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Polymer 45 (2004) 2517–2523

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Synthesis of 1,9-bis[glycidyloxypropyl]penta(1′H,1′H,2′H,2′H-perfluoroalkylmethylsiloxane)s and copolymerization with piperazine

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Received 25 October 2003; received in revised form 12 February 2004; accepted 16 February 2004

Abstract

A series of 1,9-bis[glycidyloxypropyl]pentasiloxanes (**IV–VI**) were prepared by the platinum catalyzed hydrosilylation of 1,9-dihydridodecamethylpentasiloxane (**I**), 1,9-dihydrido-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**II**), and 1,9-dihydrido-3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)heptamethylpentasiloxane (**III**) with allyl glycidyl ether. Subsequently, **IV–VI** were copolymerized with piperazine to form high molecular weight copoly(carbosiloxane)s (**VII–IX**). The structures of the 1,9-bis[glycidyloxypropyl]pentasiloxanes (**IV–VI**) and copoly(carbosiloxane)s (**VII–IX**) were 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 **VII–IX** have been characterized by gel permeation chromatography and their thermal properties measured by differential scanning calorimetry and thermal gravimetric analysis.

Keywords: Copoly(carbosiloxane); Fluoro; Piperazine

1. Introduction

The backbone of polysiloxanes consists of Si–O linkages, whereas polymers whose backbones contain both Si–C and Si–O bonds are referred to as copoly(carbosiloxane)s [1]. Si–C bonds are often prepared by platinum-catalyzed hydrosilylation reactions. In these, the anti-Markovnikov addition of a Si–H bond across a C–C double bond is usually observed [2]. Hydrosilylation copolymerizations of α,ω-dihydridosiloxanes with various divinylsilanes, α,ω-divinyloligosiloxanes, and α,ω-dienes have been utilized to obtain copoly(carbosiloxane)s [3–9]. The most frequently used catalyst for hydrosilylation copolymerization is Karstedt's catalyst (1,3-divinyltetramethyldisiloxane platinum complex) [10]. By comparison, Speier's catalyst (H_2PtCl_6) is acidic and may promote loss of vinyl groups from divinylsilanes by protodesilylation reactions [11]. This process leads to a stoichiometric imbalance which lowers copolymer molecular weight in such step growth polymerizations. Unsaturated copoly(carbosiloxane)s have also been prepared by acyclic diene metathesis (ADMET) polymerization [12]. Direct polycondensation reactions, such as the addition of piperazine to α,ω-(diepoxy)oligosiloxanes or the addition of α,ω-(diacid chloride)oligoamides to α,ω-(diamino)oligosiloxanes, have also been used to synthesize copoly(carbosiloxane)s [13,14].

The properties of polysiloxanes can be altered by the introduction of pendent functional groups attached to Si atoms of the polymer backbone. For stability, a propyl group is often placed between the functional group and the Si center. We have previously reported the synthesis of several copoly(carbosiloxane)s with pendant 3′,3′,3′-trifluoropropyl groups [4]. Such fluorinated copoly(carbosiloxane)s may achieve a blend of properties of siloxane and fluoropolymers. Siloxanes retain their properties over a broad range of temperatures. Their low temperature flexibility is evident by their low glass transition temperatures (T_g's) which are between −140 and 50 °C [15]. These depend on the type of substituents attached to the Si's of the backbone chain. Siloxanes are frequently stable to 300–350 °C [16]. Above this temperature, reversion reactions occur which converts the polymer to cyclic and oligomer residues. In addition, siloxanes possess good water-repellency, high dielectric strength, and weather-resistance as well as thermal, oxidative, biological, and chemical stability [17]. Fluorinated polymers, such as polytetrafluoroethylene (PTFE), have low surface tension and are stable to corrosive organic solvents, harsh chemicals, and high

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0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.02.029

temperatures [18]. Fluorosilicones, such as poly[(3′,3′,3′-trifluoropropyl)methylsiloxane], possess low T_g's and chemical inertness [19]. Fluorosilicones are used as aviation fuel tank sealants and gaskets and as release coatings, antifoams for organic liquids (such as crude oil), lubricants, surfactants, gels, and adhesives.

