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Antimicrobial Dye-Conjugated Polyglobalide-Based Organogels

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ABSTRACT

The straightforward coloration of polyglobalide by the covalent grafting of thiol-modified disperse dyes to afford a colored polyester is reported. The colored polymer could form physical organogels, and upon covalent crosslinking chemical organogels in a range of food-grade oils, and the fragrant and antimicrobial molecule 2-phenylethanol. Antimicrobial testing of the 2-phenylethanol-swollen chemical organogels revealed considerable antimicrobial activity against both *Staphylococcus aureus* and *Escherichia coli*. The materials reported offer a range of potential applications, particularly as simple and cost-effective antimicrobial gels.

KEYWORDS

Antimicrobial organogels, natural oil-based gels, polyester coloration, fragrance release, polyglobalide.

INTRODUCTION

Commodity plastics commonly originate from a non-renewable source and are non-biodegradable. Globally, approximately 8.3 billion metric tons of plastic have been manufactured since the commencement of mass production in the 1950s.[1] In 2017, approximately 40% of plastic produced was classified as being non-biodegradable and from a non-renewable source.[2,3] Consequently, there is an urgent demand for the creation of renewable and biodegradable polymers that can be readily applied commercially.

Aliphatic polyesters have significant potential for use in numerous artefacts in sectors ranging from packaging to personal care products owing to their degradability[4] and biocompatibility.[5-8] Additionally, many aliphatic polyesters can be created from renewable sources, for instance sweetcorn harvested to produce poly(lactic acid).[9] However, such polyesters lack chemical functionality to enable chemical conjugation to the repeat units of the polymer backbone, restricting post-polymerization functionalization that may add value to the polymer. One such functionalization is effective polymer coloration, which cannot be achieved using reactive dyes if the polymer lacks the appropriate functionality to permit dye conjugation.

Polyglobalide (PGl) is a non-cytotoxic, potentially biodegradable, aliphatic polyester that has potential use within a biomedical setting.[10-13] Polymer synthesis is achieved by the enzymatic ring-opening polymerization (ROP) of globalide, a 16-membered cyclic lactone which is widely used in the fragrance industry. Similar unsaturated cyclic macrolactones can be obtained from a renewable source, for instance the essential oil from *Angelica archangelica*.[16,17] Crucially, globalide contains a C=C double bond

within its molecular structure that is transferred to the polymer, and may be used for post-polymerization modification.[14,15] Consequently, it may be envisaged that reactive dye molecules that possess suitable functionality may be covalently conjugated to the C=C double bond of the PGl backbone to yield a polymer that boasts likely enhanced color fastness compared to polyesters colored by a non-reactive dye.

Reactive dyes that present thiol functionality are highly desirable owing to their capability to covalently couple to materials that present reactive C=C double bonds via efficient thiol-ene click chemistry reactions.[18] For instance, thermosets that originate from plant oils and possess C=C double bonds may be permanently colored by a thiol-bearing reactive dye. Previous research within our group has disclosed both the modification of linseed oil by thiol-ene coupling to yield an oil that C. I. Disperse Red 1 (DR1) can be covalently attached to by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) coupling in water,[19] and the creation of thiol-bearing DR1, thereby converting a disperse dye to a reactive dye.[20] The latter holds promise as a reactive dye for the efficient coloration of (macro)molecules that present C=C double bonds.

The C=C double bond of PGl may also be exploited for covalent crosslinking to yield a non-soluble material. Chemically crosslinked PGl may readily swell, but not dissolve, in a range of organic solvents, enabling the creation of organogels. Such materials have been cited for use in dye effluent removal,[21] oil spillage clean-up,[22] cosmetics[23] and fluorescent displays.[24] Organogels are increasingly being employed as biomaterials due to their inherent stability, ease of preparation and capability to deliver guest molecules in a controlled manner.[25-31] Organogels that aid the treatment of aliments caused or exacerbated by bacterial infection are extremely promising, and organogels with antimicrobial activity against *Escherichia coli*,[32-34] *Bacillus subtilis*,[33,35-37] *Staphylococcus aureus*[38] and *Candida albicans*[39] have been reported.

In this paper we describe the straightforward synthesis and coloration of PGl using thiol-modified DR1 and C. I. Disperse Blue 3 (DB3) to yield two permanently colored polyesters. DR1 and DB3 were selected as two reactive dyes commonly used industrially, whilst the thiol-ene reaction was pursued to achieve colored polymers and colored covalently crosslinked polymer networks in one-step. The resultant thermoset polymers were able to form organogels when independently dispersed in a range of food-grade oils and the antimicrobial compound 2-phenylethanol. The antimicrobial activity of 2-phenylethanol-swollen organogels was tested against *S. aureus* and *E. coli*. It is envisaged that such materials hold great promise as potential biomaterials, rheology modifiers for personal care products, and antimicrobial gels.

