrometer with a SmartOrbit Golden Gate Attenuated Total Reflection (ATR) attachment. Polymer film thickness was measured using a KLA Tencor Alpha-step IQ surface profiler running KLA Alpha-step IQ v2.X. Photoisomerisation was stimulated with a UVP UVGL-25 dual wavelength UV-lamp (4 W, 254/365 nm).

### 4.2. Optical Interrogation.

Interrogation of the Bragg grating at  $\sim 780$  nm was carried out with a broadband source, generated from a frequency doubled 1550 nm femtosecond laser source. A 600 nm band pass filter was used to remove any third harmonic light at 515 nm that would interfere with photoisomerisation. For interrogation at

$\sim 1550$  nm the waveguide was exposed to an Exfo IQ-2300 ASE source as part of an Exfo IQ-203 Optical Test system. The resultant signal was collected by an Ando AQ 6317B optical spectrum analyser (OSA) controlled via a PC running Labview 8.2.1. Onto this surface a sub-micron film of **6** (32.5 mg / mL in 2-butanone) was spun at 1800 rpm for 40 s. The presence of the film and its ability to photoisomerise was confirmed by diffuse-reflectance UV-visible spectroscopy using a Varian Cary 500 Scan UV-VIS-NIR spectrophotometer fitted with an internal DRA 2500 integrating sphere.

### 4.3. Materials.

Commercially available compounds were obtained from Sigma Aldrich or Fisher and, unless specified, all reagents and solvents were reagent grade or better and were used as supplied without further purification.

### 4.4. Synthesis.

#### 4-Phenylazophenol<sup>14,15</sup> (**1a**).

Freshly distilled aniline (0.50 mL, 5.37 mmol) was dissolved in a mixture of concentrated hydrochloric acid (0.50 mL, 16.4 mmol) and water (5.0 mL). This was cooled ( $<5^\circ\text{C}$ ) before subsequent dropwise addition of a solution of sodium nitrite (0.401 g, 6.04 mmol) in water (5.0 mL) until an excess was present. This was stirred for 15 minutes, before addition of phenol (0.556 g, 5.49 mmol) in an aqueous solution of sodium hydroxide (1.0 M, 2.5 mL). This was stirred for 30 minutes, before filtering, washing with cold water and drying in vacuo to yield an orange solid (0.755 g), 71 % yield. MP: decomposition at  $80^\circ\text{C}$  (Lit<sup>16</sup>:  $154^\circ\text{C}$ ).  $^1\text{H}$  NMR (MeOD):  $\delta$  6.92 (d,  $J=8.8$  Hz, 2H, Ar-H), 7.37 - 7.56 (m, 4H, Ar-H), 7.76 - 7.88 (m,  $J=8.8$  Hz, 4H, Ar-H).  $^{13}\text{C}$  NMR (MeOD):  $\delta$  116.8 (Ar), 123.50 (Ar), 126.1 (C2,6), 130.2 (Ar), 131.4 (Ar), 147.6 (Ar), 154.2 (Ar), 162.3 (Ar). IR:  $\nu/\text{cm}^{-1}$  3300-3100 (O-H), 3054 (C-H aromatic), 1602 (C=C aromatic), 1411 (N=N), 1139 (C-N), 1071 (C-O). MS (ES<sup>+</sup>, MeOH):  $m/z$  198.2 (100.0 %, [M]<sup>+</sup>), 199.1 (95.1 %, [M+H]<sup>+</sup>). MS (ES<sup>-</sup>, MeOH):  $m/z$  197.2 (100.0 %, [M-H]<sup>-</sup>).

