

Supporting Information: Covalent Polyester Colouration by *In Situ* Chromophore Creation

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Materials and Methods

Ethylene glycol, *N*-phenyldiethanolamine, antimony trioxide, propionic acid and sulfanilamide were purchased from Alfa Aesar (Lancashire, U.K.) and used as received. 2-Amino-3,5-dinitrothiophene was purchased from ChemCruz (Dallas, TX, U.S.A.) and used as received. All other reagents were purchased from Sigma-Aldrich (Dorset, U.K.) and used as received. Fourier-transform infrared (FTIR) spectra were recorded on a Perkin Elmer Spectrum One spectrometer fitted with a Specac Golden Gate attenuated total reflectance attachment. Spectra were obtained between 4000 cm⁻¹ and 550 cm⁻¹ at 1 cm⁻¹ intervals, accumulated over 100 runs. ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV4 NEO 11.75 T 500 MHz spectrometer fitted with a 5 mm Bruker C/H cryoprobe. Chemical shifts (in ppm) were referenced to a trimethylsilane standard which has a chemical shift of 0 ppm. Polymer molecular weight and dispersity values were determined using a Waters Acquity advanced polymer chromatography (APC) system using a bed of three Acquity columns (XT 125, XT 200 and XT 450) that were all 150 mm in length, had an internal diameter of 4.6 mm, and contained particles of 2.5 μm in diameter that had different pore sizes dependent on the column. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 0.5 mL min⁻¹, column temperature was set at 40 °C and detection was by refractive index measurement. The APC instrument was calibrated against standard poly(methyl methacrylate) samples in THF. UV-vis absorbance analyses were conducted on a dual beam Varian Cary 50 UV-vis spectrophotometer equipped with a xenon pulse lamp. Samples were analysed in quartz cuvettes against a blank sample in triplicate at a concentration of 1 mg mL⁻¹.

Synthesis of P1

Into a 3-necked RB flask, poly(ethylene glycol) monomethyl ether (PEGMME) (3,000 Da, 9.99 g, 3.33 mmol, 1.5 eq.), dimethyl terephthalate (3.60 g, 18.54 mmol, 8.2 eq.), ethylene glycol (1.12 g, 18.04 mmol, 8.0 eq.), *N*-phenyldiethanolamine (0.41 g, 2.26 mmol, 1 eq.), antimony trioxide (0.03 g, 0.10 mmol, 0.04 eq.), calcium acetate monohydrate (0.03 g, 0.17 mmol, 0.08 eq.) and butylated hydroxytoluene (0.02 g, 0.09 mmol, 0.04 eq.) were weighed. A magnetic stirrer bar was fitted and the bulk polymerisation reaction stirred and heated to 210 °C. The flask was fitted with a distillation apparatus and the polymerisation reaction was conducted with a flow of N₂ over seven days. The

crude polymer was purified by dialysis (2,000 Da molecular weight cut-off) against deionised water and collected by lyophilisation prior to analysis. Yield of recovered polymer = 72%.

Synthesis of P2: conjugation of 2-amino-3,5-dinitrothiophene to P1

A RB flask was fitted with a magnetic stirrer bar and cooled in ice before sodium nitrite (0.48 g, 6.96 mmol) was weighed and dissolved slowly in concentrated sulfuric acid (6 mL). To the stirring sodium nitrite solution, a solution of propionic acid (3 mL) in acetic acid (18 mL) was added slowly over a 20 minute period with stirring at 0 °C. To the stirring, cold, yellow coloured solution, 2-amino-3,5-dinitrothiophene (1.2 g, 6.34 mmol) was added slowly. After 30 minutes of stirring at 0 °C, a solution of **P1** (0.5 g, 0.05 mmol) in deionised water (20 mL) was transferred slowly followed by concentrated HCl (2 mL). The coloured solution was stirred for a further hour at 0 °C to ensure the reaction is complete before being washed by dialysis (2,000 Da MWCO) and collected by lyophilisation (yield of recovered polymer = 60%).

