7258 *Macromolecules* **2009**, *42*, 7258–7262
DOI: 10.1021/ma901506d

Macromolecules
COMMUNICATION TO THE EDITOR

Synthesis of In-Chain-Functionalized Polystyrene-*block*-poly(dimethylsiloxane) Diblock Copolymers by Anionic Polymerization and Hydrosilylation Using Dimethyl-[4-(1-phenylvinyl)phenyl]silane

Wen-Bin Zhang,[†] Bin Sun,[‡] Hui Li,[§] Xiangkui Ren,[†] Jonathan Janoski,[†] Sujata Sahoo,[†] David E. Dabney,[⊥] Chrys Wesdemiotis,[†,⊥] Roderic P. Quirk,*[,†] and Stephen Z. D. Cheng*[,†]

[†]*College of Polymer Science and Polymer Engineering, Department of Polymer Science, the University of Akron, Akron, Ohio 44325,* [‡]*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China,* [§]*School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China, and* [⊥]*Department of Chemistry, the University of Akron, Akron, Ohio 44325*

Received July 11, 2009
Revised Manuscript Received August 29, 2009

Introduction. Block copolymers with functional groups at the junction point represent an interesting class of materials because the functional groups are confined to the interface after self-assembly,[1] giving rise to novel properties and applications.[2−6] They also serve as important intermediates in the synthesis of polymers with much more complex architectures such as the heteroarm star polymers,[7−9] H-shaped multiblock polymers,[10−13] and tadpole-shaped polymers.[14] Although many synthetic methods have been developed for this purpose, such as controlled free radical polymerization[15,16] and anionic polymerization,[17,18] the former usually requires multiple synthetic steps which compromises the yields and purity of the final polymers while the latter has a limited scope of functional groups and choice of monomers. So far, a facile, general methodology to access well-defined block copolymers armed with a variety of functional groups at the junction point remains a challenge. It is very desirable to have a well-defined, general, in-chain-functionalized parent polymer that is readily available and that can be converted to other functionalities in high yield, i.e., a general functionalization methodology.

Living anionic polymerization, particularly alkyllithium-initiated polymerizations of styrene and diene monomers, offers one of the best controls over the major variables affecting polymer properties which include molecular weight, polydispersity, copolymer composition, architecture, in-chain or chain-end functionality, microstructure, etc.[17] Polymers can be synthesized with low degrees of compositional and structural heterogeneity. One of the unique features is the ability to prepare in-chain-functionalized block copolymers.[17] The reaction of polymeric organolithium compounds with substituted 1,1-diphenylethylene derivatives is an excellent system for developing a general in-chain functionalization procedure[19,20] because these additions are simple and quantitative with only monoaddition and the product is a carbanionic species that can undergo further functionalization reactions or initiate polymerization of an additional monomer.[21−23] This versatility allows one to rationally design and place functional groups at essentially any position in a polymer molecule, such as at the initiating end,[21] within the chain,[24] at the interface between blocks,[21−23] or at the terminating end.[25,26] However, the requirement of protection and deprotection and the difficulty in the preparation and handling of substituted 1,1-diphenylethylene derivatives for each different functional group severely hinder its practical application.

The silyl−hydride bond has been found to be compatible with anionic polymerization conditions[27] and can be further converted to other functional groups by hydrosilylation with a variety of readily available substituted alkenes in high efficiency.[28] We have recently demonstrated a new general functionalization method based on the combination of living anionic polymerization and hydrosilylation (Scheme 1).[29,30] This method can be extended to the synthesis of block copolymers with in-chain functionality. In this Communication, we report on the use of dimethyl-[4-(1-phenylvinyl)phenyl]silane, a silyl-hydride-functionalized 1,1-diphenylethylene (DPE-SiH), as a versatile intermediate for the anionic synthesis of in-chain-functionalized polymers (Scheme 2).

