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Biocidal activity of hydantoin-containing polyurethane polymeric surface modifiers

Stephen J. Grunzinger [a], Pinar Kurt [a], Kennard M. Brunson [a], Lynn Wood [b,c], Dennis E. Ohman [b,c], Kenneth J. Wynne [a,*]

[a] *Department of Chemical and Life Science Engineering, Virginia Commonwealth University, Richmond, VA 23284, United States*
[b] *Department of Microbiology and Immunology, Virginia Commonwealth University, Richmond, VA 23284, United States*
[c] *McGuire Veterans Affairs Medical Center, Richmond, VA 23249, United States*

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Abstract

The preparation of a new hydantoin-containing polyurethane surface modifier has been enabled by the development of a hydantoin-oxetane monomer that co-polymerizes to polyoxetane telechelics by ring-opening polymerization. After solution blending the hydantoin-containing polymer surface modifiers (2 wt%) with a conventional polyurethane, coating a substrate, and treating with dilute hypochlorite (bleach), the surfaces were challenged with Gram −ve *Pseudomonas aeruginosa* and Gram +ve *Staphylococcus aureus* in AATCC-100 'sandwich' and aerosol spray tests. Thirty-minute spray tests were used to establish concentrations at which overchallenges of the contact-kill surfaces occurred. These tests confirmed that no biocide release occurred under the test conditions. The spray test showed unambiguously the improved efficacy of biocidal action for a surface modifier with 5 mol% semifluorinated content compared to the non-fluorinated version.

Keywords: Antimicrobial coatings; Hydantoin; Poly(oxetanes)

1. Introduction

Biocidal polymers offer an approach to help curb the spread of infections by providing coatings for biomedical devices or molded articles. Biocidal polymers may be categorized by their mode of antimicrobial activity: *biocide release* or *contact-kill*. Recent work has shown that contact-kill can be combined with biocide release in a synergistic fashion [1,2]. This suggests that contact-kill based biocidal polymers may be good candidates as polymer matrixes for dual biocidal action.

Biocide release is by far the most common mode for providing antimicrobial action. These materials are made by mixing the biocidal agent with various polymeric materials during processing [3–5]. Quaternary ammonium compounds, metal salts of silver and tin, iodine, phenols, and antibiotics have been employed as antimicrobials. One commercial product, for example, is a wound dressing based on the release of silver [6,7]. However, some bacterial strains are inherently resistant to silver [8] and some develop resistance [9,10], but it is unclear whether this is a situation that is problematic compared to the buildup of antibiotic resistance.

Worley showed that polymer surface modification with hydantoin functionality generates *contact* oxidative biocidal surfaces after conversion of amide to chloramide [11,12]. Hydantoin and other cyclic amides react with hypochlorite (bleach) to generate the biocidal chloramide moiety [13–15]. Hydantoin has been grafted onto polystyrene, poly(acrylic acid), poly(vinyl acetate), and poly(vinyl chloride). Polyesters and nylons were hydantoin-functionalized first by modification to produce amide end groups followed by reaction with 1- or 3-hydroxyethyl-5,5-dimethylhydantoin [11,16–18]. Incorporation of hydantoin into polyurethanes has been effected previously via modification of the chain extender [19].

In a previous paper, we described polyurethanes with hydantoin moieties as pendent groups on soft blocks that were

* Corresponding author.
E-mail address: kjwynne@vcu.edu (K.J. Wynne).

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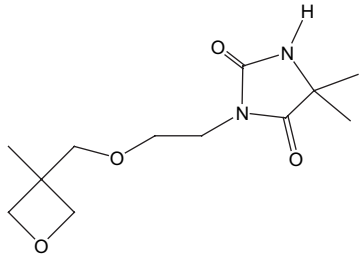
employed as surface modifiers [20]. The soft block of the surface modifying polyurethane contained semifluorinated **A** side chains to facilitate surface concentration of the biocidal hydantoin "**B**" groups (Fig. 1) [20]. Effective biocidal activity was conferred on a substrate polymer by as little as 1.6 wt% polymer surface modifier.

The preparation of these first generation hydantoin-containing polyurethane surface modifiers included a slow (72 h) and incomplete (50–60%) reaction-on-polymer step for introducing hydantoin. Therefore, a more practical preparative method was sought to incorporate hydantoin in a telechelic. After investigating several approaches, a hydantoin-containing oxetane monomer was found that would undergo cationic ring-opening polymerization. This monomer, 5,5-dimethyl-3-(2-((3-methyloxetan-3-yl)methoxy)ethyl)-imidazolidine-2,4-dione is designated Hy4Ox, **1** [21].



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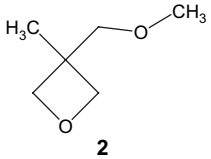

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To keep the soft block T_g low, a "companion" comonomer **2**, 3-methoxymethyl-3-methyloxetane, MOx, was prepared [21]. MOx is an easily purified oxetane with a methoxymethyl side chain. Employing the MOx "**A**" and Hy4Ox "**B**" monomers, we report the incorporation of P[MOx:Hy4Ox], **3** (Fig. 2) into a polyurethane polymer surface modifier. Here, "P" indicates that the monomers have the ring-opened structure.

