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Synthesis and chemical modification of poly(divinylsiloxane)

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Abstract

Hexavinylcyclotrisiloxane(I) has been prepared by reaction of divinyldichlorosilane with DMSO and triethylamine. Anionic ring-opening polymerization (AROP) of I catalyzed by dilithio diphenylsilanediolate yields high molecular weight poly(divinylsiloxane)(II) with a narrow molecular weight distribution. Similarly, narrow molecular weight distribution poly(vinylmethylsiloxane)(III) has been prepared by AROP of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane(IV) initiated by dilithio diphenylsilanediolate. On the other hand, III which has a broad molecular weight distribution has been synthesized by AROP of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane(V) catalyzed by phosphazene P_4-*t*-Bu superbase. Chemical modification of the C–C double bonds of II and III has been achieved by Pt-catalyzed hydrosilylation with 3,3,3-trifluoropropyldimethylsilane(VI) or 1H,1H,2H,2H-perfluorooctyldimethylsilane(VII). While Pt-catalyzed hydrosilylation reactions usually proceed in a regioselective anti-Markovnikov manner, Markovnikov addition is competitive in these examples.

Keywords: Poly(divinylsiloxane); Hydrosilylation; Poly[bis(1H,1H,2H,2H-perfluoroalkyl)siloxanes]

1. Introduction

Poly(dialkylsiloxane)s are of interest [1,2]. Numerous poly(disubstituted phosphazene)s have been prepared by chemical modification of poly(dichloro-phosphazene) (see Fig. 1) [3,4]. Analogous reactions to prepare poly(disubstituted siloxane)s are not possible since poly(dichlorosiloxane) is unknown. While, chemical modification of commercially available poly(methylsiloxane) by Pt-catalyzed hydrosilylation reactions with functionally substituted terminal alkenes permits the synthesis of poly(substituted alkyl methylsiloxane)s (see Fig. 2) [5,6], poly[bis-(substituted alkyl)siloxane]s can not be prepared by this approach since poly[bis-(Si–H)siloxane] is unknown.

Alternatively, poly(substituted alkylmethylsiloxane)s have been prepared starting from methyldichlorosilane. For example, Pt-catalyzed hydrosilylation of methyldichlorosilane with 3,3,3-trifluoropropene yields 3,3,3-trifluoropropylmethyldichlorosilane which can be converted to 1,3,5-tris(3′,3′,3′-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane. AROP of this monomer yields poly(3,3,3-trifluoropropylmethylsiloxane), a material whose low T_g and lack of permeability to hydrocarbon liquids, make it useful as a sealant, for example, in aircraft applications [7]. Despite the unusual and useful properties of poly(3,3,3-trifluoropropylmethylsiloxane) only a few other poly-(perfluoroalkylmethylsiloxanes) are known [8–12].

While hexa(1H,1H,2H,2H-perfluoroalkyl)cyclotrisiloxane [1] has been prepared by treatment of bis(1H,1H,2H,2H-perfluoroalkyl)dichlorosilanes with DMSO [13], attempts to carry out AROP of this monomer did not result in poly-[bis(1H,1H,2H,2H-perfluoroalkyl)siloxane] but rather in formation of octa(1H,1H,2H,2H-perfluoroalkyl)cyclotetrasiloxane [13]. Thus poly[bis(1H,1H,2H,2H-perfluoroalkyl)-siloxane]s are unknown.

In this paper, we report a novel approach to the preparation of these materials. AROP of hexavinylcyclotrisiloxane has been found to yield high molecular weight poly(divinylsiloxane). Chemical modification of the C–C double bonds of this materials by platinum catalyzed hydrosilylation reactions with 1H,1H,2H,2H-perfluoroalkyl-dimethylsilanes is found to yield the desired materials. This approach has also been utilized to prepare poly(1H,1H,2H,2H-perfluoroalkylmethylsiloxane)s by chemical modification of poly-(vinylmethylsiloxane). There is considerable interest in chemical modification of polymers [14,15].

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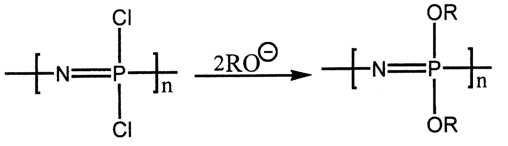

Fig. 1. Chemical modification of poly(dichlorophosphazene).

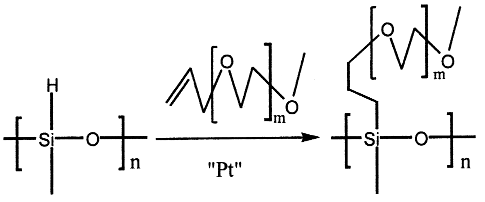

Fig. 2. Hydrosilylation of poly(methylsiloxane).

2. Results and discussion

2.1. Monomer synthesis

Hexavinylcyclotrisiloxane(I), 1,3,5-trimethyl-1,3,5-trivinylcylotrisiloxane(IV) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane(V) have been prepared by the reaction of DMSO and triethylamine with divinyldichlorosilane or vinylmethyldichlorosilane, respectively. The reaction of dichlorosilanes with DMSO to yield predominantly cyclotrisiloxanes has been reported [10,16–18]. In our initial experiments with divinyldichlorosilane and DMSO low yields (~10%) of I were obtained. Analysis of the reaction by-products suggested that protodesilylation by HCl might be a significant problem. For this reason, subsequent reactions were carried out with DMSO and triethylamine. Significantly higher yields (~50%) of I were obtained. IV and V have, likewise, been obtained by reaction of vinylmethyldichlorosilane with DMSO and triethylamine.