Synthesis of P3: sulfanilamide conjugation to P1

Analogous to the synthesis of **P2** above, a solution of propionic acid (3 mL) in acetic acid (18 mL) was added slowly to a solution of sodium nitrite (0.48 g, 6.96 mmol) in concentrated sulfuric acid (6 mL) at 0 °C. Sulfanilamide (1.09 g, 6.33 mmol) was added slowly at 0 °C and left to stir for 30 minutes for the reaction to complete. A solution of **P1** (0.69 g, 0.07 mmol) in deionised water (20 mL) was then transferred slowly to the red sulfanilamide diazotisation reaction flask followed by concentrated HCl (2 mL). The dark red coloured solution was stirred for a further hour at 0 °C before being washed by dialysis (2,000 Da MWCO) and collected by lyophilisation (yield of recovered polymer = 90%).

Simulated dye transfer inhibition of P1

A GyroWash TestWise Touch laundrometer was used to assess the capability of **P1** to reduce dye transfer from an indigo test fabric to a range of test fabrics. A 0.1 mg mL⁻¹ solution of **P1** in deionised water (50 mL) was prepared and transferred to a laundry test capsule along with a multifibre swatch. The multifibre swatch was composed of strips of regenerated cellulose, cotton, wool, nylon, polyester and acrylic. An indigo dye bleed was introduced to the laundry test capsule in the form of a piece of fabric dyed with indigo dye the same size as the multifibre swatch. 25 stainless steel ball bearings were added to the laundry test capsule to aid the simulation of the mechanical action of a domestic laundry setting. The sample was then washed at 40 °C at a rotation speed of 40 r.p.m. for 30 minutes.

The colour change of the various test fabrics was measured using a Spectraflash DataColor spectrophotometer providing L*a*b* colour system values, before and after washing in the laundrometer. Measurements were made under D65 lighting. The colour difference, ΔE , was calculated from Eqn. (1). The washings in the presence and absence of **P1** were all performed in triplicate and the average ΔE value was presented.

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

Dye transfer from P2 to test fabrics

Using the same test conditions as stated above, a solution of **P2** (0.1 mg mL^{-1} , 50 mL) was assessed in the presence of test fabric using the laundrometer, but in the absence of an indigo dye bleed. The same test was performed for a commercial polymer-dye to determine any difference in fabric colouration when the fabric undergoes simulated laundering, independently in the presence of **P2** and a patented polymer-dye. The colour difference of the fabric pre and post laundering was calculated using Eqn. (1).

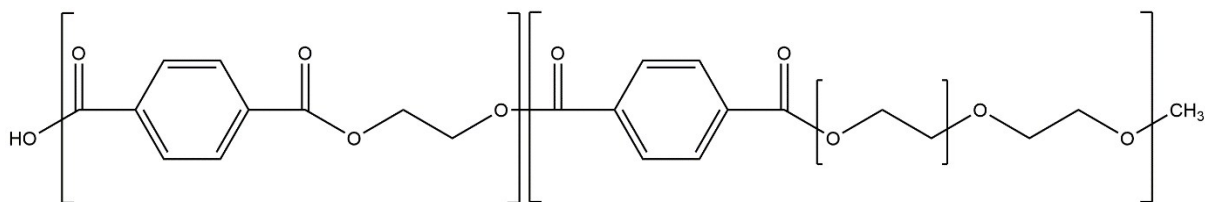


Fig. S1 Structure of a representative SRP: PET-*b*-PEG.