EXPRIMENTAL

Synthesis of PGl. Globalide was polymerized as previously described.[40] Briefly, globalide (2.11 g, 8.81 mmol) and CALB (recombinant Lipase B from *Candida antarctica* immobilized on Immobead 150, recombinant from yeast) (0.44 g, ≥2000 U g^{-1}) were dissolved in anhydrous toluene (4.6 mL) in a Schlenk tube and stirred at 60 °C for four hours under a N_2 flow. To quench the reaction, dichloromethane (DCM) (10 mL) was added and CALB removed by vacuum filtration. The filtrate was added dropwise to ice-cold methanol (30 mL) to precipitate PGl, which was collected by vacuum filtration, washed with methanol, and dried *in vacuo* to yield an off-white crystalline polymer (yield 69%).

Synthesis of DR1 3-mercaptopropionate (1) and DB3 3-mercaptopropionate (2). DR1 3-mercaptopropionate (**1**) was synthesized as reported previously.[19] Briefly, DR1 (1.04 g, 3.30 mmol), 4-dimethylaminopyridine (DMAP) (3 mg, 0.03 mmol) and 3-mercaptopropionic acid (1.49 mL, 16.50 mmol) were mixed in anhydrous DCM (100 mL) and stirred at 0 °C under a N_2 flow. Over a ten-minute period, a solution of dicyclohexylcarbodiimide (DCC) (3.41 g, 16.50 mmol) in anhydrous DCM (30 mL) was added dropwise to the DR1 mixture and the reaction allowed to stir at 0 °C for two hours. HCl (0.5 M, 300 mL)

was then added, forming a white precipitate which was removed by filtration. The organic layer was washed with $NaHCO_3$ and then water, whilst the aqueous layer was washed with DCM before the organic layers were combined and dried over $MgSO_4$. The solution was concentrated by rotary evaporator and purified by column chromatography (DCM) monitored by thin layer chromatography (TLC, DCM). The eluents collected were precipitated in ice-cold hexane and collected by centrifugation (4,500 r.p.m., 15 minutes) as a red crystalline product (yield 68.1%).

An analogous method was used to synthesize DB3 3-mercaptopropionate (**2**). DB3 (978 mg, 3.30 mmol), DMAP (3 mg, 0.03 mmol) and 3-mercaptopropionic acid (1.50 mL, 16.50 mmol) were combined with anhydrous DCM (80 mL). To this stirring DB3 mixture, a solution of DCC (3.41 g, 16.50 mmol) in anhydrous DCM (30 mL) was added dropwise over a ten-minute period at 0 °C under N_2 flow. After a further two hours of stirring at 0 °C, HCl (0.5 M, 200 mL) was added and the white precipitate that formed removed by filtration. The filtrate was washed and purified as per the procedure above, yielding a fine blue powder (yield 9.1%).

PGl gelation. To PGl (50 mg), a collection of food-grade solvents (2-phenylethanol, safflower oil, linseed oil, olive oil and corn oil) were independently added, and the suspensions sonicated to ensure thorough mixing. The mixtures were taken to and just beyond the point of maximum gelation, and the maximum point of gelation for each solvent recorded.

Dyeing of PGl with 1 and with 2. PGl (120 mg, 0.01 mmol), **1** or **2** (12 mg, 0.04 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN) (30 mg, 0.18 mmol) were dissolved in anhydrous THF (5 mL) and stirred at 60 °C under a N_2 flow. After ~46 hours, DCM (8 mL) was added and the solution added dropwise to ice-cold methanol (40 mL) to precipitate a colored product (red for **1** or blue for **2**) which was collected by centrifugation (4,500 r.p.m., 15 minutes). The dyed polymer was then washed with methanol until the washings became colorless (yield 75%).

Crosslinking PGl. Various PGl organogels were synthesized that contained various amounts of 2,2'-(ethylenedioxy)diethanethiol (EDT) crosslinker. As a representative example, PGl (300 mg, 0.01 mmol), EDT (0.5 mL, 3.07 mmol) and AIBN (50 mg, 0.30 mmol) were dissolved in anhydrous THF (10 mL) in a 15 mL sample vial. After being left to gently stir with a magnetic stirrer bar at 60 °C and under a flow of N_2 for ~26 hours, a colorless gel had formed. The crosslinked polymer was dialyzed against deionized water (2,000 Da molecular weight cut-off) and lyophilized.

