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Polymers for dye transfer inhibition in laundry applications

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Abstract

The deposition of dyes onto lightly colored garments, or onto lighter sections of multicolored garments, during laundry results in fabric discoloration. In particular, there is a requirement to restrict indigo dye transfer between garments. Polymers may be added to detergent formulations as dye transfer inhibitors to prevent dye transfer by blocking the deposition of fugitive dyes in aqueous solution. This article reports the generation of a range of dye transfer inhibitors produced by condensation reactions that are effective in preventing the transfer of unbound indigo dye to a variety of fiber types. Key design rules relating to polymer hydrophilicity and pendant polymer functionality were established for the creation of effective dye transfer inhibitors. Remarkably, polymers at concentrations as low as 0.1 mg/ml were found to be effective in inhibiting indigo deposition on a variety of fiber types, offering great promise for their inclusion within laundry detergent formulations as dye transfer inhibitors.

KEYWORDS

applications, copolymers, functionalization of polymers, polycondensation

1 | INTRODUCTION

Dye transfer occurs in the laundry process, whereby a “fugitive” dye molecule detaches from one fabric and deposits on another,[1,2] leading to the graying and discoloration of lighter garments. Such dye bleeding from fabrics is caused by a number of factors, including the pH of the aqueous medium, fabric agitation, washing time and temperature.[3] This problem is particularly noticeable for the nonreactive dyes, such as direct, sulfur and vat dyes, which account for 75% of the dyes that are used to color cotton fabrics.[4,5] To prevent dye transfer, additives may be included in detergent formulations that act as dye transfer inhibitors (DTIs). There are three major mechanisms for the action of DTIs; the prevention of dye release from the donor fabric by a fixing agent, the adsorption or degradation of dye molecules once they enter the laundry liquor, and the prevention of dye molecules in the laundry liquor from depositing onto the fabric via obstruction.[1,6]

Fixing agents included in the detergent formulation prevent dye bleeding into the wash liquor. Commonly, fixing agents are cationic, amine-containing, molecules,[7] or carbohydrates modified with cationic groups, such as imidazole groups.[8–10] The reduced dye fading is attributed to the interaction of the DTI with the fiber of the dyed garment, the “donor” fabric, preventing the loss of the dye or pigment associated with the fiber.[8] These compounds are also able to reduce physical damage to the fiber, caused by agitation in the wash.[11] However, due to their cationic nature, such DTI agents cannot readily be used in formulations containing anionic surfactants because they interfere with cleaning.[7]

The bleaching and degradation of fugitive dye molecules prevents the discoloration of lighter fabrics.[12,13] Examples of bleaches used in laundry detergents include peracids,[14] hypochlorite,[15,16] and hydrogen peroxide.[17] Water-soluble enzymatic systems that catalytically produce hydrogen peroxide are commonly used,[18] such as manganese-salen complexes,[13] porphine complexes,[19] phthalocyanine,[20] and porphyrin complexes.[21] However, the use of a bleaching agent in a detergent is non-selective, and results in fabric fading. In addition, damage to the fiber may also occur, which causes further color fading,[22] and the oxidizing agent may interfere with other laundry detergent components, potentially causing their degradation during the wash.[23]

The inclusion of (macro)molecules that inhibit unwanted dye adsorption onto fabrics within laundry detergent formulations may be exploited as a highly beneficial, and nondetrimental, mode of dye transfer inhibition. Polymers are commonly used to prevent dye transfer in laundry washing and, in contrast to bleaches, do not cause physical damage to clothing fibers.[24–26] Amine-containing polymers, such as poly(vinyl pyrrolidone) (PVP), have been widely used as DTIs in laundry detergent formulations due to the water-solubility of PVP and its ability to complex dyes.[27,28] However, anionic surfactants are often included in detergent formulations due to their exceptional cleaning and foaming qualities, and their processability into powdered forms.[29] such surfactants may compete with the dye molecules for PVP binding, thus reducing polymer efficacy,[30] and diminishing the cleaning qualities of the surfactant.

Consequently, there is a clear requirement for the development of DTIs that do not present the limitations associated with fixing agents, bleaches, and commonly used adsorbents, as described above. Amphiphilic block copolymers may be exploited to prevent dye transfer to the fabric surface in a manner analogous to anti-fouling systems used for marine paints.[31–33] The hydrophobic component of the block copolymer may be designed to adhere to the fabric surface through intermolecular interactions, while the hydrophilic block favors water interaction, forming a hydration layer between the fabric surface and the aqueous environment. This hydration layer may prevent molecular adhesion to the fiber surface.

We report a series of PEG-terminated amphiphilic macromolecules as potential DTIs, primarily to prevent unwanted indigo dye deposition. The incorporation of functional groups capable of forming hydrogen bonds with various fabrics are investigated and the DTI performance of each polymer created as a DTI reported. Polymers of relatively low molecular weight that present a very limited hydrophobic component could be dispersed well in water and were found to be extremely effective in the prevention of indigo transfer to a range of fabrics. Such materials may hold promise as DTIs in laundry detergent formulations to restrict the transfer of highly problematic indigo dye.

