Published in final edited form as:

Langmuir. 2007 January 30; 23(3): 1004–1006.

An Efficient Approach to Surface-Initiated Ring-Opening Metathesis Polymerization of Cyclooctadiene

Jianxin Feng^{†,§}, Stephanie S. Stoddart[†], Kanchana A. Weerakoon[†], and Wei Chen^{†,*}

[†]Chemistry Department, Mount Holyoke College, South Hadley, MA 01075

[§]Polymer Science & Engineering Department, University of Massachusetts, Amherst, MA 01003

Abstract

Surface-initiated ring-opening metathesis polymerization of cyclooctadiene (COD), a low ring-strain olefin, is reported for the first time. Polymerization was carried out in the vapor phase, which is advantageous compared to conventional solution methods in terms of minimizing chain transfer by reducing polymer chain mobility at the vapor/solid interface. Attachments of a norbornenyl-containing silane and a Grubbs catalyst to silicon substrates were carried out before samples were exposed to COD vapor. The thickness of grafted 1,4-polybutadiene films was controlled by reaction time and reached ~40 nm after 7 h. The polymer films were further chemically modified to afford a new polymer, head-to-head poly(vinyl alcohol).

Polymer thin films have attracted significant interest because of their application in nanopattern fabrication,¹ preparation of “smart” materials,² chemical sensing,³ and separations.⁴ Surface grafting methods have been employed to covalently attach polymer films to various inorganic substrates.⁵ Among different approaches, surface-initiated ring-opening metathesis polymerization (SiROMP) is an effective method to tether polymer chains to substrates including gold,^{6,7} silicon wafers,^{8–11} steel,¹² silicon (111),¹³ and silica nanoparticles.¹⁴ SiROMP has been used to prepare organic dielectric layers for the construction of field effect transistors; layer thickness has been controlled from less than 100 nm to more than 2 μm .⁶ This technique has also been widely used to form a variety of patterned polymer films.^{8,11} To the best of our knowledge, the monomers undergoing SiROMP have been limited to norbornene^{6,14} and its derivatives;¹⁵ there is no report on SiROMP of low-strain cyclic monomers, such as *cis,cis*-cycloocta-1,5-diene (COD), due to extensive chain transfer during polymerization.

Here we report a versatile approach to SiROMP of this low-strain cyclic monomer in the vapor phase and the subsequent chemical modifications of the grafted polybutadiene (PBd) thin films. Reduced polymer chain mobility at the vapor/solid interface minimizes chain transfer in polymerizations carried out in the vapor phase. The vapor phase also provides an efficient method for new materials synthesis - a new polymer, head-to-head poly(vinyl alcohol) (hh-PVOH) was prepared using oxidation/hydrolysis of the grafted PBd.

The 2nd generation Grubbs catalyst was chosen as the initiator for the SiROMP of COD on silicon wafers due to its high reactivity and tolerance to water, oxygen, and functional groups. As shown in Scheme 1, the catalyst was attached to silicon surfaces through a norbornenyl monolayer which was prepared in the vapor phase from norbornenyltriethoxysilane at 70 °C. The norbornenyl groups have high ring strain and can readily react with the catalyst. Closely

packed norbornenyl groups, however, can polymerize laterally on the surface upon exposure to the catalyst. This leads to a reduction of surface initiator concentration and low grafting density. To examine this issue, silicon wafers were cleaned using two different procedures: (1) simply rinsing with Milli-Q water and (2) thoroughly oxidizing with piranha solution. The thicknesses, as assessed by ellipsometry, of the norbornenyl layers formed using these two procedures are 4 Å and 7 Å, and the thickness increases after initiator attachment are 4 Å and 2 Å, respectively. Cleaning with water, rather than oxidizing solution, creates a surface with a lower density of silanol groups, hence a less thick layer of norbornenyl groups. The lower density monolayer incorporates more catalyst (by ellipsometric assessment) than the denser monolayer. This supports the contention that a too dense monolayer of norbornenyl groups is horizontally polymerized by Grubbs catalyst. The cleaning procedure of rinsing with water was used for further studies.¹⁶

SiROMP of COD was initially studied in solution. Despite every effort at increasing the grafted film thickness, including removing oxygen and water from chemicals prior to usage, carrying out all reactions under nitrogen, and distilling COD from 9-BBN and calcium hydride, very little tethered polymer formed on silicon substrates. This difficulty most certainly stems from significant chain transfer taking place between catalyst-containing propagating chain ends and alkene moieties along the polymer chains. This dramatically reduces the molecular weight of grafted polymers as well as changes their molecular structures.¹⁷ The issue of chain transfer becomes more pronounced on surfaces where polymer chains are much closer.