#### 4-(4-Nitrophenyl)azophenol (**1b**).

93 % yield. MP: decomposition at  $170^\circ\text{C}$  (Lit<sup>17</sup>:  $207^\circ\text{C}$ ).  $^1\text{H}$  NMR (MeOD):  $\delta$  6.94 (d,  $J=9.0$  Hz, 2H, Ar-H), 7.87 (d,  $J=9.0$

Hz, 2H, Ar-H), 7.97 (d, J=9.2 Hz, 2H, Ar-H), 8.36 (d, J=9.2 Hz, 2H, Ar-H). <sup>13</sup>C NMR (MeOD): δ 117.1 (Ar), 124.2 (C8,12), 125.9 (Ar), 127.0 (Ar), 147.7 (C1), 149.7 (Ar), 157.7 (Ar), 163.7 (Ar). IR: ν/cm<sup>-1</sup> 3381 (O-H), 3112 (C-H aromatic), 1584, 1603 (C=C aromatic), 1456 (N=N), 1135 (C-N), 1100 (C-O). MS (ES<sup>+</sup>, MeOH) m/z 282.1 (100.0 %, [M+K]<sup>+</sup>). MS (ES<sup>-</sup>, MeOH) m/z 242.2 (100.0 %, [M-H]<sup>-</sup>).

#### 4-(4-Methoxyphenyl)azophenol (1c).

97 % yield. MP: 132 – 133 °C (Lit<sup>18</sup>: 149.8 °C). <sup>1</sup>H NMR (MeOD): δ 3.86 (s, 3H, -OCH<sub>3</sub>) 6.90 (d, J=9.0 Hz, 2H, Ar-H) 7.03 (d, J=9.2 Hz, 2H, Ar-H) 7.76 (d, J=9.0 Hz, 2H, Ar-H) 7.82 (d, J=9.2 Hz, 2H, Ar-H). <sup>13</sup>C NMR (MeOD): δ 56.2 (CH<sub>3</sub>), 115.4 (Ar), 116.8 (Ar), 125.3 (Ar), 125.6 (Ar), 147.7 (Ar), 148.4 (Ar), 161.7 (Ar), 163.3 (Ar). IR: ν/cm<sup>-1</sup> 3411 (O-H), 3026 (C-H aromatic), 2953 (C-H), 1582, 1595 (C=C aromatic), 1436 (N=N), 1149 (C-N), 1014 (C-O). MS (ES<sup>-</sup>, MeOH): m/z 227.2 (100.0 %, [M-H]<sup>-</sup>).

#### Ethyl (4-phenylazophenoxyacetate)<sup>19</sup> (2a).

4-Phenylazophenol (1a, 0.380 g, 1.90 mmol) was dissolved in acetone (silica dried, 60 mL), followed by potassium carbonate (1.658 g, 11.9 mmol) and the mixture was warmed until everything dissolved. To this stirred solution, ethyl bromoacetate (0.125 mL, 3.75 mmol) and sodium iodide (0.287 g, 1.9 mmol, in 4.0 mL acetone) were then added. The reaction mixture was heated under reflux for 16 h. The solvent was removed in vacuo to give an orange solid. This was subsequently extracted into diethyl ether (3 x 40 mL) from water (40 mL); before drying with magnesium sulphate, filtering and removing the solvent in vacuo. The resultant solid was purified by column chromatography (50/50 diethyl ether/light petroleum (40-60)) to give an orange solid (0.307 g), 90 % yield. MP: 66 °C (Lit<sup>20</sup>: 70 °C). <sup>1</sup>H NMR (MeOD): δ 1.26 (t, J=7.1 Hz, 3H, -CH<sub>3</sub>), 4.23 (q, J=7.1 Hz, 2H, -OCH<sub>2</sub>), 4.77 (s, 2H, -OCH<sub>2</sub>C(O)), 7.05 (d, J=9.0 Hz, 2H, Ar-H), 7.39 - 7.53 (m, J=7.5 Hz, 3H, Ar-H), 7.83 (dd, J=8.2, 1.7 Hz, 2H, Ar-H), 7.87 (d, J=9.2 Hz, 2H, Ar-H). <sup>13</sup>C NMR (MeOD): δ 14.6 (CH<sub>3</sub>), 62.6 (CH<sub>2</sub>), 66.4 (CH<sub>2</sub>), 116.2 (Ar), 123.7 (Ar), 125.8 (Ar), 130.3 (Ar), 131.9 (Ar), 148.9 (Ar), 154.17 (Ar), 162.1 (Ar), 170.6 (C(O)). IR: ν/cm<sup>-1</sup> 3068 (C-H aromatic), 2937 (C-H), 1726 (C=O), 1600 (C=C aromatic), 1495 (N=N), 1149 (C-N), 1077 (C-O). MS (ES<sup>+</sup>, MeOH) m/z 285.2 (14.5 %, [M+H]<sup>+</sup>), 307.1 (64.4 %, [M+Na]<sup>+</sup>).