2 | EXPERIMENTAL

2.1 | Materials

Indigo (310 g/m^2), C.I. Sulfur Black 1 (420 g/m^2) and C.I. Direct Orange 39 (90 g/m^2) dye bleeding fabrics were purchased from Swissatest Testmaterialien AG (Switzerland). C.I. Reactive Red 141 (180 g/m^2), C.I. Reactive Brown 7 (90 g/m^2), C.I. Reactive Black 5 (180 g/m^2) and C.I. Direct Black 22 (90 g/m^2) were supplied by the Centre for Test Materials BV (Netherlands). Multifibre swatches were supplied by SDC Enterprises (Bradford, UK).

Benzoylated dialysis tubing (M_w cut-off 2 kDa), 1,2-propanediol, butylated hydroxytoluene, dimethyl terephthalate, glycerol, mPEG$_{750}$, titanium(IV) isopropoxide and mPEG$_{5000}$ were supplied by Sigma-Aldrich. mPEG$_{500}$ and 2-amino-2-methyl-1,3-propanediol was supplied by Acros Organics. Alfa Aesar supplied 2,2-dimethyl-1,3-propanediol, ethylene glycol, pentaerythritol, tris(hydroxymethyl) aminomethane and mPEG$_{13000}$.

2.2 | Instrumentation

Multifibre and dye bleeder washes were performed on a James Heal GyroWash[2] set at 40°C, for 30 min at 40 rpm. Fabric color changes were measured using a Spectraflash DataColor unit. Infrared (IR) spectra were obtained using a Bruker Alpha Platinum-ATR instrument. ^{1}H NMR spectra were obtained using a Bruker AVANCE 500 at 128 scans. A Malvern Instrument ZetaSizer Nano ZSP was used to determine zeta potentials. Three zeta runs were obtained at 25°C, using a measurement position of 2.00 mm. Waters ACQUITY Advanced Polymer Chromatography was used to determine the molecular weight of the polymers. The polymers were dissolved in THF (1 mg/ml) and passed through a 0.22 μm filter. The values are calibrated to PMMA standards. SEM images were taken using a JEOL JSM-6610LV, having used a Quorum Q150RS sputter coater to give a 30 μm gold coat over the sample.

2.3 | Simulated washing

A dye bleeding fabric, a swatch with six different adjacent fabrics (a “multifibre swatch”), 25 ball bearings and 50 ml of a polymer solution (0.1 mg/ml) were placed in a stainless steel container. This was sealed and placed on a rotor in a water bath (the GyroWash) which was set to 40°C, and the mixture spun for 30 min at 40 rpm. Color changes were measured using a Spectraflash DataColor unit, which measured the L* a* and b* coordinates, which can be compared to an unwashed sample to give a color change (ΔE) value. Measurements were made under D65 lighting. Each measurement was independently carried out three times.

2.4 | Example procedure for the synthesis of a dye transfer inhibitor (DTI1)

All reported DTIs detailed were produced by step-growth polymerization by a method analogous to this. mPEG$_{500}$ (terminal units, 11.06 g, 22.12 mmol), dimethyl terephthalate (repeat unit in central block, 2.29 g, 11.79 mol), propane-1,2-diol (repeat unit in central block, 1.79 g, 23.52 mol), butylated hydroxytoluene (antioxidant, 0.013 g, 0.059 mmol) and Ti(IV) isopropoxide (catalyst, 0.013 ml, 0.042 mmol) were weighed into a three necked round bottom flask, fitted with a distillation head, bridge and flask, with an internal thermometer and placed under a constant flow of N_2(g). The reaction mixture was heated to 150°C and over 48 hr was slowly raised to 210°C. This temperature was maintained for a further 72 hr. The reaction product was then allowed to cool and was dissolved in deionized water (100 ml) before being dialysed for 5 days and then dried in vacuo. Yield: 11.56 g, light brown oil. Mw according to APC: 3050 Da.

FTIR (cm^{-1}): 3550 (—O—H, alcohol), 2,863 (—C—H, alkyl), 1719 (—C═O, ester), 1,270 (—C—O, aromatic ester), 1,095 (—C—O, alcohol), 942 (—C═C—, alkene) 732 (—C—H, aromatic).

^{1}H NMR (500 MHz, DMSO) δ 8.23–7.89 (ArH), 4.68–4.52 (CH), 4.43 (CH_3), 3.84–3.35 (CH_2), 3.24 (CH_3), 1.53–0.92 (CH_2).

3 | RESULTS AND DISCUSSION

A series of polymers were synthesized via condensation reactions in order to produce PEG-terminated polyesters as DTIs. The polymers included a variety of diol monomers incorporated into the central polyester block to impart varied functionality. In each case, this component of the polymer was restricted to ensure that the polymers overall were sufficiently hydrophilic to disperse in aqueous solution. All reactions proceeded over a duration of days at a maximum temperature of 210°C. This contrasts to commercial poly(ethylene terephthalate) (PET) synthesis which may be completed within hours at 285°C. The similarities between the polymerisations reported and PET synthesis suggest that all the polymers disclosed may feasibly be produced on an industrial scale analogous to commercial PET synthesis. The reaction scheme for polymer production, whereby the ethylene unit highlighted in red may be substituted with other diol monomers, is provided in Figure 1. Details concerning the structure of the polymers, in terms of the monomers that were included within the central polyester section, are provided in Table 1.

