Published in final edited form as:

Langmuir. 2009 October 6; 25(19): 11250–11254. doi:10.1021/la902340z.

Acute Degradation of Surface-Bound Unsaturated Polyolefins in Common Solvents under Ambient Conditions

Maria Felisa Z. Lerum and Wei Chen *

Chemistry Department, Mount Holyoke College, South Hadley, Massachusetts 01075

Abstract

We describe the detachment of covalently grafted polybutadiene and polynorbornene chains – which were prepared by surface-initiated ring-opening metathesis polymerization (SiROMP) – from Si/SiO₂ substrates upon brief exposure to common solvents in air. Degradation and disappearance of grafted polybutadiene films after successive rinses with dichloromethane was monitored by ellipsometry. Changes in surface topography were analyzed by atomic force microscopy. The rapid auto-oxidation of allylic carbon-hydrogen bonds renders these thin films extremely susceptible to degradation under ambient conditions. Polymers in the tethered state suffer more acute degradation (on the time scale of seconds) compared to those dissolved in solution (not detectable after days). To prevent degradation, unsaturated polymers prepared by SiROMP and the subsequent conversion (of unsaturated groups) need to be carried out under inert atmosphere. For example, smooth polybutadiene thin films of ~ 100 Å thick were covalently attached to silicon substrates via SiROMP of cyclooctadiene in the vapor phase. Solvent rinsing to remove unreacted monomers and free oligomers/polymers was carried out prior to the conversion of double bonds to epoxide groups. When these steps were carried out under nitrogen, negligible film loss was observed and surface topography of the thin film was preserved. Once the unsaturation was removed from polybutadiene, the epoxidized and hydroxylated polybutadiene films were stable toward solvent exposure in air.

INTRODUCTION

Polymers attached to substrates can provide surfaces with tunable properties such as wettability, corrosion- and fouling-resistance, stimuli-responsiveness, roughness, and conductivity. Considerable efforts have been focused on techniques for the preparation of well-defined polymers on solid support. Among the available surface modification strategies, surface-initiated polymerization or the “grafting from” technique is an attractive method because it not only allows covalent attachment of a polymer of interest, but also offers control of polymer film thickness and grafting density.^{1–3} Surface-initiated polymerization methods typically involve immobilization of an initiator on a substrate and the subsequent growth of polymer chains as monomers are added. They include living radical, cationic, and anionic polymerization.^{4–6} Another simple approach to access functional polymers is surface-initiated ring-opening metathesis polymerization (SiROMP), which has been explored to synthesize, for example, photochromic polymer brushes with reversible wetting behavior,⁷ conductive surfaces,⁸ nanopatterned polymeric structures,^{9–13} and polymer dielectric layers for organic thin film transistors.¹⁴ Previous studies on SiROMP have been dominated by high ring-strain cyclic monomers, namely, norbornene and its derivatives that were tethered on surfaces including Au,^{12,14–17} Si/SiO₂,^{11,13,18} Si(111),¹⁹ and silica nanoparticles.²⁰ SiROMP offers

*weichen@mtholyoke.edu; Tel: 413-538-2224; Fax: 413-538-2327.

Supporting Information Available. Experimental details. This material is available free of charge via the internet at <http://pubs.acs.org>.

rapid synthesis of polynorbornene films under relatively mild conditions yielding up to 120 nm thick films.²¹ The double bond functionality of the monomers is preserved in resulting polymers; the olefins can be chemically modified to yield desired functionality.

Our group recently reported the SiROMP of *cis,cis*-cycloocta-1,5-diene (COD), affording polybutadiene (PBd) films with thicknesses up to ~40 nm.²² The polymerization of low ring-strain monomers such as COD is non-trivial due to the propensity of chain transfer during polymerization. Propagating chain ends can react intra- or inter-molecularly with the alkene moieties along the polymer chains and lead to high polydispersity index and low grafting yield. In comparison, polynorbornene (PNb) and its derivatives do not exhibit this propensity. We showed that SiROMP of COD in the vapor phase, in contrast to the conventional reactions in solution, is an effective strategy to minimize chain transfer by reducing the polymer chain mobility at the vapor/solid interfaces.