#### Ethyl (4-(4-nitrophenyl)azophenoxyacetate) (2b).

45 % yield. MP: 138 – 139 °C (Lit<sup>21</sup>: 150.5 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.33 (t, J=7.1 Hz, 3H, -CH<sub>3</sub>), 4.32 (q, J=7.0 Hz, 2H, -OCH<sub>2</sub>), 4.74 (s, 2H, -OCH<sub>2</sub>C(O)), 7.06 (d, J=9.0 Hz, 2H, Ar-H), 7.98 (d, J=9.2 Hz, 2H, Ar-H), 8.01 (d, J=9.0 Hz, 2H, Ar-H), 8.38 (d, J=9.0 Hz, 2H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.1 (CH<sub>3</sub>), 61.6 (CH<sub>2</sub>), 65.4 (CH<sub>2</sub>), 115.1 (Ar), 123.2 (Ar), 124.7 (Ar), 125.1 (Ar), 125.5 (Ar), 147.5 (Ar), 148.3 (Ar), 155.9 (Ar), 161.2 (Ar), 168.2 (C(O)). IR: ν/cm<sup>-1</sup> 2897, 3107 (C-H aromatic), 2909 ([C]C-H), 2847 ([O]C-H), 1755 (C=O), 1585, 1601 (C=C aromatic), 1499 (N=N), 1140 (C-N), 1082 (C-O). MS (ES<sup>+</sup>, MeOH): m/z 352.2 (98.5 %, [M+Na]<sup>+</sup>), 681.4 (100.0 %, [2M+Na]<sup>+</sup>). HRMS (ES<sup>+</sup>, MeOH) calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup> 352.0904, found 352.0910.

#### Ethyl (4-(4-methoxyphenyl)azophenoxyacetate) (2c).

53 % yield. MP: 103 – 105 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.32 (t, J = 7.2 Hz, 3H, -CH<sub>3</sub>), 3.89 (s, 3H, -OCH<sub>3</sub>), 4.30 (q, J = 7.1 Hz,

2H, -OCH<sub>2</sub>), 4.70 (s, 2H, -OCH<sub>2</sub>C(O)), 7.02 (dd, J = 9.1, 2.8 Hz, 4H, Ar-H), 7.89 (dd, J = 9.1, 1.4 Hz, 4H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.2 (CH<sub>3</sub>), 55.5 (CH<sub>3</sub>), 61.5 (CH<sub>2</sub>), 65.5 (CH<sub>2</sub>), 114.2 (Ar), 114.9 (Ar), 124.3 (Ar), 124.4 (Ar), 147.0 (Ar), 147.7 (Ar), 159.6 (Ar), 161.7 (Ar), 168.5 (C(O)). IR: ν/cm<sup>-1</sup> 3069 (C-H aromatic), 2937, 2977 (C-H), 1758 (C=O), 1579, 1599 (C=C aromatic), 1437 (N=N), 1149 (C-N), 1027 (C-O). MS (ES<sup>+</sup>, MeOH, m/z): 315.2 (100.0 %, [M+H]<sup>+</sup>), 337.2 (55.9 %, [M+Na]<sup>+</sup>). HRMS (ES<sup>+</sup>, MeOH) calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 315.1339, found 315.1343, calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 337.1159, found 337.1155.

