Articles

Synthesis of Functionalized Polycarbosilanes via One-Pot ADMET Polymerization−Macromolecular Substitution

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ABSTRACT: Three substituted unsaturated polycarbosilanes were prepared from the same parent using a two-step, one-pot ADMET polycondensation−nucleophilic substitution route. Condensation metathesis of di(4-pentenyl)dichlorosilane using Schrock's [Mo] catalyst produces a polymer backbone containing two reactive silicon−chlorine bonds per unit. Replacement of these bonds with stable alkyl moieties was performed using an excess of alkyllithium reagent without undesirable main chain alkylation or cross-linking. Upon functionalization, moisture-stable polymers were synthesized, indicating quantitative substitution was achieved. All of the resulting polymers are amorphous, elastomeric materials. Variation of the two pendant groups from phenyl to methyl resulted in a T_g change of over 85 °C.

Introduction

Macromolecular substitution is a synthetic approach that involves the functionalization of a preformed polymer backbone containing reactive groups with an appropriate reagent.[1] Using this methodology, variation of the side chains or pendant groups can be achieved, producing a family of polymers from the same parent polymer backbone. Since polymer properties are often heavily influenced by the identity of their pendant groups, a variety of different materials with a wide range of properties and applications can be synthesized from only one antecedent (Figure 1).[1]

Often, a significant drawback of this concept is the requirement that the functionalization reaction be quantitative. This can be difficult and challenging to accomplish, due to a variety of factors. Many chemical reactions are not quantitative and produce undesirable byproducts, thus severely limiting the synthetic options available. In addition, the reactivity of functional groups on a polymer backbone is often reduced compared to small molecules due to steric hindrances limiting the accessibility of the reactive site. Consequently, it is difficult for a reagent (nucleophile) to find and react with all of the reactive sites on a coiled polymer chain.

Despite these limitations, there are several successful examples of macromolecular substitution in the literature involving polymer backbones containing highly reactive silicon−chlorine bonds. It is of critical importance that each reactive site be substituted in order to form a stable, processable polymer due to the inherent hydrolytic sensitivity of all Si−Cl bonds. Interrante and co-workers have synthesized a series of substituted silylenemethylene polymers via nucleophilic substitution of di- and monochlorosilylenemethylene polymers.[2] Several nucleophilic systems were utilized, including alcohol/amine, metal alkoxide, $BF_3 \cdot Et_2O$, $LiAlH_4$, and Grignard reagents, and efficient substitution was achieved. West and co-workers have also successfully utilized macromolecular substitution in the preparation of a series of functionalized polysilanes.[3] Quantitative substitution was achieved using a nucleophilic system composed of an alcohol in tandem with an amine proton acceptor.

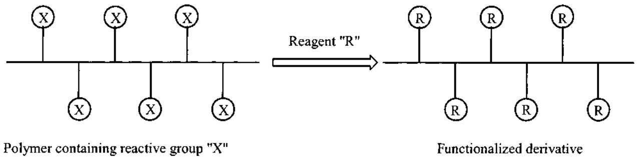

Figure 1. Macromolecular substitution of a reactive polymer backbone.

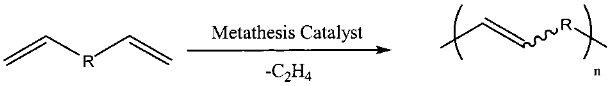

Figure 2. Acyclic diene metathesis (ADMET) polymerization.

Encouraged by these results, we decided to employ macromolecular substitution in conjunction with acyclic diene metathesis (ADMET) polymerization in the preparation of functionalized carbosilane polymers. ADMET polymerization is a true step-growth polycondensation reaction, converting an α,ω-diene to high polymer under bulk conditions, using an organometallic acid-free metathesis catalyst, with the concurrent removal of ethylene (Figure 2).[4] The ADMET route has been demonstrated to have great synthetic flexibility, and a variety of different functionalities can be incorporated into the resulting polymers.[5] Since it has been established that silicon−chlorine bonds are inert to metathesis catalysts, ADMET polymerization of an α,ω-diene containing two Si−Cl bonds produces a backbone with known micro-

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structure and reactive sites in each repeat unit.[6] Unmodified, the polymer is not very useful due to its extreme hydrolytic sensitivity, but upon substitution, a whole family of derivative polymers of increased stability, but with differing properties, can be produced.

