Polymer Bulletin 45, 471–477 (2001)

Polymer Bulletin

Surface-initiated living anionic polymerization of isoprene using a 1,1-diphenylethylene derivative and functionalization with ethylene oxide

Roderick P. Quirk (✉), Robert T. Mathers

Maurice Morton Institute of Polymer Science, University of Akron, Ohio 44325-3909
e-mail: quirk@polymer.uakron.edu, Fax: 330-972-5290

Received: 1 November 2000/Revised version: 23 November 2000/Accepted: 28 November 2000

Summary

Living anionic polymerization of isoprene on a silicon wafer was initiated by treatment of a 1,1-diphenylethylene surface-bound monolayer with *n*-butyllithium (growth from). The corresponding 1,1 diphenylhexyllithium derivative was used to initiate isoprene polymerization. The poly(isoprenyl)lithium chain ends were functionalized by addition of ethylene oxide to give a hydroxy-terminated polyisoprene brush. The thickness of the polymer brush was 9.5 ± 1.2 nm by ellipsometry. Grafting living chain ends to the 1,1-diphenylethylene monolayer and surface grafting of telechelic polymers were used for comparison (growth to). The polymer brushes were characterized by XPS, contact angle measurements, ATR-IR, and AFM.

Introduction

Polymer brushes modify surface properties and find applications in many areas including adhesion, biocompatibilility, and colloidal stabilization [1-3]. Polymer chains can be covalently attached to the surface by the "growth to" or "growth from" approach [1]. Herein is described a general method for both "growth from" and "growth to" strategies using a surface-bound 1,1-diphenylethylene monolayer that serves as a co-initiator and a linking agent, respectively. 1,1-Diphenylethylene (DPE) is a universal co-initiator group for radical, anionic and cationic polymerizations. DPE also reacts quantitatively as a linking agent with polymeric organolithiums [4]. This versatility makes 1,1-diphenylethylene desirable for many synthetic applications since 1,1-diphenylethylene will react with alkyllithium compounds and polymeric organolithiums to give the monoaddition product [4]. The absence of homopoymerization, due to steric hindrance, makes DPE chemistry very useful [4] for a surface bound monolayer since the co-initiator will not homopolymerize. Several approaches have been used to demonstrate anionic polymerization from surface bound monolayers [5-8]. We wish to demonstrate the utility of a DPE monolayer for the surface-initiated polymerization of dienes and functionalization of the living chain ends of the resulting polymer brush using ethylene oxide. For comparison with the "growth to" approach, poly(styryl)lithium was linked to the DPE monolayer. It was anticipated that the "growth from" approach would result in a higher graft density than the "growth to" approach. Mays and coworkers have recently reported "grafting from" results in a preprint for styrene polymerization using an analogous surface-bound 1,1-diphenylethylene monolayer [7].

Experimental

Materials

Solvents and monomers were purified according to known procedures before distillation into glass ampoules [9]. The polymerizations were performed in all-glass reactors using standard high-vacuum techniques [9]. The silicon wafers (American Polishing Corp.) were treated with Piranha solution (70% H_2SO_4/30% H_2O_2) for 1-2 hours at 90-100° C, rinsed with copious amounts of MilliQ water (18.2 MΩ) and absolute ethanol, and then dried under a stream of dry nitrogen.

Instruments

Size exclusion chromatographic analysis of polymers was effected using a Waters 150-C+ instrument equipped with an RI and a viscosity detector (Viscotek Model 150R). XPS was acquired using a PHI 5600 ESCA system with an Al K_α X-ray source; the take-off angle was 45 degrees. Ellipsometry data was obtained on a Gaertner Scientific Ellipsometer (Model L116C) with a fixed angle of incidence (70°) and a He-Ne laser (632.8 nm). The advancing and receding water contact angles were measured using a sessile drop (10 μL) at room temperature. AFM images were obtained with a Park Scientific Instruments AutoProbe M5 using tapping mode.