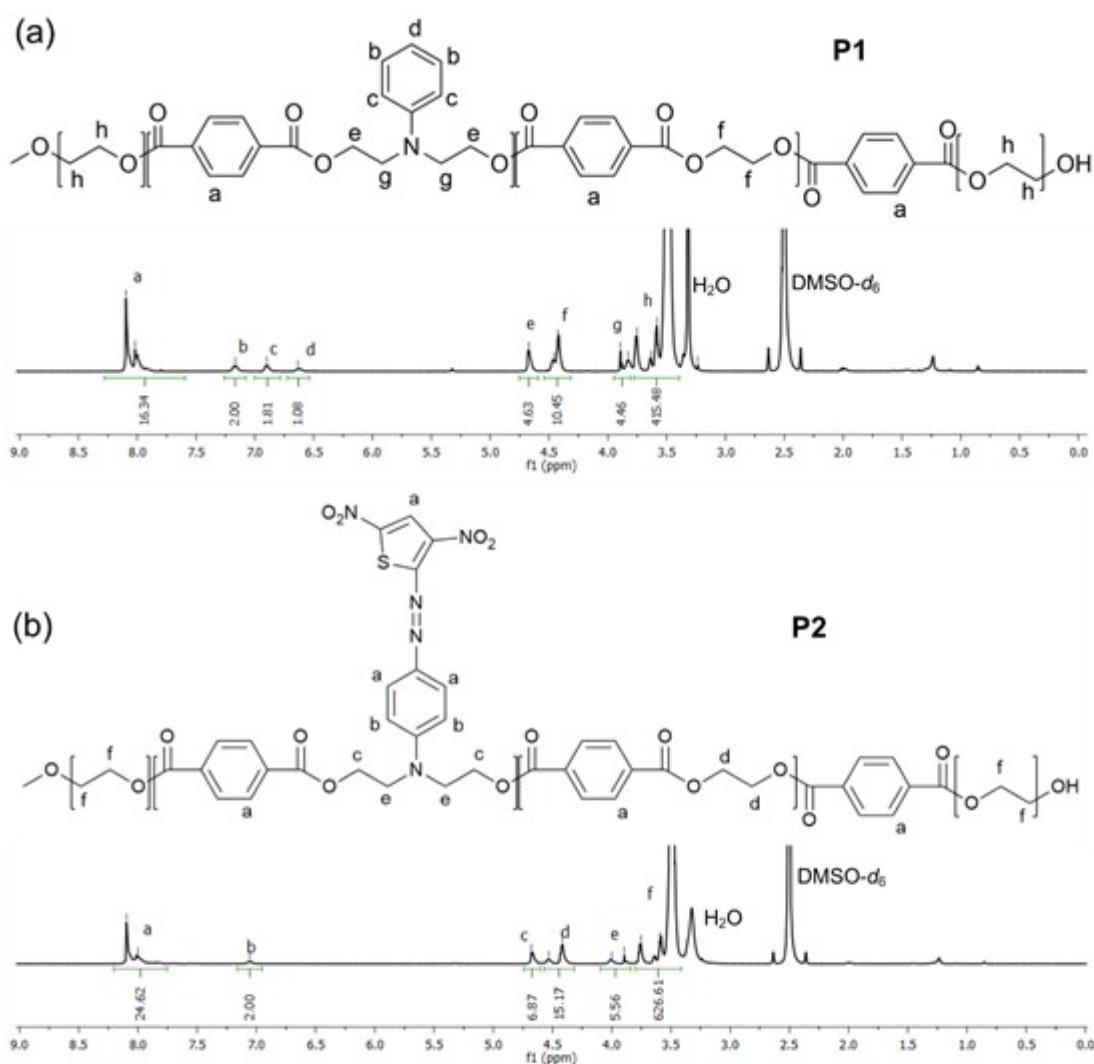


Fig. S2 ^1H NMR spectra of **P1** (a) and **P2** (b) (500 MHz, $\text{DMSO-}d_6$).