Polymerization of COD in the vapor phase affords PBd films with considerable thickness. Apparently reaction in the vapor phase suppresses the chain transfer that is prevalent in solution. The PBd film thickness increases with exposure time to COD vapor and reaches ~40 nm after a reaction time of 7 h. That little reduction of film thickness was observed at longer reaction times is an indication of minimal chain transfer during SiROMP in the vapor phase. We attribute the reduced amount of chain transfer to the lower mobility of polymers at the vapor/solid interface compared to that in the solution phase. We emphasize that vapor-phase ROMP does not entirely eliminate chain transfer - the presence of extractable free polymers on samples is observed. Chain mobility in the grafted thin films during polymerization is enhanced by monomer that can swell/plasticize the nascent polymer layer. Control experiments with no catalyst present show no thickness increase after exposure to COD vapor.

All surfaces prepared by the SiROMP process were analyzed by contact angle measurement and XPS analysis (Table 1 and Figure 1). After immobilization of the initiator on the norbornenyl layer, the surface carbon content increases slightly, from 21.1% to 26.6% and water contact angles increase correspondingly from 59°/33° (θ_A/θ_R) to 71°/49°. Neither nitrogen nor ruthenium signals were observed on the surface after treatment with the catalyst because the Ru_{3d5/2} and C_{1s} peaks overlap significantly¹³ and nitrogen content is too low to be resolved. The presence of polybutadiene thin films on silicon after polymerization is demonstrated by the intense C_{1s} peak and weak O_{1s} and Si peaks shown in Figure 1c. The water contact angles of the grafted polybutadiene samples are 94°/71°. These values are comparable to those of dip-coated films. After labeling PBd surfaces with bromine, Br_{3s}, Br_{3p} and Br_{3d} peaks were observed, indicating the presence of alkene moieties in the grafted PBd film. A fully brominated PBd would have a bromine and carbon ratio of 1:2, which is higher than the observed ratio of 2:7. The lower bromine content detected is due to x-ray beam damage during acquisition, which is common to halogens.¹⁸

Atomic force microscopy (AFM) was used to monitor the surface topographical changes during the SiROMP process. The surfaces containing norbornenyl and Grubbs initiator layers are featureless with root-mean-square roughness values of the initiator layer slightly larger (1.7

Å) than that of the norbornenyl layer (1.4 Å); grafted polybutadiene films retain the smooth morphology with a root-mean-square roughness value of 2.2 Å.

The surface chemistry of the PBd films was further modified by taking advantage of the reactive double bonds along the polymer chains. A new polymer, hh-PVOH, which has potential biomedical and industrial applications, was prepared for the first time via epoxidation of PBd using *meta*-chloroperoxybenzoic acid (MCPBA) followed by hydrolysis using HClO₄ (Scheme 1). It has been reported that epoxidation is effective at converting main-chain unsaturated carbons of polybutadiene to oxirane moieties.^{19,20} After epoxidation and hydrolysis, the advancing and receding water contact angles decreased from 94°/71° to 76°/24° and 51°/17°, respectively, indicating the expected increases in hydrophilicity (Table 1). XPS spectra indicate the appearance of oxygen after epoxidation and an increase in its intensity after hydrolysis (Figure 1). Based on the carbon and oxygen content of these surfaces and chemical compositions of the repeat units, yields for both reactions are close to 100% (Table 1). To further verify the presence of hydroxyl groups, the hydrolyzed samples were labeled with heptafluorobutyryl chloride. If the labeling yield were 100%, the ratio of carbon to fluorine content would have been 6:7. The 19% of fluorine content and 46% of carbon content detected by XPS indicates that the labeling yield is ~ 50%. The low fluorine content could be due to unreactive hydrogen-bonded hydroxyl groups and/or inaccessibility of sub-surface hydroxyl groups.

We are in the process of evaluating the vapor phase process as a general approach for SiROMP of cyclic olefins with varying degrees of ring strain. Under similar reaction conditions, SiROMP of norbornene leads to the formation of an 80 nm thick polynorbornene film after 5 h. SiROMP in the vapor phase can be a powerful method for the synthesis of new materials with varying densities of alkene moieties, epoxide groups, alcohol groups, and their derivatives.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

Financial support was provided by the National Science Foundation (CHE-0113643) and the National Institutes of Health (R15 EB00139). The authors are grateful for helpful discussions with Professor Thomas J. McCarthy at the University of Massachusetts at Amherst.