Experimental Section. *Chemicals and Solvents*. Benzene (Certified ACS, EM Science), THF (Certified ACS, EM Science), styrene (99%, Aldrich), hexamethylcyclotrisiloxane (D_3, Aldrich, 98%), chlorodimethylsilane (Aldrich, 98%), and chlorotrimethylsilane (TMSCl, Aldrich, 99%) were purified as reported.[31] *sec*-Butyllithium (Chemetall Foote Corp., 12 wt % in cyclohexane) was used as received after double titration with allyl bromide.[32] 4-Bromodiphenylethylene (DPE-Br) was prepared by a Wittig reaction (see Supporting Information, Scheme S1). 4-Bromobenzophenone (Aldrich, 98%), methyltriphenylphosphonium bromide (Aldrich, 98%), magnesium turnings (Aldrich, 98%), PSS-allyl-heptaisobutyl substituted (Allyl-POSS, Aldrich, 96%), Karstedt's catalyst, 1,3-divinyltetramethyldisiloxane−platinum (Gelest Inc., 1.2−1.4 wt % Pt in xylene), and QuadraPure TU (400−600 μm, Aldrich), were used as received. Methanol (Fisher Scientific, reagent grade) was degassed on the vacuum line before distillation into ampules and flame-sealed. Silica gel (VWR, 230−400 mesh) was activated by heating at 140 °C for 12 h.

Preparation of Dimethyl-[4-(1-phenylvinyl)phenyl]silane (DPE-SiH) (Scheme S1). 4-Bromodiphenylethylene (DPE-Br) (20.8 g, 0.080 mol) in 300 mL of dry THF was added dropwise to a three-necked, round-bottom flask containing magnesium turnings (2.31 g, 0.096 mol) and one small iodine crystal. The mixture was heated at 70 °C for 6 h under a nitrogen atmosphere, resulting in a deep green solution. After cooling in an ice bath to ~5 °C, a solution of chlorodimethylsilane (16 mL, 15.20 g, 0.160 mol) in 50 mL of dry THF was added dropwise, and the solution color changed to light brown. After stirring at room temperature overnight, 50 mL of 5% aqueous NH_4Cl solution was slowly added to the flask via syringe, followed by dilution with water and extraction with hexane (3 × 200 mL). The organic phase was separated, washed with brine, and dried over anhydrous Na_2SO_4. After filtration and solvent removal, the residue was purified by silica gel chromatography using hexanes (R_f = 0.6) followed by fractional distillation to give pure

*To whom correspondence should be addressed. E-mail: rpquirk@uakron.edu (R.P.Q.); scheng@uakron.edu (S.Z.D.C.).

 Published on Web 09/08/2009

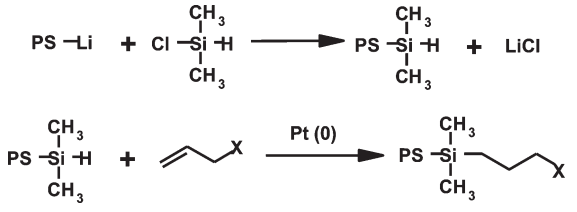
DPE-SiH as a colorless oil (13.6 g). Yield: 71%. ^{1}H NMR ($CDCl_3$, 500 Hz, ppm, δ): 7.51 (d, 2H), 7.34 (m, 7H), 5.48 (m, 2H), 4.46 (m, 1H, Si−*H*), 0.36 (d, 6H). ^{13}C NMR ($CDCl_3$, 125 Hz, ppm, δ): 149.98, 142.27, 141.36, 136.86, 133.89 (aromatic *C*−Si), 128.27, 128.15, 127.71, 127.65, 114.50 (C=*C*H$_2$), −3.77 (Si(*C*H$_3$)$_2$). FT-IR (KBr) ν (cm^{-1}): 3060, 3018, 2958, 2118 (Si−H), 1597, 1492, 1387, 1329, 1249, 1153, 1109, 1065, 1026, 880, 830, 773, 700, 664, 617, 574, 465.

Preparation of PS-(SiH)-PDMS (*Scheme 2*). The anionic polymerization was carried out in all-glass sealed reactors under high vacuum at room temperature in benzene.[33] All reagents were vacuum-distilled into calibrated ampules immediately before polymerization. The polymerization was initiated by smashing the break-seal of styrene ampule to add styrene (2.73 g, 3.0 mL) into a solution of *sec*-butyllithium (1.25 M, 1.09 mL, 1.36 mmol) in benzene (~50 mL). The mixture was stirred at room temperature for 12 h. DPE-SiH (0.42 g, 1.76 mmol) in benzene (~1.2 mL) was then added, and the solution immediately turned dark red. After stirring for 2 h, an aliquot (~5 mL) was removed by flame-sealing an ampule from the reactor and quenched with methyl iodide (~1 mL) to give PS-(SiH)-CH$_3$ (SEC: $\overline{M_n}$ = 2000, PDI = 1.02) as the base polymer sample. Ethylene oxide (0.5 mL, 10 mmol) in benzene (~5 mL) was added by breaking the corresponding ampule. The dark red color disappeared rapidly. After 20 min, an aliquot (~5 mL) was taken and quenched with methanol to give PS-(SiH)-OH (SEC: $\overline{M_n}$ = 2000, PDI = 1.02). Hexamethylcyclotrisiloxane (D_3, 3.0 g) in benzene (~5 mL) was added by smashing the break-seal for the D_3 ampule. After 0.5 h, THF (~30 mL) was added to initiate the D_3 polymerization. After 2 h, the polymerization was quenched with $(CH_3)_3SiCl$ (~1 mL). The polymer was precipitated into cold, anhydrous methanol (~500 mL). The product, PS-(SiH)-PDMS, a white solid, was filtered and dried under vacuum. The conversion was ≥99% for styrene polymerization and ~50% for D_3 polymerization. PS-(SiH)-PDMS: $\overline{M_n}$ = 3200 (^{1}H NMR), PDI = 1.03 (SEC).