3.1 | DTIs that lack pendant functionality

Initially, three polymers (DTI1, DTI2, and DTI3) that contained a variety of repeat units within the central component of the polymer backbone (Table 1), and terminal mPEG$_{500}$ units were synthesized. All three polymers were analyzed by ^{1}H NMR to confirm the inclusion of the different monomers within the polymers formed (Supporting Information, Figures S1, S2, and S3, respectively). The peak corresponding to the hydroxyl group of glycerol within DTI2 can be observed at 2.50 ppm and the peaks

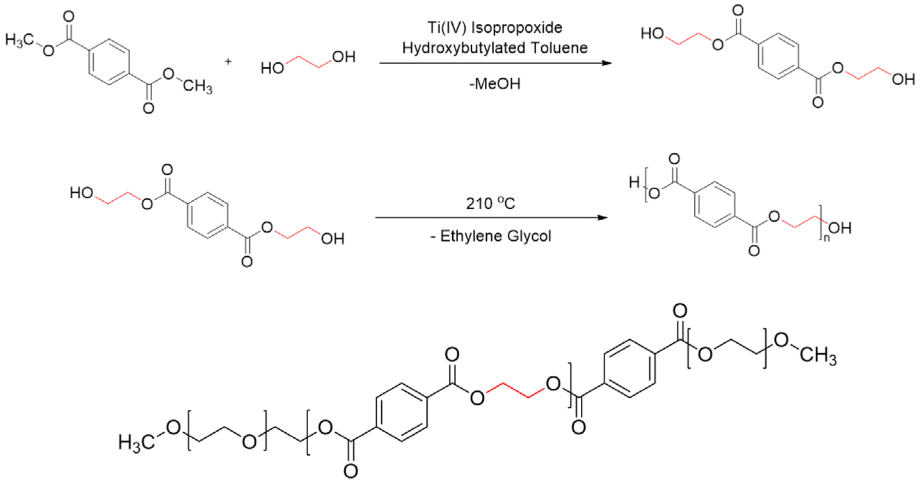
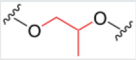
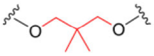
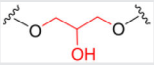
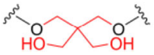
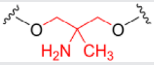
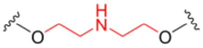
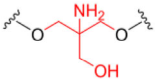


FIGURE 1 Reaction scheme for the polycondensation reaction to produce the polyester block of the polymer, incorporating various diols (highlighted in red) and the generic structure of the final, PEG-terminated polymer [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 The repeat units present in the polymers used to create the potential DTIs presented [Color table can be viewed at wileyonlinelibrary.com]

Monomer	Structure	DTI1	DTI2	DTI3, 4 and 5	DTI6 and 7	DTI8	DTI9	DTI10	DTI11	DTI12	DTI13
Ethylene glycol			✓			✓	✓	✓			✓
Propane-1,2-diol		✓									
2,2′-Dimethyl-1,3-propanediol				✓	✓					✓	
Glycerol			✓	✓					✓		
Pentaerythritol					✓						
2-Amino-2-methyl-1,3-propanediol						✓					
Diethanolamine							✓		✓		
Pentanediol								✓			
Tris(hydroxymethyl) aminomethane										✓	✓

corresponding to the methyl groups of 2,2′-Dimethyl-1,3-propanediol within DTI3 can be seen at 0.92 and 1.31 ppm. The DTI capabilities of these polymers was assessed against indigo dye by dissolving the polymers in DI water (0.1 mg/ml, 50 ml) and washing in the presence of an indigo dye bleeding fabric and a multifibre swatch. The multifibre contained six different fiber types: regenerated cellulose, cotton, nylon, polyester, acrylic, and wool. This allows the determination of indigo deposition onto a variety of fabric types, quantifiably verifies the efficacy of the DTI for each fiber, and therefore provides an excellent guide for proposed DTI efficacy. The color change (ΔE) caused by indigo onto the multifibre swatch was measured by comparing the L*a*b* values of the sample swatch and a reference, unwashed swatch. This value was compared to that of a swatch washed in the absence of polymer in order to ascertain the extent of any benefits provided by the polymers (Figure 2). A high ΔE value represents a large color difference between an unwashed reference sample, and the washed discolored sample. Therefore, a ΔE value comparable to the "No Polymer" experiment indicates an ineffective DTI.

Figure 2 reveals that DTI3 is a particularly effective DTI against indigo for a range of fiber types. A reduction in color change of over 50% for cotton and wool, in comparison to when a polymer is not included in the wash, is particularly significant considering the extremely low polymer concentration used. The efficacy demonstrated against a wide-range of fibers suggests greater polymer-fiber interaction compared to polymer-water interaction, particularly in the cases of DTI2 and DTI3. Both DTIs contain glycerol which provides an increased number of hydroxyl sites that may form additional hydrogen bonds with fabric and/or provide a site for polymer branching.