Synthesis of 1-(4-bromophenyl)-1-phenylethanol (1)

1-(4-bromophenyl)-1-phenylethanol was synthesized according to the method of Beinert and Herz [10]. Anhydrous diethyl ether (100 mL) was transferred by cannula to a flask containing 4-bromobenzophenone (2.0 g, 0.0076 mol) (Aldrich) under argon. After addition of methylmagnesium iodide (3.0 M, 3.0 mL, 0.009 mol), the solution was heated under reflux overnight. The reaction was quenched by addition of a 10 % aq. HCl/MeOH solution. The product was recovered in 95% yield and further purified using column chromatography. IR: 3447 (OH), 3000-3100 (aromatic CH st), 2963 and 2872 (aliphatic CH, st), 1392 (CH_3, sy), 1264 cm^{-1} (C-O st). ^1H NMR ($CDCl_3$): $\delta = 7.38$ (m, 9H, aromatic C-H) and 1.93 ppm (s, 3H, CH_3).

Synthesis of 4-bromodiphenylethylene (2)

1-(4-bromophenyl)-1-phenylethanol (2.01 g, 7.25 mmol) and *p*-toluenesulfonic acid (0.055g, 0.29 mmol) were added to 200 mL of toluene. The solution was heated at reflux with a Dean Stark trap for 12 hours. The product was purified by column chromatography. IR: 3079 (=CH_2 st), 3055 (ar C-H st), 3026 (=CH- st), 1610 and 1485 cm^{-1} (ar C-C). ^1H NMR ($CDCl_3$): $\delta = 7.48$ (d, 2H, aromatic C-H), 7.34 (s, 5H, aromatic CH), 7.23 (d, 2H, aromatic CH) and 5.48 ppm (d, 2H, $=CH_2$). ^{13}C NMR ($CDCl_3$): $\delta = 114.99$ ppm ($=CH_2$)

Synthesis of 4-dimethylchlorosilyl-1,1-diphenylethylene (3)

A small portion of the 4-bromodiphenylethylene (BrDPE) (0.21 g, 0.81 mmol) in 20 mL of tetrahydrofuran (THF) was added to magnesium (0.081 g, 3.32 mmol) (99+ % Aldrich) and heated at reflux with a sand bath to start the reaction. The remaining BrDPE was added dropwise using an addition funnel and the solution heated at 45-50 °C for 5 hours. The Grignard derivative was poured into a side ampoule equipped with a Rotoflo stopcock and taken into the drybox; 2.0 mL (0.080 mmol) of the Grignard solution was added to excess $(CH_3)_2SiCl_2$ (5.0 mL, 0.042 mol).

Synthesis of ω-chlorodimethylsilyl-polyisoprene and tethering reaction

Isoprene polymerization was initiated by *sec*-BuLi in benzene. The resulting poly(isoprenyl)lithium (M_n=3000 g/mol, M_w/M_n=1.06, 1.2 mmol) was added to excess $(CH_3)_2SiCl_2$ (42.0 mmol). ^1H NMR ($CDCl_3$): $\delta = 0.44$ ppm (6H, $-Si(CH_3)_2Cl$). ^{13}C NMR ($CDCl_3$): $\delta = 2.83$ ppm ($-Si(CH_3)_2Cl$). The polymer was tethered to a silicon ATR-IR crystal using known procedures for reacting silyl chlorides with hydroxyl groups [12]. ATR-IR: 2962, 2930, 2855 cm^{-1} (aliphatic C-H st.). A similar polymerization was done using 3-(*t*-butyldimethylsiloxy)-1-propylithium instead of *sec*-BuLi as initiator.

DPE Monolayer formation

The silicon wafers were taken into the drybox and added to a 20 mM solution of DPE-SiCl (3) in DMF with 0.009 g imidazole (0.13 mmol). After 30 hours at room temperature, the wafers were removed and extracted with copious amounts of methylene chloride.