The insertion of functionalized organic segments into the polymer backbone may also modify the properties of siloxanes. Hydroxy-containing organic segments distributed along the siloxane backbone would provide sites for hydrogen bonding to metallic substrates for improved adhesion [20]. Furthermore, intermolecular hydrogen bonding within the polymer matrix may enhance barrier properties to atmospheric gases [21]. For example, incorporation of the bis-allyl derivative of bisphenol A as well as 2,6-diallylphenol into polysiloxane backbones has been reported [8]. Low temperature flexibility should decrease and thermal stability increase if rigid cyclic structures, such as piperazine groups, are introduced into the polysiloxane backbone [22]. In this regard, low molecular weight multiblock copoly(carbosiloxanes/amides) having piperazine moieties in the backbone were prepared by reaction of α,ω-bis(3-aminopropyl)oligodimethylsiloxanes with α,ω-(diacid chloride)oligoamides prepared from *trans*-2,5-dimethylpiperazine and terephthaloyl chloride [14]. Piperazine also reacts with α,ω-(glycidyloxypropyl) compounds to form linear copolymers [23]. Reaction of α,ω-(glycidyloxypropyl)oligodimethylsiloxane and bisphenol-A diglycidyl ether with piperazine to form a linear copoly(carbosiloxane)s containing hydroxy-pendant groups and piperazine moieties within the polymer backbone has been reported [13].

Herein, we report a new family of copoly(carbosiloxane)s (**VII–IX**) prepared from the reaction of 1,9-bis[glycidyloxypropyl]penta(1′H,1′H,2′H,2′H-perfluoroalkylmethylsiloxane)s (**IV–VI**) with piperazine. 3′,3′,3′-Trifluoropropyl and 1′H,1′H,2′H,2′H-perfluorooctyl groups were selected because fluoroalkyl groups bonded to silicon in the α or β position are hydrolytically and thermally unstable [24].

2. Results

Our synthetic sequence begins with the known acid-catalyzed ring-opening of hexamethylcyclotrisiloxane (D_3), 1,3,5-tris(3′,3′,3′-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane, and 1,3,5-tris(1′H,1′H,2′H,2′H-perfluorooctyl)-1,3,5-trimethylcyclotrisiloxane in tetramethyldisiloxane (TMDS) to yield **I–III**, respectively [4,25,26]. This was followed by Pt-catalyzed (Karstedt) hydrosilyation of allyl glycidyl ether and **I–III** to yield 1,9-bis[glycidyloxypropyl]decamethylpentasiloxane (**IV**), 1,9-bis[glycidyloxypropyl]-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**V**), and 1,9-bis[glycidyloxypropyl]-3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)heptamethylpentasiloxane (**VI**), respectively. **IV–VI** were subsequently copolymerized with piperazine by ring-opening reaction of epoxide groups to yield high molecular weight fluorinated copoly(carbosiloxane)s: *alt*-copoly[decamethylpentasiloxane-1,9-bis(3′-propanoxylene)/piperazine-*N*,*N*-bis(2-hydroxypropanylene)] (**VII**), *alt*-copoly[3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane-1,9-bis(3′-propanoxylene)/piperazine-*N*,*N*-bis(2-hydroxypropanylene)] (**VIII**), and *alt*-copoly[3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)heptamethylpentasiloxane-1,9-bis(3′-propanoxylene)/piperazine-*N*,*N*-bis(2-hydroxypropanylene)] (**IX**), respectively (Fig. 1).

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. ^{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. ^{19}F NMR spectra were referenced to internal $CFCl_3$. ^{29}Si NMR spectra were obtained using 25% w/v chloroform-*d* solutions. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60 s delay was used to acquire ^{29}Si NMR spectra. ^{29}Si NMR spectra were referenced to internal TMS. 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)

GPC analysis of the molecular weight distribution of these polymers was performed on a Waters system equipped with 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 0.6 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)

TGA of the polymers was measured on a Shimadzu TGA-50 instrument at a flow rate of 40 $cm^3 min^{-1}$ of nitrogen or air. The temperature program was 4 °C/min from 25 to 800 °C.