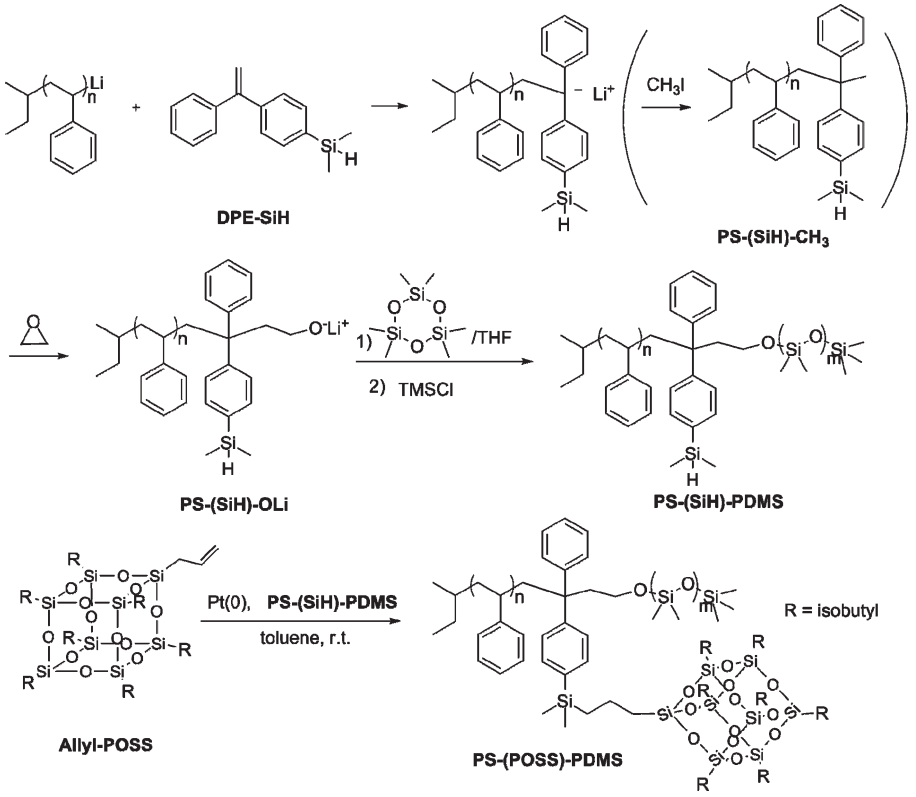
In-Chain Functionalization with Allyl-POSS (*Scheme 2*). Two drops of Karstedt's catalyst was added to a mixture of PS-(SiH)-PDMS (0.5 g, 0.14 mmol), Allyl-POSS (0.14 g, 0.16 mmol), and dry toluene (~2 mL) at room temperature. After stirring overnight, the product was precipitated into cold, anhydrous methanol (~60 mL). The solid precipitates were collected, dissolved in anhydrous toluene, and stirred with QuadraPure TU for 24 h to remove the catalyst residue. The resultant colorless solution was filtered, concentrated, and precipitated in cold, anhydrous methanol to give PS-(POSS)-PDMS as a white powder (0.41 g). Yield: 64%. $\overline{M_n}$ = 4000 (^{1}H NMR), PDI = 1.21 (SEC).