PSLi linking reaction with DPE monolayer

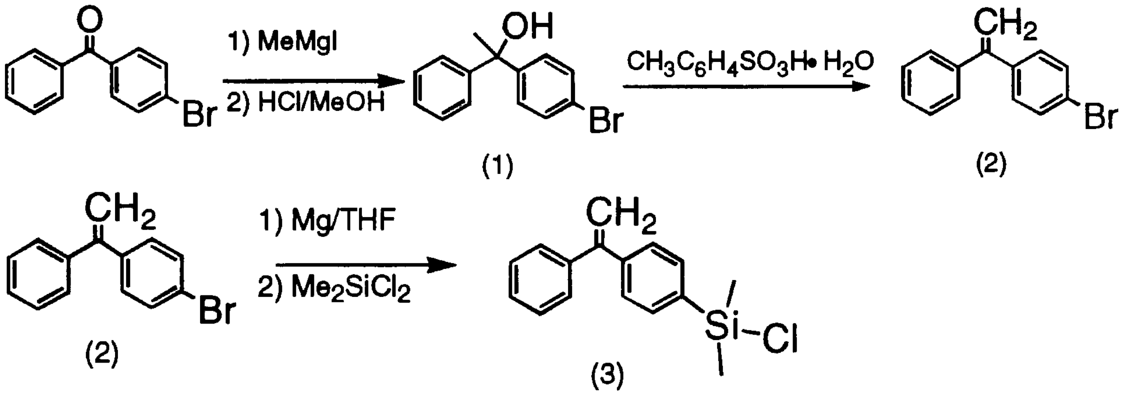
A monolayer of DPE on a silicon wafer was treated for 2 days with PSLi oligomers, made by *sec*-BuLi initiation of styrene in benzene (M_n = 940, M_w/M_n = 1.09, 4.0 mL, 60mM). The solution was then terminated with degassed methanol. The wafer was extracted overnight with methylene chloride under reflux in a Soxhlet extractor.

Polymerization of hydroxy-terminated polymer brush from DPE monolayer

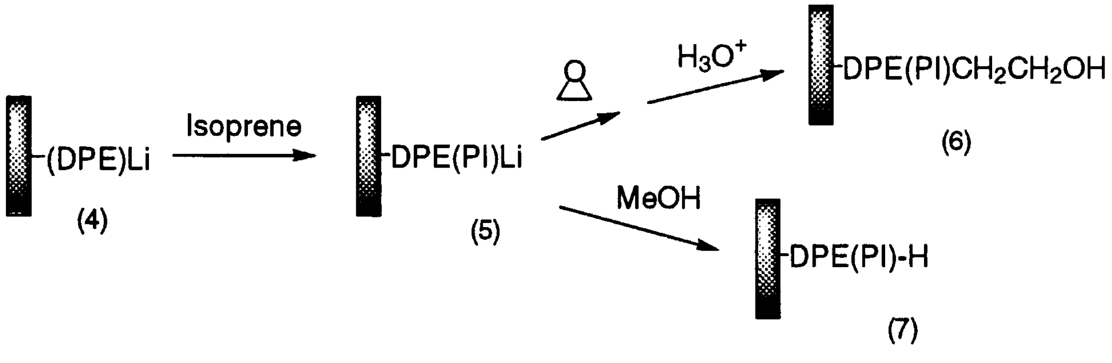
A silicon wafer with a DPE monolayer was added to an all-glass reactor and evacuated overnight. A solution of *n*-BuLi (5 mL, 1 mM) in benzene was added. After 36 hours, the excess *n*-BuLi in benzene was transferred to a side ampoule and the wafer was rinsed multiple times with benzene from the side ampoule to remove *n*-BuLi. Ampoulized isoprene (5 mL) was added by smashing the breakseal. The solution contained 50% benzene and 50% isoprene. Functionalization was effected using ethylene oxide [11,12]. After 4 days of isoprene polymerization, ethylene oxide (1.0 mL in 6.0 mL of benzene) was added and allowed to react for 2 days before quenching with 1% aq. HCl in THF. A similar reaction using another silicon wafer was terminated with degassed methanol. Non-covalently bound polymer was extracted overnight with methylene chloride under reflux in a Soxhlet extractor.