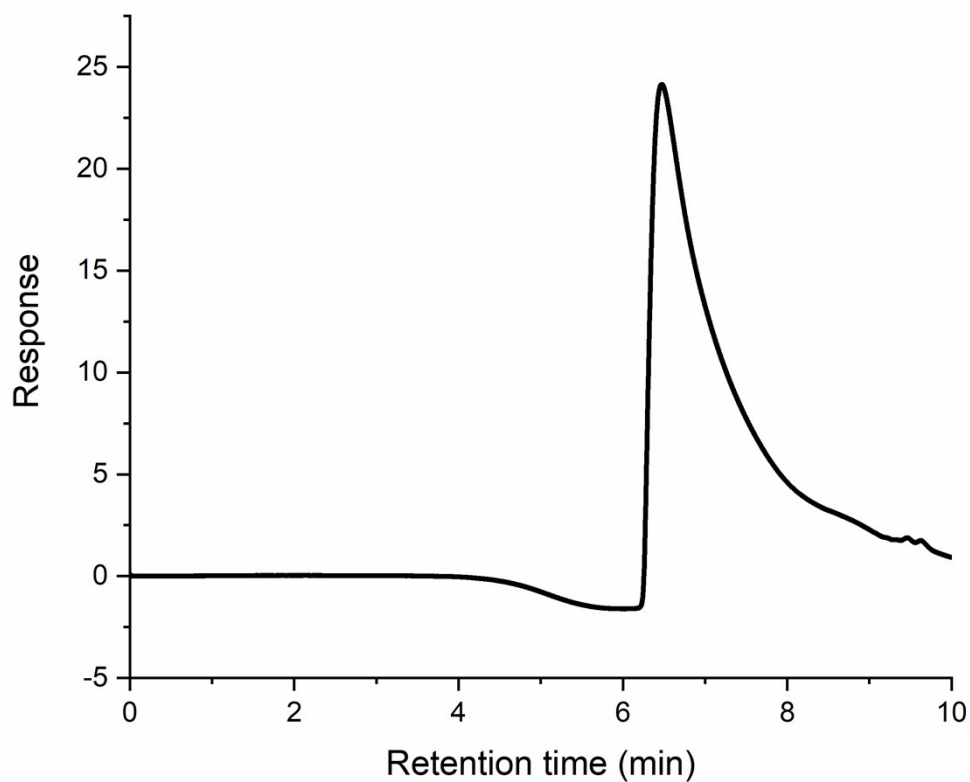


Fig. S3 APC chromatogram for P1.

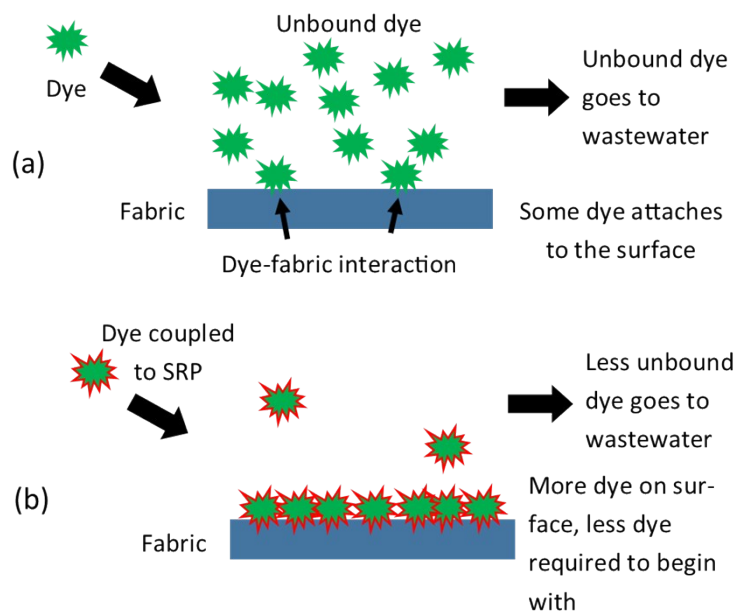


Fig. S4 Diagram showing the difference between dyeing polyester fabric using a disperse dye (a) and dyeing polyester fabric with a disperse dye coupled to a SRP (b).