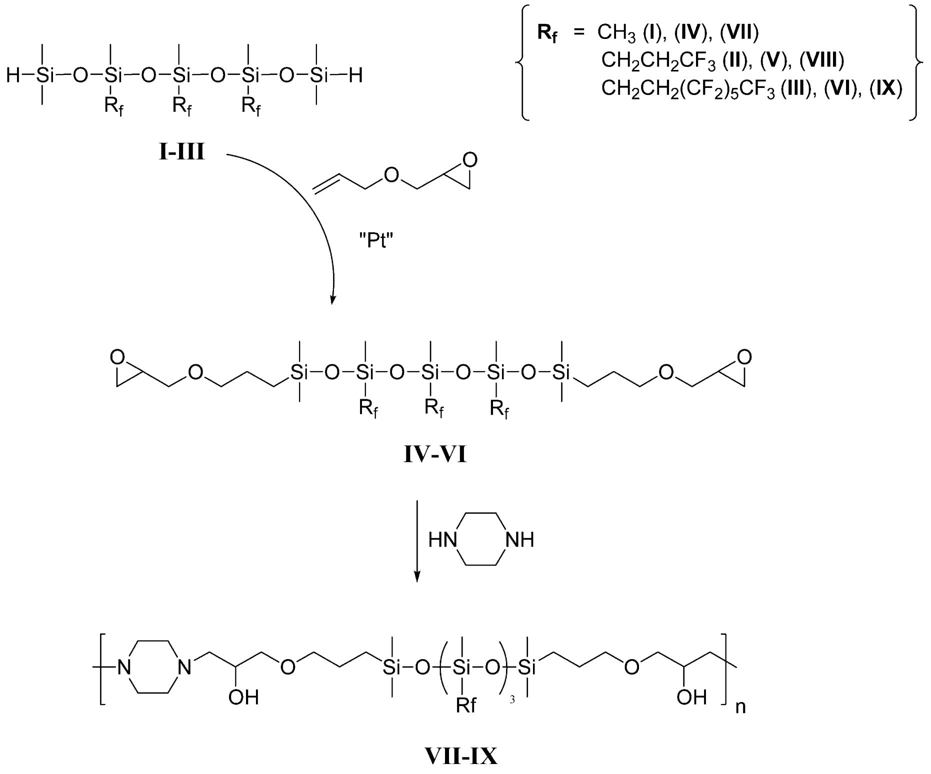

Fig. 1. Synthesis of 1,9-bis[glycidyloxypropyl]pentasiloxanes (**IV**–**VI**) and copoly(carbosiloxane)s (**VII**–**IX**).

3.4. Differential scanning calorimetry (DSC)

The T_g's of the polymers were determined on a Shimadzu DSC-50. The DSC was calibrated from the thermal transition temperature (− 87.06 °C) and melting point (6.54 °C) of cyclohexane [27]. After equilibration at − 150 °C for 5 min, the temperature was increased at a rate of 10 °C/min to 25 °C.

3.5. Materials

Pt-divinyltetramethyldisiloxane complex (Karstedt's catalyst) in xylene (2% Pt) was acquired from United Chemical Technologies, Inc. Triflic acid was bought from 3 M Co. 1′H,1′H,2′H-Perfluoro-1-octene and 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluoropropyl)cyclotrisiloxane were purchased from Lancaster. Methyldichlorosilane, hexamethylcyclotrisiloxane (D_3), TMDS, and hexamethyldisilazane (HMDZ) were purchased from Gelest. Toluene, DMSO, THF, allyl glycidyl ether, triethylamine, and piperazine were acquired from Aldrich. Solvents were purified by distillation prior to use. Piperazine was recrystallized from ethanol (mp 108–110 °C).

3.6. Synthetic procedure

All reactions were conducted in flame-dried glassware under nitrogen with Teflon covered magnetic stir bars. Three drops each of Karstedt's catalyst solution and triethylamine were added to hydrosilylation reaction mixtures. Copolymerization reactions were run at 70 °C for 48 h in sealed Ace pressure tubes.

3.6.1. 1′H,1′H,2′H,2′H-Perfluorooctylmethyldichlorosilane

1′H,1′H,2′H,2′H-perfluorooctylmethyldichlorosilane was prepared from the Pt (Karstedt) catalyzed hydrosilylation reaction of methyldichlorosilane and 1′H,1′H,2H′-perfluoro-1-octene [28].

3.6.2. 1,3,5-Trimethyl-1,3,5-tris(1′H,1′H,2′H,2′H-perfluorooctyl)cyclotrisiloxane

1,3,5-Trimethyl-1,3,5-tris(1′H,1′H,2′H,2′H-perfluorooctyl)cyclotrisiloxane was prepared by reaction of 1′H,1′H,2′H,2′H-perfluorooctylmethyldichlorosilane and DMSO in the presence of zinc [29].