Results and Discussion

4-Dimethylchlorosilyl-1,1-diphenylethylene (DPE-SiCl) was synthesized according to Scheme 1. DPE was chosen as a surface-bound co-initiator because it is a non-homopolymerizable molecule that will react quantitatively with organolithium compounds [4]. It was assumed that the surface of the silicon wafer after treatment with Piranha solution afforded approximately 5 OH groups nm^{-2} as established by other researchers using a deuterio-exchange method [13]. The monolayer was formed on the silicon wafer using well-known precedents for the reaction of hydroxyl groups with silyl chlorides [1,14]. Any remaining surface hydroxyl groups (SiOH) not protected by DPE-SiCl were rendered inactive by *n*-BuLi and thus unable to cause termination during polymerization. *n*-BuLi was chosen as initiator since it is less reactive than *sec*-BuLi [15] and should be less likely to react with the Si-O-Si bonds and damage the monolayer. To demonstrate the utility of the 1,1-DPE monolayer, PSLi oligomers (1k, 60mM) were reacted with the monolayer in a "grafting to" approach and terminated with methanol. For the "grafting from" approach, the 1,1-diphenylethylene monolayer was treated with *n*-BuLi for 1-2 days. After conversion to the corresponding 1, 1 diphenylhexyllithium derivative (4), excess *n*-butyllithium was poured into a side ampoule and the silicon wafer was rinsed 5-6 times by back distillation to ensure removal of initiator from solution. After addition of isoprene, the resulting poly(isoprenyl)lithium (5) chain ends were functionalized [11,12] by ethylene oxide (6) (Scheme 2) or methanol (7) on separate silicon wafers, respectively.



Scheme 1. Synthesis of DPE-SiCl



Scheme 2. Functionalization of poly(isoprenyl)lithium chain ends on a silicon wafer

Ethylene oxide will react with polymeric organolithiums to give a hydroxy-terminated polymer in quantitative yield without oligomerization of ethylene oxide [11,12]. Although these living chain ends of the polymer brush would be expected to exhibit different kinetics than dilute solution species [16], it is assumed that the chemistry of functionalization will be analogous to dilute solution chemistry. All polymer brushes were extracted overnight with CH_2Cl_2 under reflux to remove non-covalently bound polymer. It was found that 4-5 hours was sufficient to remove a spin-coated film of comparable thickness.

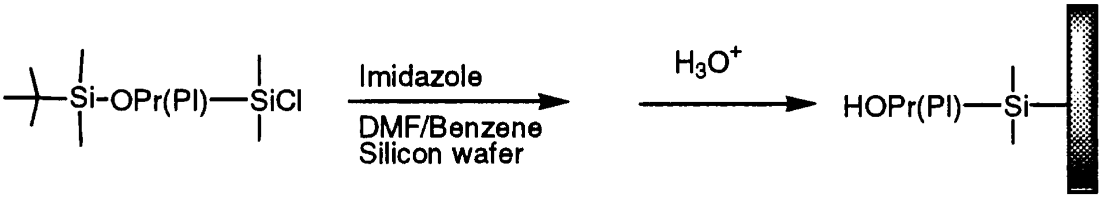
After formation of the 1,1-diphenylethylene monolayer and polymer brushes on a silicon wafer, the water contact angles were measured using a sessile drop (Table 1). The advancing contact angle is sensitive to the low-energy components of the polymer brush and the receding contact angle is sensitive to the higher-energy components [17]. The contact angle hysteresis provides insight into surface heterogeneity and surface roughness [17]. The surface roughness was determined by AFM from multiple 1x1 μm^2 regions. The surface roughness for the DPE monolayer was 4 ± 1 Å (rms) and the unfunctionalized PI brush ("growth from") had a surface roughness of 3 ± 1 Å (rms). The small variation in thickness for multiple 1x1 μm^2 regions demonstrates uniform polymerization on the silicon wafer [18].

Table 1. Contact angle measurements for DPE monolayer and the product from the linking reaction of PSLi with the DPE monolayer.