Experimental Section

Materials. Standard glovebox and Schlenk techniques were used in the preparation of air- and moisture-sensitive compounds. 5-Bromo-1-pentene was purchased from Aldrich and stored over activated 4 Å molecular sieves. 1,2-Dibromoethane (Aldrich) was distilled from CaH_2 and stored over activated 4 Å sieves. $SiCl_4$ (Aldrich) was transferred to a dried Kontes flask via cannula and stored in an Ar atmosphere glovebox. Magnesium turnings (Aldrich) were cleaned and dried in a vacuum oven at 100 °C before use. MeLi [1.4 M in Et_2O] (Acros), PhLi [1.8 M in cyclohexanes−ether] (Aldrich), and *n*-BuLi [2.5 M in hexanes] (Aldrich) were used as received and titrated according to the method of Suffert.[7] *N*-Phenyl-1-naphthylamine was dried at 56 °C under vacuum using an Abderhalden apparatus. Diethyl ether and pentane (Fisher) were dried and distilled over NaK−benzophenone ketyl. Benzene and THF (Fisher) were dried and distilled over K−benzophenone ketyl. Heptane, *o*-xylene (Aldrich), and toluene (Fisher) were dried by distillation over Na−benzophenone ketyl. Chloroform and CH_2Cl_2 (Fisher) were dried by distillation over P_2O_5. Methanol (Fisher) was dried by distillation over Mg/I_2 and stored over 3 Å sieves. Deuterated solvents (without TMS), C_6D_6 and $CDCl_3$ (CIL), without TMS were dried by distillation over CaH_2. Schrock's [Mo] catalyst **1**, $[Mo{=}CHCMe_2Ph({=}N{-}C_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)(OCMe(CF_3)_2)_2]$, was prepared using a literature procedure.[8]

Instrumentation. All NMR spectra, ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (60 MHz), were conducted on either a Varian VXR, Gemini, or Mercury series superconducting spectrometer system and referenced to residual C_6H_6 or $CHCl_3$ solvent signals. For the ^{29}Si NMR spectra, a heteronuclear gated decoupling pulse sequence with a pulse delay of 30 s was used, with a 1% internal TMS reference added. Gas chromatography was performed on a Shimadzu GC-17A gas chromatograph equipped with a 15 m Restek RTX-5 cross-bonded 5% diphenyl−95% dimethylsiloxane column using He as the carrier gas and a FID detector. Gel permeation chromatography was performed using two 300 mm Polymer Laboratories gel 5 μm mixed-C columns. The GPC instrument consisted of a Rainin SD-300 pump, a Hewlett-Packard 1047-A RI detector, a Kratos Spectroflow 757 UV detector (254 nm), a TC-45 Eppendorf column heater set to 30 °C, and a Waters U6K injector. The solvent used was $CHCl_3$ at a flow rate of 1.0 mL/min, and the peaks were referenced to narrow polydispersity polystyrene standards from Polymer Laboratories (Amherst, MA). Differential scanning calorimetry measurements were taken using a Perkin-Elmer DSC 7 instrument equipped with TAC 7/DX controller and a CCA7 cooling accessory. The samples were scanned from −95 to 75 °C at a heating rate of 10 °C/min after annealing the samples to destroy any thermal history. Liquid N_2 was used as the coolant. Spinning band distillation was performed using a B&R Instruments model 8T regulated with a dibutylphthlate-filled manostat. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