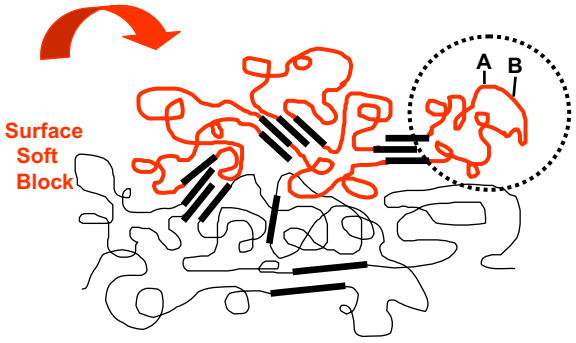
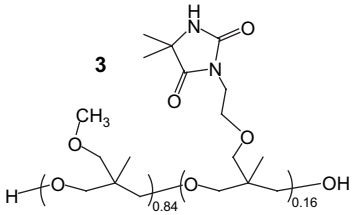


Fig. 1. A polymer surface modifier with a copolymer soft block (red chain) having **A** and **B** side chains. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



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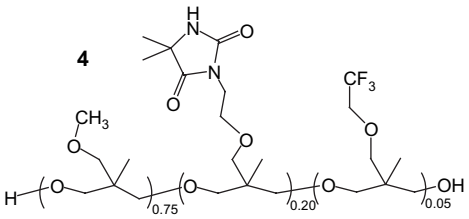

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Fig. 2. Structural representations for **3**, P[MOx:Hy4Ox-84:16], and **4**, P[MOx:Hy4Ox:3FOx-75:20:5].

The previously employed 3-(2,2,2-trifluoroethoxy)-3-methyloxetane (3FOx) [22] was copolymerized with **1** and **2** to give a 3FOx modified (5 mol%) terpolymer telechelic P[MOx:Hy4Ox:3FOx] **4** (Fig. 2). The biocidal activity of a polyurethane surface modifier containing **4** (5 mol% 3FOx) is compared with **3**, which contains only MOx and Hy4Ox. Interestingly, testing described herein unambiguously showed an improved efficacy of biocidal action for the soft block polyurethane surface modifier containing 3FOx.

2. Experimental

2.1. Composition designations

Polyurethane designations follow similar schemes as used previously [23]. For HMDI/BD(*W*)/P[MOx:Hy4Ox:3FOx-*X*:*Y*:*Z*], HMDI/BD is the hard block, *W* is the weight fraction of the hard block, P denotes the soft block with ring opened, polymerized structures. Mole percents are *X*, *Y*, and *Z* for MOx, Hy4Ox, and 3FOx, respectively. Following a previously used scheme, base polyurethane (PU-0) compositions modified with either PU-1 or PU-2 (see below) are designated as 2%PU-1 or 2%PU-2. For the latter, compositions that have been activated with hypochlorite (N–H to N–Cl), the designations are 2%PU-1-Cl and 2%PU-2-Cl.

2.2. Materials

Tetrahydrofuran (HPLC grade) (THF), methylene chloride, boron trifluoride etherate (48% BF_3), 4,4′-methylenebis(cyclohexyl isocyanate) (HMDI), trifluoroacetic anhydride (TFA), sodium thiosulfate, poly(tetramethyleneoxide) ($M_w = 1000$, PTMO-1000), and dibutyltin dilaurate were purchased from Aldrich. 1,4-Butanediol (BD) was purchased from Acros Chemicals. 3FOx was a generous gift from OMNOVA Corporation, Akron, OH. The preparation of Hy4Ox **1**, MOx **2**, P[MOx:Hy4Ox-84:16), **3** (Fig. 2) and HMDI/BD(56.7)/

P[MOx:Hy4Ox-84:16], PU-1, was described previously [21]. Glass coverslips were obtained from Corning and plain glass microscope slides (no surface treatment) were obtained from Fisher Scientific. All materials were used as received.

2.3. Preparation of HMDI/BD(50)/[PTMO-1000] matrix polyurethane, PU-0

A conventional PTMO soft block polyurethane was prepared aiming at a 50 wt% hard block content. To a 250 mL round-bottom flask was added PTMO-1000 (10 g, 10 mmol), HMDI (8.11 g, 30.9 mmol), dibutyltin dilaurate (5 drops, 10 wt% in THF) and DMF (4.49 g). The system was heated to 75 °C under an N_2 stream. The extent of the reaction was monitored by FT-IR spectroscopy. BD (1.88 g, 20.9 mmol) was added drop wise until all isocyanate (2268 cm^{-1}) was consumed. The product was precipitated by pouring the reaction mixture into a 1:4 methanol/water solution, filtered, and dried *in vacuo*. The molecular weight of the resultant polyurethane was 7.6×10^3 g/mol (GPC). The soft block T_g was −73 °C (DSC). The final hard block content was 50 wt% by ^{1}H NMR integration.

2.4. Preparation of the terpolymer telechelic P[MOx:Hy4Ox:3FOx-75:20:5], **4** (Fig. 2)

The hydantoin-containing telechelic containing 0.05 mol% 3FOx was prepared by a modification of a published procedure [22,24]. A flask was purged with N_2 and then charged with 1,4-butanediol (215.5 mg, 2.39 mmol), CH_2Cl_2 (7.0 mL), BF_3 etherate (0.70 g, 4.9 mmol BF_3) and chilled to −5 °C in an ethylene glycol bath. An addition funnel was charged with Hy4Ox (2.53 g, 9.88 mmol), 3FOx (0.44 g, 2.4 mmol), MOx (4.30 g, 37.1 mmol), and CH_2Cl_2 (10 mL). The ratio of total moles of oxetane monomer to moles BF_3 was 13.3, a value in the range previously employed [25]. The contents in the addition funnel were added over a period of 45 min. After addition was complete, the bath temperature was maintained for an additional 13 h. The flask was then allowed to warm to room temperature and quenched with deionized water. The product was extracted with CH_2Cl_2, water and CH_2Cl_2 were separated, and the CH_2Cl_2 was evaporated to yield P[MOx:Hy4Ox:3FOx-75:20:5] (5.72 g, 79% yield). The telechelic composition was determined by NMR integration (75 mol% MOx, 20 mol% Hy4Ox, and 5 mol% 3FOx), which was close to the feed ratio. The molecular weight (M_n) of P[MOx:Hy4Ox:3FOx-75:20:5] (1.3×10^3 g/mol) was determined by ^{1}H NMR end-group analysis with trifluoroacetic anhydride [25]. The telechelic T_g was −26 °C by DSC.