Surface-tethered macromolecules are presumed to be stable against bond rupture and detachment from surfaces. Theoretical and experimental studies have assessed the strength of covalent bonds in polymer chains by measuring the mechanical forces needed to rupture a covalent bond.^{25–27} In recent years, several reports have described various conditions under which detachment of covalently tethered polymers from surfaces as a result of chain scission. Studies that assess the stability of poly(ethylene glycol) anchored on self-assembled monolayers have been conducted to determine loss of the material from silica surfaces after prolonged exposure to aqueous environment,^{28,29} and from Au and SiN after aging in air.³⁰ Further, poly(poly(ethylene glycol) methacrylate) chains prepared by surface-initiated atom transferradical polymerization show detachment from silica and glass surfaces as a function of incubation time in cell culture media, as evidenced by a decrease in receding water contact angles and consequently an increase in nonspecific protein adsorption.³¹ Spontaneous bond breakage and desorption of the tethered hyperbranched polyglycidol (HPG) from the surface has been described as a consequence of the unfavorable interactions of the hydrophilic HPG macromolecule and the hydrophobic matrix.³² Similarly, spontaneous rupture of carbon-carbon bonds along the polymer backbone was seen in highly branched brush-like macromolecules due to tension caused by the spreading of the side chains upon surface adsorption.³³ In the case of polymers prepared using the SiROMP method, there was no report of degradation until Jennings and co-workers recently described the loss of PNb films during modification by sulfonation. Control experiments indicated that chain scission was not caused by the sulfonating agent.²¹ It was speculated that the loss was caused by the cleavage of polymer chains at the olefinic sites.²¹ The reaction conditions under which degradation takes place, however, were not elucidated.

Here we report the instability of surface-bound polymers containing allylic hydrogen upon brief exposure to solvent and methods to prevent such degradation. The stability of grafted polymers prepared by SiROMP, namely PBd and PNb, was examined by monitoring the loss of polymer upon rinsing with various common solvents under ambient conditions as well as under inert atmosphere. The stability of free and tethered PBd chains upon solvent exposure was also compared. To prevent polymer detachment, it is necessary to exclude oxygen in the synthesis and subsequent modification of surface-bound polymers containing allylic hydrogen.

RESULTS AND DISCUSSION

Our objective was to attach head-to-head poly(vinyl alcohol) (hh-PVOH)²² and other new polymers with controlled alcohol density along the polymer backbone to surfaces and to evaluate their properties. The synthetic route is outlined in Scheme 1. SiROMP in the vapor phase has been demonstrated to be a viable method to polymerize low ring-strain cyclic

monomers, such as COD.²² Polymerization kinetics indicated that PBd films of 80–120 Å thick were grafted to silica substrates after 30 min at room temperature, with little further growth at longer reaction time. The polymer attachment is covalent in nature because no polymer growth was observed on substrates that do not contain the immobilized catalyst or the silane layer.

Common practice after surface reactions is to rinse substrates thoroughly with a good solvent to remove unreacted reagents and by-products. In this case the substrates were rinsed with dichloromethane in a fume hood to remove unreacted monomers and extractable polymers produced by chain transfer reactions. The ellipsometric thickness of the polymer films decreased drastically as the result of successive rinses (Figure 1a). For each rinse, a sample was agitated in dichloromethane for a few seconds. After ten rinses (total ~1 minute of solvent exposure), a polymer film of only 8 Å thick (~93% loss) remained but was stable toward further degradation. Analysis of the data shown in Figure 1a indicates that the polymer films experienced a steady loss of 18 ± 6 % per rinse up to seven rinses, after which the film loss appeared erratic. A more quantitative rate-loss assessment is not attempted here since the extent of agitation and duration of each rinse varied from time to time despite of the effort to keep the rinsing process consistent. A comparable loss was observed when other good solvents, such as toluene and tetrahydrofuran, were used to rinse grafted PBd as well as PNb films.

