

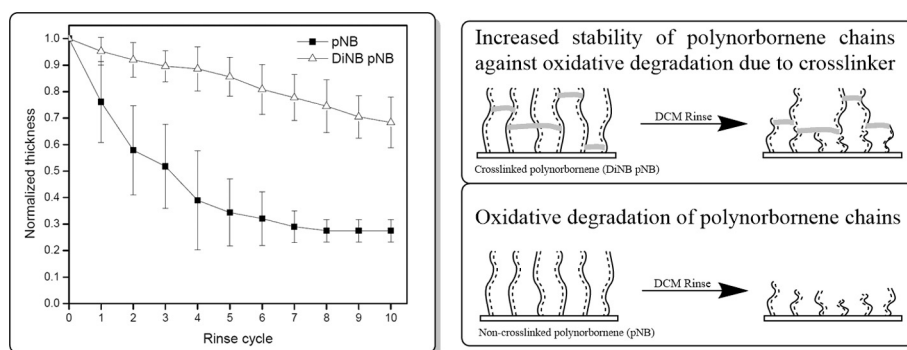


Regular Article

In situ crosslinking of surface-initiated ring opening metathesis polymerization of polynorbornene for improved stability

Ishan A. Fursule^a, Ashkan Abtahi^{b,c}, Charles B. Watkins Jr.^a, Kenneth R. Graham^b, Brad J. Berron^{a,*}^a Department of Chemical and Materials Engineering, 177 F Paul Anderson Tower, University of Kentucky, Lexington, KY 40506, USA^b Department of Chemistry, 161 Jacobs Science Building, University of Kentucky, Lexington, KY 40506, USA^c Department of Physics & Astronomy, 177 Chemistry-Physics Building, University of Kentucky, Lexington, KY 40506, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 June 2017

Revised 12 September 2017

Accepted 13 September 2017

Available online 14 September 2017

Keywords:

Surface-initiated ring opening metathesis polymerization
 ROMP
 Norbornene
 Crosslinker
 Oxidative degradation
 Film stability
 Polynorbornene

ABSTRACT

Hypothesis: In situ crosslinking is expected to increase the solvent stability of coatings formed by surface-initiated ring opening metathesis polymerization (SI ROMP). Solvent-associated degradation limits the utility of SI ROMP coatings. SI ROMP coatings have a unique capacity for post-functionalization through reaction of the unsaturated site on the polymer backbone. Any post-reaction scheme which requires a liquid solvent has the potential to degrade the coating and lower the thickness of the resulting film.

Experiments: We designed a macromolecular crosslinking group based on PEG dinorbornene. The PEG length is tailored to the expected mean chain to chain distance during surface-initiated polymerization. This crosslinking macromer is randomly copolymerized with norbornene through SI ROMP on a gold coated substrate. The solvent stability of polynorbornene coatings with and without PEG dinorbornene is quantitatively determined, and the mechanism of degradation is further supported through XPS and AFM analyses.

Findings: The addition of the 0.25 mol% PEG dinorbornene significantly increases the solvent stability of the SI ROMP coatings. The crosslinker presence in the more stable films is supported with observable PEG absorbances by FTIR and an increase in contact angle hysteresis when compared to non-crosslinked coatings. The oxidation of the SI ROMP coatings is supported by the observation of carbonyl oxygen in the polynorbornene coatings. The rapid loss of the non-crosslinked SI ROMP coating corresponds to nanoscale pitting across the surface and micron-scale regions of widespread film loss. The crosslinked coatings have uniform nanoscale pitting, but the crosslinked films show no evidence of micron-scale film damage. In all, the incorporation of minimal crosslinking content is a simple strategy for improving the solvent stability of SI ROMP coatings.

© 2017 Elsevier Inc. All rights reserved.

* Corresponding author.

E-mail addresses: iafu222@g.uky.edu (I.A. Fursule), a.abtahi@uky.edu (A. Abtahi), charles.watkinsuky@gmail.com (C.B. Watkins Jr.), kenneth.graham@uky.edu (K.R. Graham), brad.berron@uky.edu (B.J. Berron).

1. Introduction

Functionalized polymer coatings are pervasive throughout the scientific literature, including applications as self-healing materials [1,2], dielectric layers [3–5], responsive materials [6,7], membrane modifiers [8], insulating barriers [9] and conductive surfaces [10]. In particular, surface-initiated polymerization (SIP) techniques [3,11–13] are attractive owing to fine control over growth rate [3,14] and a capacity to create a conformal coating over complex morphologies [12,15,16]. While many surface properties are accessible through SIP of appropriate monomers, the post-polymerization functionalization of a coating provides an opportunity for more diverse surface chemistries than are presently attainable. For example, many ionomer systems are based on polymers which are both fluorinated and sulfonated [17]. A surface-initiated strategy to combine these functional groups requires polymerization followed by sulfonation to avoid the low polymerization rates of sulfonated monomers [18–20].

Of the SIP approaches, surface-initiated ring opening metathesis polymerization (SI ROMP) offers the simplest approach for post-polymerization modification through the unsaturated bonds in polymer backbone [14,21,22]. While most polymerization routes consume the alkene group, SI ROMP opens strained ring monomers by a metathesis catalyst which rearranges and preserves the alkene [14,21,23]. When using ruthenium based metathesis catalysts, SI ROMP can be performed in ambient environmental conditions with a high rate of polymerization and precise control over surface coating thickness [11,24]. In addition, ROMP is faster than other SIP methods like surface initiated atom transfer radical polymerization or surface initiated reversible addition-fragmentation chain transfer polymerization [25–28]. ROMP can produce micron thick coatings in minutes where as other SIP methods typically require hours.