	DPE Monolayer	After Grafting PSLi to DPE monolayer	(PI)DPE Brush "Growth from"	HO(PI)DPE Brush "Growth from"
$\theta_{\text{advancing}}$[a]	79 ± 2	86 ± 2	86 ± 2	74 ± 3
θ_{receding}[a]	65 ± 2	72 ± 4	76 ± 2	61 ± 3

[a] measured using a sessile drop

The advancing contact angle for a clean wafer is 10-20°. The contact angle measurements for the polymer brushes were in agreement with expectations compared to a spin-coated polyisoprene film (θ_{adv} = 87 ± 3°). In addition, there was good agreement between the contact angle measurements for the "grafted to " and the "grafted from" polyisoprene brushes. The relatively small difference between advancing and receding contact angles demonstrate that the brushes have relatively low degrees of heterogeneity and surface roughness. It is known that polymer chains will reorganize on the surface and that the chain ends are highly mobile [19]. Therefore, it is not surprising that the contact angle of the hydroxy-terminated brush is less than that of the unfunctionalized brush. A similar trend is seen for a hydroxy-terminated brush grafted to a silicon wafer using a functional initiator, 3-(*t*-butyldimethylsiloxy)-1-propylithium, (Scheme 3) which gave θ_{adv} = 66.8 ± 1.2 and the unfunctionalized polyisoprene brush attached in a similar fashion gave θ_{adv} = 83 ± 2.6.



Scheme 3. Surface grafting of telechelic polymers to give a hydroxy-terminated PI brush

ATR-IR spectra of the hydroxy-terminated polymer brush showed aliphatic C-H stretching bands at 2972, 2930 and 2851 cm^{-1}. A surface grafted hydroxy-terminated polyisoprene brush (Scheme 3) showed similar aliphatic stretching bands at 2962, 2930 and 2855 cm^{-1}.

The thicknesses of the polymer brushes were measured by ellipsometry using a two-layer model [20] with a refractive index of 1.51. The thickness of the DPE monolayer increased after reaction with PSLi as shown in Table 2. Although this "grafting to" approach gave a lower graft density than the "grafting from" strategy, the increase in thickness demonstrated the expected reactivity of the DPE monolayer toward polymeric organolithium compounds. The lower grafting density results from PSLi chains diffusing to the surface and forming an activation barrier towards additional grafting [21].

Table 2. Polymer brush thicknesses

	DPE Monolayer	(PS)DPE "graft to"	(PI) DPE "graft from"	HO(PI)DPE "graft from"
Thickness (nm)	0.90 ± 0.14	1.9 ± 0.2	5.0 ± 0.4	9.5 ± 1.2
Reaction time with isoprene or PSLi		2 days	2 days	4 days

The HO(PI)DPE brush was thicker than the unfunctionalized brush because of a longer polymerization time. The thickness of the hydroxy-terminated brush in Scheme 3 varied with grafting time as expected and was determined to be 6.0 nm after 7 days compared with the "grafting from" which gave 9.5 nm after 4 days. Zhou et al. [7] have recently prepared polystyrene brushes using an analogous DPE monolayer. They obtained thicknesses ranging from 3.8 nm to 16.1 nm.

X-ray photoelectron spectroscopy (XPS) can accurately determine atomic concentration of surface components using peak heights [22]. A low-energy electron gun (5-10 eV) was used to prevent charging of the polymer surface and the C_{1s} and Si_{2p} peak positions were used as charge references. The intensity of the C_{1s} binding energy at 285 eV increased after polymerization of isoprene using the 1,1-diphenylhexyllithium derivative and surface grafting of PSLi as shown in Table 3. In addition, the Si_{2p} peak from the substrate decreased as the thickness of the polymer brushes increased (see Table 2 for thicknesses). Table 3 shows the increase in the C_{1s} peak height for the polymer brushes.

Table 3. XPS atomic concentrations for linking of living chain end with DPE monolayer.

