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Synthesis of fluorinated copoly(carbosiloxane)s by Pt-catalyzed hydrosilylation copolymerization

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Abstract

A series of new 3,3,3-trifluoropropyl substituted copoly(carbosiloxane)s have been prepared by Pt-catalyzed step-growth hydrosilylation copolymerization of 1,9-dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (**I**) with various α,ω-divinylsilanes and siloxanes. The structures of the copoly(carbosiloxane)s have been determined by ^{1}H, ^{13}C, ^{29}Si, and ^{19}F NMR as well as IR spectroscopy. The molecular weight distributions (M_w/M_n) of the copolymers have been characterized by GPC and their thermal properties measured by DSC and TGA.

Keywords: Fluoro; Poly(carbosiloxane)s; Pt catalyzed Hydrosilation

1. Introduction

Polycarbosilanes include those polymers in which the backbone or pendant groups contain Si–C bonds [1,2]. Polymers that contain both Si–C and Si–O–Si linkages in their backbone are known as poly(carbosiloxane)s [3]. We have prepared copoly(carbosiloxane)s that are substituted with pendant 3,3,3-trifluoropropyl groups in an effort to achieve the useful properties of both siloxane and fluoro polymer systems. Siloxanes typically retain consistent properties over a wide range of temperature (−100 to 250 °C). These polymers possess low temperature flexibility (low T_g), high dielectric strength, and water repellency as well as thermal, oxidative, and chemical stability [4]. Fluorinated polymers, such as polytetrafluoroethylene, demonstrate excellent solvent, chemical, and temperature resistance as well as low surface tension [5]. Fluorosilicones are chemically inert and so do not dissolve in hydrocarbon fuel or fluids. This property, combined with their low T_g, has made them useful for aviation fuel tank and gasket applications. They also find utility as release coatings, antifoams for organic liquids (such as crude oil), lubricants, surfactants, gels, adhesives, and sealants. The only commercially significant fluorosilicone is poly[(3,3,3-trifluoropropyl)methylsiloxane].

Poly[(3,3,3-trifluoropropyl)methylsiloxane] has been prepared by ring-opening polymerization of 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluoropropyl)cyclotrisiloxane (D_3^F). This cyclotrisiloxane has been obtained from methyl-3,3,3-trifluoropropyldichlorosilane, which in turn has been produced via a Pt-catalyzed hydrosilylation reactions between methyldichlorosilane and 3,3,3-trifluoropropene [6]. Hydrosilylation is the anti-Markovnikov addition of an Si–H bond across a unit of unsaturation [7]. This reaction is usually catalyzed by a noble metal, typically platinum. Currently, the preferred hydrosilylation catalysts are the Pt-complex of divinyltetramethyldisiloxane known as Karstedt's catalyst [8] and hexachloroplatinic acid (H_2PtCl_6) in 2-propanol known as Speier's catalyst [9]. Pt-catalyzed hydrosilylation polymerization was first reported in 1956 by Curry [10].

Herein, we report the hydrosilylation copolymerization of a novel α,ω-bis(Si–H) pentasiloxane monomer—1,9-dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (**I**) with various α,ω-divinylsilanes or siloxanes to yield 3,3,3-trifluoropropyl substituted copoly(carbosiloxane)s. 3,3,3-Trifluoropropyl groups were selected because it has been shown that fluoroalkyl groups bonded to silicon in the α or β position lack hydrolytic and thermal stability [11]. Variations in the copolymer

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backbones were introduced by choice of appropriate α,ω-divinylsilanes or siloxanes. The effects of these changes to backbone structure on copolymer properties have been determined.

2. Results

Herein, we report the efficient synthesis of 1,9-dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (**I**) by the triflic acid-catalyzed ring-opening of 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluooropropyl)cyclotrisiloxane (D_3^F) in the presence of an excess of 1,1,3,3-tetramethyldisiloxane (TMDS). 1,9-Divinyl-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-pentasiloxane (**II**) was prepared, in a similar manner, by triflic acid-catalyzed reaction of D_3^F and 1,3-divinyltetramethyldisiloxane (**V**). It should be noted that these novel reactive α,ω-functional pentasiloxanes (**I** and **II**) are not commercially available. Acid-catalyzed equilibration of oligo and polysiloxanes is well known, however, this was not a problem in these reactions when conducted at low temperature (0 °C).

