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FORUM ARTICLE

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One-Step Photochemical Synthesis of Permanent, Nonleaching, Ultrathin Antimicrobial Coatings for Textiles and Plastics

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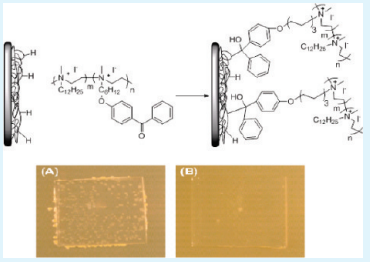
ABSTRACT: Antimicrobial copolymers of hydrophobic N-alkyl and benzophenone containing polyethylenimines were synthesized from commercially available linear poly(2-ethyl-2-oxazoline), and covalently attached to surfaces of synthetic polymers, cotton, and modified silicon oxide using mild photo-cross-linking. Specifically, these polymers were applied to polypropylene, poly(vinyl chloride), polyethylene, cotton, and alkyl-coated oxide surfaces using solution casting or spray coating and then covalently cross-linked rendering permanent, nonleaching antimicrobial surfaces. The photochemical grafting of pendant benzophenones allows immobilization to any surface that contains a C−H bond. Incubating the modified materials with either *Staphylococcus aureus* or *Escherichia coli* demonstrated that the modified surfaces had substantial antimicrobial capacity against both Gram-positive and Gram-negative bacteria (>98% microbial death).



KEYWORDS: polyethylenimine, photo-cross-linker, antibacterial, antimicrobial, antifouling

INTRODUCTION

Microbial infection is one of the most serious concerns for many commercial applications such as textiles, food packaging and storage, shoe industry, water purification, medical devices, and dental surgery equipment.[1−4] Recently, antimicrobial agents have gained significant interest from both an academic and industrial point of view because of their potential to provide safety benefits to a diverse range of materials. Some cationic polymers, like quaternary polyetheleneimines (QPEIs), have proven effective at killing bacteria because of their unique structural and hydrophobic properties.[5−10] The generally accepted hypothesis for antimicrobial activity of polycations with hydrophobic side chains is that the pendant hydrophobic groups can intercalate into the hydrophobic portion of a cell membrane, whereas the electrostatic interaction of the positively charged backbone and the negatively charged bacterial cell membrane/wall disrupts the ionic integrity of the membrane, causing cell death.[11−15] However, a more detailed mechanism for rapid contact kill of bacteria at the solid surface interface remains an important unexplored research area. To achieve this goal, the development of a new methodology for surface immobilization of antimicrobial polymers with well-defined properties is necessary. It is also of great interest to obtain biocidal effects without releasing biocide material into the environment, which means that antimicrobial coatings need to be immobilized irreversibly or covalently attached to surfaces. A significant number of literature reports discuss the preparation of antimicrobial surfaces via the covalent coupling of poly quaternary ammonium (PQA) compounds to a variety of surfaces like glass,[16−18] polymer,[19−25] paper,[26] and metal.[27] Recently, Hsu and Klibanov[28] reported a system in which an aryl azide based biocidal PEI copolymer was used to modify cotton fabrics. In this case, the nitrophenylazide based cross-linker reacts preferentially with the hydroxy functionality on the cellulose surface. Although this methodology is achievable with surfaces that contain reactive functional groups (examples include hydroxy, amine, carboxylic acid, and chloro), the covalent attachment of biocidal polymers on common and inert plastic surfaces such as polyethylene, polypropylene, and polystyrene is more challenging with very few examples in the literature.[29−32]

The ability of benzophenone (BP) to act as a cross-linking agent and abstract hydrogen from a suitable hydrogen donor has been well studied and utilized in various chemical systems for many years.[33−39] BP is an ideal choice for cross-linking organic thin films, because it can be activated using mild UV light (345−365 nm), avoiding oxidative damage of the polymer and substrate that can occur upon exposure to higher energy UV. The benzophenone moiety is more chemically robust than other organic cross-linkers and reacts preferentially with C−H bonds in a wide range of different chemical environments. Triggered by UV light, benzophenone undergoes an n−π^* transition, resulting in the formation of a biradical triplet excited state that can abstract a hydrogen atom from a neighboring aliphatic C−H group to form a new C−C bond.[40] This photoreaction has recently been used to attach thin polymer layers to metal and oxide surfaces,[41−46] along with applications in microfluidics,[47] organic semiconductors,[48] redox polymers,[49,50] and biosensors.[51]

In this article, we describe a convenient method to covalently attach ultrathin biocidal polymer coatings on surfaces with inert

Received: March 14, 2011
Accepted: June 8, 2011
Published: June 21, 2011

functionality. We have synthesized antimicrobial copolymers with pendant benzophenone groups that act as a photocross-linker for the covalent attachment of the polymer with any substrate containing a C−H bond upon irradiation with UV light. The coated substrates showed impressive antibacterial and antifouling properties. To the best of our knowledge, this is the first demonstration for the covalent immobilization of antimicrobial polymers onto inert polymer surfaces without harsh oxidative treatments to render surface functionality for further immobilization.