AFM images in Figure 2 illustrate the corresponding changes in surface topographies of the grafted polymer films upon successive rinses in dichloromethane. As shown in Figure 2a and 2f, SiROMP of COD at 30 min polymerization time affords a smooth polymer film with a root-mean-square (rms) roughness of 8 Å. After three rinses in dichloromethane, irregularly shaped cavities appear in the film (Figure 2b). The corresponding section analysis in Figure 2g indicates “holes” with depth up to 120 Å, which is comparable to the original film thickness. With successive rinses, the continual degradation is evident with more “holes” developing and feature sizes getting smaller, as seen in Figures 2c–j. Figures 2e and 2j correspond to a surface containing discrete and short polymer brushes with an average film thickness of 8 Å, which was stable toward further degradation upon rinsing.

To elucidate the origin of the film degradation, several factors were evaluated. Zhu and co-workers recently reported the spontaneous bond rupture of hyperbranched polyglycidol from surfaces upon reaching a critical size and surface coverage due to favorable interaction between the polymer and the solvent.³² We thus examined the effect of polymer film morphologies and thickness on the stability of the films against the rinsing process first. AFM images shown in Figures 3a–d reveal surface morphologies of PBd thin films at different polymerization times, 4, 10, 20, and 60 min. At relatively short reaction times, i.e. 4 and 10 min, surfaces display irregular domains with considerable roughness. As polymerization progresses, surfaces become smoother due to the continued initiation and growth of polymer chains. What is interesting is that the final morphologies have striking resemblances to the original ones. This indicates that re-attachment of the degraded segments is negligible. Another possible origin of chain scission is the cleavage of the Si–O linkages that anchor the polymer chains to the silicon substrate.³¹ To test this hypothesis, silicon substrates with silane monolayers were subjected to the same rinsing procedure. The results showed no change in ellipsometric thickness as well as water contact angles, eliminating the possibility of siloxane-bond cleavage. The most informative observation was that PBd film degradation did not occur when solvent rinsing was carried out in a glove box under nitrogen as shown in Figure 1b. The initial loss is attributed to the removal of unattached polymers and oligomers produced by chain transfer. AFM images (not shown) of these surfaces appear smooth, similar to the one shown in Figure 2a.

Based on these studies, we conclude that the observed degradation in grafted PBd and PNb upon solvent rinsing is caused by chain scission, which originates from oxidation and takes place along the macromolecular backbone. Oxidative degradation of polybutadiene solids has

been well studied in literature due to the broad technological relevance of this polymer.^{34–37} Our finding is not unexpected since unsaturated polyolefins are known to be sensitive to degradation under thermal, radiation and UV conditions, mainly due to the presence of carbon-carbon double bonds.³⁴ The allylic hydrogens in these polymers are reactive and susceptible to abstraction by oxygen. The reactivity of the radicals results in chain scission as well as cross-linking.

What is surprising is the degradation time scale of the grafted unsaturated polymers upon exposure to solvent. Is the acute degradation a general problem to unsaturated polymers – in both free and surface-bound states – in common solvents under ambient conditions? To address this question, we turn to two commercial polybutadiene samples dissolved in oxygen-saturated tetrahydrofuran. Gel permeation chromatography was carried out using the freshly prepared polybutadiene solutions as well as the ones aged for 48 h. Each of the chromatographs showed a single peak corresponding to the expected molecular weight and there was no difference between the fresh and the aged samples. These results indicate that degradation of free PBd chains in solution is negligible in comparison to that of surface-bound PBd and other polymers containing allylic hydrogens. In good solvents, polymer thin films are strongly solvated at the interface because polymer-solvent interaction is more favorable than polymer-surface and polymer-polymer interactions. Polymer degradation at the substrate-solvent interface is exacerbated by entropic gain as the result of chain scission and the polymer concentration gradient from the interface to the solvent media. All the surfaces examined have similar grafting densities due to the same preparative method used (Scheme 1). Film loss initially occurred at a constant rate of ~18% per rinse indicating that the degradation rate is relatively independent of chain length. When the chains became much shorter after ten rinses (Figures 1a, 2e and 2j), however, degradation was negligible indicating the importance of the entropic driving force for chain scission. The polymer concentration gradient drives the diffusion of the degraded segments toward solvent media so that re-attachment to the surface is not likely to take place.

