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Biocidal activity of hydantoin-containing polyurethane polymeric surface modifiers

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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

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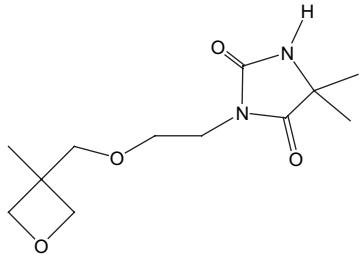
employed as surface modifiers [20]. The soft block of the surface modifying polyurethane contained semifluorinated **A** side chains to facilitate surface concentration of the biocidal hydantoin "**B**" groups (Fig. 1) [20]. Effective biocidal activity was conferred on a substrate polymer by as little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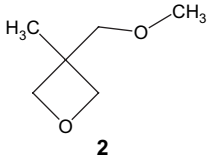

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To keep the soft block T_g low, a "companion" comonomer **2**, 3-methoxymethyl-3-methyloxetane, MOx, was prepared [21]. MOx is an easily purified oxetane with a methoxymethyl side chain. Employing the MOx "**A**" and Hy4Ox "**B**" monomers, we report 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.

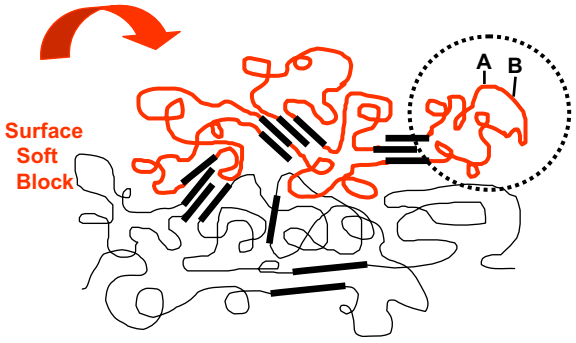
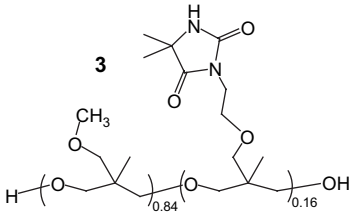


Fig. 1. A polymer surface modifier with a copolymer soft block (red chain) having **A** and **B** side chains. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



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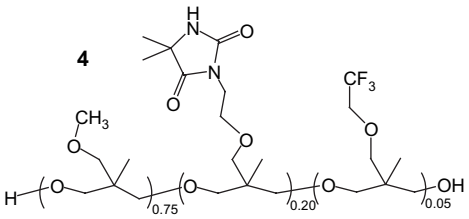

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Fig. 2. Structural representations for **3**, P[MOx:Hy4Ox-84:16], and **4**, P[MOx:Hy4Ox:3FOx-75:20:5].

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)/