3.1.1 | The prevention of C.I. reactive red 141 (RR141) and C.I. reactive black 5 deposition: DTI3 Versus PVP

DTI3 was advanced to testing against C.I. Reactive Red 141 (RR141), and C.I. Reactive Black 5 (RB5), and PVP was also assessed for comparison as a commercial DTI. In the absence of polymer, RR141 causes a color change of 2.2 for cotton (Figure S4). The presence of PVP reduces the color change to 1.5, but DTI3 reduces the ΔE value of all fibers tested to below 1.0, with exception to nylon (ΔE = 1.2). For the fiber types tested, DTI3 is a more effective DTI than commercially used PVP against RR141 under the test conditions employed. The color change to the fabrics caused by RB5 is reduced to below 1.0 when DTI3 was included, with exception to regenerated cellulose (ΔE = 1.04) (Figure S5). The reduction in color change for cotton and polyester are particularly significant, decreasing from 1.75 to 0.75 and 1.6 to 0.6, respectively, upon the addition of DTI3. Imprtantly, DTI3 out-performs PVP, which does not exhibit a statistically significant reduction in ΔE for any of the fiber types studied.

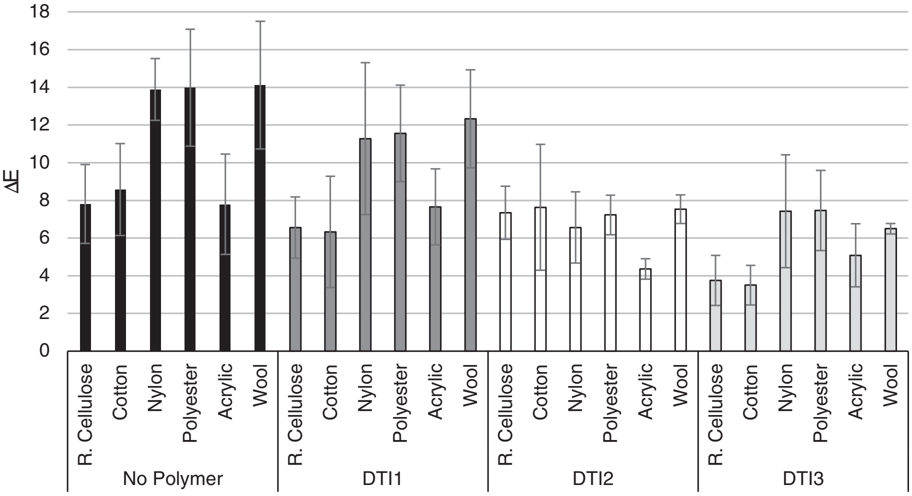


FIGURE 2 A comparison of color change caused by indigo in the presence of mPEG$_{500}$, DTI1, DTI2 and DTI3

TABLE 2 The wash conditions of the DTI3 pre-conditioning study, showing whether the dye bleeding swatch or the polymer were present in the wash

	Wash 1		Wash 2		Wash 3	
Sample name	**Dye bleeding swatch**	**DTI3**	**Dye bleeding swatch**	**DTI3**	**Dye bleeding swatch**	**DTI3**
Build-up 1	No	Yes	Yes	No	N/A	N/A
Build-up 2	No	Yes	No	Yes	Yes	No

3.1.2 | DTI3 fabric deposition and retention

In order to assess if DTI3 deposits on the fiber during the wash, and if it remains on the fabric after washing, multifibre swatches were pre-conditioned with the DTI3 without the presence of dye for either one or two washings (Build-up 1 and Build-up 2,respectively), before the multifibre swatch was combined with an indigo dye bleeding fabric in deionized water in the absence of polymer. It was proposed that if the DTI efficacy is maintained in the final wash when DTI is not included, DTI3-fabric interaction has occurred in the previous washes. This will be observable by comparable ΔE values for all washes, including the final wash cycle in which DTI3 is present. The conditions of the two independent pre-conditioning washes are outlined in Table 2.

The color change values of each swatch were determined and compared (Figure 3). The pre-conditioning (or build up) studies show a reduced color change to that without polymer. For example, in the absence of polymer, nylon has a ΔE value of 13.9, which is reduced to ΔE 7.4 in the presence of DTI3, ΔE 7.1 after one build up cycle, and ΔE 9.6 after two build up cycles. Since no additional polymer is included in the solution when the preconditioned fabrics are exposed to fugitive dye, these results suggest the polymer deposits onto the fabric to prevent dye transfer by surface modification. For all fiber types, reduced discoloration is observed in the wash in which DTI3 is not added compared to fiber discoloration in the absence of DTI3. This implies that DTI3 has some affinity for all the fiber types tested, and remains, to some extent, adhered to the fiber post-wash.