The instability of the SI ROMP coatings represents a critical obstacle in post-modification reactions. Lerum and Chen first observed the decrease in the thickness of these SI ROMP coatings during exposure to the organic solvents (Fig. 1A, B) [29]. They observed a 93% loss in film thickness following exposure of polybutadiene (PBd) to dichloromethane in an ambient atmosphere [29]. The stability of the silane linkage to the SiO₂ substrates indicated damage to the polymer coating layer. By contrasting the film loss upon solvent rinsing in ambient conditions to loss in a nitrogen environment, they proposed that the damage is the result of oxida-

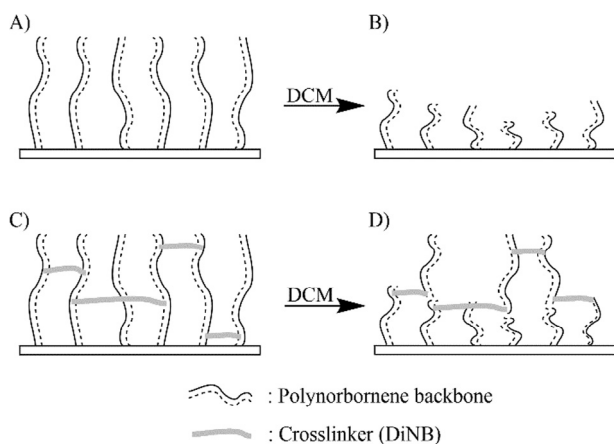


Fig. 1. The role of crosslinking in stabilizing an SI ROMP coating. (A) Non-crosslinked polynorbornene film structure. (B) Non-crosslinked polynorbornene backbone after washing with dichloromethane (DCM). (C) Crosslinked polynorbornene film structure. (D) Crosslinked polynorbornene backbone after washing with dichloromethane.

tive cleavage of the internal alkene in the ROMP backbone. As this oxidation is not commonly observed in solution phase ROMP chains, they proposed an entropic driving force to promote the cleavage of a surface-tethered chain. Other groups have also observed a decrease in SI ROMP coating thickness following exposure to organic solvents [19,30–32]. For any solution phase processing of these coatings, film loss during solvation is a critical concern. This challenge is highlighted in a previous study of the sulfonation of SI ROMP coatings. The instability of the coating resulted significant film loss during the solution phase reaction, ultimately requiring thicker initial films to achieve target thickness of the sulfonated film [19].

In the present study, we hypothesize that a crosslinking additive will improve the stability of SI ROMP coatings during solvent exposure and chemical functionalization of the deposited grown coatings. We designed a simple crosslinking molecule for ROMP polymerization consisting of a dinorbornene polyethylene glycol (PEG), and we studied changes to an SI ROMP polynorbornene (pNB) coating with and without incorporation of this crosslinker (Fig. 2). The solvent stabilities of pNB and crosslinked polynorbornene (DiNB-pNB) coatings were contrasted via repetitive exposure to dichloromethane, where minimal film loss was observed for crosslinked coating as compared to the non-crosslinked coating.

Our general approach illustrates a straightforward strategy for stabilizing SI ROMP coatings against solvation-induced degradation to facilitate complex coating chemistries. SI ROMP is a highly utilized coating technique for rapid, conformal coatings on complex surfaces. To date, nitrogen purging has been the only published approach to stabilize SI ROMP coatings to solvent accelerated degradation [29]. We anticipate these crosslinked, solvent stable SI ROMP coatings to be ideal for modification of the olefin backbone in thiol-ene click reactions [33–35]. This pairing of a highly specific, orthogonal click-type reaction and rapid growth of a stable film is expected to enable a diverse class of thick, conformal coatings containing with difficult to polymerize functional groups.

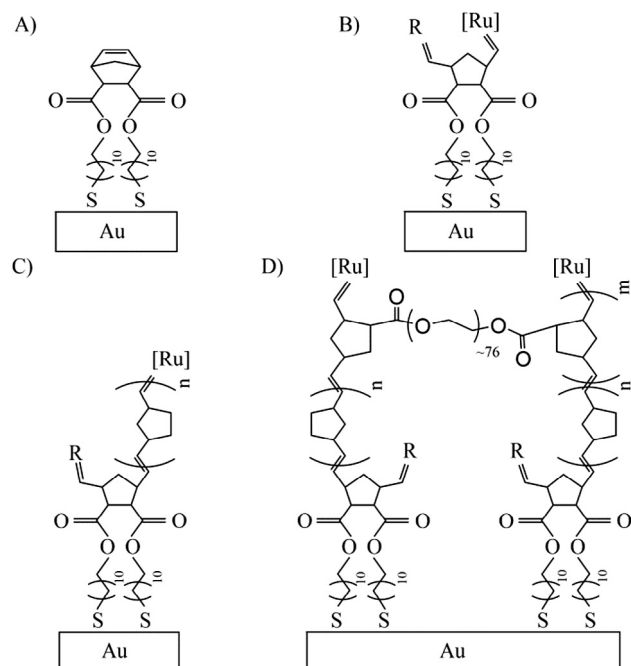


Fig. 2. Schematic representation of crosslinked SI ROMP coating preparation. (A) Norbornenyl (NBCl₂) decorated SAM, (B) Grubbs catalyst attached to norbornenyl surface, (C) SI ROMP of polynorbornene, (D) SI ROMP of crosslinked polynorbornene through random co-polymerization.

Download English Version:

<https://daneshyari.com/en/article/4984165>

Download Persian Version:

<https://daneshyari.com/article/4984165>

[Daneshyari.com](https://daneshyari.com)