Synthesis of Di(4-pentenyl)dichlorosilane (2). A 500 mL three-necked flask equipped with an addition funnel, a condenser, and a Teflon stirbar was flame-dried under vacuum. The apparatus was then flushed with Ar, and 4.9 g of Mg turnings (0.20 mol) was weighed and added to the flask. Freshly distilled dry diethyl ether (175 mL) was added to the flask via a cannula, followed by the addition of 0.2 mL of 1,2-dibromoethane. Bubbling ensued, and the gray mixture was stirred at room temperature for 1 h. 5-Bromo-1-pentene (25.3 g, 0.17 mol) was added dropwise via an addition funnel over 2 h. The reagent was refluxed overnight, followed by removal of insoluble material by filter cannulation into a 250 mL volumetric flask fitted with an air-free adapter. This gray solution was filled to the volume mark with additional dry diethyl ether via a cannula. The 4-pentenylmagnesium bromide formed was titrated by the method described in ref 9 (0.14 mol, 82.4%). Following titration, a 1000 mL three-neck, round-bottom flask equipped with a condenser, an addition funnel, and a stir bar was flame-dried under vacuum. After purging the flask with Ar, 500 mL of dry heptane was added via a cannula. $SiCl_4$ (11.4 g, 0.063 mol) was diluted with 10 mL of dry heptane in a separate 25 mL pear-shaped flask and added to the round-bottom flask via a cannula. The Grignard solution was transferred to an addition funnel via a cannula and added dropwise over 2 h. The solution was refluxed overnight, forming a white precipitate. The product was separated from magnesium salts by filter cannulation into a 1000 mL Schlenk flask; the residual salts were washed with 3 × 100 mL portions of pentane, and all organic solutions were combined. All solvent was removed in vacuo, giving a crude yellow liquid product. The product, a clear, colorless liquid, was purified by vacuum spinning band distillation. Boiling point: 90−92 °C (4 mmHg), % yield (GC): 71%, isolated: 8.8 g, 38%. ^{1}H NMR (δ, $CDCl_3$): 1.10 (Si−CH_2) (m, 4H), 1.59 (CH_2) (m, 4H), 2.10 (CH_2CH) (m, 4H), 4.98 (CH_2CH) (m, 2H), 5.74 (*CH*CH_2) (m, 2H). ^{13}C NMR (δ, $CDCl_3$): 19.7 (Si−CH_2), 21.7 (CH_2), 36.2 (CH_2CH), 115.5 (CHCH_2), 137.7 (*CH*CH_2). ^{29}Si NMR (δ, C_6D_6): 33.3 (R_2SiCl_2). Elemental Anal. for $C_{10}H_{18}SiCl_2$: Calcd (Found): C, 50.84 (50.79); H, 7.68 (7.78).

Synthesis of Poly(1,1-dichloro-1-silanon-5-ene) (3). A 25 mL round-bottom flask containing a Teflon stirbar and equipped with an air-free Schlenk adapter was taken into an inert atmosphere glovebox, and 0.72 g (0.0030 mol) of di(4-pentenyl)dichlorosilane was added. Schrock's catalyst **1** was added (4.8 mg, 6.3×10^{-6} mol) in a monomer-to-catalyst ratio of 500:1 (0.2%) to the liquid monomer; the evolution of ethylene was immediate and vigorous. The flask was closed, taken out of the glovebox, and connected to a high-vacuum line and stirred with intermittent vacuum applied. Bubbling due to the evolution of ethylene continued, and after 5 h, stirring was hindered considerably due to increased solution viscosity. The flask was then subjected to dynamic vacuum (1×10^{-4} mmHg), the temperature was increased to 40 °C, and the contents of the flask were stirred slowly for 48 h. After this time period, stirring ceased, and the polymerization procedure was stopped by exposure of the flask contents to air that was carefully dried by passing through a drierite/molecular sieve column. The flask was taken into the glovebox due to the high hydrolytic sensitivity of the polymer. The resulting dichlorocarbosilane polymer was soluble in hydrocarbon solvents such as toluene and benzene but insoluble in more polar media such as $CHCl_3$ and THF. The polymer was used for further functionalization without any additional purification. Using spectroscopy, only linear polymer and no cyclic byproducts were observed. ^{1}H NMR (δ, C_6D_6): 0.90 ($SiCH_2$) (br, 4H), 1.45 (CH_2) (br, 4H), 1.90 (CH_2CH) (br, 4H), 5.40 (CH) (br, 2H). ^{13}C NMR (δ, C_6D_6): 20.0 ($SiCH_2$), 22.6 (CH_2), 35.3 (CH_2CH), 130.6 (CH). ^{29}Si NMR (δ, C_6D_6): 33.5 (R_2SiCl_2). Elemental Anal. for $C_{10}H_{18}SiCl_2$: Calcd (Found): C, 46.15 (45.64); H, 6.78 (6.65); Cl, (33.62) 27.28.