To observe if the polymer is considerably deposited onto the fabric to the point where it might cause an effect on the hand feel of the fabric, SEM images were obtained of cotton, nylon, polyester and wool after washing with DTI3, and having been washed in the absence of DTI3 (Figure S6). In all instances DTI3 was not visible, which may be expected given the very small quantity of DTI3 incorporated in all washes.

3.2 | The effect of hydrophilic mPEG molecular weight on DTI performance

To determine the influence of the terminal mPEG blocks on the performance of DTIs, two further polymers based on the DTI3 formulation were synthesized whereby the molar ratio of the mPEG block to the polyester block remained constant, but the molecular weight of each mPEG unit increased to either 750 g/mol (DTI4) or 5,000 g/mol (DTI5). Successful synthesis of the polymers was confirmed by ^{1}H NMR (Supporting Information,

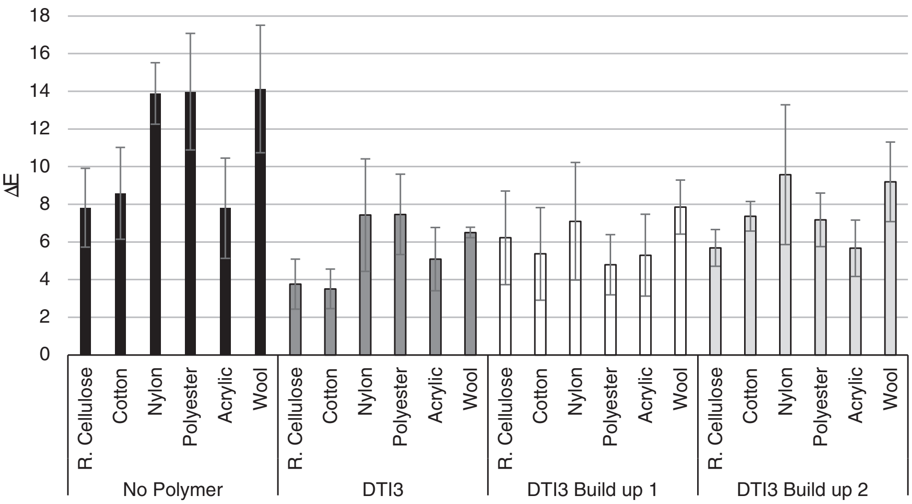


FIGURE 3 A comparison of the color change caused by indigo dye bleeder onto a multifibre swatch, without polymer, with DTI3, after pre-conditioning cycle of DTI3 and after two pre-conditioning cycles of DTI3

