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N-Halamine Copolymers for Use in Antimicrobial Paints

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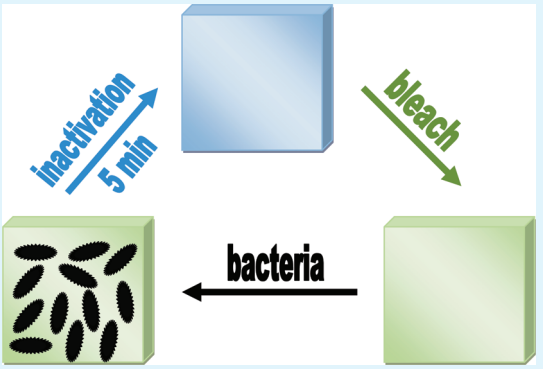
Supporting Information

ABSTRACT: A series of copolymers containing units of a novel hydantoinylacrylamide and the sodium salt of 2-(acrylamido)-2-methylpropanesulfonic acid have been synthesized. The homopolymer of the hydantoinylacrylamide compound was insoluble in water, while the copolymers with the sulfonic acid sodium salt were water-dispersible/soluble, with the solution becoming completely transparent when the feed ratio for the copolymer contained 7 parts of the hydantoin moiety to 3 parts of the sodium sulfonate moiety. The polymers were added into a commercial water-based latex paint, and upon drying, the painted surfaces treated with the water-miscible copolymers were rendered antimicrobial following chlorination with dilute household bleach. The chlorinated homopolymer failed to provide an antimicrobial property for the paint because of its tendency to isolate into aggregates in the paint, while the completely miscible copolymers were capable of 6-log inactivation of *Staphylococcus aureus* and *Escherichia coli* O157:H7 within 5 min of contact time.



KEYWORDS: antibacterial polymer, antimicrobial paint, *N*-halamine, acrylamide, latex paint, water-soluble

INTRODUCTION

Contaminated environmental surfaces serve as important sources of cross-infections due to the liberation of microorganisms into the air or transference to the surroundings through direct or indirect contact.[1−3] The microorganisms are able to survive on the surfaces for days, weeks, and even months.[4−6] The transmission of the microorganisms through contamination of surfaces in the environment can be minimized by deactivating them on the contaminated surfaces within brief contact time intervals (preferably within 5 min).

Light-activated coatings (photosensitizers),[7,8] quaternary ammonium salts,[9−12] metal ions,[13,14] and *N*-halamine compounds[15−23] are currently used for the preparation of numerous types of biocidal materials. *N*-Halamines stabilize oxidative halogens, which are highly effective disinfectants. In particular, materials incorporated with cyclic *N*-halamines are exceptionally stable over the long term in dry storage, and they efficiently inactivate a broad range of microorganisms including drug-resistant bacteria. In addition, their biocidal activities can be regenerated after the loss of oxidative halogen simply by exposure to an aqueous free chlorine solution such as household bleach, as shown in Figure 1.

Antimicrobial materials, which can be incorporated into coatings such as paints, should prove useful for a variety of surfaces. Various antimicrobial agents have been studied for possible use in commercial paints such as photoactivated metal oxides[7] and acrylics,[8] quaternary ammonium salts,[9−12] silver nanoparticles,[13,14] and *N*-halamine materials.[16−19] Among these, the *N*-halamine agents seem to offer the best alternatives because, in general, they provide the most rapid inactivation rates for pathogens,[15−23] they are relatively inexpensive to produce, they can be recharged in situ once the oxidative halogen is exhausted, the ones covalently bonded to a surface do not leach from the surface into aqueous solution,[16−18] and they generally do not adversely affect the texture of the paint.[16−19] The mechanism of action is the direct transfer of oxidative halogen from the surface-bound *N*-halamine to the microbial cell rather than the release of *N*-halamine or free halogen into aqueous solution, followed by migration to the microbe. The first report of an *N*-halamine additive for paint described a hydantoinyldiol monomer that could be copolymerized with a commercial water-borne acrylic polyol and an isocyanate to produce a polyurethane coating, which could be chlorinated on a surface to render the surface antimicrobial.[16] A complete inactivation of *Staphylococcus aureus* (4.5-log initial challenge) was obtained within 2 h of contact, which could be satisfactory for certain applications such as the prevention of biofouling. Two antimicrobial *N*-halaminehydantoinylsiloxane materials have also been studied extensively[17,18] as possible paint additives, again in polyurethane formulations. Their performances were similar to that of polyurethane discussed above. A significant advance in the use of an *N*-halamine for antimicrobial paints was realized when Cao and Sun[19] showed that an emulsion of *N*-chloro-2,2,6,6-tetramethyl-4-piperidinylmethacrylate could be added to a commercial latex

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paint to obtain 8-log inactivation of several pathogens within a few minutes of contact at high concentrations (20 wt %) and within 1−2 h at concentrations as low as 1 wt %.