EXPERIMENTAL SECTION

Materials. Silicon wafers (Universitywafer.com) with native oxide and glass slides (VWR) (cut into 2.5 × 2.5 cm pieces) were used as substrates. For plastic coatings, 100% cotton print cloth with specifications of weave 78 × 76, weight 102 g/m^2 (Testfabric, Inc.), polypropylene nonwoven geotextile (provided by TenCate Geosynthetics and Industrial Fabrics), polyethylene transparent sheets (Great Value storage bag, Wal Mart, Inc.) and polyvinyl chloride transparent sheets (Wal Mart, Inc.) were purchased. Poly(2-ethyl-2-oxazoline) (M_w = 50 000 g/mol) (Aldrich), *tert*-amylalcohol (Aldrich), 1-bromododecane (Alfa Aesar), iodomethane (Alfa Aesar), 4-hydroxybenzophenone (Alfa Aesar), 1,6-dibromohexane (Alfa Aesar), trypticase soy broth (TSB) (Difco), trypticase soy agar (TSA) (Difco), were used as received.

Instrumental Methods. Atomic force microscopy (AFM) experiments for quaternized PEI based polymer films were performed using a Multimode Nanoscope IIIa (Digital Instruments/Veeco Metrology Group). All measurements were performed using tapping mode. Null ellipsometry was performed on a Multiskop (Optrel GbR) with a 632.8 nm He−Ne laser beam as the light source. Both δ and ψ values were measured and thickness was calculated by integrated specialized software. At least three measurements were taken for every layer, and the average thickness was calculated. UV−vis spectroscopy was performed on a Cary 50 spectrophotometer (Varian). Infrared spectroscopy studies of polymer coated films were done using a Thermo-Nicolet model 6700 spectrometer equipped with a variable angle grazing angle attenuated total reflection (GATR-ATR) accessory (Harrick Scientific). The UV light source was an OmniCure, Series 1000 with 365 nm bandpass filter, equipped with a liquid filled fiber optic waveguide. The substrates were held 2 cm from the source and irradiated with a power of 180 mW/cm^2.

Antimicrobial Test Method. The antimicrobial efficacy was determined by using a modified version of test method published by Haldar et al.[5] The antimicrobial test method followed in this work mimics the practical scenario of airborne bacteria coming in contact with substrates which is simulated by spraying the bacterial aerosol. The common way of infection spreading includes respiratory droplets produced by sneezing, coughing, laugh, or breathing.

Trypticase soy broth (TSB) (10 mL) was inoculated with one loopful of bacteria *Staphylococcus aureus* (ATCC 6538) culture or *Escherichia coli* (ATCC 25922) and incubated overnight in a water shaker bath at 37 °C with 45 linear strokes per minute. The new TSB (10 mL) was again inoculated with 100 μL of an overnight bacterial culture and incubated for 4 h in the above-mentioned conditions in the shaker bath. One milliliter of this culture was transferred to a 1.5 mL centrifuge tube and was centrifuged at 5000 rpm for 1 min at 21 °C to precipitate bacteria and form a bacterial pellet. (centrifuge = accuSpin Micro 17R, Fisher Scientific, tubes = Micro Centrifuge Tube, VWR International). The supernatant solution was discarded and 1 mL of sterile water was added to the microbial pellet in the tube. The microbes were resuspended in the solution by using a vortex mixer (Vortex Genie 2) and was transferred to 9 mL of sterile water to make a bacterial concentration of ∼3 × 10^6 cfu (colony forming units) and subsequently transferred to thin layer chromatography (TLC) sprayer bottle which was connected to pneumatic dispense regulator (EFD 1500XL). The polymer coated substrates were uniformly sprayed on one side in a controlled fashion from the TLC sprayer for 1 s at 30−40 psi pressure. The distance between the sprayer and glass slide was approximately 1−1.5 feet. The sprayed sample was air-dried for approximately 1 min and the sample was carefully mounted on a Difco trypticase soy agar (TSA) plate. TSA plates were incubated for 24 h at 37 °C. Finally, the number of colonies grown on the slide was counted.

Synthesis. *Linear Polyethylenimine (PEI).* The deacylation reaction was performed according to literature procedures.[52] Three grams of poly (2-ethyl-2-oxazoline, M_w, 50 kDa) (POEZ) was added to 120 mL of 24% (wt/vol) HCl, followed by refluxing for 96 h. The POEZ dissolved completely in 1 h, but after overnight reflux a white precipitate appeared. The precipitate was filtered and then air-dried. The resultant protonated, linear PEI was dissolved in water and neutralized with aqueous KOH to precipitate the polymer. The white powder was isolated by filtration, washed with distilled water until the pH became neutral, and dried under a vacuum. Yield: 1.15 g (88%). ^{1}H NMR ($CDCl_3$): δ, 2.72 (s, 4H, NCH_2CH_2N), 1.71 (1H, NH).