Synthesis of Poly(1,1-dimethyl-1-silanon-5-ene) (4). Di(4-pentenyl)dichlorosilane (0.56 g, 0.0024 mol) was polymerized in a 25 mL flask using 350:1 monomer:catalyst ratio of [Mo] catalyst **1** under typical ADMET conditions. After backfilling the flask with Ar, the polymer was dissolved in 15 mL of dry benzene and chilled to 0 °C using an ice bath. A 2-fold excess of 1.4 M MeLi per Si−Cl bond was added (5.8 mL, 0.0093 mol) via a syringe dropwise over 15 min. White LiCl salts precipitated out of solution as the alkyllithium reagent was added. The contents of the flask were stirred overnight under Ar and slowly allowed to warm to room temperature (RT). The reaction mixture was then transferred via a cannula needle into a Schlenk flask containing 200 mL of cold, dry MeOH. The alkyllithium solution color disappeared, all LiCl salts dissolved, and a tacky white polymer precipitated from solution. All solvents were then removed via a cannula, and the resulting off-white polymer was dried for 24 h in vacuo at RT. Yield after precipitation: 0.31 g, 78%. ^{1}H NMR (δ, $CDCl_3$): −0.08 ($SiCH_3$) (s, 6H), 0.46 (CH_2) (br, 4H), 1.31 (CH_2) (br, 4H), 1.97 (CH_2CH) (br, 4H), 5.36 (CH) (br, 2H). ^{13}C NMR (δ, $CDCl_3$):

−3.4 ($SiCH_3$), 14.9 ($Si{-}CH_2$), 24.1, 36.6 (CH_2), 130.5 (CH). ^{29}Si NMR (δ, C_6D_6): 2.3 (R_4Si). Elemental Anal. for $C_{10}H_{20}Si$: Calcd (Found): C, 71.37 (71.43); H, 11.99 (11.89); Cl, 0.0 (0.0).

Synthesis of Poly(1,1-diphenyl-1-silanon-5-ene) (5). Di(4-pentenyl)dichlorosilane (0.72 g, 0.0030 mol) was polymerized using **1** in an identical fashion as discussed above in the preparation of **3**. Once the polymerization was complete, the flask was removed from the vacuum line and filled with Ar. The polymer was dissolved in carefully dried benzene (15 mL) added via a cannula. The polymer solution was cooled to 0 °C using an ice bath. An excess of 1.8 M PhLi, 2 equiv per Si−Cl bond (6.7 mL, 0.012 mol), was added via syringe dropwise over 15 min. A white precipitate appeared immediately upon addition. The flask was allowed to slowly warm to room temperature overnight while maintaining stirring under an Ar atmosphere. To ensure that all Si−Cl bonds were reacted, 1.4 M MeLi (5.0 mL, 0.0070 mol) was added to the flask via a syringe slowly (1.1 equiv per Si−Cl bond) at RT and stirred for 24 h under Ar. The reaction mixture maintained a reddish-brown color. Using a cannula, the polymer solution was then added to 200 mL of cold, dry, freshly distilled MeOH. Upon addition, the reaction mixture turned clear, and an off-white polymer precipitated out of solution. The liquids were removed by cannula filtration, and the polymer was allowed to dry in vacuo at RT for 24 h. Yield after precipitation: 0.55 g, 63%. ^1H NMR (δ, $CDCl_3$): 1.04 ($SiCH_2$) (br, 4H), 1.36 (CH_2) (br, 4H), 1.97 (CH_2CH) (br, 4H), 5.28 (CH) (br, 2H). ^{13}C NMR (δ, $CDCl_3$): 12.1 ($SiCH_2$), 23.7 (CH_2), 36.5 ($CHCH_2$), 130.4 (CH), 127.7, 129.0, 134.8, 136.3 (aromatic C). ^{29}Si NMR (δ, C_6D_6): −6.6 (R_2SiPh_2). Elemental Anal. for $C_{20}H_{24}Si$: Calcd (Found): C, 82.15 (80.56); H, 8.28 (8.19); Cl, 0.0 (trace).

Synthesis of Poly(1,1-di-*n*-butyl-1-silanon-5-ene) (6). The synthesis of this polymer was accomplished using an analogous procedure to polymer **5**. Di(4-pentenyl)dichlorosilane (0.72 g, 0.0030 mol) was polymerized using 4.6 mg of catalyst **1**. The polymer was dissolved in dry benzene, and 7.5 mL (0.012 mol) of *n*-BuLi was added, followed by 5.5 mL (0.0080 mol) of MeLi. Identical polymer workup procedures were performed. Yield: 0.79 g, 90%. ^1H NMR (δ, $CDCl_3$): −0.10 ($SiCH_3$) (s, 3H), 0.50 (br, 6H), 0.86 (CH_3) (br, 3H), 1.26 (CH_2) (br, 8H), 1.98 (CH_2CH) (br, 4H), 5.36 (CH) (br, 2H). ^{13}C NMR (δ, $CDCl_3$): −5.1 ($SiCH_3$), 12.1, 13.5 ($SiCH_2$), 13.9 (CH_3), 24.1, 26.2, 26.9, 36.8 (CH_2), 130.5 (CH). ^{29}Si NMR (δ, C_6D_6): 3.0, 3.1 (R_4Si). Elemental Anal. for $C_{13}H_{26}Si$: Calcd (Found): C, 74.22 (74.69); H, 12.47 (12.55); Cl, 0.0 (0.0).