2.5. Preparation of HMDI/BD(52.7)/P[MOx:Hy4Ox:3FOx-75:20:5], PU-2

The preparation followed a previously reported method [22]. An HMDI/BD hard block of 50 wt% feed was employed. To a 100 mL round-bottom flask was added P[MOx:Hy4Ox:3FOx-75:20:5] (0.92 g, 0.71 mmol), BD (0.12 g, 1.3 mmol), dibutyltin dilaurate (3 drops, 10 wt% in THF), and DMF (3.4 mL). An addition funnel was attached and HMDI (0.61 g, 2.3 mmol) and DMF (4.2 mL) were added. The system was heated to 70 °C and purged with N_2 for 20 min. The contents of the addition funnel were added rapidly. The extent of reaction was determined by removing small aliquots and observing the decrease of the 2268 cm^{-1} isocyanate peak in the FT-IR spectrum. BD (157.3 mg, 1.7 mmol BD and 4.5 mL DMF) was added to the reaction mixture until the isocyanate was consumed. The product was precipitated by pouring the reaction mixture into H_2O, filtering, and drying. The polyurethane was purified by dissolving in THF and precipitating by pouring into water, filtering, and drying *in vacuo*. The molecular weight (GPC, THF solution) was 11×10^3 g/mol. The T_g was 35 °C by DSC.

The ^{1}H NMR spectrum had peaks as follows: unresolved peaks from ~0.75 to ~0.90 ppm is due to the pendent soft-block methyl groups (CH_3−C−). Unresolved peaks from ~1.0 to ~1.8 is due to the hydantoin methyl groups ((CH_3)$_2$C−), the interior methylene groups of BD (−OCH_2 CH_2CH_2CH$_2$O−), and the aliphatic methylenes from HMDI. The peak at 3.14 ppm is due to the methoxymethyl group (CH_3O−). The peak at 3.21 ppm is due to the α-methylene to CF_3 (CF_3CH_2O−). The broad peak centered at 3.47 contains proton contributions from the ether methylenes from the soft block chain (−OCH_2CCH_2O−), the pendent soft block methylene ether (−OCH_2C−), and ethylene ether of the hydantoin unit (−OCH_2CH$_2$N<). The peak at 3.78 ppm is due to the HMDI proton α to the urethane (−OCONHC*H*<). The peak at 3.92 ppm is due to the ethylene imide methylene of the hydantoin unit (−OCH$_2$CH_2N<) and the 1 and 4 methylene groups from the BD (−OCH_2CH$_2$CH$_2$CH_2O−). The peak at 6.9 ppm is due to the urethane amide (−OCON*H*−). The peak at 8.25 ppm is due to the hydantoin amide (*H*N<). Integration calculations indicated that the hard block content was 52.7 wt% (*vide infra*).

The hard block weight percent was determined using ^{1}H NMR. The calculation of the polyurethane derived from telechelic **3**, HMDI/BD(56.7)/P[MOx:Hy4Ox-84:16], was reported previously [21]; the weight fraction of the hard block for **4**, HMDI/BD(52.7)/P[MOx:Hy4Ox:3FOx-75:20:5] was calculated by the same method. The region between 2.0 and 0.9 ppm contains unresolved peak integrations due to HMDI, BD, and hydantoin methyl groups. The area of this region due to each specific component was calculated using the polyurethane amide N−*H* to correlate the HMDI area and the hydantoin amide N−*H* to correlate the area due to the dimethyl group. The remaining area was assigned to BD. The integrated peak area between ~0.7 and 0.9 ppm is due to the pendent methyl group of the soft block. After normalizing for proton contributions were then multiplied by their respective molecular weights, HMDI (22 protons, 264 g/mol), BD (4 protons, 88 g/mol), and soft block (3 protons and 148.4 g/mol per repeat unit). The mass of HMDI + BD was then divided by the mass of HMDI + BD + soft block to determine the hard block percentage.

2.6. Film preparation

The pre-biocidal PSM (2 wt%) and HMDI/BD(50)/P[PTMO-1000] (98 wt%) were dissolved in THF (total, 10–15 wt% solids). A few drops of the solution were placed on the substrate. Tilting at various angles spread the solution evenly over the slide. A thin coating was generated after solvent evaporation. Glass coverslips or plain glass microscope slides were used depending on the bacterial test. The coated slides were allowed to dry in ambient atmosphere for 2 h and then vacuum dried at 45 °C overnight (15+ hours). The final films were optically clear.

2.7. Coating activation

Coated surfaces were activated by immersion in a 3 wt% NaOCl (bleach) solution for 1 h. The films were then exhaustively rinsed with deionized water and dried under a stream of nitrogen.