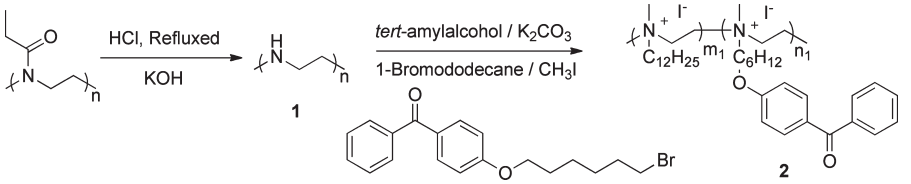
4-[(6-Bromohexyl) oxy] Benzophenone. 4-Hydroxy benzophenone (5.94 g, 30 mmol), 1,6 dibromohexane (8.05 g, 33 mmol), potassium carbonate (5.95 g, 45 mmol) and DMF (60 mL) were stirred at room temperature for 16 h under inert atmosphere. The reaction mixture was poured into ice water (300 mL) and extracted with ether (100 mL). The organic layer was collected and the solvent was removed with a rotary evaporator. The crude product was purified on a silica gel column by using 10:1 hexane:ethyl acetate mixture. Yield: 8.2 g (76%). ^{1}H NMR ($CDCl_3$): δ, 7.81 (d, 2H, J = 8.4 Hz), 7.75 (d, 2H, J = 7.8 Hz), 7.54 (t, 1H, 7.5 Hz), 7.47 (t, 2H, J = 6.9 Hz), 6.93 (d, 2H, J = 9.0 Hz), 4.06 (t, 2H, J = 6.3 Hz), 3.43 (t, 2H, 6.6 Hz), 1.86 (m, 4H), 1.50 (m, 4H). ^{13}C NMR ($CDCl_3$): δ, 25.47, 28.10, 29.11, 32.86, 33.95, 68.2, 114.2, 128.37, 129.92, 129.94, 132.06, 132.78, 138.55, 162.9, 195.7.

Linear Copolymer of N,N-Dodecyl Methyl and N,N-[(6-hexyl) oxy] Benzophenone Methyl PEI. 0.5 g (12 mmol of the monomer unit) of the PEI was dissolved in 6 mL of *tert*-amyl alcohol, followed by the addition of 2.1 g (15 mmol) of K_2CO_3, 1.99 g (8 mmol) of 1-bromododecane, and 1.44 g (4 mmol) of 4-[(6-bromohexyl) oxy] benzophenone and the reaction mixture was stirred at 95 °C for 96 h. After removing the solids by filtration under reduced pressure, 1.5 mL of iodomethane was added, followed by stirring at 60 °C for 24 h in a sealed, heavy walled pressure vessel. After reaction, the solution was dried using a rotary evaporator. The yellow solid was dissolved in a minimum volume of dichloromethane and then the solution was added to excess hexane to precipitate the polymer. The light yellow solid was filtered and dried at room temperature under vacuum for 12 h. Yield: 2.3 g (46%). ^{1}H NMR ($CDCl_3$): δ, 7.77 (bs, 4H); 7.56 (bs, 1H), 7.45 (bs, 2H); 6.96 (bs, 2H); 4.19−3.26 (m, 21H); 1.83 (bs, 6H); 1.65 (bs, 16H); 1.23 (bs, 34H), 0.87 (bs, 6H). ^{13}C NMR ($CDCl_3$): δ, 195.73, 162.88, 138.24, 132.56, 131.72, 129.71, 128.25, 114.32, 67.95, bs 53.45, 31.90, 29.65, 29.59, 29.53, 29.47, 29.36, 22.67, 14.11.

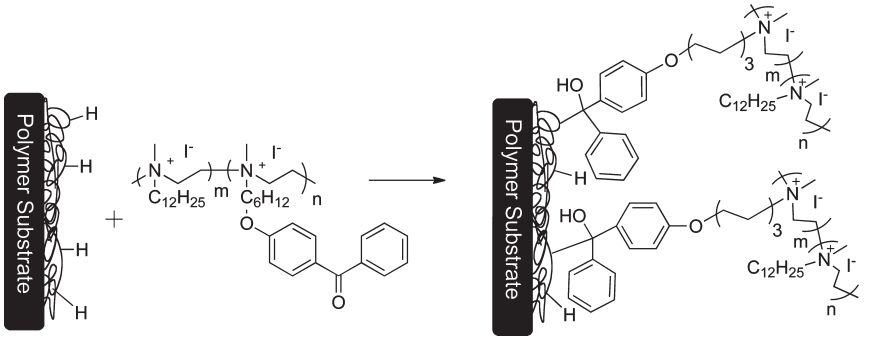
Preparation of Self-Assembled Monolayers on Glass Substates. Glass slides were cut into rectangles. The substrates were sonicated with Fisherbrand sonicating soap, 18.2 MΩ deionized water, isopropanol, and acetone for 10 min each and finally dried in an oven for 1 h. After cleaning, a self-assembled monolayer (SAM) of octyltrichlorosilane was formed from the vapor phase by suspending the substrates in a vacuum desiccator and placing two drops of silane on a glass substrate at the bottom. The substrates were kept in a vacuum flux (constant pressure of 100 mTorr) for 20 min. After venting with nitrogen, the substrates were sonicated with acetone and dried under air.