#### 4-Phenylazophenoxyacetic acid<sup>21</sup> (3a).

Ethyl (4-phenylazophenoxyacetate) (2a, 0.280 g, 0.971 mmol) was dissolved in ethanol (40 mL). To this, an aqueous solution of sodium hydroxide (0.056 M, 40 mL) was added before heating the mixture under reflux for 3 hours. The reaction mixture was acidified (conc. HCl) before it was extracted with diethyl ether (3 x 60 mL). The combined extracts were dried with magnesium sulfate, filtered and the solvent was removed in vacuo to yield a yellow solid (0.255 g), >99 % yield. MP: 180 °C (Lit<sup>21</sup>: 184 °C). <sup>1</sup>H NMR (MeOD) δ 4.72 (s, 2H, -OCH<sub>2</sub>C(O)), 7.04 (d, J=9.0 Hz, 2H, Ar-H), 7.37 - 7.54 (m, 3 H, Ar-H), 7.81 (dd, J=8.1, 1.37 Hz, 2H, Ar-H), 7.87 (d, J=9.0 Hz, 2H, Ar-H). <sup>13</sup>C NMR (MeOD) δ 66.1 (CH<sub>2</sub>), 116.2 (Ar), 123.7 (Ar), 125.8 (Ar), 130.3 (Ar), 131.9 (Ar), 148.8 (Ar), 154.2 (Ar), 162.1 (Ar) 172.3 (C(O)). IR: ν/cm<sup>-1</sup> 3068 (C-H aromatic), 2915 (C-H), 2700 broad (O-H), 1706 (C=O), 1602, 1582 (C=C aromatic), 1501 (N=N), 1143 (C-N), 1085 (C-O). MS (ES<sup>+</sup>, MeOH) m/z 257.1 (67.9 % [M+H]<sup>+</sup>), 279.1 (95.2 %, [M+Na]<sup>+</sup>), 311.1 (100.0 %, [M+Na+MeOH]<sup>+</sup>). UV-vis (MeOH): λ<sub>max</sub>/nm 320.5, 450.5 (*cis*), 342.0 (*trans*). HRMS (ES<sup>+</sup>, MeOH) calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 257.0921, found 257.0918, calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 279.0740, found 279.0737.

#### 4-(4-Nitrophenyl)azophenoxyacetic acid<sup>21</sup> (3b).

>99 % yield. MP: decomposed at 175 °C (Lit<sup>21</sup>: 236 °C). <sup>1</sup>H NMR (MeOD): δ 4.75 (s, 2H, -OCH<sub>2</sub>C(O)), 7.09 (d, J=9.0 Hz, 2H, Ar-H), 7.97 (d, J=9.2 Hz, 2H, Ar-H), 8.00 (d, J=9.0 Hz, 2H, Ar-H), 8.37 (d, J=9.2 Hz, 2 H, Ar-H). <sup>13</sup>C NMR (MeOD) δ d 72.00 (CH<sub>2</sub>), 116.0 (Ar), 124.0 (Ar), 125.6 (Ar), 126.3 (Ar), 142.6 (Ar), 149.1 (Ar), 157.2 (Ar) 159.0 (Ar), 179.7 (C(O)). IR: ν/cm<sup>-1</sup> 3108 (C-H aromatic), 2912 (C-H), 2845 ([O]C-H), 1704 (C=O), 1580, 1600 (C=C aromatic), 1496 (N=N), 1138 (C-N), 1070 (C-O). MS (ES<sup>+</sup>, MeOH): m/z 301.2 (30.6 % [M]<sup>+</sup>), 302.3 (6.7 % [M+H]<sup>+</sup>), 324.2 (9.3 %, [M+Na]<sup>+</sup>), 333.3 (5.6 % [M+MeOH]<sup>+</sup>), 356.1 (9.3 %, [M+Na+MeOH]<sup>+</sup>). MS (ES<sup>-</sup>, MeOH): m/z 300.1 (16.3 %, [M-H]<sup>-</sup>). UV-vis (MeOH): λ<sub>max</sub>/nm 367.5 (*cis*), 370.0 (*trans*). HRMS (ES<sup>+</sup>, MeOH) calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>O<sub>5</sub> [M+H]<sup>+</sup> 302.0771, found 302.0766.