Colored PGl organogel was synthesized in a one-pot procedure. For example, PGl (290 mg, 0.01 mmol), **2** (1 mg, 0.003 mmol) and AIBN (50 mg, 0.30 mmol) were dissolved in anhydrous THF (8 mL). EDT (0.5 mL, 3.07 mmol) was then added to the blue colored THF solution at which point simultaneous cross-linking and dye conjugation reactions occurred by stirring at 60 °C under a flow of N_2. The colored crosslinked PGl was dialyzed against deionized water (2,000 Da molecular weight cut-off) and lyophilized.

Crosslinked PGl gelation. Colored, crosslinked PGl (122 mg) was weighed into a small glass vial and 2-phenylethanol added until it no longer caused the crosslinked PGl to swell. The point before turning the vial upside down and the solvent could be decanted was taken to be the maximum amount of solvent required to gel (730 mg). Degree of swelling was calculated (100%*(607.8/122.3)) to be 497.0 %.

Antimicrobial activity testing of the crosslinked organogels. The antimicrobial activity of the 2-phenylethanol-swollen organogel was tested against *E. coli* National Collection of Type Cultures (NCTC) 11954 and *S. aureus* NCTC 8532 strains. Organogels with polymer concentrations of 84, 72, 60 and 48 mg mL^{-1} in 2-phenylethanol were generated in both a colorless and blue-dyed formulation by casting in 24-well plates (Corning). Crosslinked polymer (10 mg) in the absence of a solvent was tested as a control. The polymer-containing plates were UV sterilized for 30 minutes at 254 nm prior to antimicrobial testing. Polymer-free bacterial cultures acted as positive (growth) controls, whilst sterile broths functioned as negative controls.

Bacteria were cultured on Colombia Blood Agar (CBA; Oxoid) plates supplemented with 5% oxalated horse blood (Oxoid) in 5% (v/v) CO_2 at 37°C for 18 hours. Single colonies were inoculated into 5 mL brain heart infusion (BHI; Oxoid) broths, which were incubated at 37°C whilst agitated at 150 rpm (MaxQ 4450; Thermo Scientific). Optical densities (OD_{600}) of overnight cultures were measured with a Jenway 6305 spectrophotometer to estimate viable count of the undiluted suspension (based on calibration curve data). Inocula were prepared by diluting these suspensions in sterile BHI broth to a concentration of $1x10^6$ colony forming units (CFU). Inocula (500 µL) were added to polymer-containing wells and incubated overnight at 37°C with gentle agitation (70 rpm). Samples from these cultures were serially diluted in phosphate buffered saline (PBS; Oxoid) and viable bacterial populations enumerated on CBA incubated as previously. All experiments were performed in biological triplicate, with plate enumerations implemented on four separate occasions.

Statistical analysis. Statistical analysis was performed using IBM SPSS Statistics 25, groups were compared by Kruskal-Wallis test with Bonferonni adjustment; * $p<0.05$, ** $p<0.01$.

RESULTS AND DISCUSSION

Synthesis of Polyglobalide (PGl), DR1 3-Mercaptopropionate (1) and DB3 3-mercaptopropionate (2). PGl was synthesized by the enzyme-initiated ROP of globalide using CALB to initiate the polymerization.[40] To maintain the activity of lipase B, the temperature of the reaction was limited to 70 °C. An off-white crystalline solid was produced that was confirmed to be PGl by ^{1}H NMR spectroscopy (Figure S1), and ^{13}C NMR spectroscopy (Figure S2). The PGl produced was analyzed by advanced polymer chromatography, a form of size exclusion chromatography that enables relatively quick polymer analysis compared to gel permeation chromatography, which revealed a number average molecular weight of

30,727 g mol^{-1} and Đ of 1.38 (Figure S3). PGl was also analyzed by differential scanning calorimetry (DSC) and found to have a melting point of 45 °C (Figure S4).

Thiol-bearing DR1 (DR1 3-mercaptopropionate) (**1**) and thiol-bearing DB3 (DB3 3-mercaptopropionate) (**2**) were synthesized by Steglich esterification. The products, which possess pendant thiol groups for subsequent covalent conjugation to PGl, were analyzed by FTIR and ^{1}H NMR spectroscopy. The synthesis of **1** was confirmed by FTIR (Figure S5), and two further products that may be used for the coloration of PGl were also obtained from the reaction, DR1 bis(3-mercaptopropionate) and DR1 tris(3-mercaptopropiondialate) (Figures S6-S7). All spectra reveal peaks corresponding to a S-H thiol stretch at 2563 cm^{-1} and a C=O ester stretch at 1721 cm^{-1}. The formation of the thioester in DR1 bis(3-mercaptopropionate) and DR1 tris(3-mercaptopropionate) is further confirmed in the ^{1}H NMR spectra (Figures S8-S9). Figure S9 is particularly informative; the integration values of the peaks at 3.09 ppm and 3.05 ppm have increased by a factor of two, confirming the formation of DR1 tris(3-mercaptopropionate). Yields of 41.4%, 20.1% and 6.6% were obtained for **1**, DR1 bis(3-mercaptopropionate) and DR1 tris(3-mercaptopropionate), respectively (68.1% yield of colored material overall). All three products are suitable for use as a reactive dye in thiol-ene coupling reactions with PGl as they each contain a terminal thiol group and azobenzene chromophore. The UV-vis absorption spectrum of DR1 (Figure S10) was near identical to those of **1**, DR1 bis(3-mercaptopropionate) and DR1 tris(3-mercaptopropionate) (Figures S10-S12); DR1 revealed a maximum absorption at 486 nm, whereas the functionalized DR1 variants had maximum absorptions at 476 nm.