Pt-catalyzed (Karstedt) hydrosilylation copolymerization of **I** with **II**, **I** with dimethyldivinylsilane (**III**), 1,2-bis(vinyldimethylsilyl)ethane (**IV**), **V**, or 1,5-divinylhexamethyltrisiloxane (**VI**) have been carried out. These reactions produce the anticipated copolymers. Thus, Pt-catalyzed copolymerization of **I** and **II** yields alt-copoly-[1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-1,9-pentasiloxanylene/ethylene] (**VII**). Reaction of **I** and **III** produces *alt*-copoly[1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxanylene/3,3-dimethyl-3-sila-1,5-pentanylene] (**VIII**), while reaction of **I** and **IV** produces *alt*-copoly[1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-1,9-pentasiloxanylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene] (**IX**). Reaction of **I** and **V** produces *alt*-copoly[1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-1,9-pentasiloxanylene/-3,3,5,5-tetramethyl-4-oxa-3,5-disila-1, 9-heptanylene] (**X**) while reaction of **I** and **VI** yields *alt*-copoly[1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl-1,9-pentasiloxanylene/3,3,5,5,7,7-hexamethyl-4,6-dioxa-3,5,7-trisila-1,9-nonanylene] (**XI**), respectively.

3. Experimental

3.1. NMR spectroscopy

^{1}H, ^{13}C, ^{29}Si, and ^{19}F NMR spectra were acquired on a Bruker AMX-500 MHz spectrometer operating in the FT mode. Five percent w/v chloroform-*d* solutions were used to obtain ^{1}H, ^{13}C, and ^{19}F NMR spectra. ^{29}Si NMR spectra were obtained using 25% w/v chloroform-*d* solutions. ^{13}C NMR spectra were run with broad band proton decoupling. Residual chloroform was used as an internal standard for ^{1}H and ^{13}C NMR. ^{29}Si NMR spectra were referenced to internal TMS. ^{19}F NMR spectra were referenced to internal $CFCl_3$. IR spectra of neat films on NaCl plates were recorded using a Perkin–Elmer Spectrum 2000 FT-IR spectrometer.

3.2. Gel permeation chromatography

GPC analysis of the molecular weight distribution of these polymers was performed on a Waters system equipped comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector, and a model 820 Maxima control system. Two 7.8 mm × 300 mm Styragel columns packed with <5 μm divinylbenzene crosslinked polystyrene, HR4 and HR2, in series were used for the analysis. The eluting solvent was HPLC grade toluene at a flow rate of 0.3 ml/min. The retention times were calibrated against known monodispersed polystyrene standards: M_p 891 000, 212 400, 29 300, 3680, and 770 whose M_w/M_n are less than 1.09.

3.3. Thermal gravimetric analysis

TGA of the polymers was measured on a Shimadzu TGA-50 instrument at a flow rate of 40 cm^3 of nitrogen per minute. The temperature program was 4 °C/min from 25 to 800 °C.

3.4. Differential scanning calorimetry

The T_gs of the polymers were determined on a Perkin–Elmer DSC-7 (PE) or Shimadzu DSC-50 (SH).

The DSC was calibrated from the thermal transition temperature (-87.06 °C) and melting point (6.54 °C) of cyclohexane [12]. The analysis was initially begun -150 °C. The temperature was increased at a rate of 10 °C/min to 25 °C.

3.5. Materials

The α,ω-divinylsiloxanes and silane monomers **III**–**VI** are commercially available, whereas **I** and **II** are not. **III** was obtained from Aldrich. **IV**–**VI**, TMDS, and hexamethyldisilazane were purchased from Gelest. Pt-divinyltetramethyldisiloxane complex (Karstedt's catalyst) in xylene (2% Pt) was acquired from United Chemical Technologies, Inc. Triflic acid was bought from 3M Co.

3.6. Synthetic procedure

All reactions were conducted in flame-dried glassware under nitrogen with Teflon covered magnetic stir bars. Four drops of the Pt catalyst solution were placed into each polymerization reaction mixture. The tube was sealed, and heated to 120 °C. After 5 min, the color of the solution became brown. After 24 h, the reaction was stopped. The polymer was dissolved in a minimum amount of THF and precipitated into methanol.