3.6.3. 1,9-Dihydridodecamethylpentasiloxane (*I*)

I was prepared from the triflic acid catalyzed ring opening of D_3 in TMDS [25].

3.6.4. 1,9-Dihydrido-3,5,7-tris(3′,3′,3′-trifluoropropyl)-heptamethylpentasiloxane (*II*)

II was prepared by the triflic acid catalyzed ring opening of 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluoropropyl)cyclotrisiloxane in TMDS [26].

*3.6.5. 1,9-Dihydrido-3,5,7-tris(1′H,1′H,2′H, 2′H-perfluoro-octyl)heptamethylpentasiloxane (**III**)*

III was prepared by the triflic acid catalyzed ring opening of 1,3,5-trimethyl-1,3,5-tris(1′H,1′H,2′H,2′H-perfluoro-octyl)cyclotrisiloxane in TMDS [26].

*3.6.6. 1,9-bis[glycidyloxypropyl]decamethylpentasiloxane (**IV**)*

I (7.4 g, 20.7 mmol), Karstedt's catalyst, and triethylamine were placed in a 50 ml round bottom (rb) flask. Allyl glycidyl ether (8.3 g, 72.7 mmol) was placed in a pressure equalizing addition funnel and slowly added over 30 min. The mixture was allowed to stir overnight. THF (10 mL) was added and the solution was passed through a short silica gel column with additional THF to remove the Karstedt's catalyst. The volatiles were then removed under reduced pressure. **IV**, 9.2 g, 76% yield, was obtained. ^{1}H NMR δ: −0.18 (s, 12H), −0.16 (s, 6H), −0.14 (s, 12H), 0.32 (m, 4H), 1.38 (m, 4H), 2.36 (dd, 2H, $J = 5.5$ and 2.5 Hz), 2.55 (dd, 2H, $J = 5.5$ and 5.0 Hz), 2.90 (m, 2H), 3.15 (dd, 2H, $J = 11.5$ and 5.5 Hz), 3.22 (m, 4H), 3.47 (dd, 2H, $J = 11.5$ and 3.0 Hz). ^{13}C NMR δ: −0.10, 0.85, 0.94, 14.00, 23.29, 43.92, 50.56, 71.21, 71.23, 74.03. ^{29}Si NMR δ: −22.41 (s, 1Si), −21.64 (s, 2Si), 7.52 (s, 2Si). IR ν: 3046, 2960, 2938, 2873, 1476, 1438, 1409, 1341, 1255, 1185, 1153, 1102, 1032, 906, 841, 793, 704, 683, 664 cm^{-1}.

*3.6.7. 1,9-bis[Glycidyloxypropyl]-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**V**)*

V was prepared from **II** (10 g, 16.6 mmol) and allyl glycidyl ether (6.6 g, 57.9 mmol) as above. **V**, 11.4 g, 83% yield, was obtained. ^{1}H NMR δ: −0.12 (s, 12H), −0.11 (s, 6H), [−0.08 (s), −0.07 (s), −0.06 (s)] 3H, 0.35 (m, 4H), 0.49 (m, 4H), 0.53 (m, 2H), 1.37 (m, 4H), 1.82 (m, 6H), 2.34 (dd, 2H, $J = 5.0$ and 3.0 Hz), 2.53 (dd, 2H, $J = 5.5$ and 5.0 Hz), 2.90 (m, 2H), 3.13 (dd, 2H, $J = 11.5$ and 5.5 Hz), 3.22 (m, 4H), 3.47 (dd, 2H, $J = 11.5$ and 3.0 Hz). ^{13}C NMR δ: −0.99 (m), −0.27, −0.24, −0.17, 9.03, 13.89, 13.92, 23.25, 27.68 (q, $J_{C-F} = 30$ Hz), 27.81 (q, $J_{C-F} = 30$ Hz), 43.91, 43.93, 43.94, 50.62, 71.33, 73.78, 73.80, 73.86, 73.95, 124.23 (m), 126.43 (m), 128.62 (m), 130.82 (m). ^{19}F NMR δ: −69.26 (m). ^{29}Si NMR δ: [−24.0 (s), −23.80 (s), −23.78 (s), −23.48 (s), −23.43 (s), −23.29 (s), −23.23 (s), −23.13 (s)] 3Si, [8.81 (s), 9.48 (s), 9.75 (s), 9.94 (m)] 2Si. IR ν: 3057, 2954, 2863, 1444, 1417, 1366, 1312, 1266, 1207, 1126, 1073, 1022, 898, 841, 804, 774, 710 cm^{-1}.