Previously, the synthesis of a novel *N*-halamineacrylamide monomer (HA in Scheme 1) capable of stabilizing 31 wt % of chlorine was described.[22] In that study, HA was copolymerized with a siloxane comonomer and coated onto cotton, followed by chlorination with dilute household bleach (1% aqueous solution containing 0.06 wt % sodium hypochlorite) to produce antimicrobial fibers that were capable of producing 8-log inactivation of *S. aureus* and *Escherichia coli* O157:H7 within 5 min of contact time. In the current work, copolymers of HA with a sodium sulfonate monomer (Scheme 1, SA) were prepared in different compositions and then were introduced into a commercial water-based latex paint. After drying and then chlorination with household bleach, the treated paints exhibited excellent biocidal activity against Gram-positive and Gram-negative bacteria. The principle advantage of the copolymer utilizing the sodium salt over the siloxanes is the imparted water solubility rendering the copolymer miscible with commercial latex paint. It will be shown that the resulting paint had excellent antimicrobial activity even when the composition of the copolymer in the paint was only 1.5 wt %. Although most paints contain biocidal materials as preservatives to prevent the growth of microorganisms within the paint, the goal of the present work was to provide rapid antimicrobial activity to the surface of the coating so as to create antimicrobial coatings for medical, food preparation, and related applications. *N*-Halamines would not be useful as preservatives within the paint.

EXPERIMENTAL SECTION

Materials. Chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification unless otherwise stated. The preparation of hydantoinylacrylamide monomer and confirmation of its structure with NMR analysis has been described.[22] Briefly, it involved the reaction of commercial diacetone acrylamide in a Bucherer−Berg synthesis. A commercial interior white latex paint (Olympic, PPG Architectural Finishes, Inc., Pittsburgh, PA) including a total solid content of 48 wt % (titanium dioxide, vinyl acetate/ethylene copolymer, sodium potassium aluminum silicate, calcium carbonate, and aluminum silicate) was used in this study. The *N*-halamine copolymers prepared in this work did not affect the texture or color of the latex paint when used at the indicated concentrations.

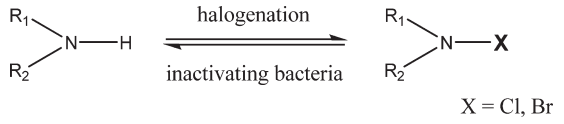


Figure 1. Regenerability of *N*-halamines.

Characterization. ^{1}H NMR spectra recorded with 16 scans were obtained using a Bruker 400 MHz spectrometer. The Fourier transform infrared (FTIR) data recorded with 64 scans at 4 cm^{-1} resolution were obtained with a Nicolet 6700 FTIR spectrometer with an attenuated total reflectance (ATR) accessory. The thermogravimetric analysis (TGA) data were obtained with a TA Instruments Q500 at a heating rate of 10 °C/min under a nitrogen atmosphere.