3.6.1. *1,9-Dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (**I**)*

The title compound **I** was prepared by reaction of D_3^F with TMDS in the presence of triflic acid (Fig. 1) [13]. Thus, D_3^F (35.1 g, 75 mmol) and TMDS (25.2 g, 188 mmol) were placed in a 200 ml round bottom flask. The flask was sealed with a rubber septum and placed in an ice-bath. Triflic acid (150 mg, 90 μl) was added. The reaction was stirred for 17 min and was then quenched by addition of hexamethyldisilazane (3.1 g, 4.0 ml). The solution was allowed to warm to rt. Salts were removed by filtration. Excess TMDS and hexamethyldisilazane were recovered by distillation. **I** was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column under reduced pressure. A fraction bp 135–136 °C/4.5 mm, 39.3 g, 87% yield was collected. ^{1}H NMR δ: 0.11 (s, 6H), 0.14 (s, 3H), 0.19 (d, 12H, $J = 2.5$ Hz), 0.74 (m, 6H), 2.04 (m, 6H), 4.72 (m, 2H). ^{13}C NMR δ: -0.96, -0.75, 0.63, 9.21, 9.30, 28.10 (m), 120.75 (m). ^{19}F NMR δ: -69.32 (m). ^{29}Si NMR δ: -22.96, (s, 1Si), -21.79 (s, 2Si), -4.84 (d, 2Si, $J = 4.5$ Hz). IR ν: 2127 (Si–H), 1069 (br) (Si–O–Si) cm^{-1}.

3.6.2. *1,9-Divinyl-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (**II**)*

The title compound **II** was, likewise, prepared in good yield by a triflic acid-catalyzed ring-opening reaction of D_3^F (35 g, 75.6 mmol) with **V** (35.2 g, 189 mmol) (Fig. 1), as above. After 15 min of reaction at 0 °C, the reaction was neutralized by addition of excess hexamethyldisilazane. The contents of the flask were filtered and the product was fractionally distilled. A fraction bp 164–165 °C/8 mm, 30.2 g, 61% yield was obtained. ^{1}H NMR δ: 0.14 (s, 4H), 0.16 (s, 2H), 0.20 (s, 7H), 0.76 (m, 4H), 2.06 (m, 4H), 5.77 (dd, 1H, $J = 21.0$ and 3.5 Hz), 5.99 (dd, 1H, $J = 15.0$ and 3.5 Hz), 6.14 (dd, 1H, $J = 20.0$ and 14.5 Hz). ^{13}C NMR δ: -0.85, -0.77, -0.03, 9.42, 28.20 (q, $J_{C-F} = 30$ Hz), 28.24 (q, $J_{C-F} = 31$ Hz), 127.93 (q, $J_{C-F} = 275$ Hz), 132.55, 138.67. ^{29}Si NMR δ: -23.23 (s, 1Si), -22.85 (s, 2Si), -2.18 (s, 2Si). ^{19}F NMR δ: -69.33 (t, 6F, $J_{H-F} = 10.8$ Hz), -69.28 (m, 3F). IR ν: 2963, 1735, 1597, 1447, 1407, 1369, 1315, 1265, 1210, 1129, 1069, 1037, 960, 901, 839, 787 cm^{-1}.

3.6.3. *alt-copoly-[1,1,3,5,7,9,9-Heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-1,9-pentasiloxanylene/ethylene] (**VII**)*

The title compound **VII** was prepared by a Pt-catalyzed reaction of **I** (1.00 g, 1.66 mmol) and **II** (1.08 g, 1.66 mmol) as above (Fig. 2). In this way, 1.62 g (78% yield) of **VII** with $M_w/M_n = 14\,092/7062$, $T_g(\mathrm{SH}) = -80$ °C, was obtained. ^{1}H NMR δ: 0.06 (m, 12H), 0.07 (s, 6H), 0.10 (s, 3H), 0.41 (s, 4H), 0.71 (m, 6H), 2.01 (m, 6H). ^{13}C NMR δ: -0.76, 9.30, 9.44, 28.01 (q, $J_{C-F} = 30.6$ Hz), 28.08 (q, $J_{C-F} = 30.4$ Hz), 127.63 (q, $J_{C-F} = 276$ Hz). ^{29}Si NMR δ: -23.43 (m, 6Si), 10.24 (s, 4Si). ^{19}F NMR δ: (-69.40 (t, $J_{H-F} = 9.4$ Hz), -69.39 (t, $J_{H-F} = 9.4$ Hz)) 6F, (-69.313 (t, $J_{H-F} = 9.4$ Hz), -69.306 (t, $J_{H-F} = 9.4$ Hz), -69.298 (t, $J_{H-F} = 9.4$ Hz)) 3F. IR ν: 3049, 2962, 2909, 2876, 2788, 1447, 1420, 1368, 1315, 1265, 1211, 1134, 1067, 1015, 901, 836, 768, 709 cm^{-1}.