2.2. NMR of monomers

The ^{13}C and ^{29}Si NMR of I are quite simple. Two signals in the ^{13}C NMR due to vinyl carbons and a single ^{29}Si resonance are detected. Three signals due to Si-methyl groups are detected in the ^{1}H NMR of IV. The signals at 0.25 and 0.26 ppm, that integrate approximately as 1:2, have been assigned to the *trans* isomer, while the signal at 0.28 ppm is attributed to the *cis* isomer. Integration of these signals is consistent with a 1:3 mixture of *cis* and *trans* isomers [19]. This mixture was not separated. V is obtained as a mixture of *cis,cis,cis,cis*; *cis,cis,trans,trans*; *cis,trans,cis,trans*; and *cis,cis,cis,trans* isomers. Six ^{29}Si NMR resonances, six ^{13}C NMR signals due to Si-methyl groups and twelve ^{13}C signals due to Si-vinyl carbons are expected if only adjacent siloxy centers affect one another. In fact, only four signals are detected in the ^{29}Si NMR. Two signals due to Si-methyl groups and twelve resonances due to vinyl carbons are observed in the ^{13}C NMR. Apparently fortuitous overlap occurs in both the ^{29}Si and ^{13}C. These isomers were not separated.

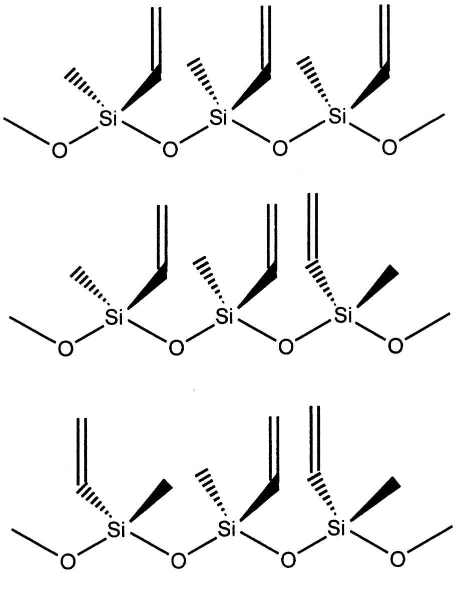

Fig. 3. Triad analysis of poly(vinylmethylsiloxane).

2.3. Preparation of poly(divinylsiloxane)(II) and poly(vinylmethylsiloxane)(III)

II has been prepared by AROP of I [20]. AROP of cyclotrisiloxanes often permits the preparation of high molecular weight polysiloxanes that have quite narrow molecular weight distributions [21]. AROP of I catalyzed by dilithio diphenylsilanediolate [22] yields II with an $M_w/M_n = 5.1 \times 10^4/4.0 \times 10^4$. The NMR spectra of II is simple. Only one ^{29}Si NMR signal, and two ^{13}C NMR resonances are observed. The T_g of II (−134 °C) is nine degrees lower than that of polydimethylsiloxane T_g (−125 °C) [23]. The T_g of III (−137 °C) is even lower. These are among the lowest T_gs reported for any polymer.

Similarly, AROP of IV by dilithio diphenylsilanediolate gave III with $M_w/M_n = 3.8 \times 10^4/2.9 \times 10^4$. The NMR spectra of III are complex. Three resonances are detected in the ^{29}Si NMR. These can be explained by a triad analysis (see Fig. 3). In the ^{13}C NMR, four signals due to the vinyl carbons and a single resonance due to methyl groups are detected. Apparently, the vinyl carbons attached to Si are sensitive to polymer microstructure, while the remote vinyl carbons are not. The reason why the Si–CH_3 carbons are not sensitive to polymer microstructure is not obvious.

Acid-catalyzed ring-opening polymerization of cyclotetrasiloxanes is often utilized rather than AROP. This is not a viable method to prepare V due the possible loss of Si-vinyl groups by protodesilylation [24]. This would lead to crosslinking. Recently, P_4-*t*-Bu superbase has been shown to be effective for the polymerization of D_4 [25–27]. We

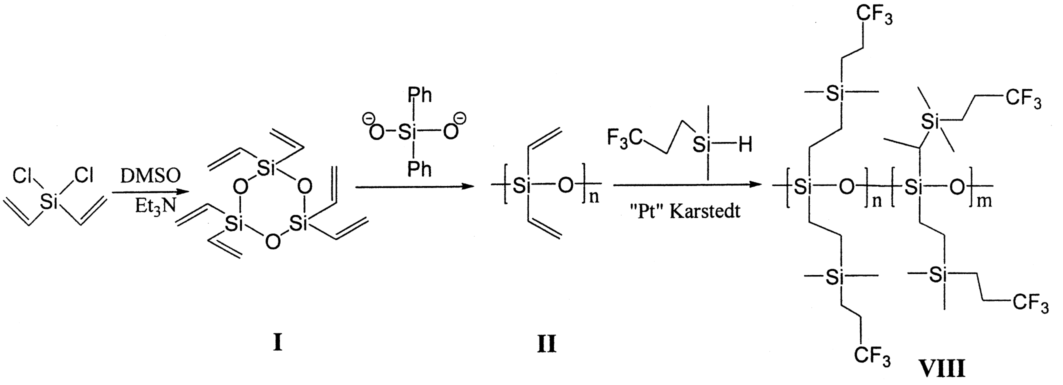

Fig. 4. Preparation of hexavinyltricyclosiloxane(I). AROP of I and Pt catalyzed modification by hydrosilylation of poly(divinylsiloxane)(II) with 3,3,3-trifluoropropyldimethylsilane.