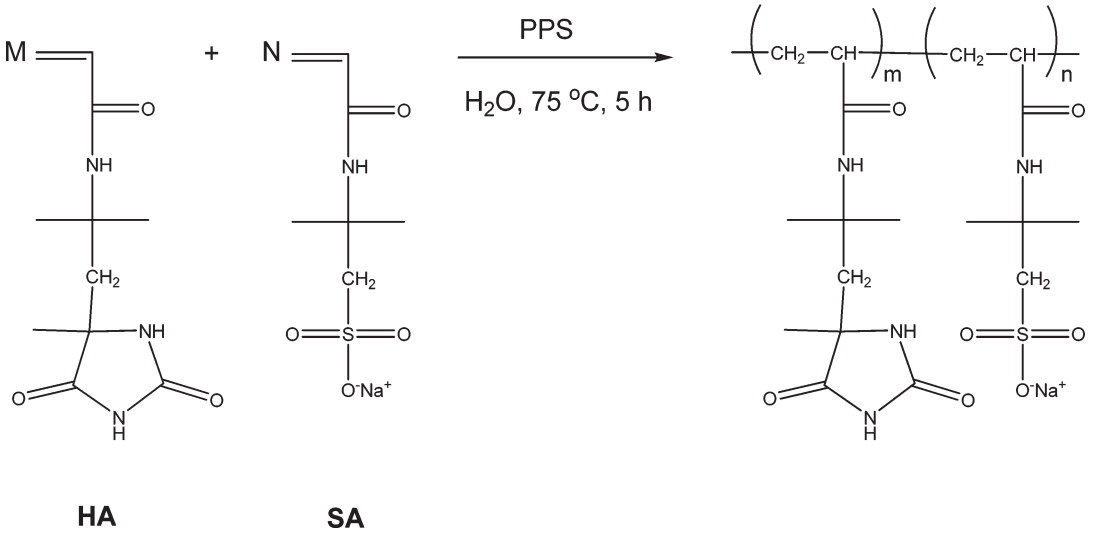
General Procedure for the Synthesis of the Polymers. The HA homopolymer and copolymers with 2-(acrylamido)-2-methyl-1-propanesulfonic acid sodium salt (SA) were synthesized by free-radical polymerization. For example, to prepare copolymer **9** (Table 1), in a 100 mL round-bottomed flask, 2.15 g (9 mmol) of HA, 0.46 g (1 mmol) of 2-(acrylamido)-2-methyl-1-propanesulfonic acid sodium salt (50 wt % solution in water), 0.01 g of potassium persulfate, and 50 mL of distilled water were added. Nitrogen was bubbled through the solution for 30 min before reaction to remove any dissolved oxygen. The mixture was stirred at 75 °C for 5 h under a nitrogen atmosphere. The precipitated homopolymer was obtained by filtration, while the copolymers were recovered by evaporation of the water solvent. The yields were about 90 wt % in all cases. Different *feed* mole ratios of SA to HA were used to synthesize four different copolymers, as summarized in Table 1. Copolymers containing SA at higher ratios than 30% (**6**, **5**, etc.) were not

Table 1. Composition of the Synthesized Polymers As Expected from the Feed Ratios of HA and SA

polymer	$M_{HA}/(M_{HA} + M_{SA})$	appearance in water
10	1.0	insoluble
9	0.9	colloid (opaque)
8	0.8	colloid (translucent)
7	0.7	soluble (transparent)

[a] M_{HA} and M_{SA}: mole fractions of HA and SA in the feed mixture.

Scheme 1. Structures of the Synthesized Copolymers



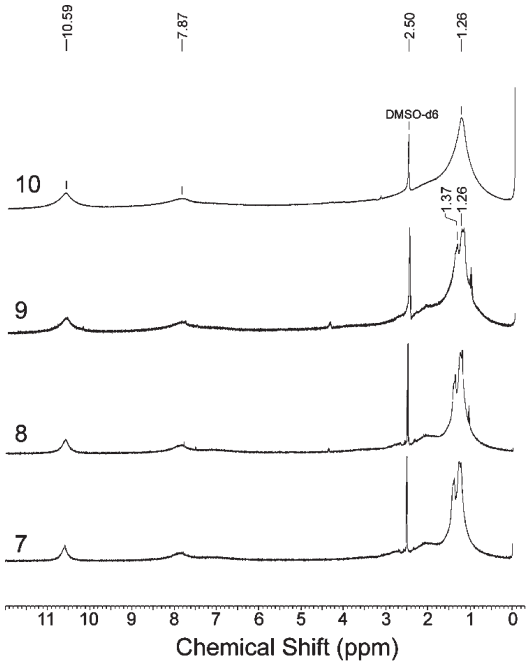


Figure 2. ^{1}H NMR spectra of the synthesized polymers (solvent: DMSO-d_6).

prepared because **7** was adequately soluble in water, and copolymers containing increased ratios of HA would load higher amounts of oxidative chlorine. The intrinsic viscosities of copolymers **10**, **9**, **8**, and **7** were 0.88, 0.92, 1.10, and 1.15 dL/g [in dimethyl sulfoxide (DMSO), 25 °C], respectively.