*Surface-Bound PEI Polymer (**2**).* Fifteen milligrams of quaternized polymer (**2**) was dissolved in 1 mL of acetone solvent. The solution was filtered through 0.25 μm filter. The polymer film was developed on functionalized glass substrate by spin coating with 0.5 mL of solution at 1000 rpm. The glass substrate was irradiated with UV light (365 nm, 180 mW/cm^2) for 15 min to covalently bind the polymer on the glass

Scheme 1. Outline of the Synthetic Protocol for the PEI Copolymer Containing Benzophenone Side Chains



Scheme 2. Covalent Attachment of the Hydrophobic Benzophenone−PEI Copolymer to C−H Alkyl-Containing Surfaces and Inert Plastics



surface through the pendant benzophenone moiety. The substrate was sonicated with acetone for 1 min and dried under air.

RESULT AND DISCUSSIONS

Copolymer **2**, which contains both hydrophobic and benzophenone side chains, was prepared by reacting linear PEI with 4-[(6-Bromohexyloxy)] benzophenone and 1-bromododecane (Scheme 1) along with subsequent quaternization using iodomethane. The copolymer composition was checked by NMR spectroscopy, which revealed that the polymer composition matched the pendant group feed ratio. Based on the NMR integration values, the benzophenone side-chain constitutes 33% of total polymer pendant groups with the dodecane constituting the other 66%. We were unable to characterize the copolymer using gel permeation chromatography but using the initial molecular weight of the poly(2-ethyl-2-oxazoline) before hydrolysis and functionalization (M_w = 50 000 g/mol), the approximate molecular weight of the quaternized copolymer was ~194 kDa. Copolymer **2** is soluble in halogenated solvents, acetone, and slightly soluble in alcohols. As described above, the benzophenone component of **2** can act as a cross-linker between the hydrophobic PEI polymer and any organic substrate through C−H activation. Initially, we have used glass and silicon wafers functionalized with alkyl SAMs to analyze the polymer film thickness before and after cross-linking, kinetics of functionalization, and to observe any surface morphology changes through atomic force microscopy. Flat substrates also simplify the antimicrobial activity assays because of the ease of analytical quantification.

The cross-linking and structure of the covalently bound polymer surfaces is shown in Scheme 2. Initially, the oxide surfaces were functionalized with octyltrichlorosilane (OTS) to generate C−H alkyl groups on the surface. To this modified surface was deposited a thin layer of polymer **2** using spin-coating (15 mg/mL in acetone, 1000 rpm). Covalent attachment was generated by exposure to UV irradiation (365 nm, 180 mW/cm^2) for 15 min. The cross-linked

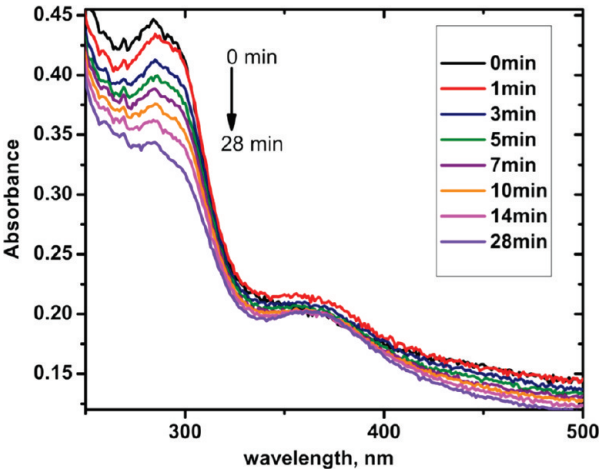


Figure 1. Change in UV spectra of benzophenone in polymer **2** with UV exposure with time (365 nm).

films were then washed with acetone and sonicated in acetone for one minute to remove any residual, unbound materials. The polymer film thickness was measured before and after sonication and was observed to be 93 and 77 nm respectively, indicating that approximately 80% of the coating remained after cross-linking. The thickness of the cross-linked coating did not change upon prolonged sonication in any organic solvent.