have found that V undergoes AROP with P_4-*t*-Bu superbase to yield III with a broad molecular weight distribution, $M_w/M_n = 11.3 \times 10^4/3.3 \times 10^4$. Broad molecular weight distributions have been previously obtained in AROP of cyclotetrasiloxanes with P_4-*t*-Bu superbase [27].

2.4. Chemical modification of II and III

Poly[bis(perfluoroalkyl)siloxane]s have been prepared by chemical modification of II by Pt-catalyzed hydrosilylation (Fig. 4) with 3,3,3-trifluoropropyldimethylsilane(VI) and 1H,1H,2H,2H-perfluorooctyldimethylsilane(VII). To minimize loss of Si-vinyl groups by protodesilylation, the Karstedt catalyst [a 1,3-divinyltetramethyldisiloxane complex of platinum(0)] was used rather than acidic H_2PtCl_6 [24]. While hydrosilylation reactions usually show a strong regioselectivity for anti-Markovnikov β-addition of the Si–H bond across a C–C double bond, in these examples, Markovnikov α-addition is competitive. Consistent with this analysis, a doublet due to the methyl group $CH_3–CHSi(CH_3)_2–CH_2CH_2R_f$ is observed in the ^1H NMR. It has previously reported that the amount of α-addition increases with the number of electronegative groups on silicon [28].

Unfortunately, even under forcing conditions, we have been unable to achieve complete hydrosilylation of II. Based on ^1H NMR integration, approximately, fifteen percent of the Si-vinyl groups were found to remain unreacted with either VI or VII.

2.5. Solubility, T_g, and GPC of poly(perfluoroalkylsiloxane)s: VIII, IX, X and XI

These modified poly(perfluoroalkylsiloxanes) materials are quite remarkable. The molar mass of the pendant side chains $CF_3CH_2CH_2Si(CH_3)_2$ (155 g/side chain) or $CF_3(CF_2)_5CH_2CH_2Si(CH_3)_2–$ (405 g/side chain) is greater than a divinylsiloxy (98 g/unit) or a methylvinylsiloxy unit (88 g/unit). The properties of these materials are determined by both the nature of the pendant side chains as well as the flexible siloxane backbone. Low T_gs are expected for flexible siloxanes. On the other hand, these perfluorinated materials have significantly different solubility properties. Unlike most polysiloxanes, they are not soluble in THF. For this reason, it was necessary to use 1,1,2-trifluoro-1,2,2-trichloroethane (CFC-113) as a solvent for GPC analysis. Unfortunately, monodispersed polystyrene standards are not soluble in CFC-113. GPC calibration for these modified polymers is a challenge. Based on $M_w/M_n = 5.1 \times 10^4/4.0 \times 10^4$ of II, we expect poly[bis(3,3,3-trifluoropropyldimethylsilylethyl)siloxane](VIII) to have an $M_w/M_n = 18.2 \times 10^4/14.2 \times 10^4$. In fact, the M_w/M_n observed by GPC is $12.6 \times 10^4/8.0 \times 10^4$. The T_g of VIII is −34 °C. For poly[bis(1H,1H,2H,2H-perfluorooctyldimethylsilylethyl)-siloxane](IX), we expect $M_w/M_n = 40.2 \times 10^4/31.5 \times 10^4$, whereas $M_w/M_n = 14.5 \times 10^4/11.7 \times 10^4$ was observed by GPC. The T_g of this material is −23 °C.

Based on $M_w/M_n = 3.8 \times 10^4/2.9 \times 10^4$ of III, the expected molecular weight distributions of poly[(3,3,3-trifluoropropyldimethylsilylethyl)methylsiloxane](X) and poly[(1H,1H,2H,2H-perfluorooctyldimethylsilylethyl)-methylsiloxane](XI) should be $10.5 \times 10^4/8.0 \times 10^4$ and $21.5 \times 10^4/16.2 \times 10^4$, respectively. In fact, molecular weight distributions of $9.9 \times 10^4/6.6 \times 10^4$ and $12.0 \times 10^4/10.0 \times 10^4$ were observed by GPC. The T_gs of X and XI are −62 and −48 °C respectively.

These differences in M_w/M_n may result from the fact that branched materials are known to have lower hydrodynamic volumes and thus give lower apparent molecular weights by GPC. In addition, problems inherent when comparisons are made between GPC results obtained with different solvent systems and standards may be significant. The T_gs of the unsymmetrically substituted siloxane polymers X and XI are lower than the symmetrically substituted polysiloxanes VIII and IX. This is expected if interchain attractions limits chain motion. The polymers that have the larger perfluoroalkyl group (IX and XI) have higher T_gs. This may be due to increase in the mutual attraction—fluorophilicity—of the larger perfluoroalkyl groups.