Results and Discussion

All of the polymers synthesized in this work were derivatives of the same carbosilane backbone produced by the ADMET polymerization of a dichlorosilyl-containing α,ω-diene. The parent diene chosen in this study, di(4-pentenyl)dichlorosilane, undergoes condensation metathesis readily using standard procedures for ADMET polymerization.[10] Since Schrock's molybdenum catalyst has been demonstrated previously to efficiently polymerize similar dienes without affecting the silicon−chlorine bonds present, it was employed as the catalyst.[6] Because of the air-sensitive nature of the catalyst, the diene monomer was carefully degassed using three freeze−pump−thaw cycles and stored in an inert atmosphere glovebox. In a reaction flask containing di(4-pentenyl)dichlorosilane (**2**) and a Teflon stirbar, Schrock's [Mo] catalyst **1** was added to effect a monomer-to-catalyst ratio of 350−500:1 (0.3−0.2% catalyst) (Figure 3). Immediately upon mixing catalyst and monomer, bubbling (ethylene evolution) occurred. The flask was promptly sealed and attached to a high-vacuum line, and the reaction mixture was stirred at room temperature under intermittent vacuum. After a few hours, stirring was hindered due to the formation of higher molecular weight product and its increased solution viscosity. The reaction flask was immersed in a 40 °C oil bath, enabling stirring to continue and full dynamic vacuum (1×10^{-4} mmHg) was applied. Slow bubbling of the reaction mixture continued, progressively forming a viscous, oily polymer product. After 48 h, stirring ceased due to the increased solution viscosity, and the polymerization was terminated by exposure of the flask contents to dried air.

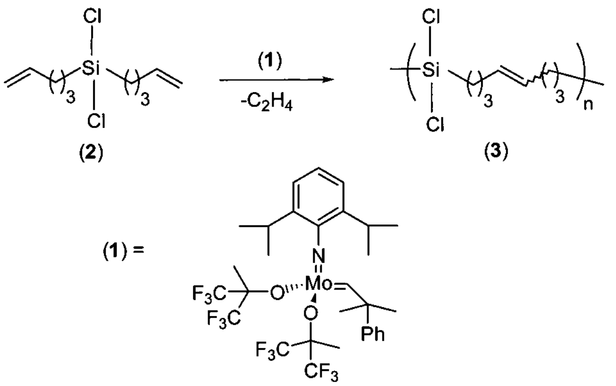

Figure 3. ADMET polymerization of di(4-pentenyl)dichlorosilane.

It was discovered that only low molecular weight oligomers were soluble in polar solvents such as $CHCl_3$ and THF. However, the polymer was quite soluble in aromatic hydrocarbon solvents such as benzene and toluene. NMR spectroscopy was utilized to confirm that high molecular weight polymer was produced by the appearance of internal olefin resonances at 5.4 ppm and the near disappearance of terminal olefin peaks at 5.8 and 5.0 ppm. No side reactions or evidence of cyclic byproducts were detected in the ^1H or ^{13}C NMR spectra, typical of ADMET polycondensation.[4,6,10] Since this polymer is extremely moisture sensitive due to the presence of two hydrolytically sensitive groups on each repeat unit, both careful technique and rigorously dried glassware/solvents must be utilized to prevent unintentional cross-linking.[11] Molecular weight determination using GPC was unable to be performed because the Si−Cl bonds on the polymer hydrolyze rapidly when exposed to the level of moisture present in chromatographic solvents. End group analysis using integration of the ^1H NMR resonance signals was not able to accurately determine the molecular weight either, as [Mo] catalyst residue peaks were present in the same region of the vinylic end group resonances, preventing precise integration. Regardless, after conversion of all the Si−Cl bonds to more stable moieties, molecular weight data can be obtained. DSC thermal analysis of this parent polymer revealed a T_g at −57 °C and no discernible T_m, indicative of an amorphous elastomer.