Preparation of the Antimicrobial Latex Paint. For example, to prepare a 1.5 wt % polymer in the paint, the synthesized polymers (0.36 g) were first dispersed/dissolved in distilled water (5.64 g) by stirring for 1 h to produce a uniform solution. In a vial, 1.1 g of the polymer dispersion/solution and around 9.1 g of the paint were added and stirred for 30 min to produce a uniform mixture. Then the mixture was poured onto a polyester transparency slide of size of 21.5 × 27.9 cm. The slide provided a nonporous surface that was easily coated uniformly with the paint. The slide itself did not absorb bleach or change shape during the chlorination and heating procedures and provided uniform contact with the bacterial suspensions. The paint was uniformly spread onto the transparency slide with a foam roller. The painted transparencies were dried for 1 week at room temperature. The amounts of the paint on the transparencies were about 15 wt % of the total weight.

The painted transparencies were generally chlorinated by soaking in a 10% aqueous solution of household bleach (6% sodium hypochlorite) at pH 7 (adjusted with 6 N HCl) for 1 h. For comparison purposes, a sample of copolymer **9** on a transparency was also chlorinated by wiping the surface with the dilute bleach for about 5 s. After rinsing with tap and distilled water, the transparencies were then dried at 45 °C for 1 h to remove any unbonded chlorine from the material. The chlorine concentrations loaded onto the coated samples were determined by a modified iodometric/thiosulfate titration procedure[23] in which the samples (2.5 × 7.6 cm) were placed in a solution containing 90 mL of ethanol and 10 mL of 0.01 N acetic acid. After the addition of 0.2 g of potassium iodide, 0.00375 N sodium thiosulfate was used to titrate until the disappearance of the yellow color at the end point. The weight percent of Cl^+ on the samples was calculated by the following formula:

$$Cl^+ (\%) = [(NV \times 35.45)/(2W)] \times 100 \quad (1)$$

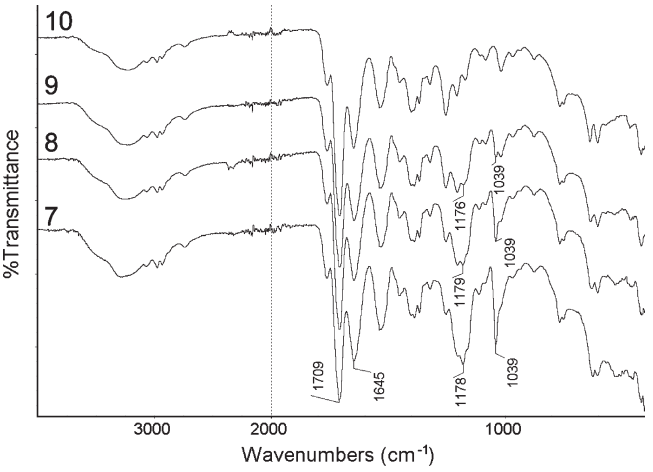


Figure 3. FTIR spectra of the synthesized polymers.

where Cl^+ (%) is the weight percent of oxidative chlorine on the samples, N and V are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and W is the weight of the sample (g).

Biocidal Efficacy Testing. A "sandwich test" was used to evaluate the biocidal efficacies. Both chlorinated and unchlorinated paint samples were challenged with *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC 43895) bacterial suspensions in a pH 7 phosphate buffer solution (100 mM). The bacteria purchased from the American Type Culture Collection (Rockville, MD) were stored at −80 °C in 10% dimethyl sulfoxide trypticase soy broth (Difco Laboratories, Detroit, MI) before use. Suspensions (25 μL) of the bacterial solution (6−7-log concentration) were added to the center of a 2.54 cm square paint sample, and a second identical sample was placed on top of the first one. The contact times for the bacteria with the samples were 5 and 10 min. At those contact times, the paint samples were quenched with a 0.02 N sodium thiosulfate solution to remove any oxidative chlorine, which could cause extended disinfection. Serial dilutions of the solutions contacting the surfaces were plated on trypticase agar, incubated for 24 h at 37 °C, and colony counts were made to determine the presence or absence of viable bacteria.[24] Unchlorinated control samples were treated in the same manner.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers. HA was copolymerized with SA in different compositions, as summarized in Table 1. The feed ratio of the copolymers $M_{HA}/(M_{HA} + M_{SA})$ varied from 1 to 0.7. The amount of HA in the copolymer composition contributes to the halogen loading capability (potential antimicrobial property), whereas the sulfonic acid (SA) amount contributes to the water dispersibility/solubility property of the copolymers. The appearance of the polymers at 5 wt % in water is summarized in Table 1. Homopolymer **10** was insoluble in water, while copolymers **9** and **8** formed stable colloids, and copolymer **7** was completely soluble in water.