3.6.4. *alt-copoly[1,1,3,5,7,9,9-Heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxanylene/3,3-dimethyl-3-sila-1,5-pentanylene] (**VIII**)*

The title compound **VIII** was prepared by a Pt-catalyzed

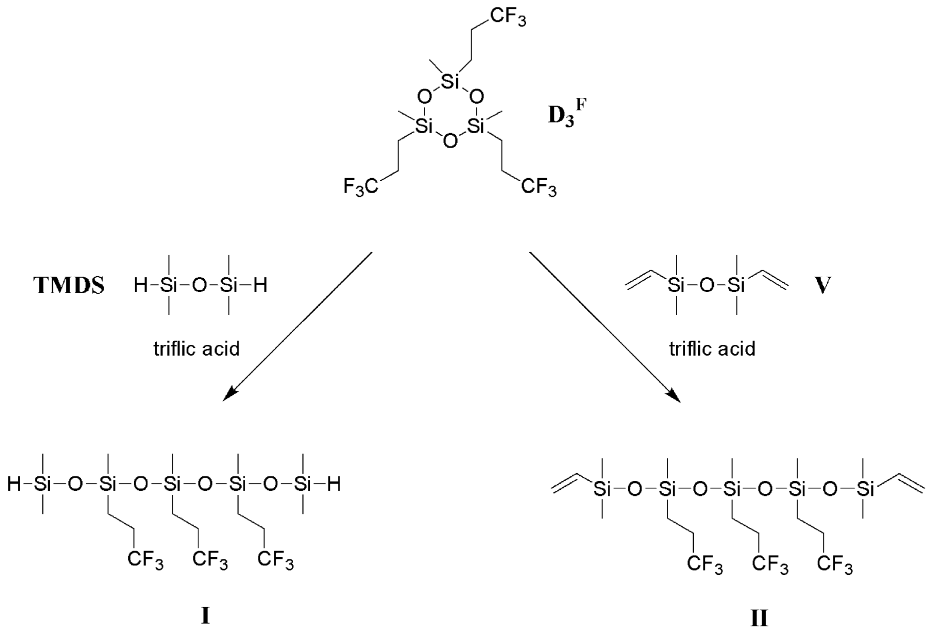
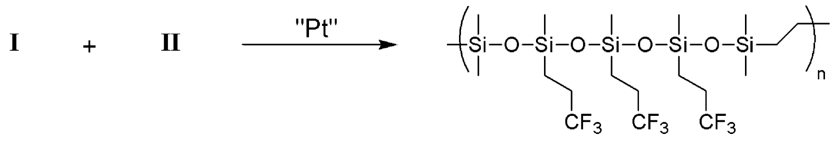


Fig. 1. Synthesis of **I** and **II** by acid-catalyzed ring-opening of D_3^F and TMDS or **V**, respectively.



VII

Fig. 2. Synthesis of **VII** by Pt-catalyzed hydrosilylation copolymerization.

reaction of **I** (1.0 g, 1.692 mmol) and **III** (0.19 g, 1.692 mmol) as above (Fig. 3). In this way, 0.76 g (64% yield) of **VIII** with $M_w/M_n = 22\,830/13\,730$, T_g(PE) = −77 °C, was obtained. ^{1}H NMR δ: −0.076 (s, 6H), 0.062 (s, 12H), 0.079 (s, 6H), 0.11 (s, 3H), 0.37 (m, 8H), 0.71 (m, 6H), 2.00 (s, 6H). ^{13}C NMR δ: −4.73, −0.73, 6.05, 9.33, 10.08, 28.03 (q, $J_{C-F} = 30$ Hz), 28.10 (q, $J_{C-F} = 31$ Hz), 127.66 (q, $J_{C-F} = 276$ Hz). ^{29}Si NMR δ: −23.60 (s, 2Si), −23.52 (s, 1Si), 6.18 (s, 1Si), 10.24 (s, 2Si). ^{19}F NMR δ: [−69.35 (t, $J_{H-F} = 9.4$ Hz), −69.34 (t, $J_{H-F} = 9.4$ Hz)] 6F, [−69.26 (t, $J_{H-F} = 9.4$ Hz), −69.25 (t, $J_{H-F} = 9.4$ Hz), −69.24 (t, $J_{H-F} = 9.41$ Hz)] 3F. IR ν: 3049, 2960, 2908, 2788, 1447, 1420, 1407, 1368, 1315, 1265, 1210, 1127, 1069, 1022, 901, 835, 784 cm^{-1}.