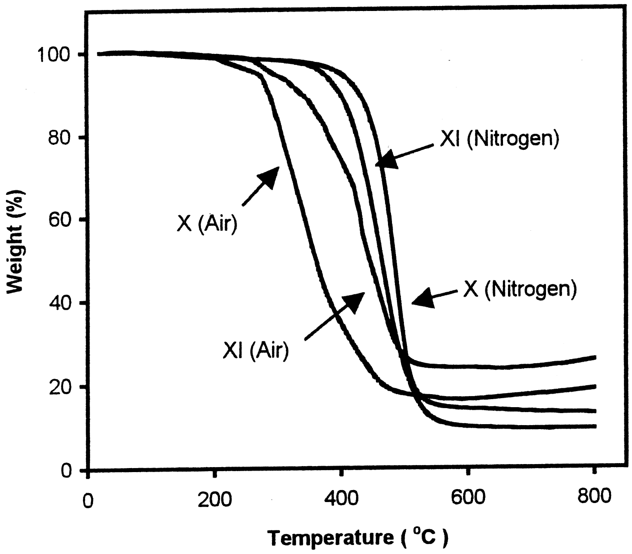

Fig. 5. TGA analysis of poly[(1H,1H,2H,2H-perfluorooctyldimethylsilylethyl)methylsiloxane](XI) and Poly(3,3,3-trifluoropropyldimethylsilylethyl)methylsiloxane(X).

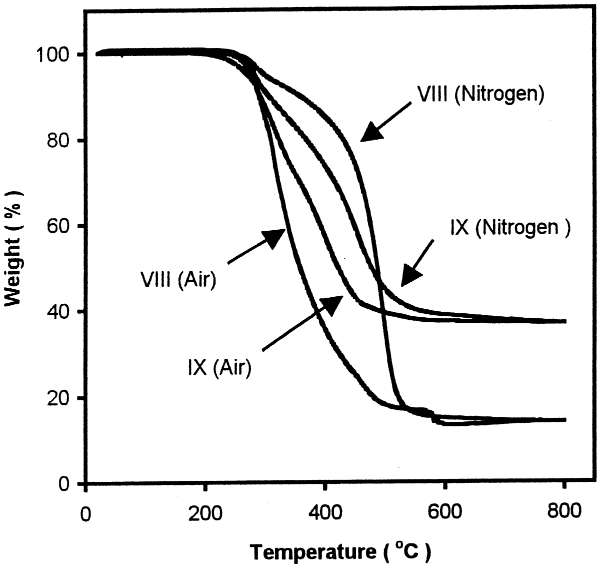

Fig. 6. TGA analysis of poly[bis-(1H,1H,2H,2H-perfluorooctyldimethylsilylethyl)siloxane](IX) and poly[bis-(3,3,3-trifluoropropyldimethylsilylethyl)siloxane](VIII).

2.6. *TGA of polymers*

The thermal stability of these polymers has been determined in both nitrogen and air by TGA. Both II and III are quite thermally stable and yield significant non-volatile char in both nitrogen and air. Similar results have been observed in the TGA of poly(1,1-divinyl-1-silabutane) [29,30]. Thus III is stable in nitrogen to more than 440 °C. Above this temperature, it slowly decomposes. Only a sixteen percent weight loss has occurred, by 800 °C. In air, III is less stable. It begins to decompose by 310 °C. A thirty-one percent weight loss has occurred by 800 °C.

II is less thermally stable. In nitrogen, it begins to decompose at 190 °C. Between 190 and 300 °C, twenty-three percent weight loss is observed. Above 475 °C, a second weight loss process begins. By 800 °C, an additional eight percent weight loss is detected. In air, II is only stable to 145 °C. Between 145 and 300 °C a weight gain of approximately five percent is detected. Above 300 °C, weight loss begins. By 650 °C, a weight loss of forty-four percent of the sample is detected.

On the other hand, poly(perfluoroalkylsiloxane)s undergo catastrophic decomposition and leave only small non-volatile residues when heated to 800 °C. X is thermally stable in nitrogen to 340 °C. Above this temperature, catastrophic decomposition occurs in nitrogen. By 550 °C, almost ninety percent of the initial sample weight has been lost. In air, the polymer is stable to 255 °C. It losses seventy-four percent of its initial weight by 500 °C. XI is stable in nitrogen to 360 °C and in air to 265 °C. The decomposition of X is similar to that of XI (see Fig. 5).

VIII is less thermally stable. It begins to decompose in nitrogen at 250 °C and at 240 °C in air. IX is stable in both nitrogen and air to 250 °C. By 500 °C in nitrogen, a sixty percent weight loss is detected, while in air a similar weight loss is observed by 450 °C (see Fig. 6).

3. Experimental

3.1. *Spectroscopy*

^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. Five percent w/v chloroform-*d* or benzene-d_6 solutions were used to acquire ^{1}H and ^{13}C NMR. ^{29}Si NMR spectra were procured of 25% w/v chloroform-*d* or benzene-d_6 solutions. CFC-113 solutions were used to acquire ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR data of poly(perfluoroalkylsiloxanes). ^{13}C NMR spectra were obtained with broadband proton decoupling. A heteronuclear gated decoupling pulse program with a 60 s delay was used to acquire ^{29}Si NMR spectra. All spectra were referenced to internal TMS. IR spectra of neat liquid films on NaCl plates were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer.

