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Synthesis and Characterization of Novel Silicon-Functional Polyisobutylenes and Their Applications: Polyisobutylene Brushes on Silicate Substrates via Living Cationic Polymerization

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Synthesis and Characterization of Novel Silicon-Functional Polyisobutylenes and Their Applications: Polyisobutylene Brushes on Silicate Substrates via Living Cationic Polymerization

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ABSTRACT

A series of novel chlorosilyl functional initiators have been prepared and applied for the first time in the living cationic polymerization of isobutylene (IB). Well-defined polyisobutylenes (PIBs) carrying mono-, di-, and tri-chlorosilyl head-group, and a *tert*-chloro end-group were synthesized using newly designed silyl-functional initiators in conjunction with TiCl_4 in Hex:MeCl (60:40, v:v) at -80°C . End-group analysis by ^1H NMR spectroscopy verified the product structure and the survival of the Si—Cl head-groups during the polymerization. The chlorosilyl functional initiators and chlorosilyl functional PIBs have been employed for the synthesis of PIB brushes on planar silicate substrates by the “grafting from” and “grafting to” techniques. The products were characterized by x-ray photoelectron spectra (XPS), atomic force microscopic (AFM), and ellipsometry. The “grafting from” approach yielded surface-bound polymer brushes with more uniform surface and higher grafting density compared to the “grafting to” technique. The film thickness of PIB brushes formed by “grafting from” increased linearly with increasing molecular weight of PIB. In contrast, PIB brushes produced by “grafting to” gave constant thickness independent of the molecular weight of PIB.

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Key Words: Chlorosilyl functional initiators; Silicon functional polyisobutylenes; Polymer brushes; Grafting from; Grafting to; Free initiator; Surface bound initiator; Surface-initiated living cationic polymerization; Grafting density.

INTRODUCTION

Functional polymers carrying reactive end-groups, are most valuable intermediates for a variety of applications and are therefore of great scientific and commercial interest.^[1-7] In particular, silicon functional polymers have attracted much attention due to the versatility of silicon chemistry in chemical reactions. With significant advances in living polymerizations, attempts increasingly focused on functionalization of living polymers.^[8-11] We recently became interested in utilizing silicon-functional initiators for the preparation of novel silicon-functional polyisobutylenes (PIBs), particularly that carrying Si—Cl end-groups that would combine the excellent properties provided by the rubbery PIB segment with the versatility and chemical reactivity of the Si—Cl bonds. An attempt has already been reported by Kennedy et al.^[11] to use chlorosilyl functional initiators in the cationic polymerization of isobutylene (IB) in conjunction with Et₂AlCl at -70°C. The results, however, indicated that the Si—Cl bond may not survive the polymerization. No other reports could be found on the use of chlorosilyl functional initiators in cationic polymerization until our recent preliminary reports on the synthesis of well-defined monochlorosilyl^[12] and dichlorosilyl^[13] functional PIBs utilizing novel monochlorosilyl and dichlorosilyl functional initiators.

Silicon functional PIBs provide multiple synthetic utilities to design macromolecular architectures and may find applications as curable elastomers,^[14] and could be used as intermediates in the combination of cationic and anionic polymerization by coupling, and in the synthesis of organic-inorganic hybrid materials.^[15] One possible application of chlorosilyl functional PIBs is the preparation of polymer brushes, which refers to tethered polymer chains on a surface or interface.^[16-18] Modification of solid surfaces by tethered polymer layers has attracted considerable attention in the last few years due to their practical and potential applications in a variety of technological fields.^[19] Generally polymer brushes can be generated by physisorption of block-copolymers,^[20] covalent attachment of end-functionalized polymers to a reactive surface (“grafting to”),^[19] and in-situ monomer by monomer growth of polymer chains from immobilized initiator (“grafting from”).^[21] Compared to physisorption, which yields polymers noncovalently attached to the surface, and to the “grafting to” technique, where the diffusion of polymer chains to the surface is kinetically and entropically hindered,^[22] the “grafting from” technique provides the most promising way to achieve sufficiently high grafting densities and film thickness. In this method, functional initiators are covalently attached onto the surface, followed by in-situ surface-initiated polymerization to prepare tethered chains. In terms of tailoring the surface, controlled/living polymerization techniques are effective methods to produce polymer chains with controlled lengths. Recently, a number of research groups have reported the use of controlled/living polymerization techniques to fabricate polymer brushes, e.g., cationic,^[23] anionic,^[24] TEMPO-mediated radical,^[25] atom transfer radical polymerization (ATRP),^[26] and cationic ring-opening polymerization.^[27] However, most surface grafting studies involved styrene and acrylate-based resins so far.



This article concerns the synthesis of mono-, di- or trichlorosilyl functional PIBs by employing mono-, di- or trichlorosilyl functional initiators for the living polymerization of IB, and their application in the preparation of tethered PIB brushes on silica surfaces by the “grafting from” and “grafting to” methods.

EXPERIMENTAL

Materials

CH_3Cl was passed through in-line gas purifier columns packed with BaO/Drierite and condensed at -80°C prior to polymerization. Hexanes were rendered olefin free by refluxing over concentrated sulfuric acid for 48 h. They were washed with 10% aqueous NaOH solution and then with deionized water until neutral, and stored over MgSO_4 for 24 h. They were refluxed over CaH_2 overnight and distilled. 2,6-di-*tert*-butylpyridine (DTBP, 99.4% by GC, Aldrich), and Titanium(IV) chloride (TiCl_4 , 99.9% Aldrich) were used as received.