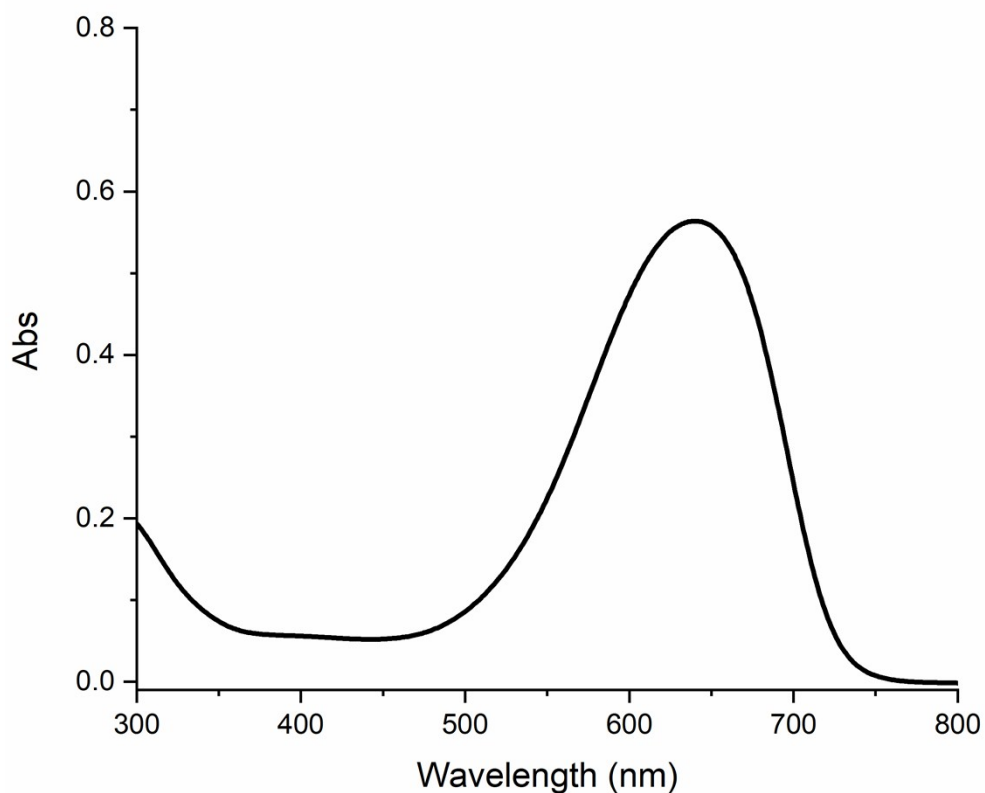


Fig. S5 UV-vis absorbance spectrum of **P2**.