Low resolution mass spectra were obtained by GC/MS on a Hewlett–Packard 5890 series II GC equipped with a Hewlett–Packard 5971 series mass selective detector and a 30 m DB-5 capillary column.

3.2. *Molecular weight distribution*

GPC analysis of the molecular weight distribution of the polymers was performed on a Waters system equipped with a 501 refractive index detector. Two 7.8 × 300 mm^2 Styragel HT 6E and HMW 6E columns in series with toluene solvent at a flow rate of 0.5 ml/min were used for analysis of

II and III. The retention times were calibrated against known monodisperse PS standards: 929 000, 114 200, 13 700, 794 g/mol. Two 7.8×300 mm Styragel HR3 and HR4 columns in series with CFC-113 solvent at a flow rate of 0.7 ml/min was used for the analysis of poly(perfluoroalkylsiloxanes). The retention times were calibrated against a PDMS standard $M_w/M_n = 5.2 \times 10^4/3.3 \times 10^4$.

3.3. Thermal analysis

TGA of the polymers was carried out on a Shimadzu TGA-50 instrument with a flow rate of 40 cm^3 of nitrogen or air per min. The temperature was increased at the rate of 4 °C per min from 25 to 800 °C. The T_g of the polymers was determined on a Perkin–Elmer DSC-7. The DSC was calibrated against the heat of transition (−87.06 °C) and the melting point of cyclohexane (6.54 °C) [31], as well as the T_g of PDMS (−125 °C) [23]. The temperature program for the analysis was begun at −150 °C and was increased at the rate of 10 °C/min to 50 °C.

3.4. Materials

Methylvinyldichlorosilane, divinyldichlorosilane, trimethylchlorosilane, sym-tetramethyldisiloxane, 3,3,3-trifluoropropyldimethylchlorosilane, 1H,1H,2H,2H-perfluorooctyldimethylchlorosilane, diphenylsilanediol, and Karstedt catalyst were obtained from Gelest. DMSO, HMPA, CFC-113 and triethylamine were purchased from Aldrich. Phosphazene Base P_4-*t*-Bu (1.0 M in hexane) was obtained from Fluka. All reactions were run in flame dried glassware under argon. Dilithium diphenylsilanediolate was prepared by titration of diphenylsilanediol with butyllithium in THF with styrene as an indicator [22]. All reactions were run in flame-dried glassware under argon.

3.5. Preparation of I

A solution of divinyldichlorosilane (10 g, 65 mmol) and triethylamine (13 g, 0.13 mol) in 50 ml of $CHCl_3$ was placed in a 250 ml three neck round bottom flask equipped with a pressure equalizing addition funnel, a reflux condenser and a Teflon covered magnetic stir bar. A solution of DMSO (5.4 g, 69 mmol) in 25 ml of $CHCl_3$ was placed in the addition funnel and was added dropwise over 0.5 h at room temperature. The solution was stirred for 3 h. $CHCl_3$ 30 ml was added and the solution was then washed with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was fractionally distilled through a 10 cm vacuum jacketed Vigreux column. A fraction bp 68 °C/0.2 mm, 2.7 g, 46.9% yield was obtained [16]. ^{1}H NMR: 5.97 (dd, 2H, $J = 16.5$ and 7 Hz), 6.10 (d, 2H, $J = 16.5$ Hz), 6.11 (d, 2H, $J = 7$ Hz). ^{13}C NMR δ: 133.4, 136.0. ^{29}Si NMR δ: −37.17. IR ν: 1597 (C=C) cm^{-1}. GC-MS m/z (rel. intensity): 294 (2%) (M^+), 267 (50%) $(M\text{-vinyl})^+$, 253 (100%).

3.6. Preparation of IV and V

A solution of vinylmethyldichlorosilane (20 g, 0.14 mol) and triethylamine (28 g, 0.28 mol) in 80 ml of $CHCl_3$ was placed in a 250 ml two neck round bottom flask equipped with a pressure equalizing addition funnel, a reflux condenser and a Teflon covered magnetic stir bar. A solution of DMSO (12 g, 0.15 mmol) in 50 ml of $CHCl_3$ was placed in the addition funnel and was added dropwise over a period of 1.5 h at room temperature. After this the solution was stirred for 3 h. The $CHCl_3$ solution was then washed with water. It was dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was fractionally distilled through a 20 cm vacuum jacketed Vigreux column. A 3:1 mixture of *trans*: *cis*, IV, bp 72 °C/11 mm Hg, 3.74 g, 31% yield was obtained. A second fraction, V, bp 90 °C/5 mm, 2.77 g, 23% yield was obtained.

IV: ^{1}H NMR δ: 0.25 (s, *trans*, 1.0H), 0.26 (s, *trans*, 1.74H), 0.28 (s, *cis*, 0.97H), 5.85–5.93 (m, 1.21H), 6.00–6.11 (m, 2.41H). ^{13}C NMR δ: −0.86, −0.83 (*trans*), −0.76, 134.2, 134.3 (*trans*), 134.4, 135.5, 135.6 (*trans*), 135.8. ^{29}Si NMR δ: −22.42, −22.38 (*trans*), −22.36. IR ν: 1597 (C=C) cm^{-1}. GC-MS *m/z* (rel. intensity): 258 (5%) (M^+), 243 (100%) $(M\text{-}CH_3)^+$, 231 (22%) $(M\text{-vinyl})^+$.