The kinetics of surface attachment of copolymer **2** was investigated by UV−vis spectroscopy on OTS functionalized quartz substrates. Time dependent changes in the absorption spectra of the film under UV light irradiation are shown in Figure 1.[53] Photon absorption at 365 nm results in the promotion of one electron from a nonbonding n orbital to an antibonding π^* orbital of the carbonyl group on the benzophenone moitey. The n−π^* transition yields a biradicaloid triplet state where the electron-deficient oxygen n-orbital is electrophilic and therefore interacts with weak

C−H δ bonds, resulting in hydrogen abstraction to complete the half-filled n orbital.[54,55] The two resulting radical species can then combine to form a new C−C bond. The reaction progress can be monitored indirectly by following the decrease in the $\pi-\pi^*$ transition of benzophenone at 290 nm. As expected, this peak decreases with increasing irradiation time. After ~30 min, the reaction is complete as observed, with no further changes in the spectrum with prolonged irradiation.

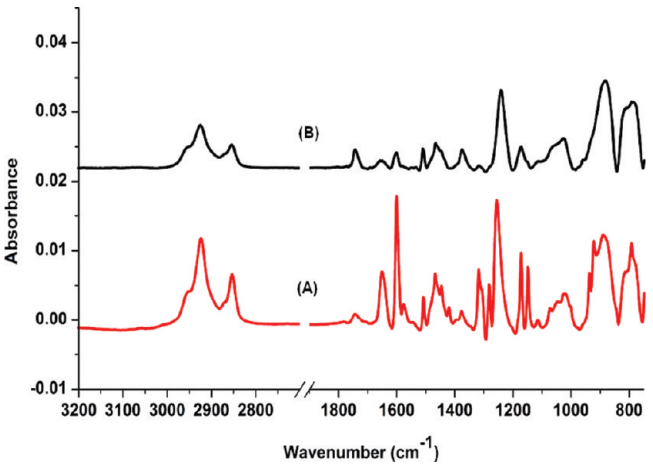


Figure 2. FTIR spectra of a thin film of copolymer **2** (A) before and (B) after UV exposure.

The photochemical attachment of copolymer **2** was also confirmed using grazing incidence attenuated total internal reflection Fourier transform infrared spectroscopy (GATR-FTIR). Copolymer **2** was spincast onto a silicon wafer that was modified with a SAM of OTS. Figure 2 shows the GATR-IR spectrum of a silicon wafer modified with copolymer **2** (A) before and (B) after UV irradiation. In Figure 2A, the peaks at 2920 and 2849 cm^{-1} are due to C−H stretching of the aliphitac backbone and pendant groups. The C═O of the benzophenone pendant group is observed at 1648 cm^{-1}. The C−C ring vibrations are assigned at 1600 cm^{-1} along with the C−N^+ stretch at 1468 cm^{-1}. Peaks at 1253 and 1020 cm^{-1} are assigned to the C−O−C asymmetric and symmetric stretches respectively. Figure 2B shows the polymer film after irradiation. A significant reduction in the C═O strecth at 1648 cm^{-1} is readily apparent, which indicates photodecomposition of the carbonyl group along with the covalent attachment of **2** onto the OTS functionalized SiO_2 surface. The overall decrease in all peak intensities

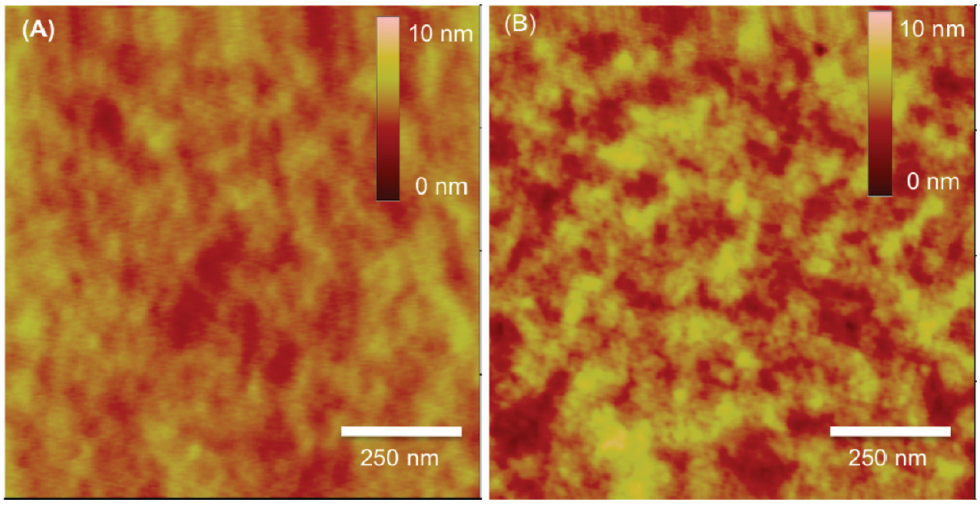


Figure 3. Tapping mode AFM image for the film of copolymer **2** (A) as cast before sonication (thickness 93 nm, rms roughness 0.48 nm) and (B) after sonication (thickness 77 nm, rms roughness 0.83 nm).