Characterization. Size exclusion chromatographic analyses (SEC) for the synthesized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/103/104 Å), mixed bed (103, 104, 106 Å)], and a triple detector system. The three detectors included a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as eluent with a flow rate of 1.0 mL/min at 30 °C. All ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ (Aldrich, 99.8% D) as solvent using a

Scheme 1. General Functionalization of Polymers via Hydrosilylation



Scheme 2. Synthesis of PS-(SiH)-PDMS and Subsequent In-Chain Functionalization by Hydrosilylation with Allyl-POSS To Form PS-(POSS)-PDMS



Varian Mercury 300 or Varian 500 NMR spectrometer. The ^{1}H NMR spectra were referenced to the residual proton impurities in the $CDCl_3$ at δ 7.27 ppm. ^{13}C NMR spectra were referenced to $^{13}CDCl_3$ at δ 77.00 ppm. Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films on KBr plates from polymer solutions with subsequent drying at 40−50 °C. The data were processed using Win-IR software. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector. Solutions of dithranol (20 mg/mL) (Alfa Aesar, 1,8,9-anthracenetriol, 97+%), polymer sample (10 mg/mL), silver trifluoroacetate (10 mg/mL) (Aldrich, 98%), or sodium iodide (10 mg/mL) (MCD, 99%) were prepared in THF (Aldrich, 99.9%). These solutions were mixed in the ratio of matrix:cationizing salt:polymer (10:1:2), and ~0.5 μL of the mixture was applied to the MALDI sample target and allowed to dry. In order to minimize polymer fragmentation, the intensity of the nitrogen laser pulses was frequently attenuated and adjusted to obtain the optimal signal intensity and minimize laser-induced fragmentation. Mass spectra were measured in the reflection mode, and the mass scale was calibrated externally using the peaks of a polystyrene standard at the molecular weight under consideration.

Results and Discussion. *Synthesis of DPE-SiH.* DPE-SiH was easily prepared from DPE-Br in good yield (Scheme S1). The synthesis has been scaled up to 24 g. Fractional distillation was necessary for the final purification because the crude product was contaminated with 1,1-diphenylethylene, which has the same chromatographic R_f as DPE-SiH. The pure product has been thoroughly characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR to confirm its structure and purity. Prior to reaction, it was further purified and ampoulized using the procedure similar to that for 1,1-diphenylethylene.[31]

Addition of Poly(styryl)lithium to DPE-SiH. The addition reaction between poly(styryl)lithium ($\overline{M}_n$ = 2000, PDI = 1.02) and DPE-SiH (1.30 equiv) in hydrocarbon solution is fast and clean, as it is with many other DPE derivatives.[19] The solution turns from orange red to dark red in seconds. The color change is due to the delocalization of charge in an additional benzene ring as compared to poly(styryl)-lithium.[19] The addition takes place much faster than that with 1,1-diphenylethylene. This is probably due to the electron-withdrawing feature of the silicon atom that activates the double bond and stabilizes the delocalized structure. The Si−H bond is stable to these organolithium compounds. To confirm this, an aliquot of the adduct solution was taken and quenched with methyl iodide to give PS-(SiH)-CH_3 as base polymer. It has been fully characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, and MALDI-TOF mass spectrometry. Figure 1 shows the ^{1}H NMR spectrum of PS-(SiH)-CH_3. The peak at δ 4.40 ppm is the characteristic resonance for the proton on silicon. In addition, as the inset shows, the integration ratio between the peaks at δ 0.70 ppm (attributed to two methyl groups from the initiator) and the peaks at δ 0.30 ppm (attributed to two methyl groups on silicon) is 6:6, confirming the desired structure. The ^{13}C NMR spectrum (Figure S1) is also consistent with the structure with the presence of the methyl groups attached to silicon at δ −3.72 ppm and the phenyl carbon attached to silicon at δ 133.71 ppm. In the FT-IR spectrum (Figure S2), a strong resonance at 2115 cm^{-1} can be clearly seen, which is characteristic of the Si−H stretching vibration.[34] The Si−CH_3 absorption bands are also observed at 1248 and 881 cm^{-1}.[34] The most convincing evidence comes from the MALDI-TOF mass spectrum which shows one major distribution with the observed molecular weight matching the calculated molecular weight of the proposed structure (Figure 2a). A representative monoisotopic mass peak at m/z 1478.0 corresponds to the 11-mer of PS-(SiH)-CH_3-Na^+, C_4H_9-$(C_8H_8)_{11}$-$C_{17}H_{21}$Si-Na^+, calculated monoisotopic mass = 1477.89 Da (Figure S3). There are two minor distributions. One of them (Figure 2b) is attributed to the oxidation of the Si−H moiety to Si−OH (i.e., with PS-(SiOH)-CH_3-Na^+ observed) which may occur during the ionization process.[29] The calculated monoisotopic mass for the 11-mer of PS-(SiOH)-CH_3-Na^+, C_4H_9-$(C_8H_8)_{11}$-$C_{17}H_{21}$SiO-Na^+, equals 1493.89 Da, which is in good agreement with the observed monoisotopic mass peak at m/z 1494.0. The other minor distribution of very small intensity with a representative monoisotopic mass peak at m/z 1566.1 is of unknown structure to us (Figure 2c).