Synthesis of Chlorosilyl Functional Initiators

Monchlorosilyl functional initiator, 3-(1-chlorodimethyl-silylmethyl)ethyl-1-(1-chloro-1-methyl)ethylbenzene (CECE) was synthesized in a two step procedure. In the first step, 1,3-di-isopropenylbenzene (Aldrich) was mono-hydrosilylated with chlorodimethylsilane. Sixty milliliters (0.35 mole) of 1,3-di-isopropenylbenzene was placed in a 250 mL three-neck round bottom reaction flask under Ar, equipped with a thermometer, condenser, magnetic stirring bar, feeding funnel, and Ar inlet. After the injection of 0.2 mL of a 10% solution of platinum divinyl-disiloxane complex in hexanes, (3–3.5% Pt in vinyl terminated polydimethylsiloxane, SOP 6831.0, Gelest) as catalyst, a drying tube containing Drierite replaced the Ar inlet. The reaction flask was warmed to 40°C in an oil bath and $\text{Cl}(\text{CH}_3)_2\text{SiH}$, (30 mL, 0.29 mole) was added dropwise. The reaction temperature was kept between 40°C and 50°C by the adjustment of the rate of addition of $\text{Cl}(\text{CH}_3)_2\text{SiH}$ and the heating of the oil bath. After the addition was complete, the reaction mixture was kept at $40\text{--}50^\circ\text{C}$ for 3 more hours. The excess 1,3-diisopropenylbenzene was distilled out under Ar, followed by the distillation of the expected material 3-(1-chlorodimethyl-silylmethyl)ethyl 1-isopropenyl-benzene. ^1H NMR spectrum: 7.10–7.50 ppm (4H, m), 5.50 ppm (1H, s), 5.20 ppm (1H, s), 3.10 ppm (1H, m), 2.20 ppm (3H, s), 1.45 ppm (2H, d), 1.30 ppm (3H, d), 0.5 ppm (6H, d).

In the second step, hydrochlorination of 3-(1-chlorodimethyl-silylmethyl)ethyl-1-isopropenylbenzene was carried out. Five milliliters of 3-(1-chlorodimethylsilylmethyl)-ethyl-1-isopropenylbenzene was dissolved in 100 mL of dried and distilled CH_2Cl_2 and cooled to 0°C . Dry HCl was bubbled through the solution for 5 h. The solution was then allowed to warm up to room temperature and the solvent was evaporated on the rotavap. Characterization of the product by ^1H NMR spectroscopy confirmed quantitative hydrochlorination. ^1H NMR spectrum: 7.10–7.60 ppm (4H, m), 3.10 ppm (1H, m), 2.05 ppm (3H, s), 1.45 ppm (2H, d), 1.30 ppm (3H, d), 0.5 ppm (6H, d).



Dichlorosilyl functional initiator, 3-(1-dichloromethyl-silylmethyl)ethyl-1-(1-chloro-1-methyl)ethylbenzene (DECE) and trichlorosilyl functional initiator, 3-(1-trichlorosilylmethyl)ethyl-1-(1-chloro-1-methyl)ethylbenzene (TECE) were prepared by the same procedure as CECE except that instead of chlorodimethylsilane, dichloromethylsilane and trichlorosilane were used. After mono-hydrosilylation with dichloromethylsilane and trichlorosilane, the expected material, 3-(1-dichloromethyl-silylmethyl)ethyl 1-isopropenylbenzene and 3-(1-trichlorosilylmethyl)ethyl 1-isopropenylbenzene was distilled off respectively. The ^1H NMR spectrum of 3-(1-dichloromethylsilylmethyl) ethyl 1-isopropenylbenzene: 7.10–7.50 ppm (4H, m), 6.40 ppm (1H, s), 6.10 ppm (1H, s), 3.20 ppm (1H, m), 2.20 ppm (3H, s), 1.60 ppm (2H, d), 1.45 ppm (3H, d), 0.5 ppm (3H, s). The ^1H NMR spectrum of 3-(1-trichlorosilylmethyl)ethyl 1-isopropenylbenzene: 7.10–7.50 ppm (4H, m), 6.40 ppm (1H, s), 6.10 ppm (1H, s), 3.20 ppm (1H, m), 2.20 ppm (3H, s), 1.85 ppm (2H, d), 1.45 ppm (3H, d).

After hydrochlorination of mono-hydrosilylated intermediates, ^1H NMR spectroscopy confirmed quantitative hydrochlorination. The ^1H NMR spectrum of DECE: 7.10–7.60 ppm (4H, m), 3.20 ppm (1H, m), 2.05 ppm (6H, s), 1.60 ppm (2H, d), 1.44 ppm (3H, d), 0.5 ppm (3H, s). The ^1H NMR spectral assignments of TECE: 7.10–7.60 ppm (4H, m), 3.30 ppm (1H, m), 2.05 ppm (3H, s), 1.85 ppm (2H, d), 1.40 ppm (3H, d). Detailed procedures and characterization methods are described in Ref.^[12].

Synthesis of Silicon Functional Polyisobutylenes

The living cationic polymerization of IB was carried out using mono-, di-, and trichlorosilyl functional initiators/ TiCl_4 /hexanes : CH_3Cl (60 : 40, v : v)/ -80°C system in the presence of 2,6-di-*tert*-butylpyridine (DTBP). Typical concentrations of reactants were as follows: [Chlorosilyl function initiators] = 0.002 M, [TiCl_4] = 0.036 M, and [DTBP] = 0.003 M. All polymerizations were carried out in a 250 mL round bottom glass flask. After a predetermined reaction time, aliquots of the solution were transferred to 75 mL test tubes equipped with a teflon-lined cap and quenched with dried and pre-chilled methanol.

Preparation of Substrates and Surface Bound Initiator on Silicon Wafers

The silicon (100) wafers (4 cm \times 1 cm) were put into an ultrasonic bath of a 1% Chem-Solv[®] (NaOH/ CH_3OH) for 3 h, 30 min and were rinsed with a copious amount of deionized water and dried with a stream of nitrogen. Freshly cleaned silicon wafers were then immersed into 2×10^{-3} M solution of chlorosilyl functional initiator in hexane with 1 mL of DTBP at room temperature. After 1 h, the silicon wafers were removed and rinsed repeatedly with hexanes followed by CH_2Cl_2 .

Preparation of Polymer Brushes by “Grafting From” Technique

A typical surface-initiated carbocationic polymerization was carried out as follows. To prechilled 75 mL test tubes containing Si wafers with the chemically attached initiator, a mixture of DTBP and TiCl_4 , in hexanes : CH_3Cl (60 : 40, v : v) was added, followed by the



addition of “free initiator,” 3-(1-chlorodimethyl-silylmethyl)ethyl-1-(1-chloro-1-methyl)-ethyl-benzene, to control the molecular weight of PIB. Then polymerization was started by injection of IB with different concentration at -80°C . The initial concentrations of reactants were [“free initiator”] = 0.002 M, $[\text{TiCl}_4]$ = 0.036 M, and $[\text{DTBP}]$ = 0.009 M. After 1 h polymerization (100% conversion), the reaction was quenched with dried and prechilled methanol. Addition of this solution to methanol precipitated the soluble PIB produced from the added non surface-bound initiator, which was analyzed using standard techniques. The silicon wafer was then removed, rinsed several times with hexanes, and continuously extracted with hexanes in a soxhlet extractor overnight.