*3.6.5. alt-copoly[1,1,3,5,7,9,9-Heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-1,9-pentasiloxanylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene] (**IX**)*

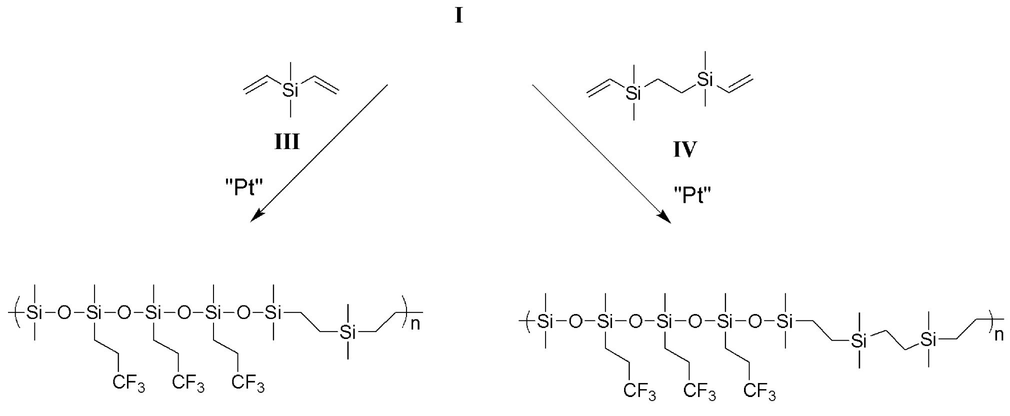
The title compound **IX** was prepared by a Pt-catalyzed reaction of **I** (2.0 g, 3.3 mmol) and **IV** (0.66 g, 3.3 mmol) as above (Fig. 3). In this way, 1.94 g (73% yield) of **IX** with $M_w/M_n = 47\,660/11\,080$, T_g(PE) = −78 °C, was obtained. ^{1}H NMR δ: −0.05 (s, 12H), 0.09 (s, 12H), 0.11 (s, 6H), 0.14 (s, 3H), 0.37 (s, 4H), 0.40 (m, 8H), 0.74 (m, 6H), 2.05 (m, 6H). ^{13}C NMR δ: −4.63, −0.69, −0.61, 1.13, 6.05, 6.61, 9.28, 9.33, 10.12, 28.03 (q, $J_{C-F} = 31$ Hz), 28.10 (q, $J_{C-F} = 31$ Hz), 126.5, 128.8, 130.9, 131.5. ^{29}Si NMR δ: −23.61 (s, 2Si), −23.50 (s, 1Si), 5.94 (s, 2Si), 10.29 (s, 2Si). ^{19}F NMR δ: [−69.32 (t, $J_{H-F} = 9.4$ Hz), −69.30 (t, $J_{H-F} = 9.4$ Hz)] 6F, [−69.23 (t, $J_{H-F} = 9.4$ Hz), −69.22 (t, $J_{H-F} = 9.4$ Hz), −69.21 (t, $J_{H-F} = 9.4$ Hz)] 3F. IR ν: 3044, 2958, 2907, 2876, 2793, 1447, 1407, 1368, 1315, 1263, 1211, 1132, 1069, 1020, 901, 831, 777, 711 cm^{-1}.

*3.6.6. alt-copoly[1,1,3,5,7,9,9-Heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-1,9-pentasiloxanylene/-3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,9-heptanylene] (**X**)*

The title compound **X** was prepared by the Pt-catalyzed polymerization reaction of **I** (2.00 g, 3.32 mmol) and **V** (0.62 g, 3.32 mmol) as above (Fig. 4). In this way, 1.78 g (68% yield) of **X** with $M_w/M_n = 51\,500/19\,570$, T_g(PE) = −78 °C, was obtained. ^{1}H NMR δ: 0.04 (s, 12H), 0.09 (s, 12H), 0.11 (s, 6H), 0.14 (s, 3H), 0.41 (m, 8H), 0.74 (m, 6H), 2.05 (m, 6H). ^{13}C NMR δ: −0.72, −0.63, −0.48, 1.13, 9.27, 9.32, 9.52, 9.65, 28.01 (q, $J_{C-F} = 29$ Hz), 28.08 (q, $J_{C-F} = 30$ Hz), 127.64 (q, $J_{C-F} = 276$ Hz). ^{29}Si NMR δ: −23.56 (s, 2Si), −23.47 (s, 1Si), 8.21 (s, 2Si), 10.44 (s, 2Si). ^{19}F NMR δ: [−69.34 (t, $J_{H-F} = 9.4$ Hz), −69.332 (t, $J_{H-F} = 9.4$ Hz)] 6F, [−69.26 (t, $J_{H-F} = 9.4$ Hz), −69.25 (t, $J_{H-F} = 9.4$ Hz), −69.22 (t, $J_{H-F} = 9.4$ Hz)] 3F. IR ν: 2961, 2909, 2876, 2784, 1585, 1447, 1405, 1368, 1315, 1262, 1210, 1130, 1070, 1022, 901, 799 cm^{-1}.