Anionic Synthesis of PS-(SiH)-PDMS. One excellent feature of 1,1-diphenylethylene addition to poly(styryl)lithium is that the adduct is still a living carbanionic polymer that is amenable to further functionalization or block copolymerization.[19] Its reaction with ethylene oxide has been known to

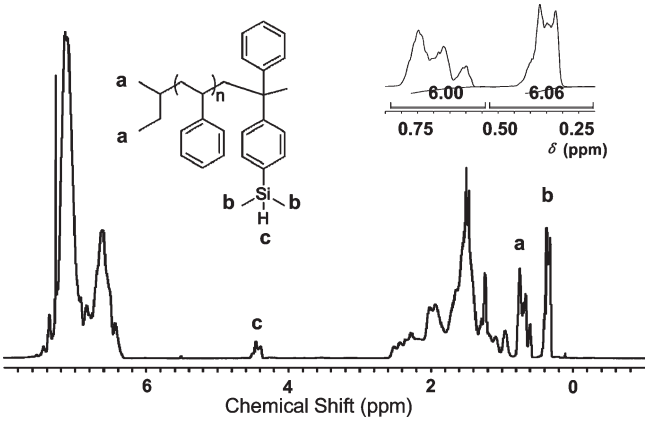


Figure 1. ^{1}H NMR spectrum of PS-(SiH)-CH_3.

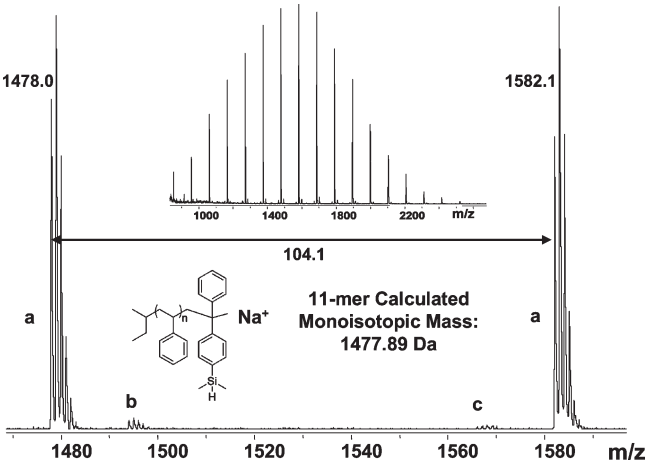


Figure 2. MALDI-TOF spectrum of PS-(SiH)-CH_3 shows three distributions: (a) major distribution corresponding to the desired structure as shown in the inset; (b) minor distribution attributable to the oxidation of Si−H bond of the product; and (c) another minor distribution with unknown structure (see text for detailed discussion).

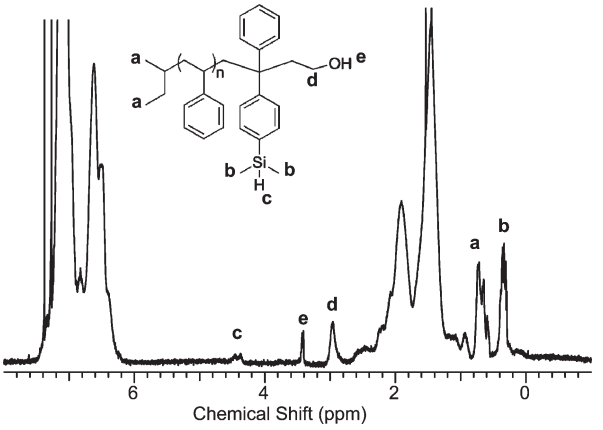


Figure 3. ^{1}H NMR spectrum of PS-(SiH)-OH.

be one of the few simple, efficient functionalization reactions that proceed smoothly in quantitative yield with only monoaddition product.[35,36] In this case, the adduct was reacted with 10 equiv of ethylene oxide. An aliquot was taken and quenched with methanol to give PS-(SiH)-OH. Indeed, the ^{1}H NMR spectrum of PS-(SiH)-OH (Figure 3) shows no oligomerization of ethylene oxide, and the ^{13}C NMR spectrum (Figure S4) shows clearly the appearance of the carbon near hydroxyl group at δ 59.60 ppm. The preservation of Si−H bond is demonstrated by both the peak at δ 4.40 ppm in the ^{1}H NMR spectrum (Figure 3) and the absorption band at 2115 cm^{-1} in the FT-IR spectrum (Figure S5). The reaction product, PS-(SiH)-OLi, was then used as a macroinitiator for synthesis of the second block, polydimethylsiloxane.