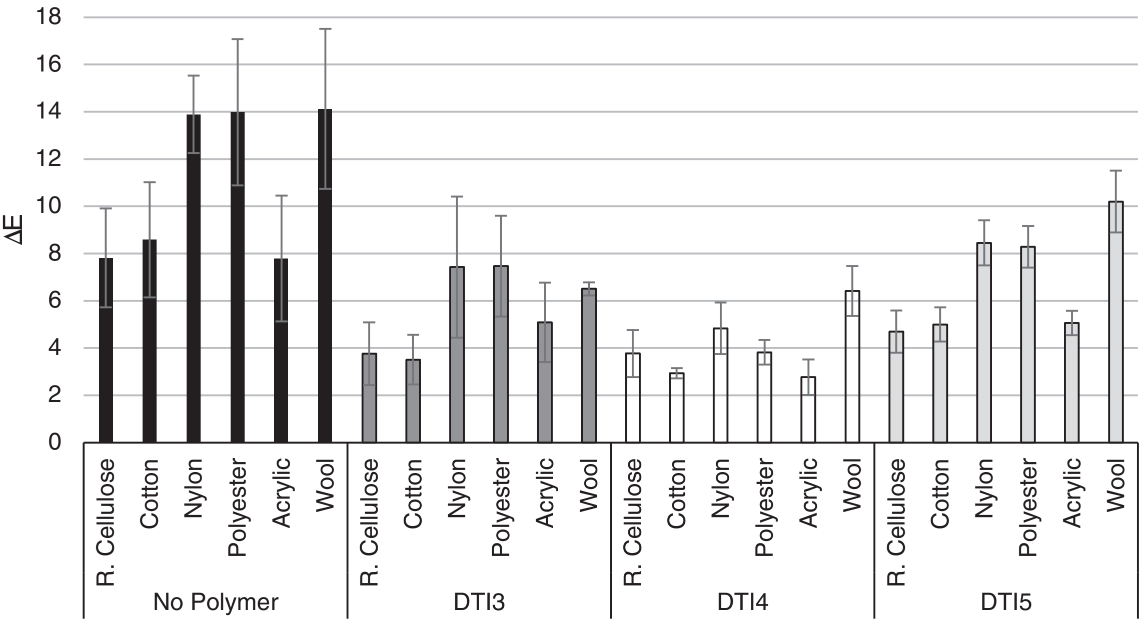


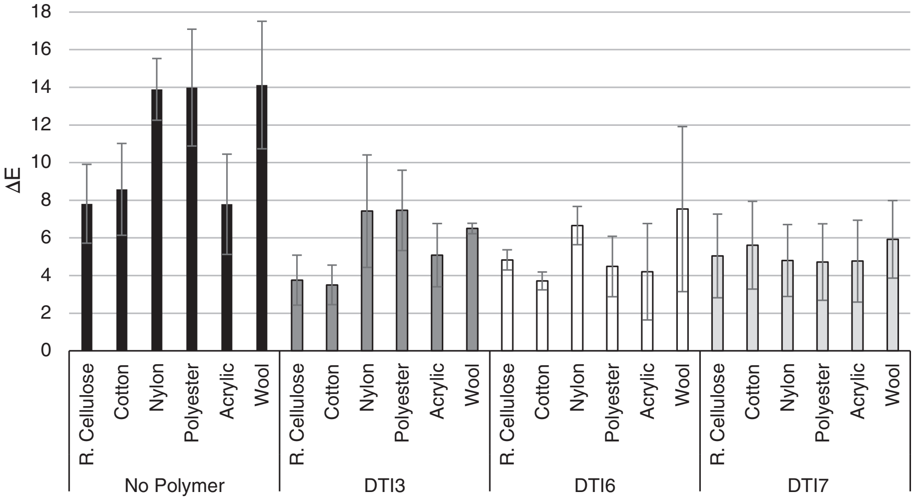
FIGURE 4 A comparison of the color change caused by indigo in the presence of DTI3, and DTI4 or DTI5

Figures S7 and S8). The two polymers were washed with indigo dye bleeding fabric and a multifibre swatch, and the ΔE values recorded.

The hydrophilicity of the polymer had a moderate overall effect on the efficacy of the polymer as a DTI against indigo (Figure 4). Increasing the molecular weight of the mPEG block to 750 g/mol (DTI4) resulted in the mean color change value caused by indigo adsorption on nylon (ΔE = 4.8) and polyester (ΔE = 3.8) reducing significantly compared to washing in the absence of DTI. These values are an improvement of those of DTI3 (ΔE = 7.4 and 7.5, respectively). The color change for acrylic and wool also improved; a reduction from ΔE = 7.8 to 2.8 for acrylic, and from ΔE = 14.1 to 6.4 for wool were observed, although these values are more comparable to washes in presence of DTI3.

In contrast, a worsening effect in mean color change in comparison to DTI3 when the terminal PEG sections have molecular weights of to 5,000 $g.mol^{-1}$ (DTI5) was observed, particularly for nylon (ΔE = 7.4 for DTI3 to 8.5 for DTI5), polyester (ΔE = 7.5 for DTI3 to 8.3 for DTI5) and wool (ΔE = 5.5 for DTI3 to 10.2 for DTI5). The increased hydrophilicity of the polymer suggests that polymer-water interactions are increasingly favored over polymer-fabric interactions, thus reducing DTI adsorption on the fiber surface is lower for DTI5 compared to DTI3.

FIGURE 5 A comparison of the color change caused by indigo in the presence of the pentaerythritol containing polymer with $mPEG_{500}$ (DTI6) and $mPEG_{750}$ (DTI7)



3.3 | DTIs with increased pendant hydroxyl functionality

Attempts to produce more effective DTIs by including monomers that contained more than two hydroxyl groups were then made. To achieve this, pentaerythritol replaced glycerol in the DTI3 formulation to determine the effect of increased hydroxyl content and/or polymer branching (DTI6). The ^{1}H NMR spectrum shows a small hydroxyl peak at 2.75 ppm (Supporting Information, Figure S6), indicating that some free OH groups of pentaerythritol remain, which is in agreement with the FTIR spectrum (Supporting Information, Figure S7, strong OH band at 3,460 cm^{-1}). The incorporation of hydroxyl groups provides further hydrogen bonding capability to the polymer and may be exploited for polymer-fiber interaction, as well as enhanced polymer solubility in aqueous solution. The presence of free hydroxy groups is further confirmed by measuring the zeta potential of polymeric particles, which was found to be −33.3 mV in comparison to −20 mV for DTI3.

A second polymer (DTI7) was synthesized with $mPEG_{750}$ and pentaerythritol. Both polymers are effective DTI agents against indigo, particularly for hydrophobic fibers, nylon and polyester (Figure 5). A mean decrease in color change (ΔE) onto nylon from 13.9 in the absence of polymer, to 4.8 in the presence of DTI7, and from 14.0 to 4.7 for polyester, was observed. This is also an improvement on the mean color change recorded for DTI3 (7.4 and 7.5, respectively).

3.4 | DTIs with amine functionality

Polymers were then produced that independently contained pendant primary amine (2-amino-2-methyl-1,3-propanediol) and secondary amine (diethanolamine) groups incorporated into the formulation of DTI2, in the place of glycerol (DTI8 and DTI9, respectively). Polymer synthesis was confirmed by ^{1}H NMR and FTIR spectroscopy, which revealed peaks ascribed to the amine groups of DTIs 8 and 9 (Figures S13–S15). DTI efficacy tests against indigo revealed that DTI9 improved DTI efficacy compared to DTI3 (Figure 6). In particular, a reduction in the ΔE value from 7.4 (DTI3) to 4.0 (DTI9) for nylon, and a reduction of color change for polyester from 7.5 (DTI3) to 2.5 (DTI9) was found. DTI8 was also an effective DTI, although not as effective as DTI3, in general.