NMR and FTIR analyses were used to confirm the structures of the synthesized polymers. ^{1}H NMR spectra of the polymers **10**, **9**, **8**, and **7** are shown in Figure 2. The primary evidence for the polymer formation is the disappearance of the vinyl proton signals between 5.5 and 6.5 ppm (see the Supporting Information for the spectra of the monomers). For the homopolymer **10**, the signal at 1.26 ppm (c) can be assigned to the protons of the methyl groups. The signals at 7.87 and 10.59 ppm can be assigned to the amide and imide protons of the hydantoin ring,

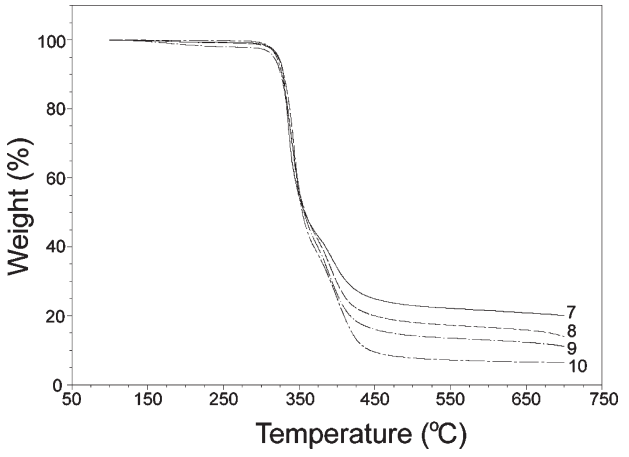


Figure 4. TGA traces of the synthesized polymers.

respectively. In the spectrum for **9**, a new signal appeared at around 1.37 ppm, compared to the spectrum for **10**, due to the methyl groups of the comonomer SA. The intensity of this band is enhanced by increasing the amount of SA in the copolymer (**9** to **7**). Unfortunately, the resolution in Figure 2, even for dilute samples, was not sufficient for an accurate determination of the mole ratios of units HA and SA in the copolymers. However, the mole feed ratios should give a reasonable account of the copolymer compositions because the acrylamide monomer units in HA and SA are the same in structure.

The FTIR spectra of the polymers shown in Figure 3 were also suggestive of the copolymer formation and the monomer composition. First, the stretching vibration for the vinyl bonds of the monomers at around 1630 cm^{-1} disappeared for the polymers. Also, the bands in the spectra were broader compared to those of the comonomers (see the Supporting Information) due to polymerization. The bands at 1709 and 1760 cm^{-1} are characteristic of the presence of the hydantoin ring in the polymers; the intensities of these bands decreased concomitantly with a reduction in the amount of HA in the copolymers. The intensities of the SO^{-} group asymmetric stretching band at around 1180 cm^{-1} and the symmetric stretching band at 1039 cm^{-1} increased with an increase in the SA amount in the copolymers.[25]

TGA traces of the synthesized polymers are shown in Figure 4. All polymers started to degrade at about 300 °C, which makes them suitable for many applications requiring elevated processing temperatures such as melt extrusion (150−300 °C).[26] The weight loss of the polymers above 500 °C decreased upon an increase in the SA amount in the polymers. This was due to an increased amount of nonvolatile char, which resulted during degradation of the sodium salt. This had been observed previously for the thermal degradation of acid salts.[27]

Preparation of the Antimicrobial Paints. The polymers were mixed with the latex paint in varying concentrations. The treated paints were coated onto polyester transparencies and then chlorinated with dilute household bleach. The amounts of the chlorine loadings, both weight percent with respect to the paint and chlorine atoms per centimeter squared on the treated paints, are summarized in Table 2. The paint containing no polymer could be chlorinated at a very low chlorine loading of about 0.04 wt %. The chlorine loadings of the treated paints with 1 wt % polymer were between 0.21 and 0.32 wt %. The chlorine