*3.6.7. alt-copoly[1,1,3,5,7,9,9-Heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl-1,9-pentasiloxanylene/3,3,5,5,7,7-hexamethyl-4,6-dioxa-3,5,7-trisila-1,9-nonanylene] (**XI**)*

The title compound **XI** was prepared by a Pt-catalyzed reaction of **I** (0.49 g, 0.813 mmol) and **VI** (0.21 g, 0.813 mmol) as above (Fig. 4). In this way, 0.44 g (63% yield) of **XI** with $M_w/M_n = 20\,050/13\,550$, $T_g = -90$ °C, was obtained. ^{1}H NMR δ: −0.014 (s, 3H), 0.03 (s, 12H),



VIII **IX**

Fig. 3. Preparation of **VIII** and **IX** by Pt-catalyzed hydrosilylation copolymerization.

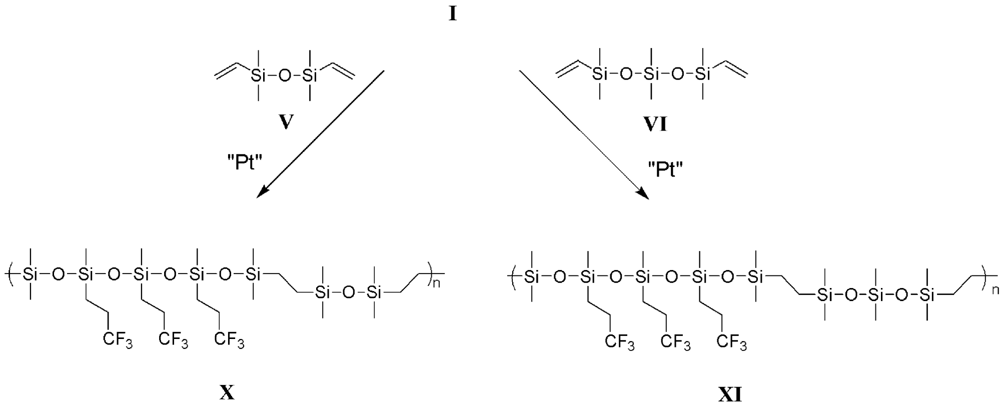


Fig. 4. Synthesis of **X** and **XI** by Pt-catalyzed hydrosilylation copolymerization.

0.046 (s, 6H), 0.06 (s, 12H), 0.076 (s, 6H), 0.11 (s, 3H), 0.40 (m, 8H), 0.70 (m, 6H), 2.01 (m, 6H). ^{13}C NMR δ: -0.60, 1.13, 1.25, 9.34, 9.49, 9.56, 28.03 (q, $J_{C-F} = 31$ Hz), 28.10 (q, $J_{C-F} = 29$ Hz), 120.76 (q, $J_{C-F} = 279$ Hz). ^{29}Si NMR δ: -23.57 (s, 2Si), -23.50 (s, 1Si), -21.00 (s, 1Si), 7.99 (s, 2Si), 10.45 (s, 2Si). ^{19}F NMR δ: [-69.35 (t, $J_{H-F} = 9.4$ Hz), -69.34 (t, $J_{H-F} = 9.4$ Hz)] 6F, [-69.27 (t, $J_{H-F} = 9.4$ Hz), -69.26 (t, $J_{H-F} = 9.4$ Hz), -69.25 (t, $J_{H-F} = 9.4$ Hz)] 3F. IR ν: 3049, 2961, 2909, 2876, 2792, 1447, 1408, 1368, 1315, 1262, 1210, 1132, 1071, 1024, 901, 832, 796 cm^{-1}.

4. Discussion

4.1. Synthesis

4.1.1. Synthesis of *I* and *II*

Compound **I** was synthesized in excellent yield (87%). However, the yield of **II** was somewhat lower (61%). This may be due to protodesilylation or acid-catalyzed equilibration of the pentasiloxane product. Protodesilylation of vinyl silanes is known to occur under acidic conditions [14]. **II** is also susceptible to acid-catalyzed equilibration, which causes redistribution of siloxane bonds.