2.8. Bacterial suspension preparation

Pseudomonas aeruginosa and *Staphylococcus aureus* used were strains PAO1 and ATCC-25904, respectively. Cultures were streaked on a Luria agar plate and incubated overnight at 37 °C. A single colony was used to inoculate 5 mL Luria broth and grown overnight at 37 °C with vigorous shaking. The next day, 20 mL Luria broth was inoculated using 200 μL of this culture followed by growth at 37 °C with vigorous shaking. A stock solution of 10^7–10^8 colony forming units (CFU) per milliliter of the desired bacteria was prepared. The required optical density was monitored by UV–vis spectroscopy at a wavelength of 600 nm by comparing absorption against a standard curve (Fig. 3) [26]. If the concentration of the stock solution was higher than the desired it was diluted to the appropriate concentration with saline prior to challenging the film surface. The stock solution concentration was subsequently confirmed by serial dilution and plating onto nutrient agar plates and incubating at 37 °C for 24 h. Stock solutions of 10^9 CFU/mL or greater resulted in an overchallenge and yielded irreproducible results.

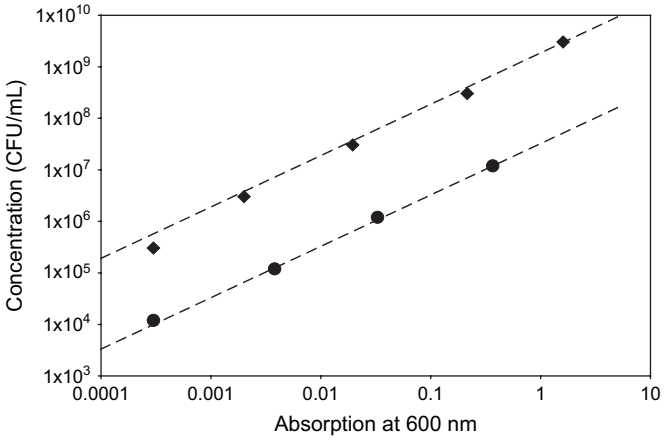


Fig. 3. Optical density standard curve for *Pseudomonas aeruginosa* (◆) and *Staphylococcus aureus* (●). Absorption measurements were taken using serial dilution of a prepared bacterial suspension and bacterial counts were made from cultured agar plates. The dashed lines represent regression fits for PA ($1.9 \times 10^9 \pm 2.8 \times 10^7$ CFU/mL) and SA ($3.3 \times 10^7 \pm 1.7 \times 10^5$ CFU/mL).

2.9. AATCC-100 test

A modified version of the AATCC-100-1999 was used [15,20,27]. A 1 μL drop of a bacterial suspension was placed on the coated coverslip surface. An identical second coverslip was then used to 'sandwich' the drop. A sterile cuvette was placed on top of the sandwich as a spacer. The cuvette/sandwich were covered with Petri dish to isolate the sample and maintain sterility and humidity. Finally, a 100 mL beaker (a convenient mass) was placed on Petri dish to ensure contact. The bacteria were kept between the coverslips for a predetermined duration, typically 30–60 min. The coverslips were separated and all bacteria (dead or alive) were removed via vortexing in a 3 wt% sodium thiosulfate solution for 2+ min. Thiosulfate reduces chloramide to amide thus inactivating biocidal action of the coated slide [15,27]. A 100 μL aliquot of the vortexed supernatant sodium thiosulfate solution was plated onto a nutrient agar plate (designated as 'plate-0'). Two 10-fold serial dilutions were performed. All plates were incubated at 37 °C for 24 h. Tests on both the chlorinated films (experimental) and the non-chlorinated films (control) followed the same procedure.

2.10. Spray test

A chromatography sprayer was used to challenge the polymer surfaces with a bacterial aerosol as described by Klibanov et al. [28]. To assure the delivery of a predictable mass of challenge, the spray pressure was regulated using the pumping system shown in Fig. 4. A Barnant Air Cadet Pump (model# 400-1901) was used to pressurize the system with air. An oxygen regulator was used to deliver a uniform flow of gas. The flow was then metered using a Gilmont 65 mm Flowmeter (Fisher Scientific) with a tunable range of 0.8–6.3 L/min airflow rate.

Cautionary Note: Spraying an aerosol of pathogenic bacteria must be carried out with caution (disposable gloves, mask). For the tests described below, spraying was done in

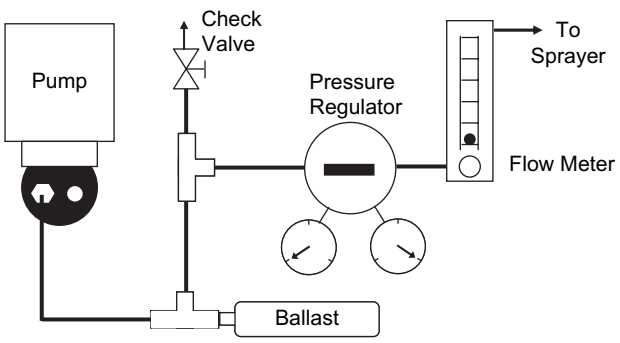


Fig. 4. Air pumping system for smooth and reproducible airflow.

a laboratory hood. Coated glass microscope slides were placed at a distance of 25 cm from the sprayer. The sprayer was charged with ~10 mL of stock bacterial suspension, which was gently stirred to prevent settling of the bacteria. A spray time of 1 ± 0.1 s was used. After spraying, the slides were quickly weighed to estimate the amount of bacteria deposited. A flow rate of 5.1 L/min was found to deliver a visibly uniform film. These conditions were confirmed to be non-lysing by spraying directly on an agar plate and confirming bacterial growth after incubation. After aerosol deposition the slides were incubated in a 90+% humidity chamber in a covered Petri dish for 30 min. All bacteria (dead or alive) were removed via vortexing in a 3 wt% sodium thiosulfate solution, worked up, and analyzed in the same manner as the AATCC-100-1999 test described above.