Preparation of Polymer Brushes by the “Grafting To” Technique

The living cationic polymerization of IB was carried out using the 3-(1-chlorodimethyl-silylmethyl)ethyl-1-(1-chloro-1-ethyl)ethylbenzene/ TiCl_4 /hexanes : CH_3Cl (60 : 40, v : v) / -80°C system in the presence of DTBP. Typical concentrations of reactants were as follows: [chlorosilyl function initiator] = 0.002 M, $[\text{TiCl}_4]$ = 0.036 M, and $[\text{DTBP}]$ = 0.003 M. After complete polymerization of IB (1 h), the polymer was tethered to a silicon wafer by condensation reaction of silyl chlorides with silanol groups for 12 h at -80°C , and quenched with dried and pre-chilled methanol. The wafer was then removed, rinsed several times with hexanes and continuously extracted with hexanes in a soxhlet extractor overnight.

Characterization

^1H NMR spectra were obtained on a Bruker 250 MHz spectrometer. Molecular weights and molecular weight distributions were determined using a Waters HPLC system equipped with a model 510 HPLC pump, model 712 sample processor, model 486 tunable UV/VIS detector, and a model 250 dual detector (refractometer/viscometer, Viscotek) and five Ultrastaygel columns (Waters) connected in the following series: 500, 10^3 , 10^4 , 10^5 , and 100 \AA . Tetrahydrofuran (THF) was used as a carrier solvent at a flow rate of 1 mL/min.

X-ray photoelectron spectra (XPS) were recorded on VG ESCA LAB II spectrometer equipped with a $\text{MgK}\alpha$ x-ray source. The x-ray source was operated at 13 kV and 20 mA. The kinetic energy of the photoelectrons was measured by a concentric hemispherical analyzer operated at a pass energy of 20 eV. All binding energies are reported with respect to the Fermi level. Atomic force microscopic (AFM) measurements were performed by advanced surface microscopy (ASM), Indianapolis, IN. Specimens were examined using a Digital Instruments NanoScope Dimension 3100 in tapping mode head and an electronics extender ($3 \times 3 \mu\text{m}^2$ scan range). The samples were scanned with standard silicon nitride tips under ambient conditions. The images were recorded in constant amplitude mode with a resolution of 512×512 pixels at scanning rates from 0.7 to 1.0 Hz. Thickness measurements were carried out with a Rudolph Research AutoEL III ellipsometer with a 632.8-nm He-Ne laser as the light source and a fixed angle of incidence of 70° . For the calculation of the layer thickness, a refractive index of $n = 1.462$ for the self assembled monolayer (SAM) and $n = 1.481$ for the polymer layer was used. Thickness data were average values obtained from at least four different points on a given sample.



RESULTS AND DISCUSSION

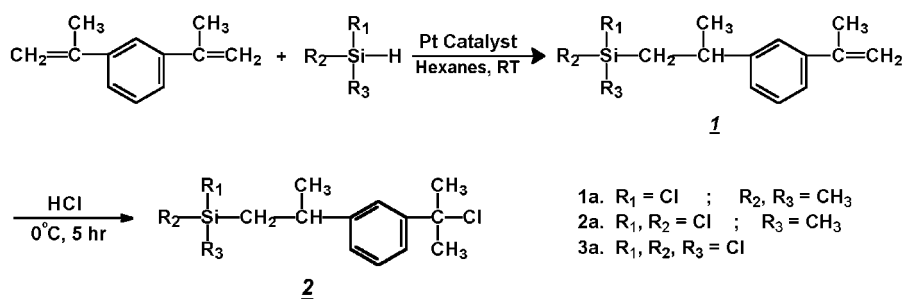
Synthesis of Novel Chlorosilyl/Methoxysilyl Functional Polyisobutylenes

The mono-, di-, and trichlorosilyl functional initiators were readily synthesized by platinum catalyzed hydrosilylation of 1,3-di-isopropenylbenzene with chlorodimethyl-, dichloromethyl-, and trichlorosilane as presented in Sch. 1. These initiators combine the highly reactive Si—Cl functional groups and the benzyl chloride group, which is able to initiate carbocationic polymerization in conjunction with suitable cointiators.^[28–30]

In a recent work, we have reported a new one-pot synthesis of moisture curable dimethoxysilyl telechelic PIB.^[13] This process utilized novel dichlorosilyl functional initiators for the polymerization of IB, and was based on a finding that the dichlorosilyl head-group remains unreacted during polymerization when TiCl₄ is employed as Lewis acid. As shown in Sch. 2, PIB bearing chlorosilyl-, or methoxysilyl head groups was synthesized using the chlorosilyl functional initiators in conjunction with TiCl₄.