DTI8 and DTI9 were then tested against C.I. Direct Orange 39 (DO39) (Supporting Information, Figure S16). DO39 is a highly water-soluble dye with affinity for cellulose fibers, and therefore shows a high level of discoloration in the absence of a DTI. Figure S13 reveals that for the cellulosic fibers there is not a significant reduction in color change. However, DTI9 provides an improvement in color change for the hydrophobic fibers nylon, polyester and wool, showing that this type of polymer is effective as a DTI against DO39 for many fiber types.

3.5 | Pentanediol-containing DTIs

In order to assess whether the increased performance of DTI9 versus DTI3 was due to the hydrogen bonding capability of the amine, or the increased length of diethanolamine in comparison to glycerol, pentanediol was substituted into the structure (DTI10). Pentanediol is a diol of comparative molar mass to diethanolamine, and the structure was confirmed by ^{1}H NMR spectroscopy which revealed peaks corresponding to pentanediol at 2 ppm and below (Supporting Information, Figure S17).

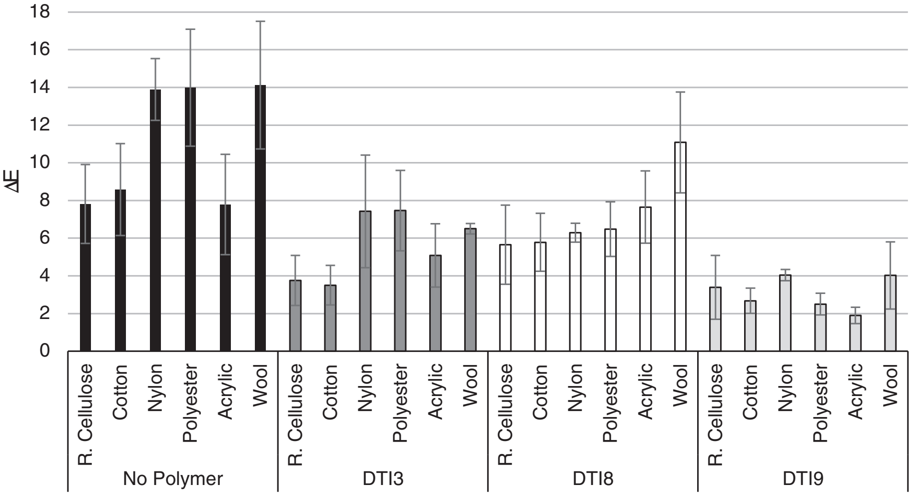


FIGURE 6 A comparison of the color change caused by indigo in the presence of DTI3, the 2-amino-2-methyl-1,3-propanediol containing polymer (DTI8) and the diethanolamine containing polymer (DTI9)

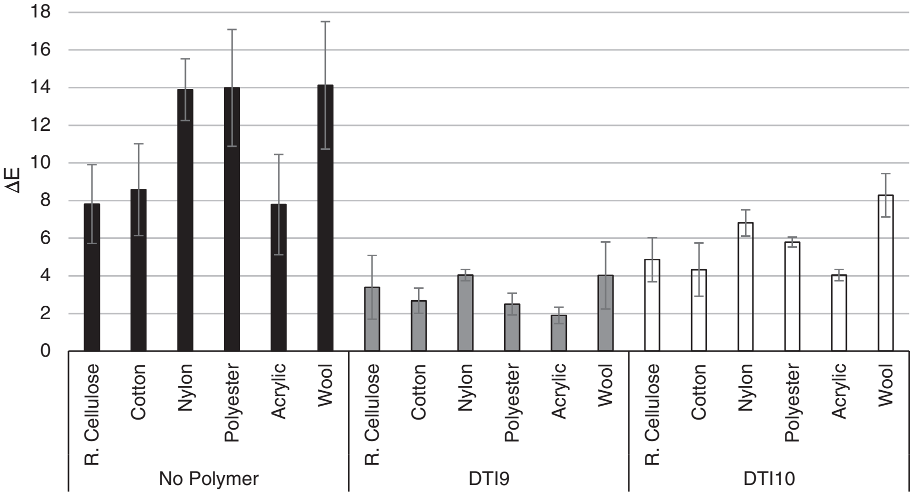


FIGURE 7 A comparison of the color change caused by indigo in the presence of the diethanolamine containing polymer (DTI9) and the pentanediol containing polymer (DTI10)