	DPE	(PS)DPE "grafting to" using PSLi	(PI)DPE "graft from"	HO(PI)DPE "graft from"
% C_{1s}	17	30	37	51
% Si_{2p}	45	38	29	20

The hydroxy-terminated graft polymer was compared with the analogous methanol terminated graft polymer. As expected, the amount of carbon increased for longer polymerization time and use of the "grafting from" approach. The "grafting to" approach using a telechelic polymer (Scheme 3) gave 24 % C_{1s} for the atomic concentration.

Conclusions

It has been shown that living anionic polymerization of isoprene on a silicon wafer can be initiated using a surface-bound 1,1 diphenylhexyllithium derivative. The resulting poly(isoprenyl)lithium chains ends were functionalized [11,12] by addition of ethylene oxide to give a hydroxy-terminated polyisoprene brush. The thickness of the polymer brush was 9.5 ± 1.2 nm compared to 1.9 ± 0.2 nm for a "grafting to" approach using poly(styryl)lithium. To the best of the authors' knowledge, this is the first report of ethylene oxide functionalization of living poly(isoprenyl)lithium chain ends of a polymer brush initiated from a 1,1-diphenylethylene surface-bound monolayer. Future work will include anionic diblock synthesis as well as free radical and cationic polymerizations using the surface grafted DPE layers.

Acknowledgements.
The authors are grateful to the National Science Foundation (UKRF 463675-00-297), FMC Lithium Division and the Army Research Office (ARO-MURI-R4575-C1/BRI) for support of this work. We thank Dr. Wayne Jennings at the CWRU Center for Surface Analysis of Materials for advice on XPS. RTM thanks Professor Lynn Penn for instruction on contact angle measurements. Special thanks to Professor W.J. Brittain and Randy Sedjo for use of the ATR-IR spectrometer and to Professor Mark D. Foster, Shijun Jia and Tricia Cregger for the AFM images and use of the ellipsometer.

References

1. Zhao B, Brittain WJ, (2000) Prog Polym Sci 25:677
2. Milner ST (1991) Science 251:905
3. Perahia D, Wiesler DG, Satija SK, Fetters LJ, Sinha SK, Milner ST (1994) Phys Rev Lett 72:100
4. Quirk RP, Yoo T, Lee Y, Kim J, Lee B (2000) Adv Polymer Sci 153:67
5. Jordan R, Ulman A, Kang JF, Rafailovich MH, Sokolov J (1999) J Am Chem Soc 121:1016
6. Oosterling ML, Sein A, Schouten AJ (1992) Polymer 33:4394
7. Zhou Q, Nakamura Y, Inaoka S, Park M, Wang Y, Mays J, Advincula R (2000) Polym Mater Sci Eng 82:290
8. Ingall MDK, Honeyman CH, Mercure JV, Bianconi PA, Kunz RR (1999) J Am Chem Soc 121, 3067
9. Morton M, Fetters LJ (1975) Rubber Chem Technol 48:359
10. Beinert G, Herz J (1980) Makromol Chem 181:59
11. Quirk RP, Ma J-J (1988) J Polym Sci Part A: Polym Chem 26, 2031
12. Hsieh HL, Quirk RP (1996) Anionic Polymerization: Principles and Practical Applications. Marcel Dekker, New York.
13. Zhuravlev LT (1987) Langmuir 3:316
14. Greene TW, Wuts PGM (1991) Protecting Groups for Organic Synthesis, 2nd ed. John Wiley & Sons, New York
15. Wakefield BJ (1974) The Chemistry of Organolithium Compounds. Pergamon, Oxford
16. Wittmer JP, Cates ME, Johner A, Turner MS (1996) Europhys Lett 33, 397
17. Neumann AW, Good RJ (1972) J Colloid Interface Sci 38:341
18. Zhao B, Brittain WJ (2000) Macromolecules 33, 342
19. Ruckenstein E, Gourisankar SV (1985) J Colloid Interface Sci 107:488
20. Wasserman SR, Whitesides GM, Tidswell IM, Ocko BM, Pershan PS, Axe JD (1989) J Am Chem Soc 111:5852
21. Ligoure C, Leibler L (1990) J Phys (Paris) 51:1313
22. Stamm M (1992) Adv Polymer Sci 100:357