^{1}H NMR spectroscopy confirmed the successful formation of **2** (Figure S13). Notably, the peak at 1.60 ppm that appears in the spectrum of **2** and which corresponds to the thiol proton, is absent from the ^{1}H NMR spectrum of unmodified DB3. In addition, peaks at 2.73 ppm and 3.13 ppm that originate from conjugated 3-mercaptopropionate are present in the spectrum of **2** but are lacking in the spectrum of DB3. FTIR analysis of **2** revealed a weak peak corresponding to the S-H thiol stretch at 2567 cm^{-1} and a

strong peak representing the C=O ester stretch at 1739 cm^{-1} (Figure S14). UV-vis spectroscopy analysis of **2** revealed maximum absorbance values of 554 nm, 594 nm and 641 nm that are comparable to the spectrum of DB3, which has maximum absorbance values of 559 nm, 599 nm and 646 nm (Figure 1).

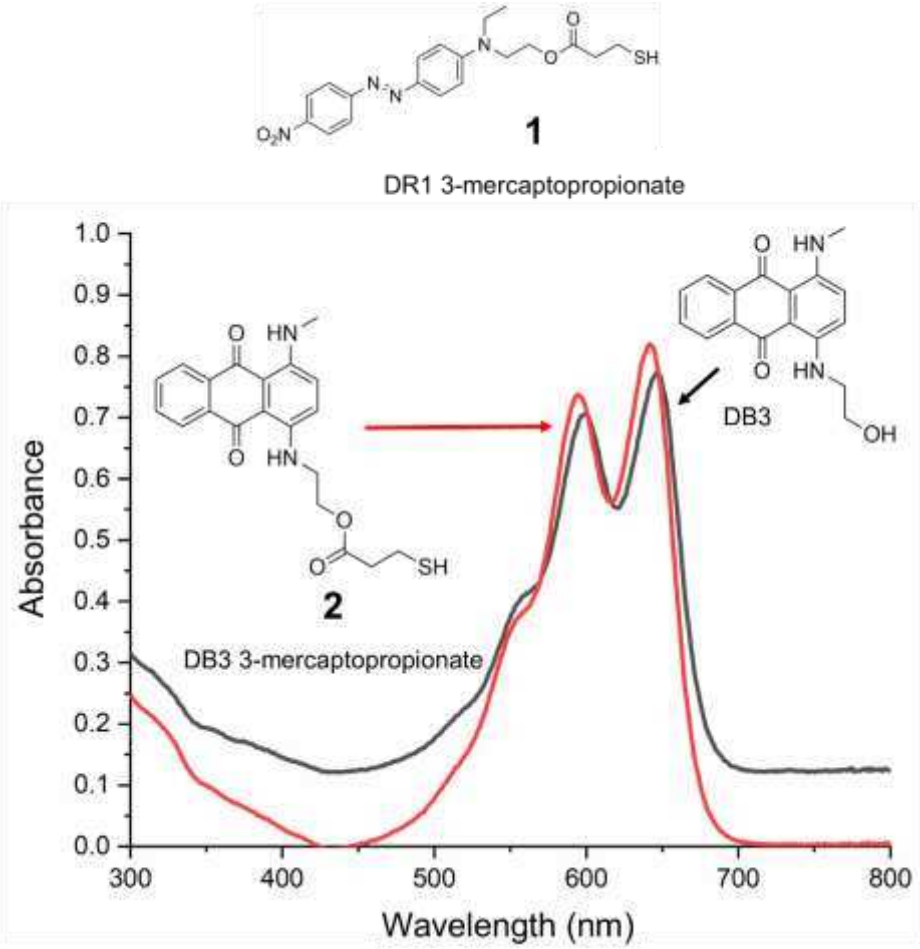

Figure 1. The UV-vis spectra corresponding to DB3 and DB3 3-mercaptopropionate (**2**).

Covalent Coloration of PGl with DR1 3-Mercaptopropionate (1) and DB3 3-Mercaptopropionate (2).