4.1.2. Synthesis of *VII–XI*

Pt-catalyzed hydrosilylation using Karstedt's catalyst was effective in producing high molecular weight copolymers **VII–XI** in good yields. High molecular weight copolymers are often difficult to achieve via step-growth polymerization due to the requirement of precise stoichiometry. In this regard, IR analysis of copolymers **VII–IX** and **XI** shows an absorbance at ~3050 cm^{-1}, consistent with the presence of terminal vinyl groups. This may be due to a slight excess of α,ω-divinyl monomers in the reaction mixture. Copolymer **X** does not exhibit an IR band at ~3050 cm^{-1}. While the other possible end group is an Si–H, no IR absorption is observed at ~2125 cm^{-1} in the spectrum.

4.2. NMR spectroscopy

The structure of the copolymers was studied by NMR spectroscopy. The ^{1}H, ^{13}C and ^{29}Si NMR spectra are consistent with the structures proposed. The ^{19}F NMR spectra are more complicated. The fluorine signal due to each trifluoromethyl group is split to a triplet by the hydrogens of the adjacent methylene to which it is bonded with a coupling constant of approximately 9 Hz. In each 1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-1,9-pentasiloxanylene unit there are two chemically equivalent terminal 3,3,3-trifluoropropyl units and one chemically unique central 3,3,3-trifluoropropyl units. Thus, one would anticipate two independent triplets in a 2:1 integration ratio. In fact, however, five triplets are observed. Two of these are due to the terminal 3,3,3-trifluoropropyl groups while three result from the central 3,3,3-trifluoropropyl groups. The silyl centers to which the 3,3,3-trifluoropropyl groups are bound are chiral. Thus, the relationship between the terminal 3,3,3-trifluoropropyl group and the adjacent central 3,3,3-trifluoropropyl group can be *RR*′, *SS*′ or *RS*′, *SR*′. These are two magnetically non-equivalent diastereotopic environments, which result in two distinct triplet signals. Similar analysis of the environments of the central 3,3,3-trifluoropropyl group predicts that there are three magnetically non-equivalent diastereotopic environments *RR*′*R*, *SS*′*S*; *RR*′*S*, *SS*′*R*; or *RS*′*R*, *SR*′*S*. These give rise to three distinct triplet signals (Fig. 5).

4.3. Molecular weight distribution

The expected molecular weight distribution (M_w/M_n) for a high molecular weight linear step-growth polymer is 2 [15]. The molecular weight distribution (M_w/M_n) for copolymers **VII**, **VIII**, **X**, **XI**, determined following precipitation, are 2.0, 1.7, 2.6 and 1.5, respectively. These values are reasonably close agreement with the expected value of 2.0. However, the M_w/M_n value (4.3) of **IX** was unusually high. Low molecular weight fractions of copolymer **IX** were removed during their precipitation from