Table 1. Antimicrobial Test with *S. aureus* along with Percent Bacterial Reduction[a]

	control (CFU)	5 mg/mL polymer conc.		10 mg/mL polymer conc.		15 mg/mL polymer conc.	
	uncoated glass slides	SUV[b] film thickness 35 nm	SUVS[c] film thickness 31 nm	SUV film thickness 55 nm	SUVS film thickness 53 nm	SUV film thickness 93 nm	SUVS film thickness 77 nm
1	258	1	15	0	3	0	4
2	247	4	16	0	4	0	2
3	158	0	10	0	3	3	2
average	221	1.66	13.66	0	3.33	1	2.66
% reduction		99.24	93.81	100	98.49	99.54	98.79

[a] There were four sets of samples tested: (1) control glass substrate with OTS coated SAM, (2) spin-coated glass substrate with 5 mg/mL polymer concentration, (3) spin-coated glass substrate with 10 mg/mL polymer, and (4) spin-coated glass substrate with 15 mg/mL concentration. Copolymer **2** was spin-coated on the glass sample and irradiated with UV light (365 nm, 180 mW/cm^2) for 15 min and sonicated in acetone for 1 min. The coated and control samples were sprayed with *S. aureus* solution and incubated for 24 h at 37 °C. [b] SUV = Spin-coated UV radiated unsonicated glass slides. [c] SUVS = Spin-coated UV radiated sonicated glass slides.

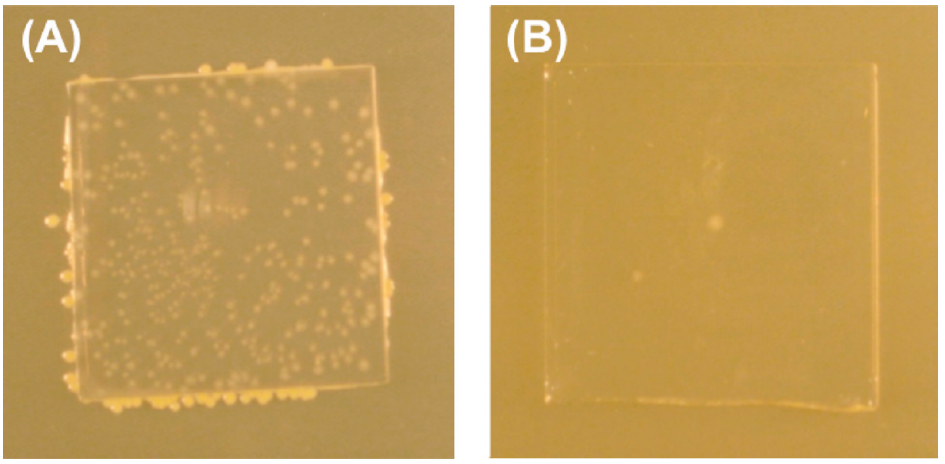


Figure 4. Digital pictures of the glass substrates sprayed with *S. aureus* and incubated for 24 h at 37 °C: (A) control substrate and (B) glass substrate modified with polymer **2** after sonication.

Table 2. Antimicrobial Test with *E. coli* along with Percent Bacterial ReductionT[a]

	control (CFU)	5 mg/mL polymer conc.		10 mg/mL polymer conc.		15 mg/mL polymer conc.	
	uncoated glass slides	SUV[b] film thickness 35 nm	SUVS[c] film thickness 31 nm	SUV film thickness 55 nm	SUVS film thickness 53 nm	SUV film thickness 93 nm	SUVS film thickness 77 nm
1	91	0	11	1	0	0	1
2	81	2	24	0	11	0	0
3	136	2	26	0	6	0	1
average	102.66	1.33	20.33	0.33	5.66	0	0.66
% reduction		98.70	80.19	99.67	94.48	100	99.35

[a] There were four sets of samples tested: (1) control glass substrate with OTS coated SAM, (2) spin-coated glass substrate with 5 mg/mL polymer concentration, (3) spin-coated glass substrate with 10 mg/mL polymer, and (4) spin-coated glass substrate with 15 mg/mL concentration. Copolymer **2** was spin-coated on the glass sample and irradiated with UV light (365 nm, 180 mW/cm^2) for 15 min and sonicated in acetone for 1 min. The coated and control samples were sprayed with *S. aureus* solution and incubated for 24 h at 37 °C. [b] SUV = Spin-coated UV radiated unsonicated glass slides. [c] SUVS = Spin-coated UV radiated sonicated glass slides.