V: ^{1}H NMR δ: 0.17 (s, 0.5H), 0.18 (s, 1.1H), 0.20 (s, 1.0H), 0.21 (s, 0.4H), 5.79–5.87 (m, 1H), 5.94–6.07 (m, 2H). ^{13}C NMR δ: −0.84, −0.81, 133.30, 133.35, 133.40, 133.43, 133.48, 133.50, 136.17, 136.21, 136.26, 136.33, 136.39, 136.45. ^{29}Si NMR δ: −32.52, −32.44, −32.41, −32.40. IR ν: 1598 (C=C) cm^{-1}. GC-MS *m/z* (rel. intensity): 344 (2%) (M^+), 329 (100%) $(M\text{-}CH_3)^+$, 317 (30%) $(M\text{-vinyl})^+$.

3.7. Preparation of VI

$LiAlH_4$ (0.8 g, 26 mmol) was placed in a three-necked round bottom flask equipped with a pressure equalizing addition funnel and a reflux condenser. Anhydrous diethyl ether (50 ml) was added to the flask by syringe. A solution of 3,3,3-trifluoropropyldimethylchlorosilane (9 g, 47 mmol) in diethyl ether (20 ml) was added dropwise at room temperature. After stirring for an additional hour, the mixture was filtered. The solution was fractionally distilled through a 10 cm vacuum jacketed Vigreux column. In this way, 3,3,3-trifluoropropyldimethylsilane (4.7 g), bp 78 °C, was obtained in 64% yield [32]. ^{1}H NMR δ: 0.06 (d, 6H, $J = 3.5$ Hz), 0.76 (dt, 2H, $J = 3.5$ and 8.5 Hz), 2.01 (m, 2H), 3.84 (septet, 1H, $J = 3.5$ Hz). ^{13}C NMR δ: −4.92, 5.98, 29.25 (q, $J_{C–F} = 30$ Hz), 127.64 (q, $J_{C–F} = 276$ Hz). ^{19}F NMR δ −69.19 (t, $J_{F–H} = 10.4$ Hz). ^{29}Si NMR δ: −11.62. IR ν: 2122 (Si–H) cm^{-1}.

3.8. Preparation of VII

1H,1H,2H,2H-Perfluorooctyldimethylchlorosilane and $LiAlH_4$ were reacted as above. 1H,1H,2H,2H-Perfluorooctyldimethylsilane(VII) was obtained in 91% yield, bp

77 °C/28 mm [33]. ^{1}H NMR δ: 0.13 (d, 6H, $J = 4.0$ Hz), 0.84 (dt, 2H, $J = 4.0$ and 8.5 Hz), 2.07 (m, 2H), 3.93 (septet, 1H, $J = 4.0$ Hz). ^{13}C NMR δ: -4.82, 3.90, 26.62 (t, $J_{\text{C–F}} = 24.1$ Hz), 108.98(m), 109.29(m), 111.17(m), 111.44(m), 117.56 (qt, $J_{\text{C–F}} = 288$ and 33.3 Hz), 118.61 (tt, $J_{\text{C–F}} = 286$ Hz and 31.5 Hz). ^{19}F NMR δ: -126.84, -123.99, -123.52, -122.57, -116.74 (t, 2F, $J_{\text{F–H}} = 16$ Hz), -81.58 (t, 3F, $J_{\text{F–F}} = 3$ Hz). ^{29}Si NMR δ: -11.31. IR ν: 2126 (Si–H) cm^{-1}.

3.9. AROP of IV

IV (2 g, 7.74 mmol) was placed in a test tube equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. The system was purged with argon three times. THF (500 μl), HMPA (10 μl) and 50 μl of a THF solution of dilithio diphenylsilanediolate (0.316 mol/l, 15.8 μmol) initiator were added. The reaction was stirred for 3 h at room temperature. Trimethylchlorosilane (10 μl) and triethylamine (10 μl) were sequentially added to quench the reaction. The polymer was taken up in a minimum amount of diethyl ether and was precipitated into methanol. This procedure was repeated three times. III was dried under vacuum. In this way, 1.9 g, 95% yield of III, $M_w/M_n = 3.8 \times 10^4/2.9 \times 10^4$, and $T_g = -130$°C was obtained. ^{1}H NMR δ: 0.37 (s, 3H), 5.96–6.24 (m, 3H). ^{13}C NMR δ: -0.16, 133.55, 137.12, 137.14, 137.18. ^{29}Si NMR δ: -34.15, -34.16, -34.18. IR ν: 1598 (C=C) cm^{-1}.

3.10. AROP of V

V (0.5 g, 1.4 mmol) was placed in a 5 ml test tube that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. The system was purged with argon three times. The tube and the content were heated to 80 °C and P$_4$-*t*-Bu (1 μl, 1 μmol) was added. After 3 h at 80 °C, trimethylchlorosilane (5 μl) and triethylamine (5 μl) were sequentially added to quench the reaction. III was taken up in a minimum amount of diethyl ether and was precipitated into methanol. This procedure was repeated three times. III was dried under vacuum. In this way, 0.4 g, 80% yield of III, $M_w/M_n = 11.3 \times 10^4/3.3 \times 10^4$, $T_g = -130$°C was obtained. ^{1}H NMR δ: 0.37 (s, 3H), 5.98 (d, 2H, $J = 17$ Hz), 6.21 (d, 1H,$J = 17$ Hz). ^{13}C NMR δ: -0.17, 133.57, 137.11, 137.14, 137.17. ^{29}Si NMR δ: -34.11, -34.13, -34.16.