#### 4-(4-Methoxyphenyl)azophenoxyacetic acid (3c).

>99 % yield. MP: 182 – 183 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 3.85 (s, 3H, -OCH<sub>3</sub>) 4.79 (s, 2H, -OCH<sub>2</sub>C(O)), 7.09 (d, J = 9.0 Hz, 2H, Ar-H) 7.10 (d, J = 9.0 Hz, 2H, Ar-H) 7.83 (d, J=9.0 Hz, 2H, Ar-H) 7.84 (d, J=9.0 Hz, 2H Ar-H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 55.6 (OCH<sub>3</sub>), 64.8 (CH<sub>2</sub>), 114.6 (Ar), 115.1 (Ar), 124.1 (Ar), 124.2 (Ar), 146.3 (Ar), 146.6 (Ar), 160.0 (Ar), 161.6 (Ar), 169.9 (C(O)). IR: ν/cm<sup>-1</sup> 3419, 3515 (O-H), 2998 (C-H aromatic), 2972 (C-H), 1704 (C=O), 1579, (C=C aromatic),

1437 (N=N), 1144 (C-N), 1018 (C-O). MS (ES<sup>+</sup>, MeOH): m/z 287.2 (16.9 % [M+H]<sup>+</sup>), 309.2 (25.7 %, [M+Na]<sup>+</sup>), 341.2 (15.3 %, [M+Na+MeOH]<sup>+</sup>) 572.6 (29.6 % [2M]<sup>+</sup>). MS (ES<sup>-</sup>, MeOH) m/z 285.2 (18.3 %, [M-H]<sup>-</sup>). UV-vis (MeOH)  $\lambda_{\text{max}}/\text{nm}$  444.0 (*cis*), 356.0 (*trans*). HRMS (ES<sup>+</sup>, MeOH) calcd for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 287.1026, found 287.1027.

#### 4-(4-Methoxyphenyl)azophenoxyacetyl chloride<sup>22</sup> (4).

4-(4-Methoxyphenyl)azophenoxyacetic acid (**3c**, 0.110 g, 0.359 mmol) was refluxed in thionyl chloride (5 mL, 68.5 mmol) overnight under nitrogen. The remaining thionyl chloride was removed by distillation under vacuum (50 °C), before drying the red solid under vacuum (assumed quantitative yield and used immediately without further purification). MP: 164 – 165°C. MS (ES<sup>+</sup>, MeOH): m/z 323.2 (100.0 %, [N+Na]<sup>+</sup>), N represents the molecular ion for methyl [4-(4-methoxyphenyl)azophenoxyacetate] formed from the reaction of **4** with the methanol MS solvent. The formation of the methyl ester was not seen with samples of **3c** and as such can be used as an indicator for successful synthesis of **4**.

#### Poly(methyl methacrylate)(hydroxyethyl methacrylate), P(MMA)(HEMA) (49:51)<sup>11</sup> (5).

A mixture of methyl methacrylate (MMA, 0.89 mL, 8.3 mmol) and hydroxyethyl methacrylate (HEMA, 0.94 mL, 7.5 mmol) was dissolved in methanol (6.0 mL) under a slow stream of nitrogen at 60 °C for 30 minutes prior to the addition of azobisisobutyronitrile (AIBN, 51.3 mg, 0.316 mmol). The reaction was then stirred overnight before heating at 60 °C for 24 hours. The viscous solution was poured into diethyl ether (200 mL) to yield a white precipitate. The cloudy solution was centrifuged before decanting the eluent. The solid was redissolved in methanol and precipitated from diethyl ether a further two times, before drying the white solid under vacuum (1.5857 g), 88 % yield.