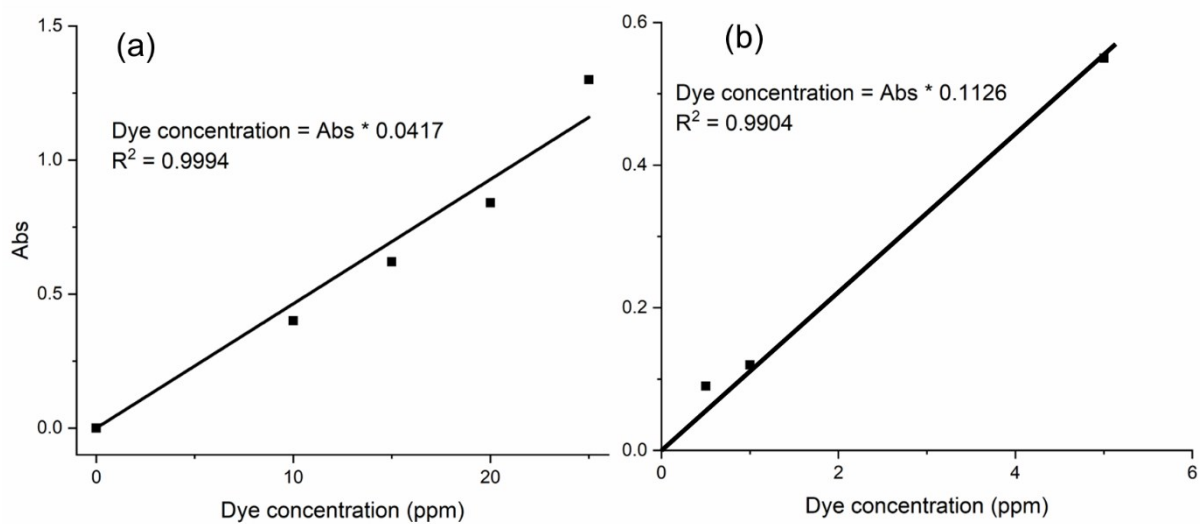


Fig. S6 Calibration curves for the dye concentration outside the dialysis media for commercially-available SRP (a) and the novel SRP **P2** (b).

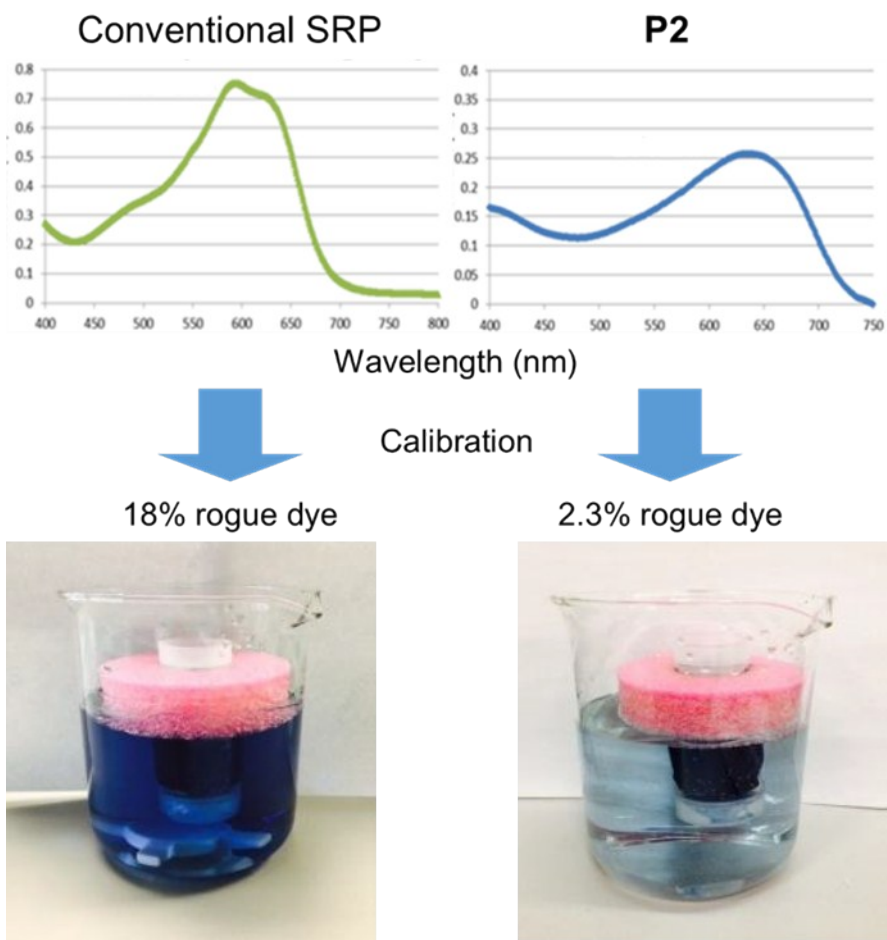


Fig. S7. UV-vis absorbance spectra of the media outside the dialysis membrane for conventional and this novel approach. Amount of dye leached was quantified from a calibration curve of known concentrations.