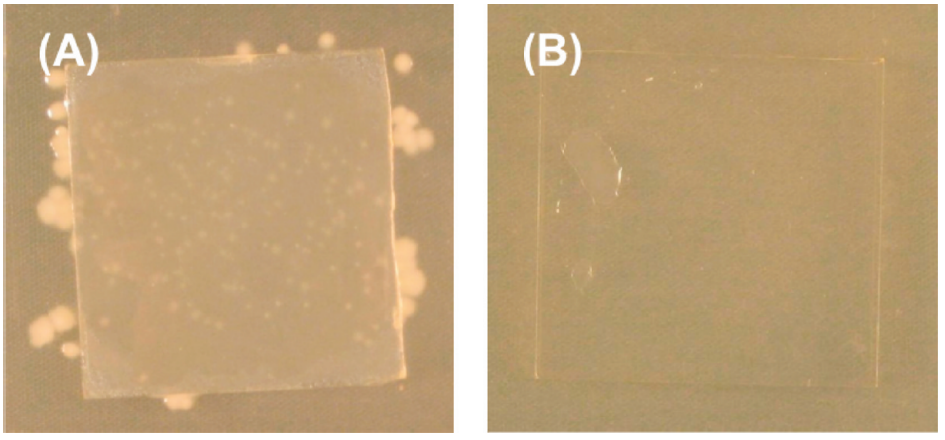


Figure 5. Digital pictures of the glass substrates sprayed with *E. coli*: (A) control substrate and (B) glass substrate modified with **2** after sonication.

correlates with the decrease in film thickness after cross-linking and subsequent sonication.

AFM was used to characterize the surface morphology of copolymer (**2**) film before and after sonication to remove any noncovalently bound polymer from the surface. Before and after sonication, the irradiated film of **2** was very smooth. A representative morphology for both is shown in Figure 3. The thickness of the film is 93 nm (measured with ellipsometry) with an rms roughness 0.48 nm by AFM. Figure 3B shows the morphology of the film after sonication. The overall film