2.11. Physical methods

Glass transition temperatures (T_gs) were measured using a TA Instruments DSC Q1000 Differential Scanning Calorimetry at 10 °C/min from −90 to 150 °C over two heating and cooling cycles. The second heating cycle was used for all calculations. ^{1}H NMR spectra were obtained on a Varian Spectrometer (Inova 400 MHz). Infrared spectra were collected using a Nicolet Magna IR 760. Polyurethane molecular weights were obtained with a Viscotek GPCmax VE2001 GPC Solvent/Sample Module.

Dynamic contact angle (DCA) data are summarized in Supplementary data (Table S-1). DCA measurements were performed with a Cahn DCA-312 at a stage speed of 100 mm/min. Samples were examined over five immersion/emersion cycles. The DCA probe liquid was 18.2 MΩ cm MilliQ water. Purity was verified before and after sample analysis by testing a flamed glass coverslip in the probe liquid. If oil- or detergent-like species diffuse into water during analysis, migration to the water surface takes place resulting in a surface tension change that is readily detected [29].

3. Results and discussion

Polymer surface modifiers have previously been employed to introduce biodurable, hydrophobic polydimethylsiloxane domains [30–33] or to generate semifluorinated surfaces that are both hydrophobic and oleophobic [34–38]. A polymer surface modifier relies on surface concentration of a minor constituent (Fig. 5) so that ideally, the surface properties closely mimic that of the modifier.

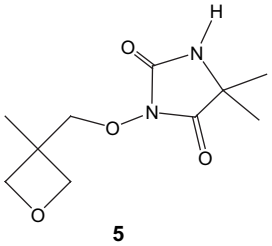
Because soft blocks are surface-concentrated [20,39,40], the surface modification strategy herein employs functional soft blocks to generate a polyurethane surface modifying domain (Fig. 1). In this approach, copolymer soft blocks with **A** and **B** side chains are employed (Fig. 1). Surface concentration is enhanced by P[**A**–**B**] side chains that act as pseudo chain ends [41]. Side chain **A** may be (1) a semifluorinated chaperone to assist with surface concentration of functional group **B**, (2) a diluent for **B** so that soft block T_g remains low, or (3) a synergistic facilitator for **B**. The presence of interactive **A** and **B** groups can even produce unexpected surface phenomena as in our recent report of ''contraphilic'' wetting [42].

Fig. 5. Schematic for a polymer surface modifier.

3.1. Telechelic synthesis

The polyurethane soft block precursors are poly((2,2-functionized)-1,3-propylene oxide) telechelics, often referred to as polyoxetanes [43]. These telechelics are prepared by oxetane ring-opening polymerization (ROP) catalyzed by BF_3 and a butanediol co-catalyst. Prior work has shown that the reaction is tolerant of many functional groups in the 3-position of the oxetane ring, including bromomethyl, methoxy-ethoxy substituents of general formula $CH_3O(CH_2CH_2O)_n$ [25], semifluorinated-alkoxy groups such as CF_3CH_2O- [44,45], mesogenic moieties [46], and others [47].

Our first incorporation of hydantoin into precursors to biocidal surface modifying additives was through a reaction-on-polymer approach [20]. In seeking simpler materials' preparation, our initial target for incorporation of hydantoin moieties by ROP was Hy1Ox, **5** where hydantoin is separated from the main chain by a single methylene group. Hy1Ox is easily prepared by reaction of bromomethyl-methyloxetane with 5,5-hydantoin, but fails to undergo copolymerization to an isolable cotelechelic. Previously, Motoi showed that BF_3 catalyzed ROP yields an internally cyclized product for 3-methyl-3-(phthalimidomethyl)oxetane which, like Hy1Ox, contains a carbonyl group positioned 1,6-relative to the oxonium carbon [47]. Presumably, the failure of Hy1Ox to polymerize is due to the formation of cyclic structures such as those isolated by Motoi.



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The high biocidal activity of previously reported hydantoin-containing soft block polyurethanes [20] led to a search for a hydantoin-containing oxetane that would tolerate ROP conditions. Synthesis of the hydantoin monomer Hy4Ox, **1** that successfully underwent ring-opening polymerization enabled the preparation of telechelics and polyurethanes with controllable fractions of hydantoin-containing repeat units in the soft block. Fig. 2 shows the two hydantoin-containing telechelics incorporating **1** that are the focus of this paper: **3**, P[MOx:Hy4Ox-84:16] and **4**, P[MOx:Hy4Ox:3FOx-75:20:5].

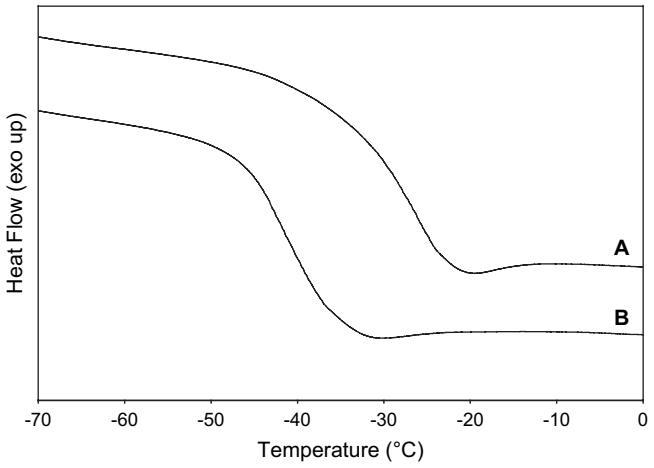

Fig. 6. DSC thermograms for **A**, P[MOx:Hy4Ox:3FOx-75:20:5], and **B**, P[MOx:Hy4Ox-84:16].