After elucidating the degradation mechanism of surface-bound unsaturated polymers, experimental protocols were modified to minimize PBd film loss during subsequent chemical modification. SiROMP of COD, solvent rinsing, and epoxidation of PBd films were carried out in a nitrogen-filled glove box, followed by solvent rinsing and hydrolysis under ambient conditions (Scheme 1). Negligible loss of surface polymer was observed in the process.

CONCLUSIONS

Severe degradation of surface-bound PBd and PNB films upon brief exposure to common solvents was realized and examined. The presence of allylic hydrogen in these polymers renders them susceptible to oxidative degradation, which leads to chain scission and polymer detachment. The extreme sensitivity of the tethered polymers, in comparison to the free counterparts in solution, is attributed to the entropic gain as the result of chain scission and the diffusion of degraded segments from high concentration interface to low concentration solution media. We showed that it is necessary to carry out experimental protocols of SiROMP and subsequent modification of unsaturation to other functionality under inert atmosphere to prevent polymer degradation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The financial support is provided by the National Institutes of Health (2R15EB139-2) and the National Science Foundation (DMR 0604899). We would like to thank Surangkhan Martwiset for assisting us with the GPC analysis. We are grateful to Professor Thomas J. McCarthy's helpful suggestions. The use of the NSF-MRSEC central facilities at the University of Massachusetts is also acknowledged.