3.11. AROP of I

I (1.5 g, 5.1 mmol) was placed in a 10 ml round bottom flask, equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. THF (3.0 ml), HMPA (5 μl) and 40 μl of a THF solution of dilithio diphenylsilanediolate (0.33 mol/l, 13.2 μmol) initiator were added. After stirring for 2 h at room temperature, trimethylchlorosilane (10 μl) and triethylamine (10 μl) were sequentially added to quench the reaction. II was taken up in a minimum amount of diethyl ether and was precipitated into methanol. This procedure was repeated three times. II was dried under vacuum. In this way, 1.32 g, 88% yield of II, $M_w/M_n = 5.1 \times 10^4/4.0 \times 10^4$, $T_g = -134$°C was obtained. ^{1}H NMR δ: 6.04 (dd, 2H, $J = 14.5$ and 3.5 Hz), 6.09 (dd, 2H, $J = 20.5$ and 3.5 Hz), 6.24 (dd, 2H, $J = 20.5$ and 14.5 Hz). ^{13}C NMR δ: 135.09, 135.33. ^{29}Si NMR δ: -49.9. IR ν: 1598 (C=C) cm^{-1}.

3.12. Preparation of XI by chemical modification of III

III (0.15 g, 1.7 mmol, $M_w/M_n = 3.8 \times 10^4/2.9 \times 10^4$), VII (0.75 g, 1.7 mmol), CFC-113 (2 ml), and Karstedt catalyst (5 μl) were placed in a Ace-pressure tube equipped with a Teflon-covered magnetic stir bar. The tube was sealed with a Teflon-threaded stopper. The reaction was allowed to proceed at 85 °C overnight. VIII was precipitated from a mixture of CFC-113/Et$_2$O/MeOH (1:1:5). It was dried under vacuum. In this way, 0.73 g, 81% yield of material, $T_g = -48$°C and $M_w/M_n = 12.0 \times 10^4/10.0 \times 10^4$ was obtained. ^{1}H NMR δ: 0.06 (s, 3.76H), 0.15 (m, 5.95H), 0.49–0.56 (m, 2.97H), 0.80 (m, 2.08H), 1.02–1.13 (m, 0.77H), 2.04 (m, 2H). ^{19}F NMR δ: -126.89, -123.86, -123.49, -122.50, -116.86, -81.75. ^{29}Si NMR δ: -22.75 (br, s), 4.91 (s), 5.44 (s).

3.13. Preparation of X by chemical modification of III

III (0.2 g, 2.3 mmol), $M_w/M_n = 3.8 \times 10^4/2.9 \times 10^4$ and VI (0.36 g, 2.3 mmol) were reacted as above. In this way, 0.5 g, 96% yield, $M_w/M_n = 9.9 \times 10^4/6.6 \times 10^4$, $T_g = -62$°C was obtained. ^{1}H NMR δ: 0.12 (s, 3H), 0.19 (m, 6H), 0.51 (m, 1.56H), 0.58 (m, 1.56H). 0.84 (m, 2H), 1.05 (m, 0.22H), 1.16 (d, 0.56H), 2.10 (m, 2H). ^{13}C NMR δ: -4.49 (br. s), -3.60 (br. s), -3.22 (br. s), -1.12 (br. s), -0.92 (br. s), 6.28 (br. s), 6.87 (br. s), 7.68 (br. s), 8.63 (br. s), 9.41 (br. s), 28.8 (q, $J_{\text{C–F}} = 30$ Hz), 28.9 (q, $J_{\text{C–F}} = 30$ Hz), 127.75 (q, $J_{\text{C–F}} = 276$ Hz), 127.9 (q, $J_{\text{C–F}} = 276$ Hz). ^{19}F NMR δ: -69.34. ^{29}Si NMR δ: -22.5, -21.8, 4.65, 5.19.

3.14. Preparation of IX by chemical modification of II

II (0.1 g, 1.0 mmol, $M_w/M_n = 5.1 \times 10^4/4.0 \times 10^4$), VII (0.9 g, 2.2 mmol), CFC-113 (1.5 ml) and Karstedt catalyst (5 μl) were place in a 20 ml Ace-pressure tube equipped with a Teflon-covered magnetic stir bar. The tube was sealed with a Teflon-threaded stopped. After 12 h at 80 °C and 72 h at 145 °C, X was precipitated from a mixture of CFC-113/Et$_2$O/MeOH (1:1:4). X was dried under vacuum. In this way, 0.53 g, 57% yield of X with $T_g = -23$°C, $M_w/M_n = 14.5 \times 10^4/11.7 \times 10^4$ was obtained. ^{1}H NMR δ: 0.03 (s, 3.36H), 0.12 (s, 2.86H), 0.56 (br. s, 2.27H), 0.75 (br. s, 2.14H), 1.02–1.15 (m, 1.33H), 1.99 (br. s, 2H), 5.93–6.06 (m, 0.5H, due to Si-vinyl groups). ^{19}F NMR δ: -126.83 (br. s), -123.73 (br. s), -123.37 (br. s), -122.30 (br. s), -116.72 (br. s), -81.76 (br. s). ^{29}Si

NMR δ: -37.63 (br. s), -23.74 (br. s), 4.86 (s), 5.74 (s). IR ν: 1597 (C=C) cm^{-1}.