After the physical properties of the parent dichlorocarbosilane polymer had been elucidated, it was functionalized with several different alkyl groups via nucleophilic substitution reactions using alkyllithium reagents (Figure 4).

Several important factors outline the rationale behind the choice of reagent utilized. Since the parent polymer has solubility in nonpolar aromatic solvents, which are compatible and miscible with most alkyllithiums, they are an ideal reagent for this medium. Since alkyllithium reagents are strong and efficient nucleophiles, they react with silicon−chlorine bonds in high conversion.[12] An additional advantage of utilizing carbanion nucleophiles lies in the stability of the resulting bonds formed.

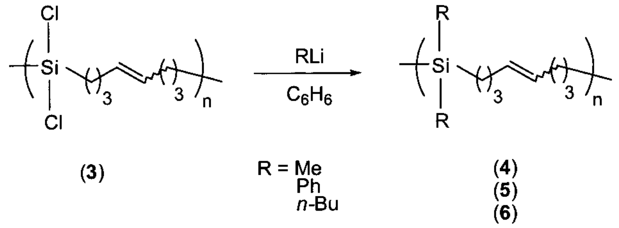

Figure 4. Macromolecular substitution of reactive ADMET polymer **3**.

Silicon−carbon bonds are similar in bond strength to carbon−carbon bonds and, most importantly, are stable to hydrolysis.[13] After replacement of all of the silicon−chlorine bonds present, the polymer will be stable and can be exposed to the atmosphere without significant degradation.

The first reagent utilized for macromolecular substitution reactions was methyllithium. A 0.5 g sample of poly(1,1-dichloro-1-silanon-5-ene), prepared using typical ADMET polymerization techniques, was dissolved in freshly distilled, rigorously dried benzene in an Ar-purged and dried Schlenk flask. The polymer solution was cooled to 0 °C in an ice bath, and a 4-fold excess of 1.8 M MeLi in cyclohexanes−ether (2 equiv per Si−Cl bond) was added dropwise over 15 min using a gastight syringe. A cloudy white precipitate of LiCl formed immediately upon addition of MeLi, indicating that substitution of the Si−Cl bonds was occurring. Under a continuous Ar stream, the reaction mixture was allowed to warm slowly to ambient temperature and stirred overnight. After no additional precipitate formation was observed, the polymer solution was cannulated into an excess volume of rigorously dried, chilled MeOH, precipitating out a clear, viscous, oily material. This enabled the excess MeLi to be destroyed by the protic nonsolvent as well as dissolving all of the LiCl precipitate. The solvents were removed via filter cannulation, and the product, poly(1,1-dimethyl-1-silanon-5-ene), was then dried in vacuo at room temperature.

The alkylated derivative polymer was readily soluble in $CHCl_3$, and no gel formation was observed. When the polymer was exposed to atmospheric moisture, it remained soluble without gelation or cross-linking observed. This evidence strongly supports the assumption that quantitative substitution of all silicon−chlorine bonds occurred, since any residual Si−Cl bonds will hydrolyze rapidly, producing stable siloxane bonds and creating a cross-linked polymer. An insoluble network will form with less than 1% cross-links present.[14] Since this did not occur, all of the chlorine atoms have been replaced with methyl groups. This was confirmed by NMR spectroscopic evidence, and the elemental analysis of the polymer found no chlorine content. The ^{29}Si NMR spectrum illustrated only one peak at 2.3 ppm, indicative of a silicon atom bonded to four alkyl groups, and the signal at 33 ppm from the parent dichlorocarbosilane polymer disappeared. The ^{1}H and ^{13}C NMR spectra illustrated that no side-reactions, cross-linking, or alkylation of the polymer backbone occurred during the nucleophilic substitution reaction. Vinyl end groups were almost completely obscured in the ^{1}H NMR spectrum, evidence of the formation of a moderately high molecular weight polymer (Figure 5). Quantitative ^{13}C NMR spectroscopy indicated a ~80% trans olefin content, which is typical for ADMET polymers. Since polymer **4** contained no residual Si−Cl bonds, molecular weight determination was easily accomplished by GPC. The number-average molecular weight (M_n) was determined to be 16 000 g/mol with a polydispersity index of 2.1, typical of condensation polymers.[15] DSC thermal analysis was also performed, indicating a T_g of −89 °C, and no T_m was observed. This is a consequence of a high degree of chain flexibility in the polymer backbone combined with small pendant groups.