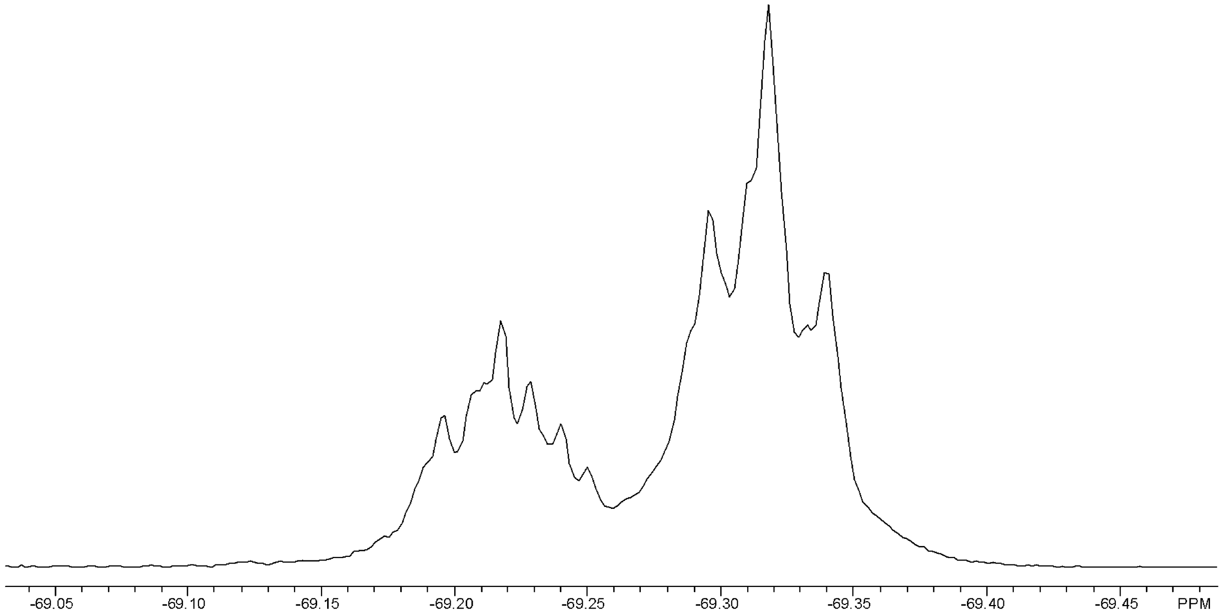


Fig. 5. ^{19}F NMR spectrum of **IX**.

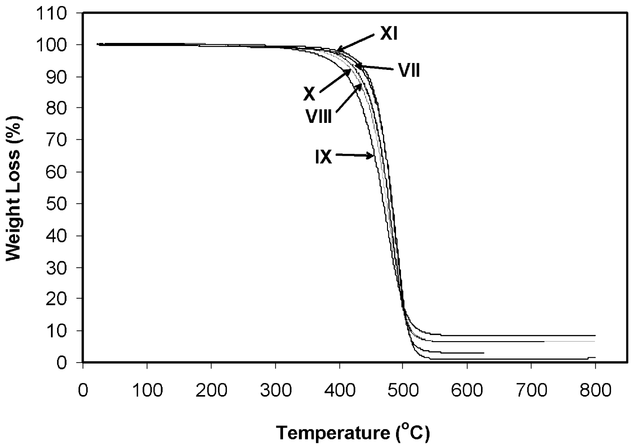


Fig. 6. TGA in nitrogen of **VII–XI**.

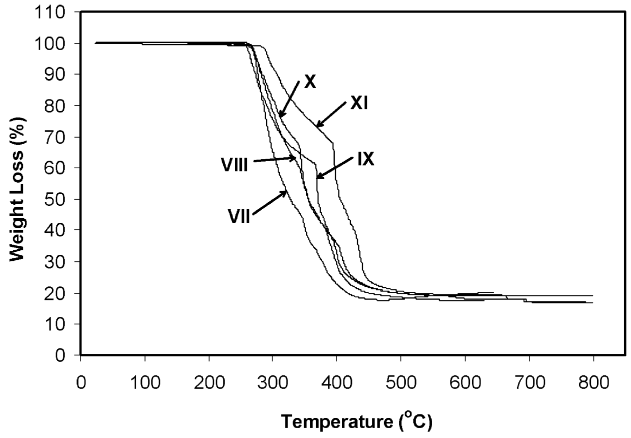


Fig. 7. TGA in air of **VII–XI**.

methanol. It is unclear why the molecular weight distribution for **IX** is high.

4.4. Glass transition temperature

The glass transition temperatures (T_gs) of polydimethylsiloxane (PDMS) and poly[(3,3,3-trifluoropropyl)methylsiloxane] are -123 and -70 °C, respectively [16,17]. Almost all the copolymers (**VII–X**) have T_gs that are between -77 and -80 °C. Adjacent CF_3 groups would be anticipated to electronically repel one another and thereby cause the propyl groups to become rigid, resulting in an increase in T_g [11]. The T_g of **XI** (-90 °C) is lower. This is consistent with the increased number of the dimethylsiloxanylene subunits in the backbone. Polysiloxanes low T_gs arise from large bond angles and bond lengths associated with the dimethylsiloxane backbone to produce greater conformational flexibility.

4.5. Thermal analysis

Despite changes in the nature of the copolymer backbones, the thermal stabilities of copolymers **VII–XI** are very similar in both nitrogen (Fig. 6) and in air (Fig. 7). As expected, decomposition in air began at a lower temperature than in nitrogen and resulted in a higher char yield. The copolymers are stable in nitrogen to approximately 380 °C. Between 380 and 575 °C, catastrophic decomposition occurs. At 575 °C, about 90% of initial weight is lost. No further weight loss occurs on heating to 800 °C. Stability in air is observed to approximately 270 °C. Between 270 and 550 °C decomposition occurs. At 550 °C about 80% of initial weight is lost. No further weight loss occurs on heating to 800 °C.

Acknowledgements

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