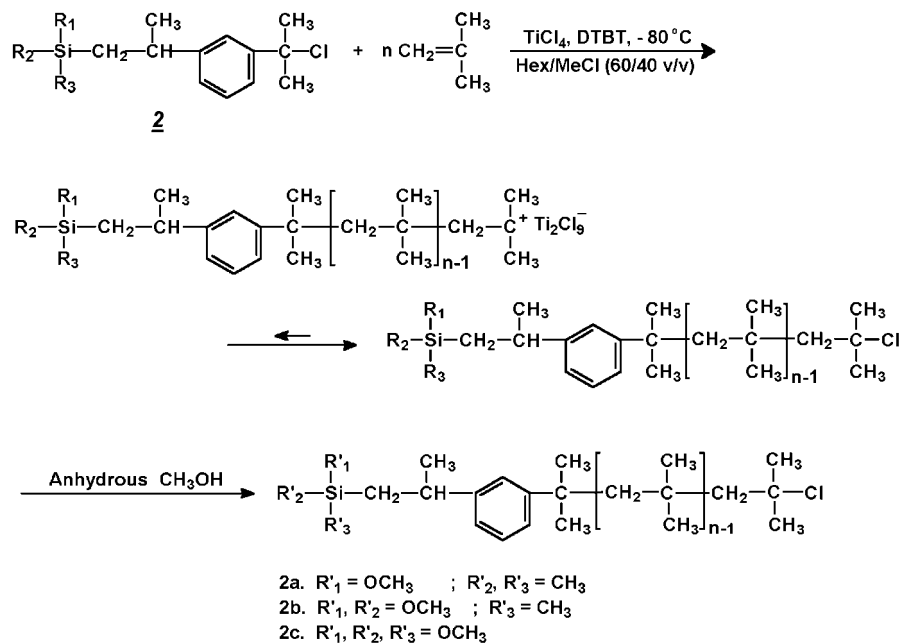
To examine the living nature of the polymerization, ln([M]₀/[M]) vs. time (Fig. 1) and M_n vs. conversion plots (Fig. 2) were constructed. The linearity of the first-order kinetic plots indicates that the number of active chains is constant (absence of irreversible termination). The linear plot of M_n vs. conversion plot demonstrates the absence of chain transfer. The slight upward curvature of the first-order plots at low monomer conversion suggests slow initiation due to the negative inductive effect of the chlorine atom next to the silicon, which destabilize the intermediate carbocation of initiator.^[31] It can be observed that the magnitude of this effect increases with the number of chlorine atoms connected to the silicon atom. Slow initiation is manifested by the slightly higher than theoretical molecular weights at low monomer conversion as shown in Fig. 2. The polymers however, exhibited close to theoretical M_n (M_n^{theoretical} = 50,000, M_n^{experimental} = 52,000) indicating close to 100% initiator efficiency (I_{eff}) and narrow molecular weight distributions reaching 1.05–1.10 at complete IB conversion.

To investigate the stability of Si—Cl head group during the polymerization and polymer purification, PIBs with low molecular weight (M_n = 2100 and M_w/M_n = 1.06 by GPC) were prepared for polymer head-group analysis by ¹H NMR spectroscopy. Representative ¹H NMR spectra of mono-, di-, and trimethoxysilyl functional PIBs obtained upon quenching with methanol are shown in Fig. 3. As indicated by the ¹H NMR spectra, the chlorosilyl head-groups underwent quantitative methanolysis to yield



Scheme 1. Synthesis of mono-, di-, and trichlorosilyl functional initiators.





Scheme 2. Synthesis of mono-, di-, and trimethoxysilyl functional PIBs.

(CH₃O)_{3-x}Si— head-groups wherein x is 1, 2, or 3. Comparison of the characteristic resonance signals of the α-methoxysilyl head-group [(CH₃O)_{3-x}Si— at δ = 3.4 ppm] to that of the ω-chloro end-group (—CH₂—C(CH₃)₂Cl at δ = 1.96 and 1.67 ppm), indicates perfect head- and end-group functionality.

α-Chlorosilyl functional PIB could also be obtained when the polymerization was quenched with dry triethylamine. The resulting polymers exhibited characteristic signals at

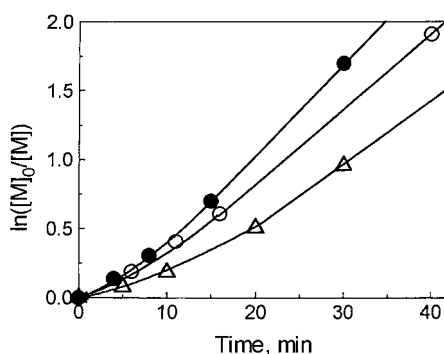


Figure 1. ln([M]₀/[M]) vs. time plot for the polymerization of IB using mono- (●)/di- (○)/tri- (△) chlorosilyl functional initiators in hexanes:CH₃Cl (60:40, v:v) at -80°C. Polymerization conditions: [chlorosilyl functional initiator] = 0.002 M, [TiCl₄] = 0.036 M, [DTBP] = 0.003 M, and [IB] = 1.78 M.



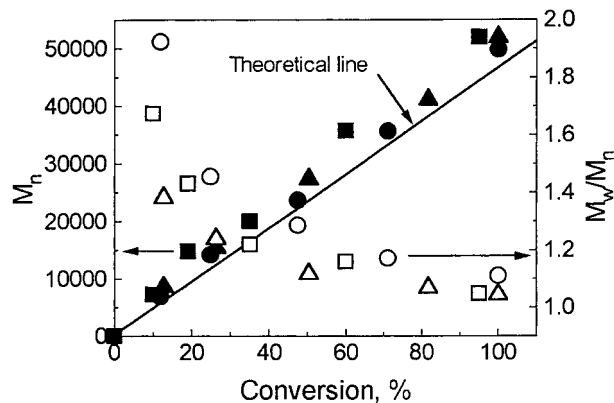


Figure 2. The M_n (filled symbols) and M_w/M_n (open symbols) vs. conversion plots for the polymerization of IB using mono- (■, □)/di- (●, ○)/tri- (▲, △) chlorosilyl functional initiators in hexanes:CH₃Cl (60:40, v:v) at -80°C . Polymerization conditions: [chlorosilyl functional initiator] = 0.002 M, [TiCl₄] = 0.036 M, [DTBP] = 0.003 M, and [IB] = 1.78 M.

0.2–0.3 ppm, corresponding to Cl–Si(CH₃)₂– head-group. According to the result of our preliminary experiment on monochlorosilyl functional PIB, dry triethylamine formed insoluble complex with TiCl₄ and Zn(CH₃)₂, and polymer purification was difficult.

Formation of Polymer Brushes by “Grafting From” Technique

Tethered PIB brush was fabricated by surface-initiated living cationic polymerization of IB. In the work described here we first synthesized self-assembled initiator monolayers, which are immobilized onto the clean surface of SiO₂ substrates as illustrated in Sch. 3. 2-6-Di-*tert*-butylpyridine was added to catalyze the condensation reaction of chlorosilyl functional initiator with surface silanol groups of silicon wafers. Our study to find the optimal deposition time revealed that 1 h was needed to obtain an equilibrium state (Table 1).

X-ray photoelectron spectra was used to confirm the covalent attachment of the chlorosilyl functional initiator. Figure 4 (e) and (f) show the XPS spectrum for the SAM on the silicon wafer and a reference spectrum of cleaned silicon wafer, respectively. A small chlorine peak at 200 eV and the increase of carbon peak at 285 eV indicate the presence of the chlorosilyl functional initiator monolayer. The ratio of carbon and chlorine peak areas is in good agreement with the molar ratio between these atoms in the chlorosilyl functional initiator monolayer.