Anionic ring-opening polymerization of cyclosiloxanes has been thoroughly studied and shown to possess the features of living polymerization under certain conditions, namely, when the initiation is fast and quantitative.[37] This is usually accomplished by addition of various promoters such as THF and use of the more strained D_3 monomer. Under these conditions, the difference in rates of propagation and the undesired backbiting and chain randomization processes should be sufficient to maintain a narrow PDI. There are basically two ways to control the molecular weight of the PDMS block.[38] If the polymerization is carried out at room temperature, it has to be terminated at relatively low conversion to avoid side reactions, and the molecular weight is controlled kinetically by conversion. If the polymerization is carried out first at room temperature to ~50% conversion and then at lower temperature (e.g., −20 °C) for an extended time, it can reach complete conversion without side reactions, and the molecular weight is controlled by monomer/initiator ratio. Here, the first method was used. After D_3 was allowed to oligomerize in the presence of PS-(SiH)-OLi, THF was added to promote the polymerization.[39] The reaction was stopped after 2 h at ~50% conversion. In this way, the polydispersity of the block copolymer remained narrow (PDI = 1.03). In the SEC trace, a symmetric peak was observed at lower retention volume compared to the base polymer, PS-(SiH)-CH_3 (Figure 4), which is consistent with efficient block copolymer formation. The ^{1}H NMR spectrum (Figure 5a) confirms the presence of Si−H proton by the peak at δ 4.40 ppm. It should be noted that there is no peak around δ 3.50 ppm, indicating no ethylene oxide polymerization even with the promoter THF. The ^{13}C NMR spectrum (Figure S6a) is also in good agreement with the expected structure, evidencing the methylene carbon near oxygen (−CH_2O−) at δ 58.90 ppm, the methyl groups on the PDMS block (−OSi(CH_3)$_2$−) at δ 1.04 ppm, and the methyl

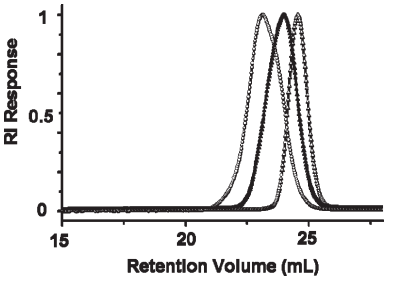


Figure 4. SEC overlay of PS-(SiH)-CH_3 (Δ, $\overline{M_n}$ = 2000, PDI = 1.02), PS-(SiH)-PDMS (▲, $\overline{M_n}$ = 3200, PDI = 1.03), and PS-(POSS)-PDMS (○, $\overline{M_n}$ = 4000, PDI = 1.21).

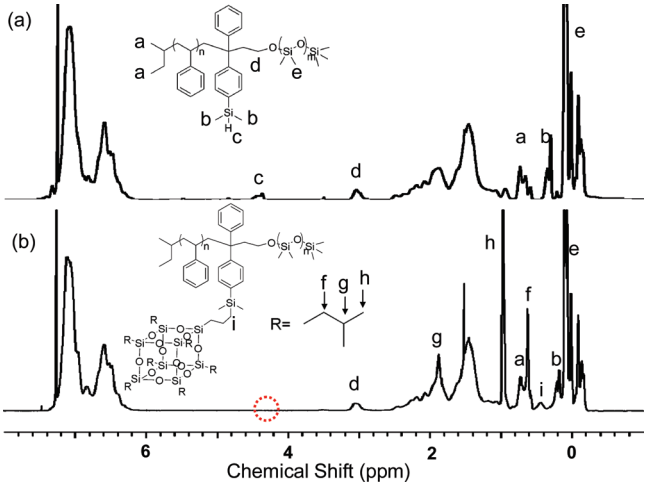


Figure 5. ^{1}H NMR spectra of (a) PS-(SiH)-PDMS and (b) PS-(POSS)-PDMS.

groups attached to silane (−SiH(CH_3)$_2$) at δ −3.77 ppm. The FT-IR spectrum (Figure S7a) showed a characteristic resonance around 2100 cm^{-1}, which also indicates that the Si−H bond is retained. The new absorption bands at 1261, 1094, 1021, and 800 cm^{-1} are characteristic of the PDMS block.[34] All of this evidence is consistent with the formation of the expected diblock copolymer.