*3.6.8. 1,9-Bis[glycidyloxypropyl]-3,5,7-tris(1′H,1′H,-2′H,-2′H-perfluorooctyl)heptamethylpentasiloxane (**VI**)*

VI was prepared from **III** (10 g, 7.4 mmol) and allyl glycidyl ether (3.0 g, 26.3 mmol) as above. **VI**, 10.2 g, 87% yield was obtained. ^{1}H NMR δ: −0.12 (s, 12H), −0.09 (s, 6H), [−0.06 (s), −0.05 (s), −0.04 (s)] 3H, 0.37 (m, 4H), 0.53 (m, 2H), 0.58 (m, 4H), 1.40 (m, 4H), 1.85 (m, 6H), 2.33 (m, 2H), 2.51 (m, 2H), 2.88 (m, 2H), 3.12 (dd, 2H, $J = 11.5$ and 5.5 Hz), 3.22 (m, 4H), 3.46 (dd, 2H, $J = 11.5$ and 3.0 Hz). ^{13}C NMR δ: −2.10 (m), −1.39 (m), −0.75 (m), 6.06 (m), 6.49, 13.75, 13.79, 13.83, 23.18, 23.20, 24.79 (m), 29.75, 43.38, 43.43, 43.47, 50.34, 50.38, 71.22, 73.59, 73.66, 73.77, 108.47 (m), 110.65 (m), 112.80 (m), 115.88 (m), 118.17 (m), 120.09 (m). ^{19}F NMR δ: −126.88 (m, 2F), −124.02 (m, 2F), −123.49 (m, 2F), −122.47 (m, 2F), −116.72 (m, 2F), −81.81 (m, 3F). ^{29}Si NMR δ: [−23.75 (s), −23.50 (s), −23.45 (s), −22.87 (m), −20.31 (s), −20.26 (s), −20.01 (s), −19.95 (s), 19.87 (s)] 3Si, [8.94 (s), 9.67 (s), 9.68 (s), 9.95 (s), 9.97 (s), 10.09 (s), 10.18 (s)] 2Si. IR ν: 3051, 2960, 2863, 1441, 1363, 1317, 1250, 1142, 1043, 949, 895, 844, 788, 734, 704, 645 cm^{-1}.

*3.6.9. alt-Copoly[decamethylpentasiloxane-1,9-bis(3′-propan-oxylene)/piperazine-N,N-bis (2-hydroxy-propanylene)] (**VII**)*

VII was prepared by reaction of stoichiometric amounts of **IV** and piperazine. In an Ace pressure tube equipped with a Teflon covered magnetic stir bar, **IV** (1.5 g. 2.6 mmol) was dissolved into 2 mL of THF and heated to 70 °C. Next, piperazine (0.22 g, 2.6 mmol) was added to the solution. The mixture was allowed to stir at 70 °C for 48 h. The THF was evaporated under high vacuum to quantitatively isolate **VII** having $M_w/M_n = 63,300/45,000$ and $T_g = -41$ °C. ^{1}H NMR δ: −0.19 (s, 12H), 0.17 (s, 6H), −0.16 (s, 12H), 0.29 (m, 4H), 1.37 (m, 4H), 2.19 (m, 8H), 2.43 (bs, 4H), 3.19 (m, 8H), 3.64 (m, 2H). ^{13}C NMR δ: 0.04, 1.03, 1.11, 14.00, 23.23, 53.28, 60.65, 66.01, 73.07, 74.30. ^{29}Si NMR δ: −22.25 (s, 1Si), −21.46 (s, 2Si), 7.65 (s, 2Si). IR ν: 3442, 2950, 2812, 1942, 1664, 1457, 1410, 1327, 1297, 1256, 1137, 1024, 960, 925, 861, 784, 740, 701 cm^{-1}.