References

1. (a) Kaholek M, Lee WK, Lamattina B, Caster KC, Zauscher S. *Nano Lett* 2000;4:373–376. (b) Iwata R, Suk-In P, Hoven VP, Takahara A, Akiyoshi K, Iwasaki Y. *Biomacromolecules* 2005;6:2427–2448. [PubMed: 16153077] (c) Teare DO, Schofield WCE, Roucoules V, Badyal JPS. *Langmuir* 2003;19:2398–2403.
2. (a) Feng J, Haasch RT, Dyer DJ. *Macromolecules* 2004;37:9525–9537. (b) Li D, Sheng X, Zhao B. *J Am Chem Soc* 2005;127:6248–6256. [PubMed: 15853330] (c) Sidorenko A, Minko S, Schenk-Meuser K, Duschner H, Stamm M. *Langmuir* 1999;15:8349–8355. (d) Motornov M, Minko S, Eichhorn KJ, Nitschke M, Simon F, Stamm M. *Langmuir* 2003;19:8077–8085.
3. (a) Kitano H, Anraku Y, Shinohara H. *Biomacromolecules* 2006;7:1065–1071. [PubMed: 16602722] (b) Wolkenhauer M, Bumbu GG, Cheng Y, Roth SV, Gutmann JS. *Appl Phys Lett* 2006;89Art. No. 054101
4. (a) Kawai T, Saito K, Lee W. *J Chromatogr, B: Anal Technol Biomed Life Sci* 2003;790:131–142. (b) Miller MD, Baker GL, Bruening ML. *J Chromatogr, A* 2004;1044:323–330. [PubMed: 15354455]
5. Edmondson S, Osborne V, Huck WT. *Chem Soc Rev* 2004;33:14–22. [PubMed: 14737505]
6. Rutenberg IM, Scherman OA, Grubbs RH, Jiang W, Garfunkel E, Bao Z. *J Am Chem Soc* 2004;126:4062–4063. [PubMed: 15053568]

7. Weck M, Jackiw JJ, Rossi RR, Weiss PS, Grubbs RH. *J Am Chem Soc* 1999;121:4088–4089.
8. Jeon NL, Choi IS, Whitesides GM. *Appl Phys Lett* 1999;75:4201–4203.
9. Harada Y, Girolami GS, Nuzzo RG. *Langmuir* 2003;19:5104–5114.
10. Liu X, Guo S, Mirkin CA. *Angew Chem Int Ed* 2003;42:4785–4789.
11. Kim NY, Jeon NL, Choi IS, Takami S, Harada Y, Finne KR, Girolami GS, Nuzzo RG, Whitesides GM, Laibinis PE. *Macromolecules* 2000;33:2793–2795.
12. Detrembleur C, Jérôme C, Claes M, Louette P, Jérôme R. *Angew Chem Int Ed* 2001;40:1268–1271.
13. Juang A, Scherman OA, Grubbs RH, Lewis NS. *Langmuir* 2001;17:1321–1323.
14. Jordi MA, Seery TM. *J Am Chem Soc* 2005;127:4416–4422. [PubMed: 15783224]
15. (a) Moon JH, Swager TM. *Macromolecules* 2002;35:6086–6089. (b) Buchmeiser MR, Sinner F, Mupa M, Wurst K. *Macromolecules* 2000;33:32–39. (c) Lubbad S, Buchmeiser MR. *Macromol Rapid Commun* 2003;24:580–584.
16. To improve reproducibility, silanization of wafers (cleaned by piranha solution) at shorter amounts of time and using a mixture of norbornenyltriethoxysilane and an inert silane is being evaluated.
17. Bielawski CW, Grubbs RH. *Angew Chem Int Ed* 2000;39:2903–2906.
18. Artyushkova K, Fulghum JE. *Surf Interf Anal* 2001;31:352–361.
19. Schilling FC, Bovey FA, Tseng S, Woodward AE. *Macromolecules* 1983;16:808–816.
20. Roland CM, Kallitsis JK, Gravalos KG. *Macromolecules* 1993;26:6474–6476.

Figure 1.

XPS survey spectra of various surfaces prepared by SiROMP of COD and subsequent chemical modifications obtained at 15° take-off angle: (a) norbornenyl, (b) Grubbs (II) initiator, (c) grafted polybutadiene of 14 nm thick, (d) epoxidized polybutadiene, and (e) hh-PVOH.

Scheme 1.
SiROMP of COD in the vapor phase and further chemical modifications of the grafted polybutadiene.

Table 1

Dynamic water contact angles and XPS analysis of various surfaces prepared by SiROMP of COD and subsequent chemical modifications.

Substrate	Contact angles (θ_A/θ_R) ^a	XPS (15° take-off angle) ^b		
		C	O	Si
Norbornenyl	59°/33°	21.1	49.2	29.7
Grubbs catalyst	71°/49°	26.6	45.1	28.3
Polybutadiene	94°/71°	96.4	3.6	~0
Polybutadiene-epoxidized	76°/24°	72.8	25.2	2.0
Polybutadiene-hydroxylated	51°/17°	64.7	31.9	3.5

The reported values are averages of at least three trials:

^a the standard deviation for contact angle data is 2° and

^b the relative error for XPS atomic composition is less than 5%.