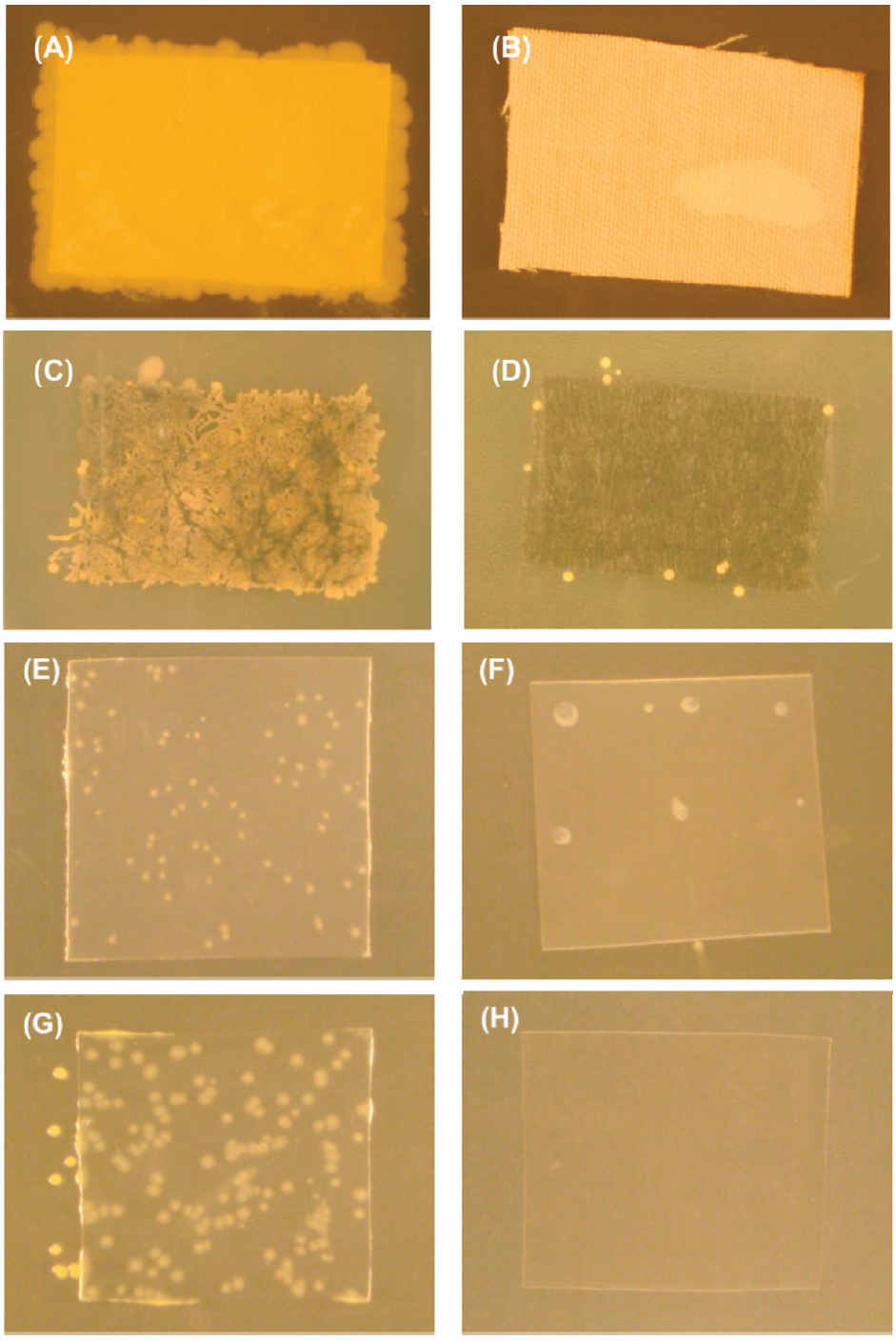


Figure 6. Digital pictures of the textiles and plastic substrates sprayed with *S. aureus*: (A) untreated cotton, (B) cotton spray-coated with 15 mg/mL polymer **2**, (C) untreated polypropylene (nonwoven geotextile fabric), (D) polypropylene spray-coated with 15 mg/mL polymer **2**, (E) untreated poly(vinyl chloride) substrate, (F) poly(vinyl chloride) substrate spray-coated with 15 mg/mL polymer **2**, (G) untreated polyethylene substrate, and (H) polyethylene substrate spray-coated with 15 mg/mL polymer **2**.

thickness decreased to 77 nm after sonication, with an increase in surface roughness to 0.83 nm due to removal of noncovalently attached polymer from the surface.

The effectiveness of the polymer-coated surfaces to kill bacteria was tested on different plastics, fabrics, and alkyl-functionalized glass substrates. For covalently bonded biocides, direct contact of the organism with the antimicrobial moiety is required for the antibacterial activity.[56,57] In these experiments, microbes were uniformly sprayed on the polymer-coated surfaces using a TLC sprayer connected to pneumatic dispense regulator. The sprayed sample was air-dried and mounted on a TSA plate, which was incubated for 24 h at 37 °C. The number of colonies grown on the slide was then counted by visualization under an optical microscope. To examine the influence of polymer coating thickness on the biocidal activity, was spin-cast copolymer **2** onto flat substrates using solutions of different concentration. This allowed uniform,

reproducible thickness that varied between 30 and 93 nm after irradiation and sonication. The thickness of the coating had an impact on the biocidal activity (Table 1). The surface grafted with a high density of polymers exhibited relatively high biocidal activity. When the thickness of the polymer layer is greater than 35 nm, the coating was >99% effective and all bacterial colonies were killed. Figure 4 shows the digital photograph of the control and polymer functionalized surfaces after spraying with *S. aureus* and incubated for 24 h at 37 °C. As seen in Figure 4A, numerous colonies of *S. aureus* are grown on the control slide after spraying the bacterial suspension onto the surface. On the other hand, a bacterial reduction greater than 99% is observed on the same substrate coated with copolymer **2** (Figure 4B).

To establish the generality of the effectiveness of our polymer coatings, we also tested against the human pathogenic bacterium *Escherichia coli* (*E. coli*, which is a Gram-negative bacterium), the results of which are shown in Table 2. As also seen in Figure 5, the polymer-coated slides once again afforded a 99% killing efficiency against *E. coli*.

To investigate the versatility of these copolymers on commodity plastics and textile fabrics, we photochemically modified a variety of substrates such as cotton, polypropylene, polyethylene, and poly(vinyl chloride) with copolymer **2** using a simple spray-coating technique. The copolymer, dissolved in acetone, was uniformly spray-coated with a laboratory TLC sprayer. The substrates were air-dried and irradiated (365 nm, 180 mW/cm^2) to covalently attach the polymer to the plastic surface. After UV curing, the substrates were thoroughly washed in acetone to remove any noncovalently attached copolymer. For all substrates, there were no major changes observed to either the hand or physical properties. On the cotton pieces, the coated samples showed mild yellowing after UV irradiation. The copolymer treated and untreated fabrics were challenged against *S. aureus* with the antibacterial test method described earlier. Figure 6 shows bacterial proliferation on the untreated fabrics and excellent antibacterial activity on the treated fabrics. The results demonstrate covalent immobilization of polymer **2** on all substrates, including those with with reactive functional groups such as cotton as well as on inert plastic surfaces such as polypropylene, poly(vinyl chloride), and polyethylene.

CONCLUSIONS

In this study, we have demonstrated a novel and efficient approach to covalently attach antimicrobial polymer on any substrate with a C−H bond. A hydrophobic PEI copolymer substituted with benzophenone side chain (**2**) was spin-casted or spray-coated on a wide range of surfaces from cotton to inert plastics and photocross-linked by UV irradiation. After the covalent attachment of polymer on the surface, the biocidal activity was investigated against both Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria. The surface grafted with a high density of polymers exhibited relatively high biocidal activity. When the thickness of the polymer layer was greater than 50 nm, essentially almost all the bacteria were killed. This one step photochemical attachment process of an ultrathin antimicrobial coating is both simple and scalable for industrial applications.

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ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from the University of Georgia Office of Vice President for Research and the Traditional Industries Program (TIP^3) from the State of Georgia.

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