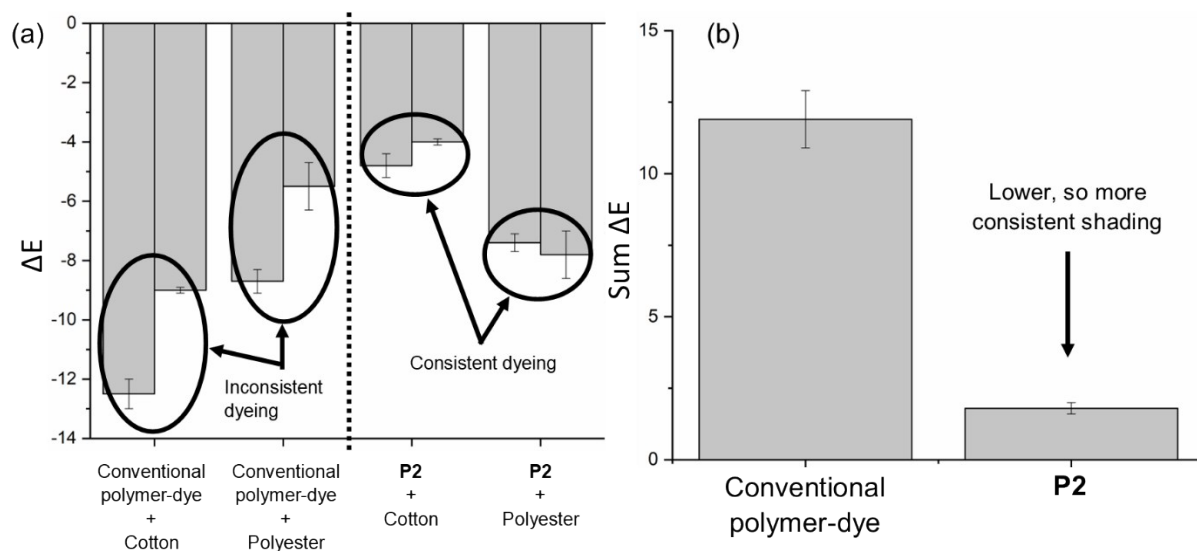


Fig. S8. Graph comparing the consistency of dye deposition onto cotton and polyester for a commercial unmodified polymer-dye and **P2** (a). Graph comparing the consistency of the shading across a mixed washing load containing cotton, polycotton and polyester (b).