*3.6.10. alt-Copoly[3,5,7-tris(3′,3′,3′trifluoropropyl)hepta-methylpentasiloxane-1,9-bis(3′propanoxylene)/-piperazine-N,N-bis(2-hydroxypropanylene)] (**VIII**)*

V (1.5 g, 1.8 mmol) and 0.16 g (1.8 mmol) of piperazine were reacted in 2 mL of THF as described above to quantitatively produce **VIII** having $M_w/M_n = 71,300/56,300$, $T_g = -36$ °C. ^{1}H NMR δ: −0.08 (m, 18H), −0.02 (m, 3H), 0.36 (m, 4H), 0.55 (m, 6H), 1.41 (m, 4H), 1.86 (m, 6H), 2.34 (m, 8H), 2.49 (bs, 4H), 3.25 (m, 8H), 3.70 (m, 2H). ^{13}C NMR δ: −0.93 (m), −0.12 (m), −0.07, 0.01, 9.11 (m), 13.91, 13.95, 13.98, 23.20, 23.22, 27.86 (m), 53.20, 60.52, 60.55, 66.06, 73.15, 74.06, 74.08, 74.13, 74.21, 124.23 (m), 126.42 (m), 128.62 (m), 130.82 (m). ^{29}Si NMR δ: [−23.92 (s), −23.74 (s), −23.72 (s), −23.45 (s), −23.36 (s), −23.21(s), −23.14 (s), −23.10 (s)] 3Si, [8.89 (s), 9.60 (s), 9.89 (s), 10.09 (m)] 2Si. ^{19}F NMR δ: −69.2 (m). IR ν: 3442, 2930, 2818, 1449, 1366, 1310, 1250, 1206, 1101, 1021, 900, 831, 765, 704, 632 cm^{-1}.

*3.6.11. alt-Copoly[3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)heptamethylpentasiloxane-1,9-bis(3′propanoxylene)/piperazine-N,N-bis (2-hydroxypropan-ylene)] (**IX**)*

IX was prepared by reaction of **VI** (1.0 g. 0.63 mmol) and piperazine (0.05 g, 0.63 mmol) in 1 mL of THF as above. In this way, **IX** was obtained quantitatively with $M_w/M_n = 48,200/32,700$ and $T_g = -34\,°C$. ^{1}H NMR δ: − 0.08 (m, 18H), 0.01 (m, 3H), 0.37 (m, 4H), 0.58 (m, 6H), 1.42 (m, 4H), 1.88 (m, 6H), 2.24 (m, 8H), 2.45 (m, 4H), 3.25 (m, 8H), 3.70 (s, 2H). ^{13}C NMR δ: − 0.85 (m), 0.07, 0.06, 0.17, 6.65 (m), 7.05, 14.21, 14.24, 14.31, 23.48, 23.51, 25.20 (m), 46.35, 53.55, 54.92, 60.88, 60.92, 61.16, 61.68, 66.28 (m), 66.50, 73.51, 74.33 (m), 74.42, 108.87 (m), 111.27 (m), 113.65 (m), 116.24 (m), 118.55 (m), 120.46 (m). ^{19}F NMR δ: − 126.83 (m, 2F), − 124.15 (m, 2F), − 123.55 (m, 2F), − 122.58 (m, 2F), − 116.82 (m, 2F), − 81.55 (m, 3F). ^{29}Si NMR δ: [− 23.71 (s), − 23.51 (s), − 23.44 (s), − 22.52 (m), − 20.31 (s), − 20.62 (s), − 20.01 (s), − 19.95 (m), − 19.88 (s)] 3Si, [8.99 (s), 9.73 (bs), 10.02 (bs), 10.17 (s), 10.25 (s)] 2Si. IR *ν*: 3401, 2944, 2859, 2817, 1643, 1442, 1360, 1317, 1248, 1145, 1063, 891, 836, 783, 740, 701, 667 cm^{-1}.

4. Discussion

4.1. Synthesis

*4.1.1. Synthesis of **IV–VI***

Pt-catalyzed hydrosilylation reaction of allyl glycidyl ether and **I–III** was effective in producing **IV–VI** in good yields. IR analysis of **IV–VI** shows no absorbance at ~ 2100 cm^{-1}. This confirms that all of the Si–H groups of **I–III** were consumed during the hydrosilylation reaction. It is critical to add a small amount of triethylamine to the Pt-catalyzed hydrosilylation reaction of allyl glycidyl ether with the α,ω-dihydridopentasiloxanes (**I–III**) to avoid premature ring-opening of the epoxide by acidic impurities.

*4.1.2. Synthesis of **VII–IX***

Condensation reactions between piperazine and **IV–VI** produced high molecular weight copoly(carbosiloxane)s (**VII–IX**). It is critical to have exact stoichiometric conditions to achieve high molecular weights in step-growth copolymerization reactions [30]. In this regard, the high molecular weights obtained for **VII–IX** are noteworthy.