1 and **2** were used to covalently dye PGl via thiol-ene coupling (Figure 2). After dyeing, the colored polymer was washed thoroughly with methanol, a solvent that readily solubilizes both modified dye

molecules, until the washings were colorless to ensure that any dye remaining was covalently bound to PGl.

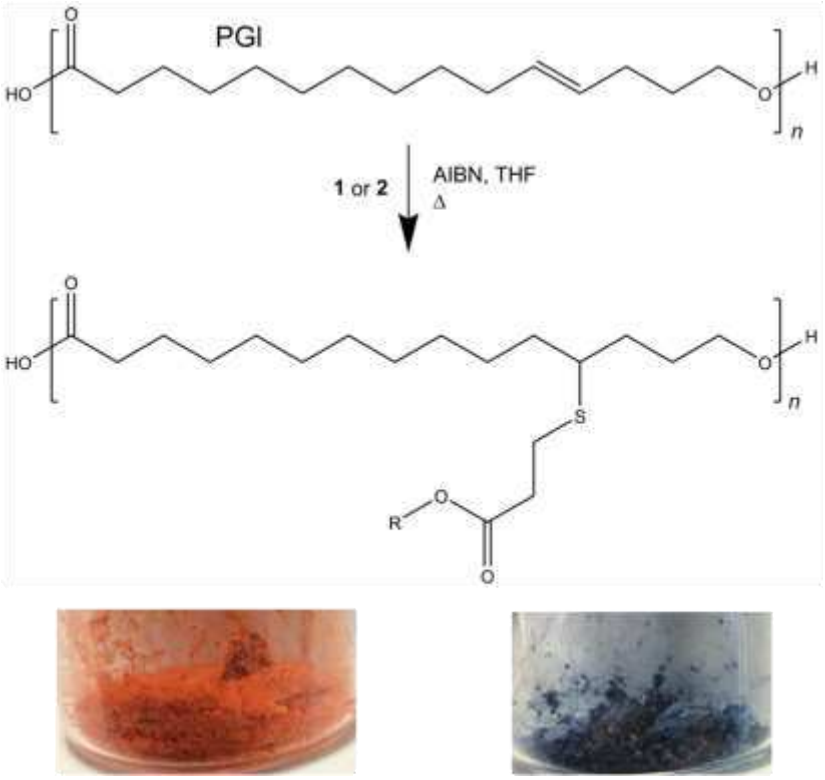

Figure 2. Thiol-ene coupling of PGl with **1** or **2** to yield PGl that is dyed red (left inset = photo of collected red PGl) or blue (right inset = photo of collected blue PGl).

FTIR analysis of the polymer dyed with **1** revealed peaks that are attributed to PGl, and additional peaks at 1604 cm^{-1}, which corresponds to the azobenzene group of **1**, and 1520 cm^{-1}, which represents the NO_2 asymmetric stretch of **1** (Figure S15). The FTIR spectrum of PGl dyed with **2** contains the peaks that are attributed to PGl, plus an additional peak at 1677 cm^{-1}, which corresponds to the aromatic ketone of **2** (Figure S16). ^{1}H NMR analysis confirmed the successful conjugation of **1** (Figure 3a) and **2** (Figure 3b) to PGl. Based on comparing the integrals of peaks corresponding to the methylene group adjacent to the terminal hydroxyl group of PGl with peaks corresponding to the aromatic groups of **1**

and **2**, dye conjugation to PGl was found to be approximately 2% for both dyes. It was also found that the melting transition of PGl increased slightly from 45 °C for linear PGl (Figure S4) to ~51 °C for dyed PGl (Figures S17-S18). This increase in melting point is likely due to restricted polymer flexibility as a result of the conjugated pendant groups.