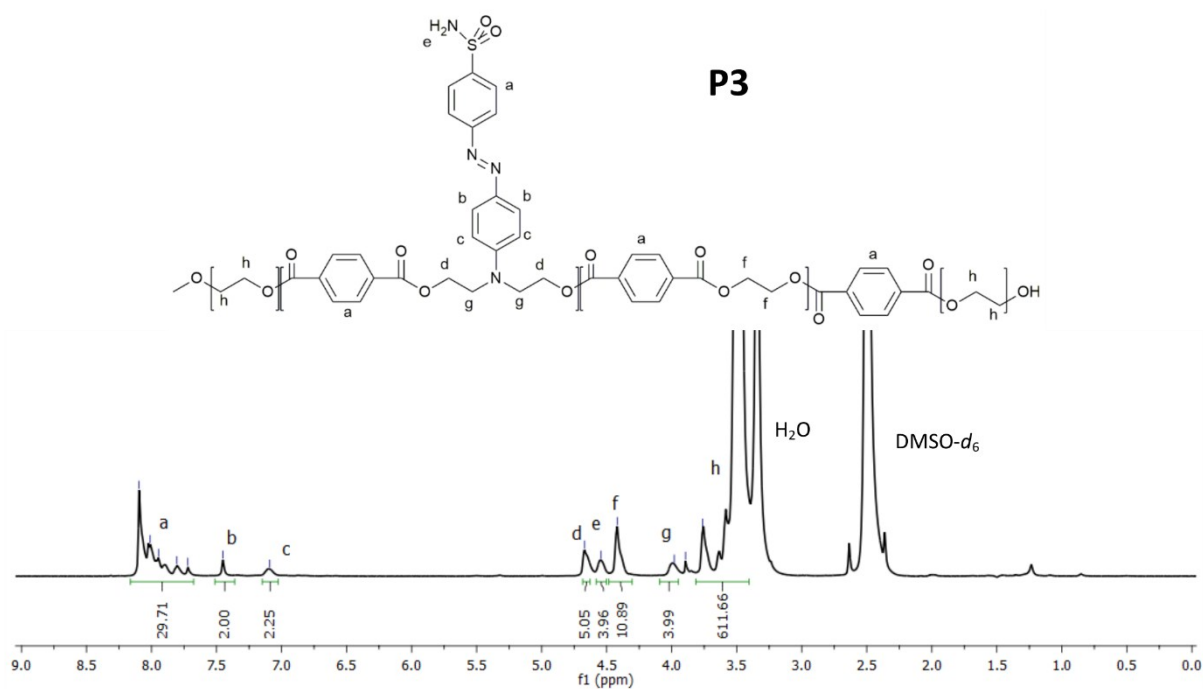


Fig. S9 ^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **P3**.

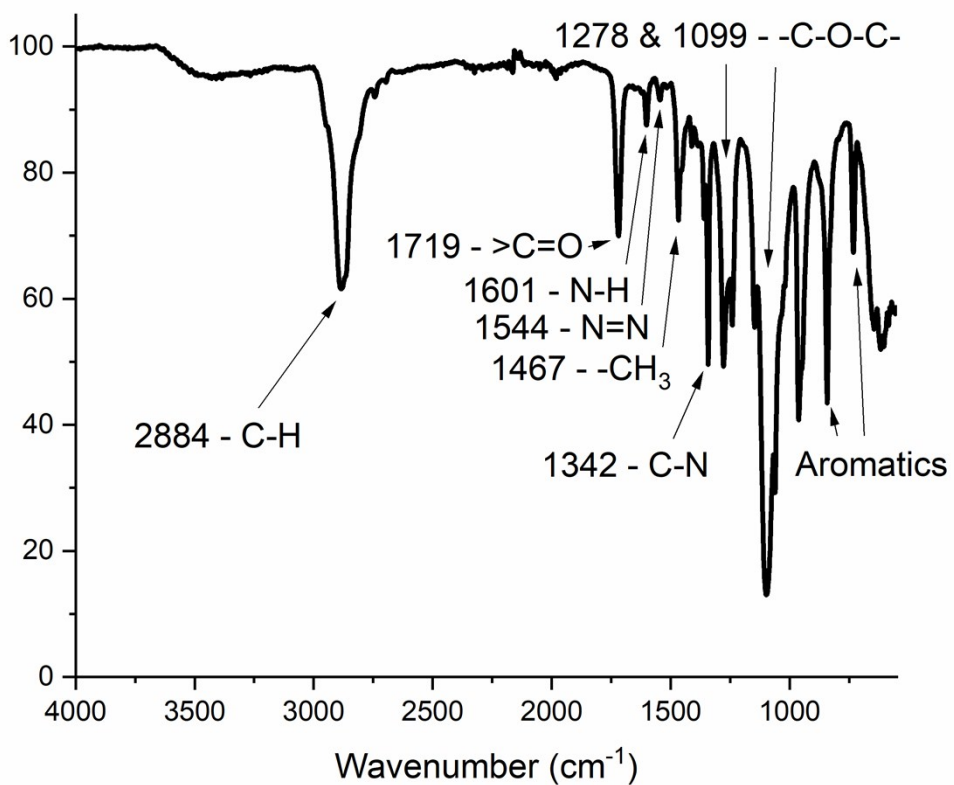


Fig. S10 FTIR spectrum of **P3**.