<sup>1</sup>H NMR (MeOD):  $\delta$  0.92 and 1.10 (br.s., 6H, -CH<sub>3</sub>), 1.96 (br.s., 4H, -CH<sub>2</sub>) 3.65 (br.s., 3H, -OCH<sub>3</sub>) 3.80 and 4.07 (br.s., 2H, -CH<sub>2</sub>CH<sub>2</sub>-). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  16.2 (CH<sub>3</sub>), 18.5 (CH<sub>3</sub>), 44.0 (C $\alpha$ ), 44.3 (C $\alpha$ ), 51.6 (OCH<sub>3</sub>), 53.6 (C $\beta$ H<sub>2</sub>), 58.5 (CH<sub>2</sub>OH), 66.3 (OCH<sub>2</sub>), 176.3 (C(O)), 177.3 (C(O)). IR:  $\nu/\text{cm}^{-1}$  3500 (broad, O-H), 2991 (C-H), 2948 (C-H), 1716 (C=O). UV-vis (MeOH):  $\lambda_{\text{max}}/\text{nm}$  215. GPC (M<sub>w</sub>, expressed as ‘PMMA equivalent’ molecular weight) 190,500.

#### Poly(methyl methacrylate) (hydroxyethyl methacrylate)(4-(4-methoxyphenyl) azophenoxyacetyethyl methacrylate), P(MMA)(HEMA)(Azo-HEMA) (49:46:5) (6).

P(MMA)(HEMA) (**5**, 1.005 g, 7.72 mmol of HEMA) was dissolved in 2-butanone (12.0 mL) under a slow stream of nitrogen followed by triethylamine (TEA, 1.89 mL, 14 mmol) to give a colourless solution. 4-(4-Methoxyphenyl)azophenoxyacetyl chloride (**4**, 0.401 g, 1.4 mmol) was dissolved in 2-butanone (4.0 mL) to give an orange solution, before adding to the stirred polymer solution, instantaneously forming an orange precipitate. After stirring for 36 hours the viscous solution was poured into diethyl ether (150 mL) to yield a caramel precipitate. This was centrifuged and decanted before trituration in water (50 mL) to leave an orange solid. This was dissolved in 2-butanone (150 mL), centrifuged and precipitated from diethyl ether a further two times. The resultant orange solid was dried under vacuum

(0.8366 g), 62 % yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  0.76 and 0.90 (br.s., 4.26H, -CH<sub>3</sub>), 1.78 (br.s., 1.98H, -CH<sub>2</sub>) 3.53 (br.s., 3.0H, -OCH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>-) 3.90 (br.s., 1.30H, -CH<sub>2</sub>CH<sub>2</sub>-), 4.80 (br.s., 0.54H, -OH) 7.12 (br.s., 0.25H, Ar-H) 7.85 (br.s., 0.25H, Ar-H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  16.21 (CH<sub>3</sub>), 18.3 (CH<sub>3</sub>), 44.0 (C $\alpha$ ), 44.3 (C $\alpha$ ), 51.6 (OCH<sub>3</sub>), 53.5 (C $\beta$ H<sub>2</sub>), 55.6 ((Azo) OCH<sub>3</sub>), 58.5 (CH<sub>2</sub>OH), 66.3 (OCH<sub>2</sub>), 114.5 ((Azo) Ar), 115.1 ((Azo) Ar), 124.0 ((Azo) Ar), 124.2 ((Azo) Ar), 161.6 ((Azo) C(O)), 176.3 (C(O)), 177.0 (C(O)). IR:  $\nu/\text{cm}^{-1}$  3500 (broad, weak O-H), 2992 (C-H), 2949 (C-H), 1718 (C=O), 1598 (C=C). UV-vis (2-butanone):  $\lambda_{\text{max}}/\text{nm}$  356, 447. GPC (M<sub>w</sub>, expressed as ‘PMMA equivalent’ molecular weight) 301,500.

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