The composition of telechelics **3** and **4** was determined by ^{1}H NMR integration and closely matched the monomer feed ratio in ring-opening polymerization. The molecular weights (M_n) by NMR end-group analysis for P[MOx:Hy4Ox-84:16] and P[MOx:Hy4Ox:3FOx-75:20:5] are relatively low: 2030 and 1300 g/mol, respectively. P[MOx:Hy4Ox:3FOx-75:20:5] exhibits a single T_g at −26 °C (Fig. 6 (**A**)), which is higher than that for P[MOx:Hy4Ox-84:16] (**B**, −42 °C) [21]. The higher T_g for P[MOx:Hy4Ox:3FOx-75:20:5] is correlated with a higher Hy4Ox content. A broad inflection at both T_g endotherms suggests hydrogen bonding involving the Hy4Ox moiety.

3.2. Polyurethane synthesis and characterization

Telechelics **3** and **4** were incorporated into HMDI-BD hard block polyurethanes HMDI/BD(56.7)/P[MOx:Hy4Ox-84:16], PU-1, and HMDI/BD(52.7)/P[MOx:Hy4Ox:3FOx-75:20:5], PU-2, by a conventional method [21]. The matrix polyurethane HMDI/BD(50)/P[PTMO-1000], PU-0, was prepared in the same manner using PTMO-1000 in place of the hydantoin-containing telechelics. The hard block mass fraction for each polyurethane was close to the feed weight percent (50 wt%).

The GPC molecular weights for HMDI/BD(52.7)/P[MOx:-Hy4Ox:3FOx-75:20:5] and HMDI/BD(50)/[PTMO-1000] were 11 and 76 × 10^3 g/mol, respectively. The soft block T_g for (HMDI/BD(56.7)/P[MOx:Hy4Ox-84:16] is 13 °C with a range of −15 to 34 °C [21]. HMDI/BD(52.7)/P[MOx:-Hy4Ox:3FOx-75:20:5] has a soft block T_g of 35 °C with a range of −20 to 47 °C. The matrix polyurethane, HMDI/BD(50)/[PTMO-1000] has a soft block T_g at −24 °C (−38 to 5 °C).

The previously reported T_g of the polyurethane prepared from the homo-MOx telechelic was −33 °C and occurred in a narrow range (−29 to −38 °C) [21]. In contrast, both the HMDI/BD(56.7)/P[MOx:Hy4Ox-84:16] and the HMDI/BD(52.7)/P[MOx:Hy4Ox:3FOx-75:20:5] show higher T_gs with broader transition temperature ranges. The higher T_gs are consistent with an increased interaction between the soft block and the hard block, which indicates the presence of hydantoin in the soft block. HMDI/BD(52.7)/P[MOx:Hy4Ox:3-FOx-75:20:5] has a higher hydantoin content and T_g than HMDI/BD(56.7)/P[MOx:Hy4Ox-84:16], which is consistent with that previously observed for soft blocks of varying hydantoin content [21].

3.3. Film preparation and characterization

THF solutions (10–15 wt% solids) were prepared containing the hydantoin polymer surface modifier and base polyurethane. These solutions were then used to generate coatings for antimicrobial testing. The resulting films were uniform and optically transparent indicating a single microscopic phase. The AATCC-100 test employed untreated glass coverslips while glass microscope slides were used for spray testing.

3.4. Contact angle data

In favorable cases the presence of a polymer surface modifier is easily detected by contact angle measurements [31]. Success depends on the modifier having different wetting characteristics compared to the substrate polymer. To ascertain whether wetting behavior would be useful in providing evidence for modifier surface concentration, dynamic contact angle data using water were obtained for pure constituents and modified coatings. Several cycles were obtained as wetting behavior for polyurethanes can be time dependent due to polymer chain surface reorganization. The contact angle data are summarized in Supplementary data, Table S-1.

The matrix polyurethane PU-0 exhibits an initial force distance curve from which the advancing (θ_a) of 90° and receding (θ_r) of 49° contact angles are obtained. After three cycles, the corresponding values are θ_a, 85° and θ_r, 49°. This change in advancing contact angle is due to thermodynamically driven surface reorganization, as the same sequence is observed when the coating is dried and run again.

DCA on HMDI/BD(56.7)/P[MOx:Hy4Ox-84:16], PU-1, provided θ_a, 92°, and θ_r, 53°. After four cycles, the corresponding values are θ_a, 83° and θ_r, 55°. The similar wetting behavior for the matrix polyurethane PU-0 and the surface modifier PU-1 precluded the use of contact angle measurements for establishing surface concentration of PU-1 in 2%PU-1 or 2%PU-1-Cl.

HMDI/BD(53)/P[MOx:Hy4Ox:3FOx-75:20:5], PU-2, gave first cycle DCA of θ_a, 98° and θ_r, 53°. The higher advancing contact angle for PU-2 gives evidence for the surface concentration of 3FOx. However, the receding contact angle is similar to PU-0 and PU-1, again due to rapid surface reorganization. For cycles 3–5, PU-2 contact angles are θ_a, 93° and θ_r, 53°. The higher value of θ_a continues to provide evidence for surface concentration of the soft block. The initial value of θ_a for 2%PU-2 (95°) encourages the idea that PU-2 is surface-concentrated. However, θ_r is 53°, a value similar to the base

polyurethane PU-0. Furthermore, on repeated immersion, θ_a for 2%PU-2 decreases to values (~84°) comparable to PU-0.