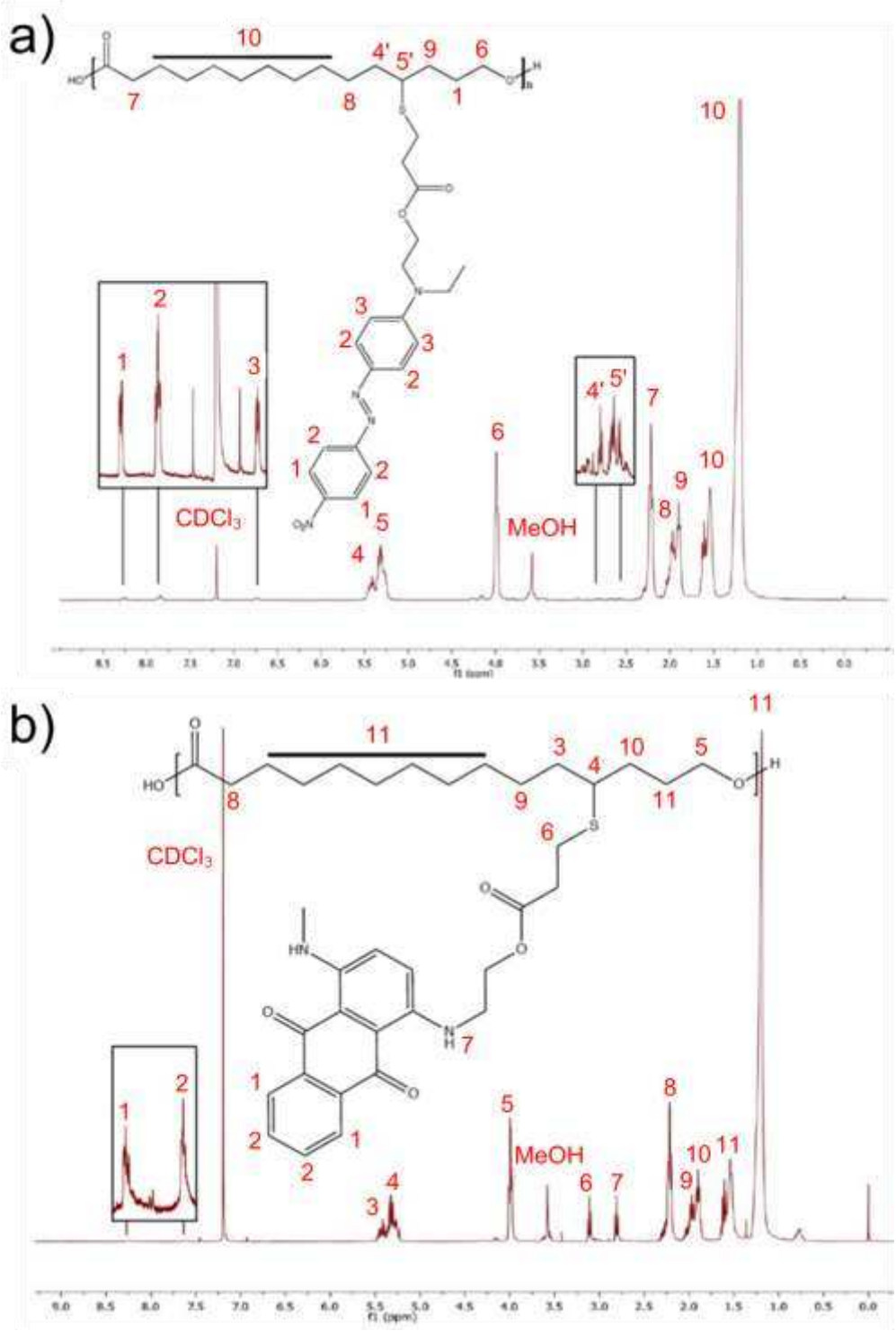

Figure 3. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) spectra of a) **1**-dyed PGl and b) **2**-dyed PGl.

The Creation of PGl-Based Organogels. The capability of linear PGl to form physical organogels via organic solvent uptake was assessed using various non-aqueous solvents as the continuous phase (Table 1). 2-Phenylethanol was selected as it is a fragrant and antimicrobial molecule, and so any gel formed has potential application as a perfumed, antimicrobial, gel.[41] The gel swollen in 2-phenylethanol was a physical gel whereby the elastic modulus (G') exceeds the viscous modulus (G'') at higher angular frequency owing to relative freedom of the polymer chains within the physically crosslinked network (Figure S19). The other oils tested are certified food grade and so gels formed have potential *in vivo* application. In all cases, self-supporting materials were formed, with the lowest and highest quantity of polymer (disperse phase) required for organogel formation being when corn oil (11.3% PGl) and 2-phenylethanol (24.8% PGl) were used as the continuous phase, respectively (Table 1).

Table 1. The minimum weight percentage of PGl required to form a self-supporting organogel in various continuous phases.

Weight % of Polymer Required for Gel Formation				
2-phenylethanol	**Safflower Oil**	**Linseed Oil**	**Olive Oil**	**Corn Oil**
24.8	15.5	20.8	21.1	11.3

Covalently crosslinking PGl with EDT using thiol-ene coupling was then performed. Successful PGl crosslinking was confirmed by DSC analysis; the thermogram produced revealed an exothermic peak at 123 °C that is attributed to crosslinker degradation and lacked the sizeable endothermic melting point peak at 42 °C that linear PGl possesses (Figure S20). Such thermal stability is advantageous for using materials in applications in which it must retain structural integrity at elevated temperatures, for instance as a recyclable polymer that undergoes washing in hot liquids between uses. The crosslinked polymer was robust when handled.