The stability of the Si−O−C bond connecting the PS block and PDMS block toward moisture was of concern. However, SEC analysis (Figure 4) and other characterizations suggest the stability of diblock copolymers at ambient conditions, either in solution or as solids. In fact, the samples have been stored in a desiccator for months without any appreciable change in physical characterization. Therefore, the Si−O−C bonds do not hydrolyze easily, which is also consistent with literature reports on diblock copolymers with a similar connection.[39]

In-Chain Functionalization with POSS Nanoparticle. Polyhedral oligosilsequioxanes, regarded loosely as the smallest possible silica nanoparticle with diameter up to 1.5 nm including the side chains, are known for their chemical and thermal robustness and have found wide applications in coating, nanocomposites, electronic devices, and space shuttles.[40] Its incorporation in polymers can impart valuable properties such as oxidative stability and fire retardance.[40,41] Allyl-functionalized POSS (Allyl-POSS) was reacted with PS-(SiH)-PDMS using Karstedt's catalyst. The reaction proceeded efficiently and was essentially complete after overnight stirring. The product was obtained as a white powder. In the ^{1}H NMR spectrum (Figure 5b), the peak around δ 4.40 ppm completely disappeared, and characteristic

peaks attributable to the side-chain isobutyl groups of POSS (δ 1.90, 0.90, 0.60 ppm) appeared. The characteristic resonance peaks for isobutyl groups of POSS are also present in the ^{13}C NMR spectrum (Figure S6b, δ 25.70, 23.87, 22.56 ppm). The FT-IR spectrum (Figure S7b) also showed complete disappearance of the Si−H band at 2115 cm^{-1}. In the SEC trace, the peak completely shifts to a lower elution volume (Figure 4). The significant influence of the rigid POSS cage (with diameter up to 1.5 nm) to the overall hydrodynamic volume of the polymer is evidenced. The product, PS-(POSS)-PDMS, is of unique structure in that a conformationally rigid, monodisperse, inorganic nanoparticle is attached right at the junction point of two conformationally flexible, strongly segregated, organic polymers of comparable dimension. Their interaction and self-assembly in solution, bulk, and thin film are of great interest to us. We are currently working on its physics, and the details will be discussed in future publications.

Conclusions. In summary, we have successfully developed dimethyl-[4-(1-phenylvinyl)phenyl]silane, a silyl-hydride-functionalized 1,1-diphenylethylene (DPE-SiH), as a versatile intermediate for the anionic synthesis of in-chain-functionalized polymers. PS-*b*-PDMS block copolymer has been prepared possessing a reactive Si−H bond at the junction point, and it serves as a versatile parent polymer from which a large variety of in-chain-functionalized diblock copolymers can be synthesized. As an example, a polyhedral oligosilsequioxane (POSS) cage has been incorporated at the block junction by hydrosilylation to give a block copolymer with a nanoparticle tethered in between the two blocks. The polymers are stable at ambient conditions. The methodology has more implications than what is described in the paper in that the scope can be further extended to other diblock copolymer systems (e.g., PS-*b*-PMMA, PS-*b*-PLLA, etc.) accessible by anionic polymerization or a combination of anionic polymerization and other living/controlled polymerization mechanisms. It is also important in the area of understanding polymeric interfaces, as different functional groups can be incorporated which can be detected by various techniques (e.g., fluorimetry, neutron scattering, etc.).

Acknowledgment. We thank the Collaborative Center in Polymer Photonics of Air Force Research Office, the Ohio Board of Regents, and National Science Foundation (DMR-0906898, DMR-0821313, CHE-0517909, DMR-0414599, and CHE-0341701) for financial support. W.B.Z. acknowledges Lubrizol Corporation for a fellowship. We also thank FMC Corporation, Lithium Division, and Chemtall Foote Corporation for providing samples of *sec*-butyllithium and dibutylmagesium.