Table 2. Chlorine Loadings of the Antimicrobial Paints

	1 wt % copolymer in paint		1.5 wt % copolymer in paint	
sample	$[Cl^+]$ %[a]	$[Cl^+]$ atoms/cm^2	$[Cl^+]$ %[a]	$[Cl^+]$ atoms/cm^2
10	0.31	1.7×10^{17}	0.47	2.2×10^{17}
9	0.27	1.3×10^{17}	0.40	1.7×10^{17}
8	0.24	9.6×10^{16}	0.39	1.7×10^{17}
7	0.21	7.4×10^{16}	0.32	1.2×10^{17}
paint[b]	0.04	1.7×10^{16}	0.04	1.7×10^{16}

[a] $[Cl^+]$ is the chlorine loading on the treated paint samples in weight percent with respect to the paint weights (before exposure to light). [b] Paint with no polymer added (before exposure to light).

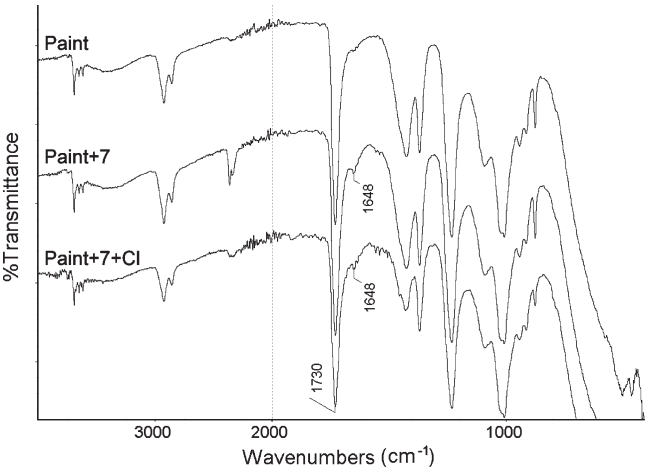


Figure 5. FTIR spectra of the paint, treated paint with copolymer **7**, and treated paint with chlorinated copolymer **7**.

loadings of the treated paints with 1.5 wt % polymer were higher compared to those containing 1 wt % polymer as expected. The measured chlorine loadings of the treated paints were near the theoretical chlorine loadings, indicating that most of the N−H moieties in the paint matrix could be chlorinated. A sample treated with copolymer **9**, wiped with dilute bleach for about 5 s, then dried, rinsed, and further dried at 45 °C for 1 h provided 0.25 wt % chlorine loading. The immersion technique described in the Experimental Section used on an identical sample containing **9** provided 0.38 wt % loading, which was higher than that for the wiping technique as expected. However, the loading provided by the wiping procedure would be easily adequate for an antimicrobial application.

The paint matrix allowed halogenation of the *N*-halamine polymers not only on the surface but also within the paint. Moreover, even the water-soluble copolymer **7** was well trapped in the paint matrix as well as on the surface. As shown in Figure 5, an additional band appeared at 1648 cm^{-1} when copolymer **7** was added into the paint (Paint+7), and this band remained after chlorination, indicating that the copolymer was well trapped in the paint matrix. Similar FTIR spectra were also observed with the other polymers.

Chlorine Stability. Under ambient lighting in air, the paint samples slowly lose their chlorine contents. For example, a sample of **9** at the 1.5 wt % concentration level in the latex paint loaded initially with 0.38 wt % chlorine declined in chlorine loading to 0.16 wt % over an 8 week period. However, at that

Table 3. Biocidal Tests (Log Reduction)

		Exp 1		Exp 2	
sample/Cl$^+$ %	contact time (min)	*S. aureus*	*E. coli*	*S. aureus*	*E. coli*
Paint-Cl	10	0.18	0.05	0.14	0.10
10	10	0.01	0.01	0.11	0.09
9	10	0.09	0.14	0.06	0.12
8	10	0.13	0.01	0.15	0.04
7	10	0.02	0.25	0.13	0.22
10-Cl	5	0.05	0.03	0.12	0.07
0.41	10	0.04	0.12	0.25	0.05
9-Cl	5	6.60	6.52	6.38	6.24
0.28	10	6.60	6.52	6.38	6.24
8-Cl	5	6.60	6.52	6.38	6.24
0.29	10	6.60	6.52	6.38	6.24
7-Cl	5	6.60	6.52	6.38	6.24
0.18	10	6.60	6.52	6.38	6.24