4.2. NMR spectroscopy

^{1}H NMR spectra peak assignments for protons of **IV–VI** were made based on homonuclear decoupling NMR experiments and coupling constants. The ^{1}H NMR spectrum of **V** is shown in Fig. 2a. Irradiation of **V** at the frequency of protons ‘c’ (δ = 1.37 ppm) causes a loss of coupling which simplifies the multiplets due to protons ‘b’ and ‘d’ at δ = 0.35 and 3.22 ppm (Fig. 2b). Based on this decoupling experiment, the peaks at δ = 0.35, 1.37, and 3.22 ppm are assigned to protons ‘b’ (4H), ‘c’ (4H), and ‘d’ (4H), respectively. Irradiation of the peak at δ = 2.90 ppm causes the peaks at δ = 2.34, 2.53, 3.13 and 3.47 ppm to simplify (Fig. 2(c)). This is expected if the signal at δ = 2.90 ppm is due to protons ‘f’ (2H). The dd’s at δ = 2.34 (2H) and 2.53 (2H) ppm both have $^2J = \sim 5.5$ Hz. Each of these resonances is due to two of the protons ‘e’. These are diastereotopic because they are adjacent to the chiral carbon of the epoxide. The remaining dd’s δ = 3.13 (2H) and 3.47 (2H) ppm, which both have $^2J = 11.5$ Hz, are assigned to the diastereotopic protons ‘g’.

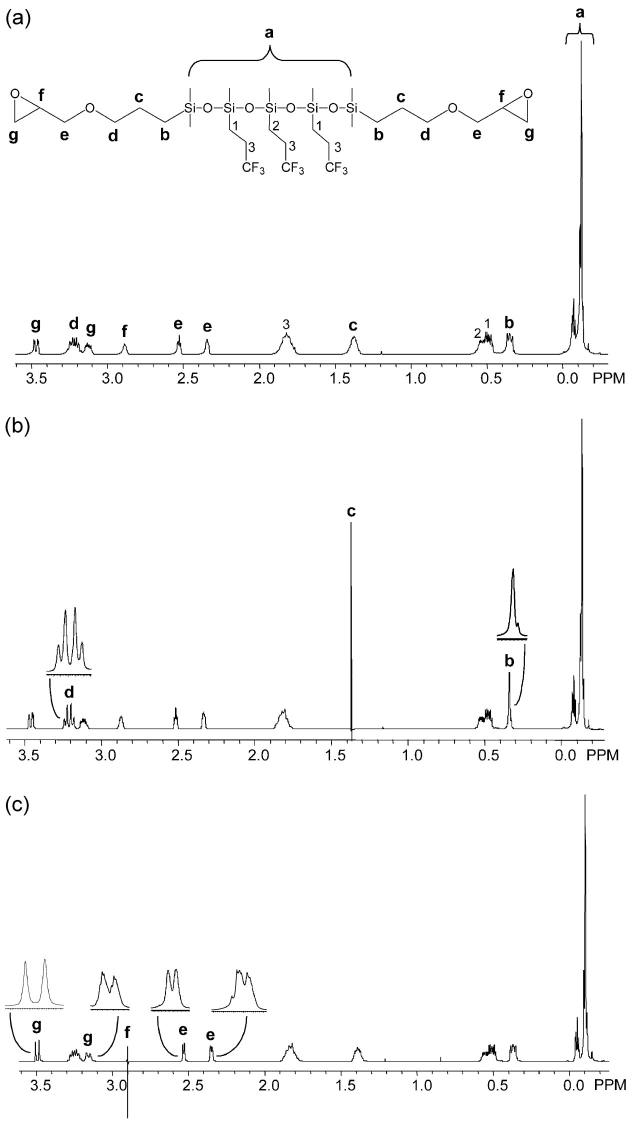

Fig. 2. (a) ^{1}H NMR spectrum peak assignments for **V**. (b) Homonuclear (proton–proton) decoupled ^{1}H NMR spectrum peak of **V** with irradiation at frequency δ = 1.37 ppm. (c) Homonuclear (proton–proton) decoupled ^{1}H NMR spectrum peak of **V** with irradiation at frequency δ = 2.90 ppm.