References

1. Edmondson S, Osborne VL, Huck WTS. *Chem Soc Rev* 2004;33:14–22. [PubMed: 14737505]
2. Zhao B, Brittain WJ. *Prog Polym Sci* 2000;25:677–710.
3. Jennings GK, Brantley EL. *Adv Mater* 2004;16:1983–1994.
4. Tsujii Y, Ohno K, Yamamoto S, Goto A, Fukuda T. *Adv Polym Sci* 2006;197:1–45.
5. Dyer DJ. *Adv Polym Sci* 2006;197:47–65.
6. Advincula R. *Adv Polym Sci* 2006;197:107–136.
7. Samanta S, Locklin J. *Langmuir* 2008;24:9558–9565. [PubMed: 18642863]
8. Voccia S, Claes M, Jerome R, Jerome C. *Macromol Rapid Commun* 2005;26:779–783.
9. Liu X, Guo S, Mirkin CA. *Angew Chem, Int Ed* 2003;42:4785–4789.
10. Lee WK, Caster KC, Kim J, Zauscher S. *Small* 2006;2:848–853. [PubMed: 17193132]
11. Jeon NL, Choi IS, Whitesides GM, Kim NY, Laibinis PE, Harada Y, Finnie KR, Girolami GS, Nuzzo RG. *Appl Phys Lett* 1999;75:4201–4203.
12. Fu D, Weng LT, Du B, Tsui OKC, Xu B. *Adv Mater* 2002;14:339–343.
13. Harris RF, Ricci MJ, Farrer RA, Praino J, Miller SJ, Saleh BEA, Teich MC, Fourkas JT. *Adv Mater* 2005;17:39–42.
14. Rutenberg IM, Scherman OA, Grubbs RH, Jiang W, Garfunkel E, Bao Z. *J Am Chem Soc* 2004;126:4062–4063. [PubMed: 15053568]
15. Weck M, Jackiw JJ, Rossi RR, Weiss PS, Grubbs RH. *J Am Chem Soc* 1999;121:4088–4089.
16. Kong B, Lee JK, Choi IS. *Langmuir* 2007;23:6761–6765. [PubMed: 17489620]
17. Berron BJ, Graybill EP, Jennings GK. *Langmuir* 2007;23:11651–11655. [PubMed: 17929844]
18. Harada Y, Girolami GS, Nuzzo RG. *Langmuir* 2003;19:5104–5114.
19. Juang A, Scherman OA, Grubbs RH, Lewis NS. *Langmuir* 2001;17:1321–1323.
20. Jordi MA, Seery TAP. *J Am Chem Soc* 2005;127:4416–4422. [PubMed: 15783224]
21. Berron BJ, Payne PA, Jennings GK. *Ind Eng Chem Res* 2008;47:7707–7714.
22. Feng J, Stoddart SS, Weerakoon KA, Chen W. *Langmuir* 2007;23:1004–1006. [PubMed: 17241005]
23. Netz RR, Andelman D. *Phys Rep* 2003;380:1–95.
24. Klein J. *Annu Rev Mater Sci* 1996;26:581–612.
25. Grandbois M, Beyer M, Rief M, Clausen-Schaumann H, Gaub HE. *Science* 1999;283:1727–1730. [PubMed: 10073936]
26. Beyer MK. *J Chem Phys* 2000;112:7307–7312.
27. Beyer MK, Clausen-Schaumann H. *Chem Rev* 2005;105:2921–2948. [PubMed: 16092823]
28. Branch DW, Wheeler BC, Brewer GJ, Leckband DE. *Biomaterials* 2001;22:1035–1047. [PubMed: 11352085]
29. Sharma S, Johnson RW, Desai TA. *Langmuir* 2004;20:348–356. [PubMed: 15743077]
30. Cerruti M, Fissolo S, Carraro C, Ricciardi C, Majumdar A, Maboudian R. *Langmuir* 2008;24:10646–10653. [PubMed: 18729528]
31. Tugulu S, Klok HA. *Biomacromolecules* 2008;9:906–912. [PubMed: 18260637]
32. Deng Y, Zhu XY. *Journal of the American Chemical Society* 2007;129:7557–7561. [PubMed: 17523642]
33. Sheiko SS, Sun FC, Randall A, Shirvanyants D, Rubinstein M, Lee H-i, Matyjaszewski K. *Nature (London, United Kingdom)* 2006;440:191–194. [PubMed: 16525468]
34. Li GY, Koenig JL. *Rubber Chem Technol* 2005;78:355–390.

35. Coquillat M, Verdu J, Colin X, Audouin L, Neviere R. Polym Degrad Stab 2007;92:1334–1342.
36. Fan S, Kyu T. Macromolecules 2001;34:645–649.
37. Bussiere PO, Gardette JL, Lacoste J, Baba M. Polym Degrad and Stab 2005;88:182–188.

Figure 1.
Decrease in ellipsometric thickness of grafted PBd films upon successive rinses in dichloromethane carried out in a) a fume hood (●) and b) a nitrogen-filled glove box (○).

Figure 2.

AFM images ($1.25 \times 5 \mu\text{m}$, height scale is 20 nm) of PBd films before and after successive rinses in dichloromethane: (a) no rinse, after termination with ethyl vinyl ether, (b) after three rinses, (c) after six rinses, (d) after nine rinses, and (e) after twelve rinses. Section analyses of the corresponding surfaces are shown in f – j.

Figure 3.

AFM images ($1.25 \times 1.25 \mu\text{m}$, height scale is 20 nm) of PBd films prepared at different polymerization times: (a) 4 min, (b) 10 min, (c) 20 min, (d) 60 min, and the resultant films (e) – (h) after three rinses in dichloromethane.

Scheme 1.

SiROMP of COD in the vapor phase and subsequent chemical modifications: thickness (T) and dynamic water contact angle (CA) data of various surfaces prepared.