Generally, the concentration of surface bound initiator is extremely low compared to the monomer concentration.^[23] In order to control the polymer growth from the surface bound initiators, predetermined amount of free chlorosilyl functional initiator was added to the reaction mixture. Therefore, the molecular weight of a covalently attached PIB chains and PIB layer thickness can be easily controlled by adjusting the concentration of free initiator in solution. The polymer originated from the addition of free initiator was easily separated from the covalently bound polymer brushes by washing with hexanes.



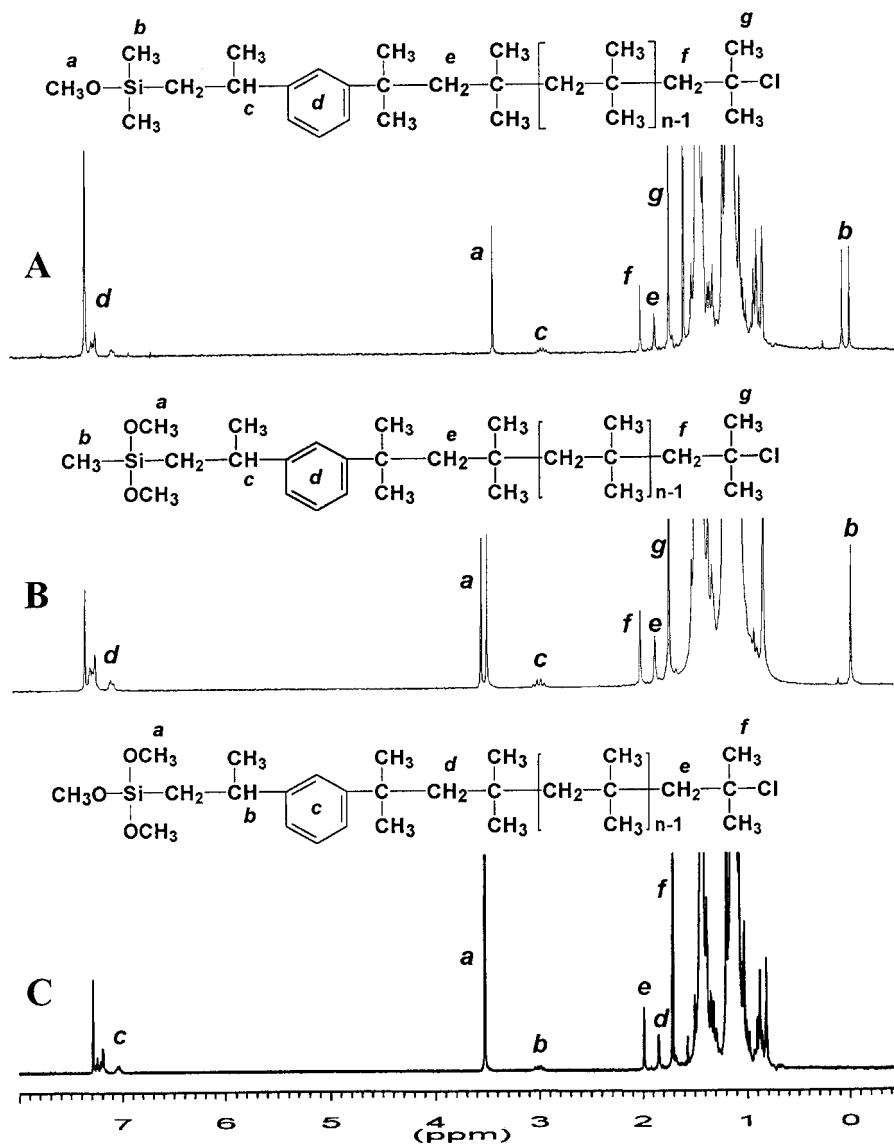
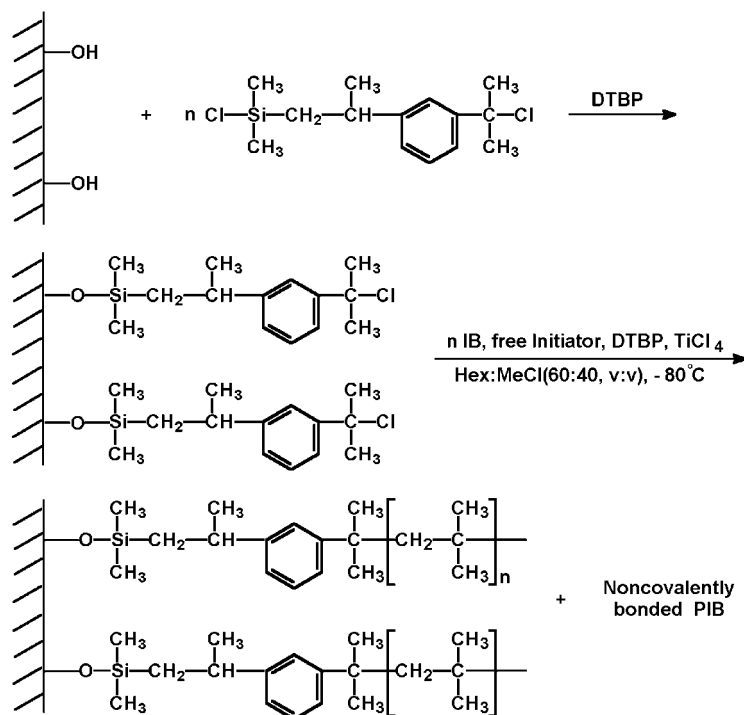


Figure 3. ¹H NMR spectra (CDCl₃) of α-methoxysilyl-, ω-chloro functional PIBs: (A) methoxy-dimethylsilyl functional PIB; (B) dimethoxymethylsilyl functional PIB; (C) trimethoxysilyl functional PIB.

Non-bonded polymer chains were removed through the continuous extraction of the silicon wafer with hexanes overnight. Figure 4 shows the XPS spectra of PIB brush formed by “grafting from” approach. As expected, the intensity of the C_{1s} binding energy at 285 eV increased and the Si_{2p} and O_{1s} peaks from the substrate decreased with increasing molecular weight of free PIB (Table 2).





Scheme 3. Synthesis of PIB brushes.