The hydantoin surface modifier requires chlorination for biocidal activity [14,15]. This reaction (1 h, 3% hypochlorite) replaces the amide proton of the hydantoin with chlorine [20]. Previously examined polyurethanes had soft block structures wherein the hydantoin moiety was separated from the main chain by only one carbon atom (as shown for monomer **1**) [22]. For these polyurethanes, large changes in initial values for θ_a are observed upon conversion of amide and chloramide [22]. This large change in the first advancing contact angle for amide (θ_a, 70–80°) and chloramide (θ_a ca. 103°) is due to the amide version exhibiting "contraphilic" behavior [48]. PU-2 displays conventional amphiphilic wetting, not contraphilic behavior. A 9° decrease is seen for the initial advancing contact angle for 2%PU-2-Cl (θ_a, 86°) compared to 2%PU-2 (θ_a, 95°) providing some evidences for PSM surface concentration for the dry coating. However, once the surface is wetted, succeeding cycles show contact angles very similar to PU-0 and other coatings.

Overall, contact angle data provide only modest evidence for surface concentration of PU-2 hydantoin surface modifier. For PU-1, the combination of polar hydantoin and non-polar methoxy side chains results in a surface with wetting behavior not much different from the matrix polyurethane PU-0. However, results from biocidal testing described below show that the hydantoin polymer surface modifier must be surface-concentrated because after hypochlorite activation effective contact biocidal behavior is observed.

3.5. Spectroscopic testing

In favorable cases, ATR-IR can be very useful in providing evidence for surface concentration of 3FOx containing surface modifiers [49]. For HMDI/BD(53)/P[MOx:Hy4Ox:3FOx-75:20:5] and the 2%PU-2 the C–F absorption was too weak to detect. Another method that has proved useful in other cases is X-ray photoelectron spectroscopy. Unfortunately, a combination of low atom% F and F-contamination precluded this approach as well. Unexpectedly, the biotesting provides the best measure of surface concentration of hydantoin.

3.6. AATCC-100 "sandwich" test

A modified version of the AATCC-100 biocidal testing protocol was employed. Films prepared on plain glass microscope coverslips were used. The control films for each experiment were the non-chlorinated version of each film. Coatings were challenged with either *P. aeruginosa* (Gram −ve) or *S. aureus* (Gram +ve) bacteria.

The results of the AATCC-100 tests are shown in Table 1. Calculation of log reduction takes into account two (×10) serial dilutions prior to culture. For cases where there are no surviving bacteria (zero CFU) the calculation of % kill includes an assumption of one survivor. In this way, log kill can be estimated as a lower limit. For example, % kill (reported to three significant figures) and log reduction for 2%PU-1-Cl (Table 1, line 5) are calculated as follows:

$$\text{Lower limit (in percent) bacteria killed} = \frac{5080-1}{5080}\times 100 = 99.98\%$$

$$\text{Log reduction} = \log(1-0.9998) = \log(0.0002) = -3.71$$

In all cases greater than 90% kill was observed for 30 min of incubation with the exception of *P. aeruginosa* on 2 wt%PU-2-Cl which took 60 min to obtain >99% kill. These results are consistent with previous reports that chloramide surface modifier biocides are effective against both *P. aeruginosa* and *S. aureus* [20]. The results also provide evidence for surface concentration of chloramide. The cause of the slower kill rate for the *P. aeruginosa* on the 2 wt%PU-2-Cl film is not known, though may be connected to the test method as the aerosol test procedure (*vide infra*) showed a higher kill.

The stability of the chloramide was examined by annealing a chlorinated 2%PU-1-Cl film at 65 °C under vacuum for 24 h. The biocidal activity is actually enhanced after annealing (Table 1). This result indicates that the chloramide moiety is thermally stable at the polymer–air interface. Perhaps annealing facilitates surface concentration of chloramide (N–Cl), which is a relatively non-polar group with little tendency for hydrogen bonding.

Table 1
Modified AATCC-100 test using *Pseudomonas aeruginosa* (PA) and *Staphylococcus aureus* (SA)

PSM polyurethane	Bacteria	Challenge concentration (CFU/mL)	Challenge time[a] (min)	CFU control[c,d]	CFU N–Cl[c]	% Kill	Log reduction
2%PU-1-Cl	PA	3.8×10^7	30	292.5	27.5	90.6	1.03
2%PU-2-Cl	PA	2.5×10^8	30	188	27.5	85.4	0.83
2%PU-2-Cl	PA	8.4×10^7	60	88.3	0.25	99.7	2.55
2%PU-1-Cl[b]	PA	2.5×10^8	30	238.5	0	100.0	4.38
2%PU-1-Cl	SA	9.0×10^7	30	50.8	0	100.0	3.71
2%PU-2-Cl	SA	2.1×10^8	30	230	1	99.6	2.36

[a] This is the amount of time the 1 μL drop (~1×10^8 CFU/mL) spent between the films before vortexing.
[b] Prior to testing, the sample was annealed by heating at 65 °C under vacuum for 24 h after chlorination.
[c] CFU counts are the average of duplicate runs.
[d] Control films are non-chlorinated versions of the biocidal films (i.e., 2%PU-1 or 2%PU-2).

The nature of the AATCC-100 test underscores an important point about contact biocidal interfaces: bacteria must contact the interface for the biocide to be effective. In the sandwich test, this is facilitated by application of a small weight to eliminate the liquid cavity between the films [20]. The sandwich test thus provides evidence that there is no release of biocide (e.g., chlorine, hypochlorite) during the test.

3.7. Spray test

Surfaces were challenged by delivering bacteria in an aerosol form to mimic a cough or sneeze [28]. The stock solution for the spray test was prepared and verified as described for the AATCC-100 test. In order to gain preliminary information on kill kinetics, bacteria were left on the slide for 30 min in a humid environment before removal by vortexing in a solution of sodium thiosulfate. This solution reduces chloramide to amide thereby eliminating antimicrobial activity [15,27].