The crosslinked polymer also holds great potential to form an organogel with increased mechanical properties when swollen in an organic continuous phase. Once more, 2-phenylethanol was probed to determine if it can form a chemical organogel that includes a fragrant antimicrobial molecule as the continuous phase (Table 2). Figure S21 demonstrates the solid-like behavior of the covalent gel whereby values of the storage modulus are significantly increased with respect to values of the loss modulus, regardless of the angular frequency. The rheogram also shows the significantly increased storage modulus of this organogel compared with the non-crosslinked organogel. THF was also used to create organogels owing to its ability to readily solubilize linear PGl, rendering it ideal to demonstrate PGl crosslinking by organogel formation as linear PGl dissolves in THF, whereas crosslinked PGl should swell in THF.

Table 2. The PGl : EDT ratio, weight percentage of PGl in the organogels formed, and the solvent loss rate (mL/h) of the organogels created in THF or 2-phenylethanol.

Sample	Polymer : Crosslinker Ratio	THF		2-Phenylethanol	
		% PGl	Solvent loss	% PGl	Solvent loss (mL/h)
1	1 : 0.11	15	0.3	11	0.07
2	1 : 0.22	19	0.29	16	0.06
3	1 : 0.44	21	0.24	22	0.05
4	1 : 0.85	23	0.24	20	0.04

In general, as the PGl : EDT ratio converges to parity, the weight percentage of PGl in the organogels formed increases. This was anticipated as reduced gel swelling typically corresponds to increased crosslink density. Organogels formed using 2-phenylethanol had a solvent loss rate, determined by organogel mass, of 0.07 mL h^{-1} over 24 h, which proved to be much reduced compared with that of THF. 2-Phenylethanol retention capability provides the material with potential use as an antimicrobial gel that provides prolonged fragrance release; control over solvent loss ensures the material does not dry prematurely. SEM analysis revealed that such structures possessed a porous morphology and so may

also be feasibly deployed as scaffolds for three-dimensional cell culture owing to the non-cytotoxic components of the material (Figure 4a). The porous morphology is also relevant when aiming to achieve uptake of antibacterial compound within the pores rather than only in the polymer free volume.

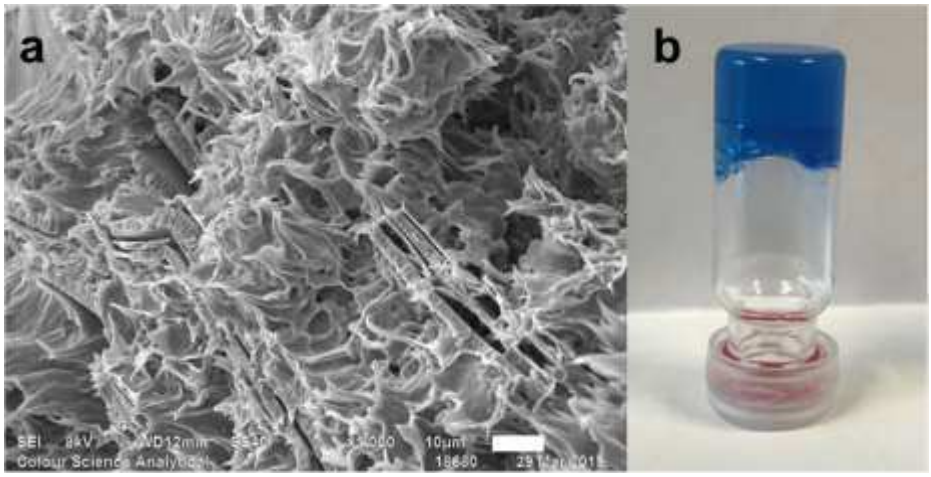

Figure 4. (a) SEM image of PGl crosslinked with EDT. The scale bar represents 10 µm. (b) DB3-dyed PGl crosslinked with EDT and dispersed in 2-phenylethanol.

PGl was simultaneously dyed with **2** and crosslinked with EDT to yield a polymer that may form a blue organogel (Figure 4b). DB3-dyed and EDT-crosslinked PGl expanded to 497% the original polymer mass, when dispersed in 2-phenylethanol. Figure S22 demonstrates this dyed organogel is stronger than the non-crosslinked organogel (Figure S19) as the G' value is much greater than the G'' value. However, the G' value is less than that of the non-dyed organogel (Figure S21) (G' of ~17,000 Pa and ~10,250 Pa for the non-dyed and dyed organogels, respectively).