The thickness of the grafted polymer layers was determined by ellipsometry and the results are summarized in Table 3. A cross-sectional area per chain, A_x , and graft density can be determined from the film thickness, t , and the molecular weight of the chain, M , by

$$A_x = \frac{M}{t\rho N_A} \quad (1)$$

where ρ is the mass density (0.92 g/cm³ for PIB) and N_A is avagadro's number. Similarly to previous reports that the thickness of the polymer layer is a function of graft density and

Table 1. Atomic fraction on silicon substrates with monolayers of chlorosilyl functional initiator as measured by XPS.

	Silicon wafer	SAM 1 (30 min) ^a	SAM 2 (1 h) ^a	SAM 3 (3 h) ^a	SAM 4 (4 h) ^a
Si _{2p} (%)	43.3	40.1	35.4	33.8	35.2
O _{1s} (%)	44.3	42.2	37.7	35.3	37.2
C _{1s} (%)	12.4	16.7	25.6	29.6	26.3
Cl _{2p} (%)	0	1.0	1.3	1.3	1.3

^aDeposition time in hexanes at 25°C.



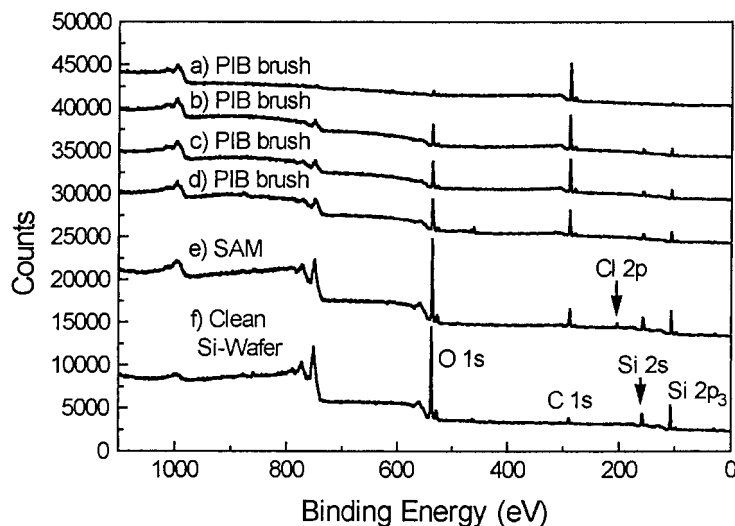


Figure 4. X-ray photoelectron spectra of (f) cleaned silicon wafer, (e) self-assembled monolayer, and tethered PIB films obtained with varying molecular weight (M_n) of “bulk” polyisobutylene by “grafting from” approach: (a) PIB brush ($M_n = 12,000$); (b) PIB brush ($M_n = 16,000$); (c) PIB brush ($M_n = 25,000$); (d) PIB brush ($M_n = 60,000$).

the molecular weight of the attached polymer chains,^[32] a linear increase in thickness with chain length (assuming that the M_n of the surface bound and bulk chains are related) was clearly observed and the graft density was high (~ 0.5 chains/nm²), and constant independent of the chain length (Table 3 and Fig. 5). These results indicate that the polymer chains are very highly stretched from the surface, which is in good accord with previous reports.^[32,33] A typical morphological characterization of PIB layer on a molecular scale is shown in Fig. 6. This topographic image shows a smooth and uniform polymer brush surface with a typical surface roughness of 1–3 nm (rms) within $3 \times 3 \mu\text{m}^2$ area. The small variation in height values on the nanometer scale confirms the assumption of a uniform reaction throughout the substrate surface and a small polydispersity, as expected from living cationic polymerization.

Table 2. X-ray photoelectron spectra analysis for determination of the atomic fraction on PIB brush formed by the “grafting from” technique.

	Silicon wafer	SAM	PIB brush ^a	PIB brush ^b	PIB brush ^c	PIB brush ^d
Si _{2p} (%)	40.3	35.4	23.0	19.8	18.5	6.3
O _{1s} (%)	50.6	37.8	27.4	19.0	16.5	5.4
C _{1s} (%)	9.1	25.6	49.6	61.2	65.0	88.3
Cl _{2p} (%)		1.2				

^{a,b,c,d}PIB brush obtained with $M_n = 12,000$, 16,000, 25,000, and 60,000 of “bulk” polyisobutylene, respectively.



Table 3. Thickness and graft density of PIB brush with molecular weight.

	"Grafting from"			
	PIB brush ^a	PIB brush ^b	PIB brush ^c	PIB brush ^d
Thickness (nm)	10.1 ± 0.3	14.9 ± 0.5	21.2 ± 0.4	50.3 ± 0.5
A_x (Å) ^c	214.4	193.8	212.8	215.3
Graft density (chains/nm ²)	0.47	0.52	0.47	0.46

^{a,b,c,d}PIB brush obtained with $M_n = 12,000, 16,000, 25,000,$ and $60,000$ of "bulk" polyisobutylene, respectively.

^cCross-sectional area per chain.

Formation of Polymer Brushes by "Grafting To" Technique

Chlorosilyl functional PIB was first synthesized via living cationic polymerization and then reacted with silanol groups on the silicon wafers. As illustrated in Fig. 7 and Table 4, XPS analysis shows that the content of carbon atom does not increase with increasing molecular weight of PIB, which means low grafting density. Since diffusion of chlorosilyl functional PIBs is hindered through the formed polymer layer to reach the reactive sites, lower grafting densities of these films are obtained. In agreement with the XPS results the thickness of the PIB brush remained approximately constant and independent of the M_n of PIB (Table 5). In contrast with the grafting from approach much higher cross-sectional area and lower graft density were achieved with increasing molecular weight of polymer chain. Figure 8 depicts a typical topographical image of the polymer layer, featuring an irregular surface morphology with 7–10 nm (rms) roughness. Several small dimples with 7–10 nm depth were observed. It is interesting to note that the surface roughness of the film is nearly same as that of the film thickness itself (4.9–7.4 nm) as measured by ellipsometry (Table 5).^[24] We speculate that the PIB chains dropped as soon as it grafted to the substrate, which prevents end-functionalized PIB from further

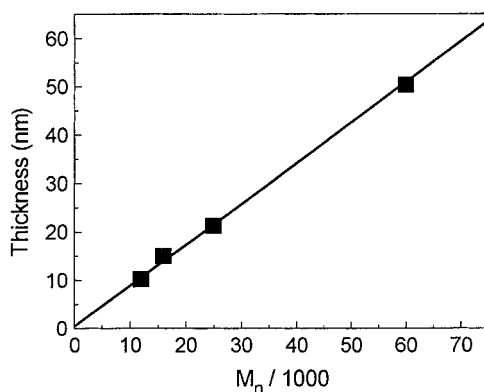


Figure 5. Variation in thickness of polymer brushes with molecular weight, M_n , of bulk polymers produced in solution.