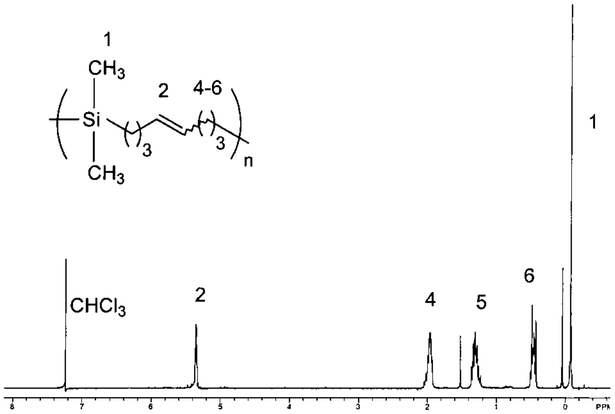

Figure 5. 300 MHz ^{1}H NMR spectrum of poly(1,1-dimethyl-1-silanon-5-ene).

The next reagent utilized for macromolecular substitution reactions was phenyllithium. Substituted polycarbosilane **5** containing two phenyl groups per repeat unit was synthesized using analogous methodology to polymer **4**. Two equivalents of phenyllithium per Si−Cl bond was added in a fashion similar to that discussed above, and after stirring overnight under Ar, 1 equiv of methyllithium per Si−Cl bond was added to the reaction mixture. This was to ensure that any residual Si−Cl bonds remaining on the polymer backbone would be substituted, since MeLi is a sterically unencumbered nucleophile, and it was previously shown to promote quantitative substitution under identical reaction conditions. The tacky, elastomeric polymer was readily soluble in $CHCl_3$ and did not show any evidence of cross-linking upon exposure to atmospheric moisture, indicating complete substitution of the Si−Cl bonds occurred. Using GPC analysis, the number-average molecular weight was determined to be 22 000 g/mol with a polydispersity index of 2.0, typical of condensation polymers. DSC analysis of the polymer indicated no observable melting point and a T_g of −2 °C, which is significantly higher than that observed for the dimethyl functionalized carbosilane polymer. Since the backbone of **5** is identical to **4**, this observation is due to the presence of two bulky and rigid phenyl substituents on the silicon atom. This is dramatic evidence for the effect that the substituents have on the physical properties of the polymer. NMR spectroscopy was used to confirm the polymer structure and quantify the percentage of phenyl and methyl groups in the polymer. No resonance peaks from Si−CH_3 groups were observed in either the ^{1}H or ^{13}C NMR spectra. The ^{29}Si NMR spectrum illustrated only one peak at 6.6 ppm, representative of a silicon atom bound to two alkyl and two phenyl groups.[13] Consequently, it can be concluded that the phenyllithium substitution was quantitative, and no methyl−phenyl exchange transpired on the silicon atom. The ^{13}C NMR spectrum of the phenyl-substituted derivative polymer is illustrated in Figure 6, showing typical 80% trans-olefin stereochemistry, and confirms that the polymer has a well-defined microstructure and

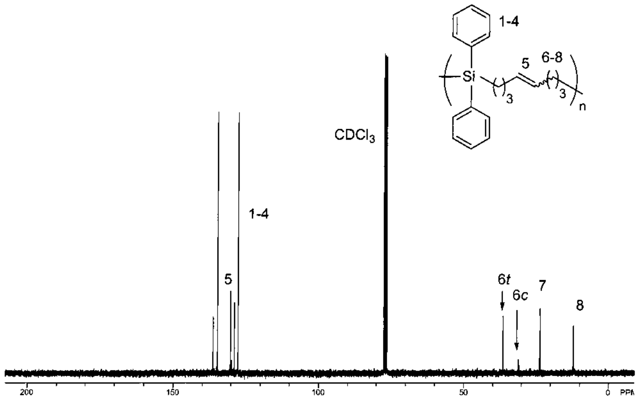

Figure 6. 75 MHz ^{13}C NMR spectrum of poly(1,1-diphenyl-1-silanon-5-ene).