3.15. Preparation of VIII by chemical modification of II

II (0.1 g, 1.0 mmol, $M_w/M_n = 5.1 \times 10^4/4.0 \times 10^4$) and VI (0.34 g, 2.2 mmol) were reacted as above. In this way, 0.26 g, 65% yield of XI, $M_w/M_n = 12.6 \times 10^4/8.0 \times 10^4$, $T_g = -34$°C was obtained. ^{1}H NMR δ: 0.12 (s, 3.61H), 0.20 (s, 2.28H), 0.59 (br. s, 2.15H), 0.83 (br. s, 2.19H), 1.02–1.09 (m, 1.27H), 2.10 (br. s, 2H), 5.98–6.12 (m, 0.46H). ^{19}F NMR δ: -69.34. ^{29}Si NMR δ: -38.01 (br. s), -23.77 (br. s), 4.18 (s), 5.01 (s).

4. Conclusions

Novel poly[bis(1H,1H,2H,2H-perfluoroalkyl)siloxane]s have been prepared by chemical modification of poly(divinylsiloxane) by Pt-catalyzed hydrosilylation with 1H,1H,2H,2H-perfluorodimethylsilanes. Poly(1H,1H,2H,2H-perfluoroalkylmethylsiloxane)s have been prepared in a similar manner by hydrosilylation of poly(vinylmethylsiloxane). These materials have unusual solubility properties and have been characterized by spectroscopy, DSC, and TGA.

References

[1] Out GJJ, Klok H-A, Schwegler L, Frey H, Möller M. Macromol Chem Phys 1995;196:185.

[2] Out GJJ, Turetskii AA, Möller M, Olefin D. Macromolecules 1994;27:3310.

[3] Allcock HR, Dembek AA, Kim C, Devine RLS, Shi Y, Steier WH, Spangler CW. Macromolecules 1991;24:1000.

[4] Allcock HR, Kim C. Macromolecules 1991;24:2846.

[5] Hideyuki A, Tetsuya W, Yoshuki N. Jpn Kokai Tokkyo Koho 1995; Jpn Patent 07316166.

[6] Masakazu S, Tadashi Y, Akihiro K. Jpn Kokai Tokkyo Kohno, 1996; Jpn Patent 08012536.

[7] Noll W. Chemistry and technology siloxanes. New York: Academic Press, 1968. p. 145–7.

[8] Paulasaari JK, Weber WP. Polym Prepr 1998;39(2):583–4.

[9] Paulasaari JK, Weber WP. Polym Prepr 2000;41(1):133–4.

[10] Goossens JC. French Patent 1964. 1456981. CA 1967;7:54259.

[11] Nagase Y, Ochiai J, Matsui K, Uchikura M. Polymer 1988;29:740.

[12] Kobayashi H. European Patent, EU 0 563 902 A1, 3rd March 1993.

[13] Paulasaari JK. PhD Thesis. University of Southern California, 1999.

[14] Benham JL, Kinstle JE, editors. Chemical reactions on polymers ACS Symposium Series 364. Washington, DC: American Chemical Society, 1988.

[15] Carraher Jr CE, Moore JA, editors. Modification of polymers. New York: Plenum Press, 1983.

[16] Cai G, Weber WP. Macromolecules 2000;33:6310.

[17] Cai G, Weber WP. Macromolecules 2000;33:8976.

[18] Cai G, Weber WP. Macromol Chem Phys 2000;201:2234.

[19] Belyakova NR, Mileshkevich NR. Zhur Obshch Khim 1990;60(10):2287.

[20] Kossmehl G, Fluthwedel A, Schaefer H. Makromol Chem 1992;193(9):2289.

[21] Bouleau S. Anionic polymerization of cyclosiloxanes with cryptates as counterions in ring opening polymerization. In: McGrath JE, editor. ACS Symposium Series 286. Washington, DC: American Chemical Society, 1985. p. 23.

[22] Battjes K, Kuo C-M, Miller RL, Saam JC. Macromolecules 1995;28:790.

[23] Clarson SJ, Dodgson K, Semlyen JA. Polymer 1985;26:930.

[24] Dvornic PR, Gerov VV. Macromolecules 1994;27:1068.

[25] Molenberg A, Möller M. Macromol Rapid Commun 1995;165:449.

[26] Clarson SJ, Van Dyke ME. J Inorg Organometal Polym 1998;8:111.

[27] Hupfield PC, Taylor RG. J Inorg Organometal Polym 1999;9:17.

[28] The hydrosilylation of unsaturated organosilicon compounds. In: Marciniec B, editor. Comprehensive handbook on hydrosilylation. Oxford, England: Pergamon Press, 1992. p. 178–9, Chapter 5.

[29] Liao X, Weber WP. Macromolecules 1992;25:1639.

[30] Sargeant SJ, Zhou SQ, Manuel G, Weber WP. Macromolecules 1992;25:2832.

[31] Aston JG, Szabz GJ, Fink HL. J Am Chem Soc 1943;65:1135.

[32] Steward OW, Pierce OR. J Am Chem Soc 1961;83:1916.

[33] Ameduri B, Boutevin B, Nouiri M, Talbi MJ. Fluorine Chem 1995;74:191.