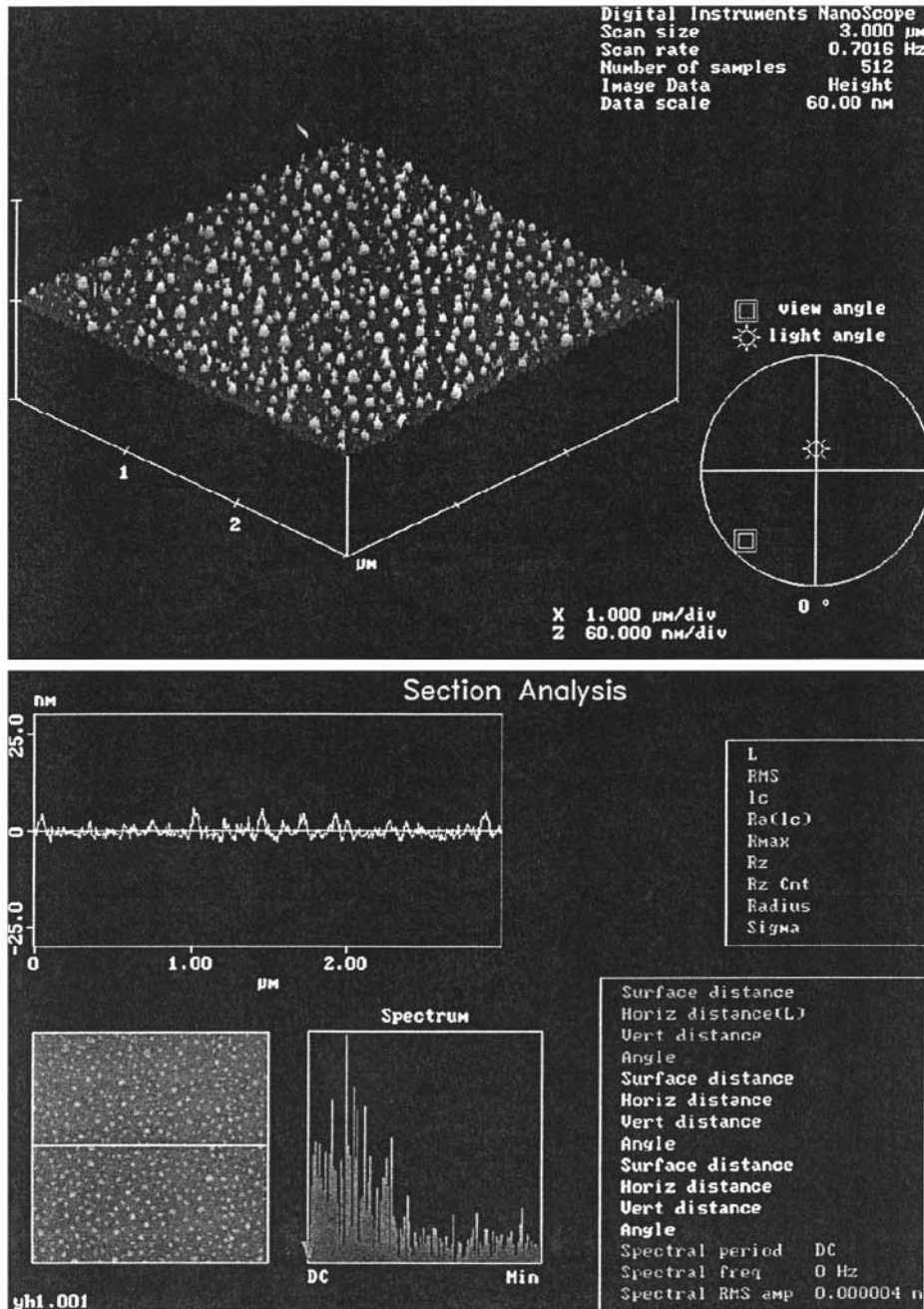


Figure 6. Atomic force microscopic image of a tethered PIB brushes with 21.2 nm thick PIB layer generated by “grafting from” approach and depth profile.



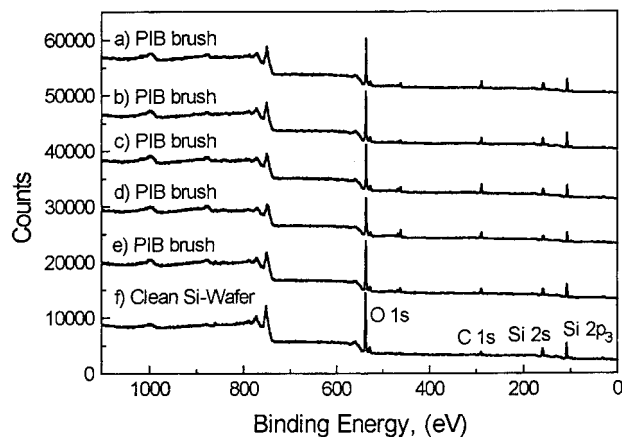


Figure 7. X-ray photoelectron spectra of (f) a cleaned silicon wafer and tethered PIB films obtained with varying molecular weight (M_n) of PIB layer by “grafting to” approach: (a) PIB brush ($M_n = 21,000$); (b) PIB brush ($M_n = 29,000$); (c) PIB brush ($M_n = 40,000$); (d) PIB brush ($M_n = 74,000$); (e) PIB brush ($M_n = 83,000$).

Table 4. X-ray photoelectron spectra analysis for determination of the atomic fraction on PIB brush prepared by the “grafting to” technique.

	PIB brush ^a	PIB brush ^b	PIB brush ^c	PIB brush ^d	PIB brush ^e
Si _{2p} (%)	37.7	31.8	33.8	38.8	35.1
O _{1s} (%)	45.6	46.5	43.4	44.5	43.4
C _{1s} (%)	16.7	21.7	22.8	16.7	21.5

^{a,b,c,d,e}PIB brush obtained with $M_n = 21,000, 29,000, 40,000, 74,000,$ and $83,000$, respectively.