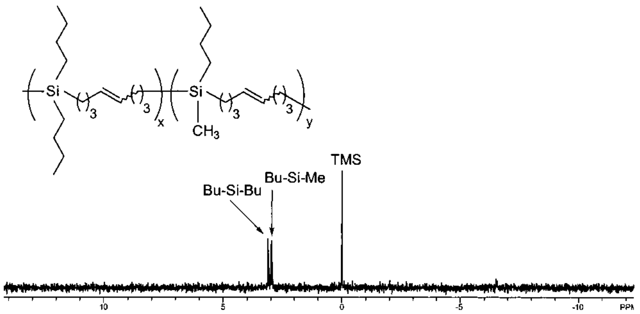

Figure 7. 60 MHz ^{29}Si NMR spectrum of hybrid butyl/methyl-substituted polymer **6**.

that no side reactions such as main chain alkylation, observed by Interrante while substituting silylene-methylene polymers, occurred.[2]

The third polymer produced in this series was functionalized using *n*-butyllithium. The parent polymer **3** was again synthesized using Schrock's [Mo] catalyst **1** utilizing typical ADMET methodology. The functionalization reaction was performed under conditions identical for polymer **5**. After drying in vacuo, the resulting polymer was a clear, viscous oily liquid that is readily soluble in $CHCl_3$. Using NMR spectroscopy, it was determined that butyl group substitution was not quantitative in this reaction. It is possible that this reduced efficiency is due to anionic aggregration of the nucleophilic sites, which are often observed in nonpolar hydrocarbon environments.[12] Evidence of methyl group incorporation on the polymer was observed in both the ^{1}H and ^{13}C NMR spectra. The peaks at −0.10 ppm in ^{1}H NMR and at −5.1 ppm in the ^{13}C NMR are clearly indicative of $Si-CH_3$ groups. The determination of methyl incorporation was accomplished using peak integration, indicating 18% methyl groups present on the polymer. There are three possibilities for the substitution pattern: butyl−Si−butyl, butyl−Si−methyl, and methyl−Si−methyl. Figure 7 illustrates the ^{29}Si NMR spectrum of the hybrid butyl/methyl carbosilane polymer, clearly showing only two Si peaks at 3.0 and 3.1 ppm. Since there are only two types of silicon environments present, one of the three possibilities outlined above did not occur. The silicon on the dimethyl functionalized carbosilane resonates at 2.3 ppm in the ^{29}Si NMR, whereas both peaks present for the butyl polymer were downfield, thereby ruling out the dimethyl possibility.

The butyl/methyl functionalized polycarbosilane was also stable in the atmosphere, allowing molecular weight determination by GPC analysis. Using this technique, the M_n of polymer **6** was determined to be 12 000 g/mol with a polydispersity index of 2.2. Thermal analysis of this amorphous elastomer illustrated a low T_g of −75 °C with no observed T_m. The low T_g is attributed to the both flexibility of the butyl side groups and the resulting irregular polymer structure.

Table 1. Properties of Alkyl Functionalized Polycarbosilanes

carbosilane polymer	T_g(°C)	M_n (g/mol)[a]	M_w/M_n[a]
3	−57	*b*	*b*
4	−89	16 000	2.1
5	−2	22 000	2.0
6	−75	12 000	2.2

[a] Determined by GPC referenced to narrow polydispersity PS standards. [b] GPC unable to be determined due to hydrolytic sensitivity.

We have demonstrated in this work that the glass transition temperature can be varied by over 85 °C on the same polymer backbone by simple variation of the pendant group (Table 1). Although the molecular weights of this series of polymers are not identical, this is not a result of pendant group variation. Each macromolecular substitution reaction was performed on a different batch of poly(1,1-dichloro-1-silanon-5-ene). Therefore, the molecular weight discrepancies observed are attributed to variations of experimental conditions during each polymerization of the parent polymer, particularly the difficulty of stirring the polymer as its molecular weight (and viscosity) increases.

Conclusions

Three functionalized polycarbosilanes were produced by macromolecular substitution of the same parent dichlorocarbosilane polymer synthesized by ADMET polycondensation. These alkylated polymers are tacky, elastic materials that are stable when exposed to the atmosphere, indicating that complete replacement of hydrolytically sensitive silicon−chlorine bonds with stable silicon−carbon bonds occurred. In reactions using phenyllithium or methyllithium, backbone substitution of the polymers proved to be quantitative, whereas *n*-butyllithium was unable to affect complete substitution; hence, exhaustive substitution with added methyllithium was required.

Since main chain proton abstraction was not observed during the substitution reactions when exposed to strong bases such as alkyllithium reagents, considerable flexibility in the choice of substitution reagent is permitted. This unlocks the potential to prepare a series of stable polymers with a wide range of properties. We are continuing our investigation into the synthesis of functionalized polycarbosilanes with the incorporation of new pendant groups.

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