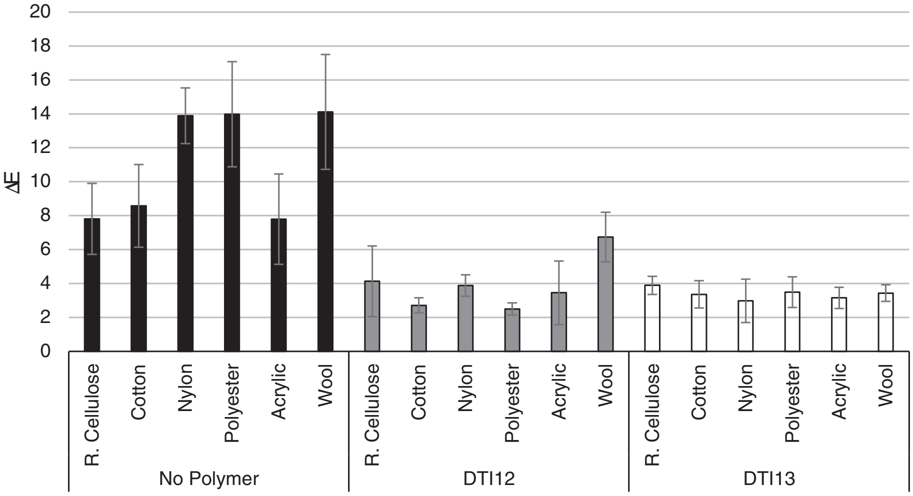


FIGURE 8 A comparison of the color change caused by indigo in the presence of two tris(hydroxymethyl) aminomethane-containing polymers

Figure 7 reveals that whilst DTI10 remains an effective DTI against indigo, it is not as effective as the diethanolamine-containing polymer (DTI9). For example, the ΔE on nylon was 6.8 for DTI10. DTI11 shows a lower color change across all fiber types compared to DTI9, suggesting that the additional hydrogen bonding site the diethanolamine is essential for improved DTI performance, particularly for nylon, polyester and wool.

3.6 | DTIs possessing both amine and hydroxyl functionality

A DTI containing both 2-amino-2-methly-1, 3-propanediol and glycerol, DTI11, was created and its efficacy against indigo assessed to determine the effect of two different sites that may participate in hydrogen bonding and/or branching (secondary amine and hydroxyl) on DTI performance. Figure S19, reveals that the inclusion of glycerol (DTI11) instead of ethylene glycol (DTI9) does not improve the DTI efficacy of the polymer against indigo. However, DTI11 is still an effective DTI agent, particularly for polyester whereby the color change reduces to 3.3 from 14.0 (no polymer).

Tris(hydroxymethyl)aminomethane was then incorporated into the polymer structure to determine any positive effect that DTIs which contain both primary amine and hydroxyl functionality may have. The monomer was incorporated into the structure of DTI2 and DTI3 in place of glycerol (DTI12 and DTI13, respectively) and the structures confirmed by ^{1}H NMR and FTIR, which revealed the presence of the amine groups (Figures S20–S23). The two polymers were tested for their DTI efficacy against indigo (Figure 8), which revealed that tris(hydroxymethyl) aminomethane-containing polymers are successful DTI agents. In particular, DTI13 provides a significant reduction in color change from 8.6 to 3.4 for cotton, from 13.9 to 3.0 for nylon, and from 14.1 to 3.4 for wool. DTI12 is similarly effective but shows a higher level of discoloration onto wool (6.8), although this is a significant reduction compared to washing in the absence of a DTI. Such promising results further highlight the necessity to include repeat units that contain sites for branching and hydrogen bond formation within the structure of effective polymeric DTIs.

DTI12 and DTI13 were then investigated for their DTI efficacy against DO39 (Figure S24). DTI13 reduces DO39 deposition onto the cellulosic fibers and nylon in particular, reducing the mean color change from 24.1 to 19.7. This suggests that barrier-type DTI polymers can be effective against DO39, as an alternative to commercially deployed polymers that complex the dye, for instance PVP, which have been used as the dominant solution to DO39 dye transfer inhibition.

4 | CONCLUSIONS

Several novel polymers that have potential for use as DTIs against indigo dye at very low concentrations (0.1 mg/ml are reported. All the polymers created were designed to present a central hydrophobic region intended for fiber interaction, and terminal hydrophilic regions intended to form a hydration layer that prevents fiber-dye interaction. Initially, the glycerol containing polymer, DTI3, was found to be a highly effective DTI against indigo, showing a mean reduction of 50% in color change for cotton. It was proposed that the presence of unreacted hydroxyl groups provide the polymer with hydrogen bonding capability that improve fiber-polymer interactions. Further testing revealed that the polymer deposits onto multifibre swatches, and that DTI efficacy was maintained in further washes in which polymer was not added. Further polymers were synthesized that are also excellent candidates for use as DTIs. DTI9 incorporated diethanolamine within the polymer structure and revealed a significant reduction in dye transfer caused by indigo (82% reduction in color change onto polyester). Additionally, DTI13, which contains tris(hydroxymethyl)aminomethane within the polymer structure, showed an 80% reduction for the color change caused by indigo onto nylon fabric. The results obtained highlight the necessity that amphiphilic polymers present multiple hydrogen bond donor/acceptor sites in order to be effective DTIs. The positive results presented, which have instigated consumer trials featuring DTIs 3, 9, and 13 within detergent formulations, demonstrate the significant potential that very low concentrations of amphiphilic macromolecules have to perform as effective DTIs within commercial laundry detergent formulations.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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