Finally, the antimicrobial activity of the blue colored and uncolored chemically-crosslinked 2-phenylethanol-swollen PGl-based organogels was assessed versus *S. aureus* and *E. coli*. Preliminary testing revealed comparable antimicrobial activity for gels at all concentrations (data not shown),

therefore subsequent experiments focused only on the gel with the lowest solvent concentration, 84 mg mL^{-1}. Figure 5 shows the bacterial viability following incubations of *S. aureus* and *E. coli* in the positive growth control, with the 2-phenylethanol-free PGl control and the colored/non-colored organogels. The antimicrobial effect of colored and non-colored PGl in the absence of 2-phenylethanol was minimal, but when swollen to form an organogel the material displayed clear antimicrobial capabilities. As expected, there was no marked difference in the antimicrobial activity between crosslinked PGl dyed with **2** or not, although some difference was found when assessed against *S. aureus*. Additionally, OD_{600} readings were made of the suspensions incubated with the organogels. For *S. aureus*, the OD_{600} values for both the colorless and dyed 84 mg mL^{-1} organogel were reduced by >95% compared with the positive growth control. Similarly, the OD_{600} values for both *E. coli* organogels decreased by >97% from the positive growth control, further demonstrating the pronounced antimicrobial capabilities of the reported organogels.

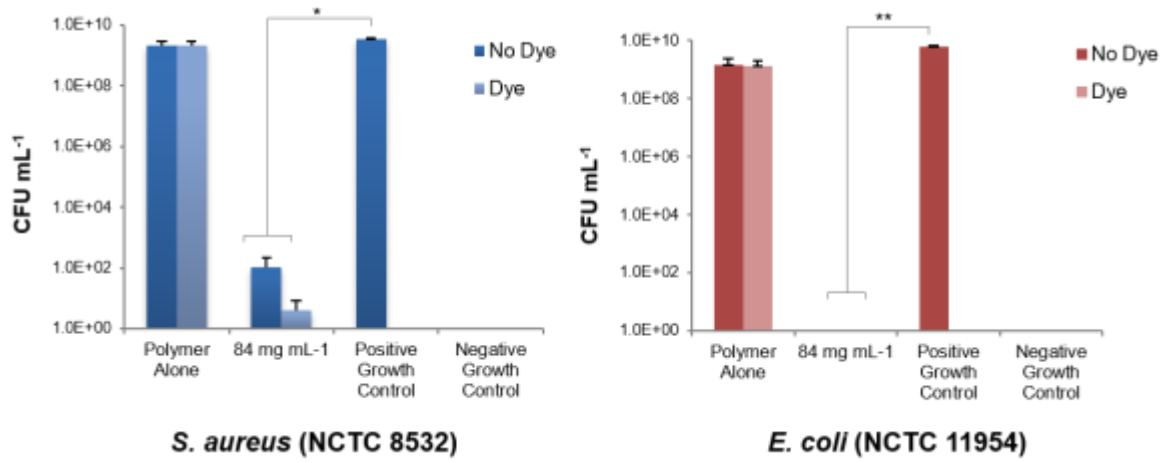

Figure 5. Bacterial viability of *S. aureus* (left) and *E. coli* (right) following incubation with DB3-conugated and DB-3 crosslinked PGl samples, and respective 2-phenylethanol-swollen PGl organogel.

CONCLUSIONS

The thiol modification of DR1 and DB3 was carried out to yield two reactive dyes that are able to color (macro)molecules that possess C=C double bonds, through covalent coupling. PGl, a biocompatible and potentially biodegradable polyester, was both colored by such dyes, and crosslinked via a one-step thiol-ene reaction to yield a non-soluble polymer that lacks a melting point. Crosslinked PGl was used as the gelating component for various food-grade solvents, including the fragrant, food-grade, molecule 2-phenylethanol. Chemically crosslinked PGl-based organogels that have 2-phenylethanol as the continuous phase demonstrate a predominantly elastic behavior with increased storage modulus with respect to both the loss modulus and the storage modulus of the 2-phenylethanol-swollen linear polymer. Such organogels display excellent antimicrobial activity against both *S. aureus* and *E. coli* regardless of dye conjugation to the crosslinked network. Consequently, the PGl-based, 2-phenylethanol-containing, organogels reported are highly promising candidates to be employed for the prolonged release of a fragrant molecule, and as antimicrobial gels.

ASSOCIATED CONTENT

Supporting information. The following supporting information is available free of charge: materials, equipment and settings; NMR spectra of the PGls and thiol-modified dyes; advanced polymer chromatography chromatogram of the PGl; DSC thermograms of the PGl, dyed PGl and crosslinked PGl; FTIR spectra of the dyes and the dyed PGl; UV-vis absorbance spectra and rheological graphs.

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Author Contributions. J.V.R. and P.W. synthesized the polymers, crosslinked polymers and organogels. J.V.R., P.W. and H.Y. carried out characterization. J.J.V. tested the antimicrobial activity. All authors contributed to the writing of the paper.

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