Table 5. Thickness of PIB brush with molecular weight.

	“Grafting to”				
	PIB brush ^a	PIB brush ^b	PIB brush ^c	PIB brush ^d	PIB brush ^e
Thickness (nm)	5.6 ± 0.8	6.5 ± 1.2	7.4 ± 1.5	5.8 ± 1.3	4.9 ± 1.4
A_x (Å) ^f	676.7	805.1	975.5	2302.518	3056.9
Graft density (chains/nm ²)	0.15	0.12	0.10	0.04	0.03

^{a,b,c,d,e}PIB brush obtained with $M_n = 21,000, 29,000, 40,000, 74,000,$ and $83,000$, respectively.

^fCross-sectional area per chain.



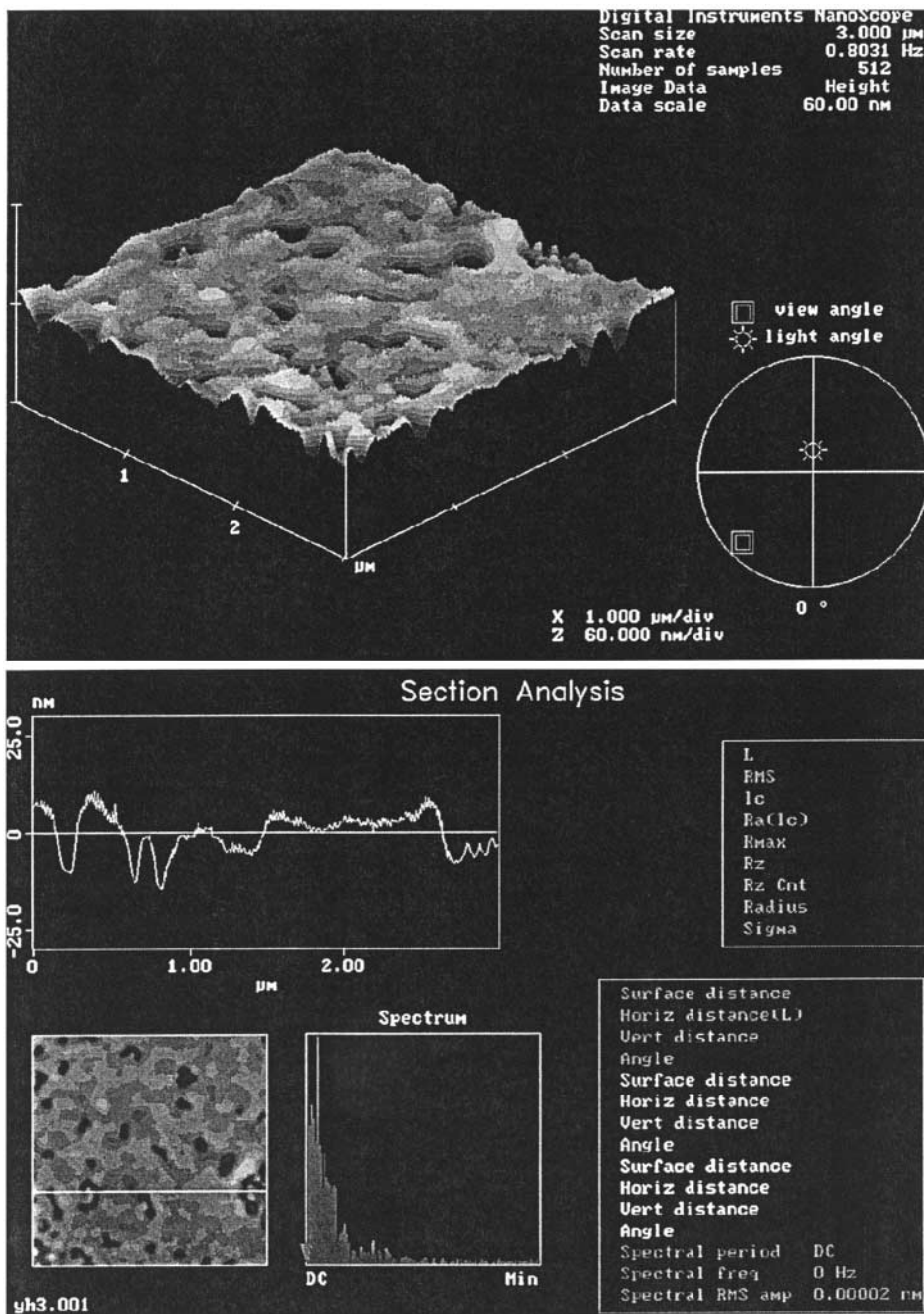


Figure 8. Atomic force microscopic image of a tethered PIB brushes with 6.5 nm thick PIB layer generated by “grafting to” approach and depth profile.





attachment to the silicate substrate surface. There is also some segregation of PIB indicating a possibility for the tethered polymer having intermediate surface density,^[18] since the morphology of the polymer layer tethered to the surface in the air is similar to that of films formed in poor solvent conditions.^[34]

CONCLUSION

Novel mono-, di-, and trichlorosilyl-functional initiators have been developed and applied for the first time in the living cationic polymerization of IB. Well-defined PIBs carrying mono-, di-, and trichlorosilyl head-group and a *tert*-chloro end-group could be readily obtained using silyl-functional initiators in conjunction with TiCl₄ in hexanes : MeCl (60 : 40, v : v) at -80°C. The identification of the product structure and the survival of the Si—Cl head-groups during the polymerization were confirmed by quantitative end-group analysis using ¹H NMR spectroscopy. Tethered PIB films on flat silicate substrates could also be prepared by living cationic polymerization both by the “grafting from” and “grafting to” techniques. Surface-initiated living cationic polymerization of IB (“grafting from” approach), however, gives PIB brushes with more uniform surface and higher grafting density compared to PIB brushes formed by the “grafting to” method. For PIB brushes formed by “grafting from” the film thickness increased linearly with increasing molecular weight of PIB, but PIB brushes produced by the “grafting to” technique gave constant thickness with increasing molecular weight of PIB. Other applications of chlorosilyl functional PIBs are in progress in our laboratories and will be reported in due time.

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