The results of aerosol spray testing are shown in Table 2. The overall biocidal log reduction ranges from 0.22 to 3.94. The extent of antimicrobial activity is dependent on the extent of overchallenge, the nature of the PSM, and the bacteria type.

The pairs of tests shown in Table 2 comprise a higher and lower bacterial challenge concentration. For example, the first two challenge concentrations for *P. aeruginosa* were 2.6×10^8 and 3.0×10^8 CFU/mL, respectively. Although these concentrations are similar, aerosol spray followed by vortexing and plating resulted in an average of 783 and 3402 CFUs on the control and 158 and 2059 CFUs on the activated 2%PU-1-Cl. A log reduction of 0.69 was observed for the lower count control (783) versus activated 2%PU-1-Cl (158). A much lower log reduction (0.22) was seen for the higher challenge control (3402) compared to activated 2%PU-1-Cl. The decreased kill with increasing concentration of the *P. aeruginosa* challenge is consistent with bacterial stacking, which results in enhanced survival and not with exhaustion of available biocide. In our test, overchallenge conditions correspond to 3.4×10^3 CFUs on the serially diluted ($\times$100) control. Survival of bacteria under overchallenge conditions is additional evidence that the surface modifier provides only contact-kill and that biocide release does not occur.

For comparable sets of challenges, biocidal activity is consistently in the order 2%PU-2-Cl > 2%PU-1-Cl. For example, the log kill for *S. aureus* is 3.94 for 2%PU-2-Cl but only 3.08 for 2%PU-1-Cl. These two log reductions were the highest observed for any of the coatings. The same relative order is observed for high and low challenges of both Gram +ve and Gram −ve bacteria. Even though only 5 mol% 3FOx repeat unit is employed, the PSM surface concentration is clearly enhanced. Cationic ring-opening polymerization probably results in a random incorporation of monomers [44] resulting in some soft blocks having more or less 3FOx repeat units. Even at 2 wt%, there are orders of magnitude more surface modifier chains than are necessary to occupy a nano-layer of polymer molecules. Perhaps soft blocks that have more than the average 5 mol% 3FOx groups selectively surface-concentrate, thereby enhancing the concentration of Hy4Ox.

Whether measured by bacterial concentration or control colony forming units (CFUs), the *S. aureus* challenges were somewhat lower than those for *P. aeruginosa.* However, it is clear that even at the lower concentrations overchallenge occurs with *S. aureus*. For example, with 88 CFUs on the control, a log reduction of 3.84 (no surviving CFUs) occurs for 2%PU-2-Cl. In contrast, with a challenge resulting in 559 CFUs on the control, a log reduction of 0.81 is found for 2%PU-2-Cl. Clearly, the latter test resulted in overchallenge and a large reduction of biocidal activity ($\times$1000) compared to the lower challenge.

Changing concentrations/control CFUs for *P. aeruginosa* results in less dramatic differences in log reductions. However, it appears that even at the lower challenge concentrations, the coatings are overchallenged.

4. Conclusions

Polyurethane polymer surface modifiers with hydantoin-containing soft blocks were prepared. One polymer surface modifier soft block contained only MOx and Hy4Ox repeats (PU-1), while the other (PU-2) included 5 mol% semifluorinated side chain chaperone (3FOx). The resulting PSMs were blended (2 wt%) with a model polyurethane. Evidence for PU-2 surface concentration from wetting behavior was

Table 2
Spray test with *Pseudomonas aeruginosa* (PA) and *Staphylococcus aureus* (SA)

PSM polyurethane	Bacteria	Challenge concentration[a] (CFU/mL)	CFU control[b,c]	CFU chlorinated[c]	% Kill	Log reduction
2%PU-1-Cl	PA	2.6×10^8	783	158	79.8	0.69
		3.0×10^8	3402	2059	39.5	0.22
2%PU-2-Cl	PA	1.8×10^7	897	27	97.0	1.52
		3.0×10^8	4959	1540	68.9	0.51
2%PU-1-Cl	SA	1.3×10^8	12	0	100.0	3.08
		2.1×10^8	227	133	41.4	0.23
2%PU-2-Cl	SA	1.3×10^8	88	0	100.0	3.94
		2.1×10^8	559	87	84.4	0.81

[a] After spraying, coatings were kept covered for 30 min at 90+% relative humidity.
[b] Control films were identical to the biocidal films except for chlorination (i.e., 2%PU-1 or 2%PU-2).
[c] CFU counts are the average of duplicate runs.

fairly clear, but the similarity of wetting behavior for PU-1 and the base polyurethane precluded evidence of surface concentration.

After activation with hypochlorite, the AATCC-100 ''sandwich'' test and an aerosol spray test were used to evaluate antimicrobial effectiveness. Thirty-minute challenges with *P. aeruginosa* and *S. aureus* showed that 2%PU-1-Cl and 2%PU-2-Cl are effective biocidal PSMs. Thirty-minute spray tests were useful in clarifying concentrations at which overchallenges of the contact-kill surfaces occurred and confirmed no biocide release under the test conditions. The spray test also showed unambiguously the improved efficacy of biocidal action for 2%PU-2-Cl versus the non-fluorinated 2%PU-1-Cl. Under comparable challenge conditions, the presence of only 5 mol% 3FOx in the PSM soft block significantly enhances biocidal effectiveness.

The polymer surface modifier soft block concentration depicted in Fig. 1 should be modified for HMDI/BD(52.7)/P[MOx:Hy4Ox:3FOx-75:20:5] to include a ''**C**'' chaperone side chain, viz., 3FOx. 3FOx enhances surface concentration by mimicking a chain end and providing a low surface free energy group.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.06.010.

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