[a] Exp 1: The inoculum concentrations were 6.60 and 6.52 logs for *S. aureus* and *E. coli* O157:H7, respectively. [b] Exp 2: The inoculum concentrations were 6.38 and 6.24 logs for *S. aureus* and *E. coli* O157:H7, respectively.

time, it could be rechlorinated with dilute household bleach to a chlorine level of 0.39 wt %, indicating that there was no decomposition of the copolymer in the paint. In an application, surfaces coated with the treated paints could be periodically rechlorinated to maintain antimicrobial efficacy. Because the copolymers are water-soluble, their retention in the dried paint was assessed. Sample transparencies treated with **7** and **9** were exposed to flowing tap water (750 mL/min) for 24 h. The chlorine content for **7** declined from 0.31 to 0.23 wt % over the time period, but it could be rechlorinated to 0.29 wt %. For **9**, the decline was from 0.38 to 0.29 wt % with rechlorination to 0.37 wt %. Thus, loss of the copolymers from the dried paint samples upon exposure to flowing water was minimal.

Antimicrobial Efficacies. The treated paint samples were stored for 10 days to remove the noncovalently bonded, occluded chlorine from the paint matrix and then were challenged with *S. aureus* and *E. coli* O157:H7 at concentrations of about 10^7 CFUs (colony-forming units). The control samples, chlorinated paint sample (**Paint-Cl**), and unchlorinated copolymers (**10**, **9**, **8**, and **7**) provided only about 0.10-log reduction because of the adhesion of bacteria to the paint samples, within 10 min of contact time (Table 3). Thus, the in-can paint preservatives in the latex paint provided little, if any, biocidal activity. It is of interest that the chlorinated homopolymer sample (**10-Cl**) also did not provide an antimicrobial property. This was probably due to the insufficient contact of microorganisms with the chlorine-loaded polymer particles, which could not be dispersed uniformly in the paint. Because the mechanism of antimicrobial action of *N*-halamines is the direct transfer of oxidative halogen to microbial cells, spaces among the aggregates of **10-Cl** on the paint had no direct contact of the polymer with the bacteria, resulting in undetectable biocidal action. On the other hand, copolymers **9**, **8**, and **7**, which were dispersible/soluble in the paint provided a total inactivation of both *S. aureus* and *E. coli* O157:H7 within 5 min of contact time in the repeated experiments. This observation underlines the importance of using soluble *N*-halamine copolymers in latex paints. Insoluble *N*-halamine homopolymers are not satisfactory for use with water-based paints. It should be noted that in one experiment a paint sample treated with copolymer **7**, tested at a chlorine loading of 0.16 wt % for antimicrobial efficacy, then rechlorinated to 0.16 wt %, and retested for antimicrobial efficacy provided a complete inactivation (about 6.5 logs) for both bacteria. Thus, there was no decline in efficacy brought about by a rechlorination process.

CONCLUSIONS

A series of *N*-halamine copolymers and the homopolymer of hydantoinylacrylamide were successfully synthesized. The hydantoinylacrylamide was copolymerized with a sodium sulfonate monomer so as to render the copolymers soluble in water-based latex paint formulations. The synthesized polymers were mixed at 1.5 wt % into a commercial water-based latex paint. The treated dried paints were chlorinated with a dilute household bleach treatment. The homopolymer-added paint did not provide an antimicrobial property because of insufficient contact with the microorganisms. On the other hand, the copolymers that were dispersible/soluble in water, and therefore in the paint, inactivated about 6−7 logs of both Gram-positive and Gram-negative bacteria within 5 min of contact time. This represents an excellent antimicrobial performance, particularly given the low percentage of polymer (1.5 wt %) necessary to achieve it. The stabilities and performance of the new polymers under extended laboratory and UVA light exposure are under investigation.

ASSOCIATED CONTENT

Supporting Information. Additional FTIR and NMR spectra of the monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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