Supporting Information Available: Additional information on the synthesis and characterization of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Haliloglu, T.; Balaji, R.; Mattice, W. L. *Macromolecules* **1994**, *27*, 1473–1476.
(2) Goldbach, J. T.; Lavery, K. A.; Penelle, J.; Russell, T. P. *Macromolecules* **2004**, *37*, 9639–9645.
(3) Wang, X. F.; Zhang, Y. F.; Zhu, Z. Y.; Liu, S. Y. *Macromol. Rapid Commun.* **2008**, *29*, 340–346.
(4) Yang, J.; Lou, X. D.; Spiro, J. G.; Winnik, M. A. *Macromolecules* **2006**, *39*, 2405–2412.
(5) Gohy, J. F.; Lohmeijer, B. G. G.; Alexeev, A.; Wang, X. S.; Manners, I.; Winnik, M. A.; Schubert, U. S. *Chem.—Eur. J.* **2004**, *10*, 4315–4323.
(6) Saito, N.; Liu, C.; Lodge, T. P.; Hillmyer, M. A. *Macromolecules* **2008**, *41*, 8815–8822.
(7) Hadjichristidis, N.; Pispas, S.; Pitsikalis, M.; Iatrou, H.; Vlahos, C. *Adv. Polym. Sci.* **1999**, *142*, 71–127.
(8) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.
(9) Hirao, A.; Inoue, K.; Higashihara, T.; Hayashi, M. *Polym. J.* **2008**, *40*, 923–941.
(10) Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 6232–6233.
(11) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 7378–7385.
(12) Lee, C.; Gido, S. P.; Poulos, Y.; Hadjichristidis, N.; Tan, N. B.; Trevino, S. F.; Mays, J. W. *J. Chem. Phys.* **1997**, *107*, 6460–6469.
(13) Hadjichristidis, N.; Xenidou, M.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Lohse, D. J.; Schulz, D. N.; Fetters, L. J.; Wright, P. J.; Mendelson, R. A.; Garcia-Franco, C. A.; Sun, T.; Ruff, C. J. *Macromolecules* **2000**, *33*, 2424–2436.
(14) Dong, Y. Q.; Tong, Y. Y.; Dong, B. T.; Du, F. S.; Li, Z. C. *Macromolecules* **2009**, *42*, 2940–2948.
(15) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921–2990.
(16) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.
(17) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(18) Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A.; Higashihara, T. *Prog. Polym. Sci.* **2005**, *30*, 111–182.
(19) Quirk, R. P.; Yoo, T.; Lee, Y.; Kim, J.; Lee, B. *Adv. Polym. Sci.* **2000**, *153*, 67–162.
(20) Hirao, A.; Hayashi, M.; Haraguchi, N. *Macromol. Rapid Commun.* **2000**, *21*, 1171–1184.
(21) Quirk, R. P.; Zhu, L. F. *Br. Polym. J.* **1990**, *23*, 47–54.
(22) Zhao, Y. L.; Higashihara, T.; Sugiyama, K.; Hirao, A. *J. Am. Chem. Soc.* **2005**, *127*, 14158–14159.
(23) Quirk, R. P.; Kim, J.; Rodrigues, K.; Mattice, W. L. *Makromol. Chem., Macromol. Symp.* **1991**, *42*−*3*, 463–473.
(24) Quirk, R. P.; Zhu, L. F. *Polym. Int.* **1992**, *27*, 1–6.
(25) Quirk, R. P.; Zhu, L. F. *Makromol. Chem.* **1989**, *190*, 487–493.
(26) Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206–1212.
(27) Hirao, A.; Hatayama, T.; Nakahama, S. *Macromolecules* **1987**, *20*, 1505–1509.
(28) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, 1992.
(29) Quirk, R. P.; Kim, H.; Polce, M. J.; Wesdemiotis, C. *Macromolecules* **2005**, *38*, 7895–7906.
(30) Quirk, R. P.; Janoski, J.; Chowdhury, S. R.; Wesdemiotis, C.; Dabney, D. E. *Macromolecules* **2009**, *42*, 494–501.
(31) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211–3234.
(32) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447–454.
(33) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359–409.
(34) Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds*, 7th ed.; John Wiley & Sons: Hoboken, NJ, 2005.
(35) Quirk, R. P.; Ma, J. J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031–2037.
(36) Quirk, R. P.; Mathers, R. T.; Ma, J. J.; Wesdemiotis, C.; Arnould, M. A. *Macromol. Symp.* **2002**, *183*, 17–22.
(37) Jones, R. G.; Ando, W.; Chojnowski, J. *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications*; Kluwer Academic Publishers: Dordrecht, 2000.
(38) Bellas, V.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 6993–6997.
(39) Lee, J.; Hogen-Esch, T. E. *Macromolecules* **2001**, *34*, 2805–2811.
(40) Li, G. Z.; Wang, L. C.; Ni, H. L.; Pittman, C. U. *J. Inorg. Organomet. Polym.* **2001**, *11*, 123–154.
(41) Wu, J.; Mather, P. T. *Polym. Rev.* **2009**, *49*, 25–63.