The peaks in the ^{1}H NMR spectra which are due to the methyl protons of the central Si atom are unique to **IV–VI**. In the case of **IV**, the protons of the central silyl atom produce a singlet at $\delta = -0.16$ (6H) ppm. However, the chirality of the methyl(3′,3′,3′-trifluoropropyl)-and methyl(1′H,1′H,2′H,2′H-perfluorooctyl) siloxane centers produces complexity. For **V** and **VI**, three unique resonances due to the protons of the methyl group attached to the central silyl atom are observed. The silyl centers to which the 3′,3′,3′-trifluoropropyl (**V**) or 1′H,1′H,2′H,2′H-perfluorooctyl groups (**VI**) are bound are chiral. The relationship between the central silyl center and the two adjacent silyl centers can be (*RR'R, SS'S*); (*RR'S, SS'R*); or (*RS'R, SR'S*). Thus, there are three magnetically non-equivalent diastereotopic environments which results in the three peaks for these methyl protons.

In the ^{13}C NMR of **VI**, six multiplets are detected between 109 and 120 ppm due to the terminal trifluoromethyl groups and the five distinct difluoromethylene groups. ^{13}C–^{19}F coupling produces multiplets for the carbons which are bonded to fluorine atoms. Thus, while the ^{13}C NMR is run with broad band proton decoupling, we are unable to simultaneously decouple the fluorine atoms.

The ^{29}Si NMR spectrum of **IV** shows the three expected silicon resonances in a 1:2:2 ratio. The three central silicon atoms are each bonded to two oxygen atoms and give rise to two resonances at approximately -22.4 (1Si) and -21.6 (2Si) ppm. The signal at approximately 7.52 (2Si) ppm is due to the terminal silicon atoms which are each bonded to only one oxygen atom. ^{29}Si NMR spectra of **V** and **VI** are complicated due to the presence of chiral centers. The effect of chiral centers is also manifested in the ^{29}Si NMR spectra of **II** and **III**.[26]

The ^{19}F signals due to terminal trifluoromethyl groups are found at approximately -69 ppm for **V** and -82 ppm for **VI**. In addition, the difluoromethylene groups of **VI** give rise to five multiplets in the ^{19}F NMR between -127 and -117 ppm.

The NMR spectra of **VII–IX** may be interpreted in a similar manner on the basis of spectra of the corresponding 1,9-bis[glycidyloxypropyl]pentasiloxanes (**IV–VI**).

4.3. Molecular weight and molecular weight distribution

The molecular weights of the copoly(carbosiloxane)s (**VII–IX**) are quite high for step growth polymerization. Achieving such high molecular weights requires exact balance in stoichiometry. The expected molecular weight distribution (M_w/M_n) for a high molecular weight linear step-growth polymer is 2 [31]. The molecular weight distribution (M_w/M_n) for copolymers **VII**, **VIII**, and **IX** are 1.4, 1.3, and 1.5, respectively. Because **VII–IX** were not purified by precipitation, their narrow polydispersities cannot be attributed to fractionation. The reason for the narrower then expected molecular weight distribution is not known.

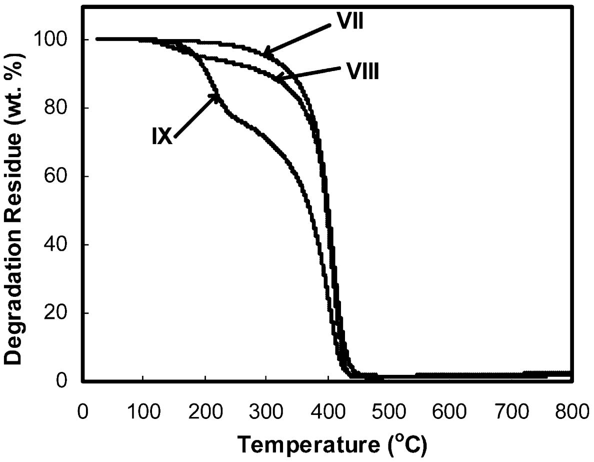

Fig. 3. TGA in nitrogen of **VII–IX**.

4.4. Glass transition temperature

The glass transition temperature (T_g) of polydimethylsiloxane (PDMS) is -123 °C whereas the T_g of poly[(3,3,3-trifluoropropyl)methylsiloxane] is -70 °C [32,33]. Introduction of rigid piperazine moieties into the siloxane backbone as well as pendant hydroxyl groups should significantly increase T_g of the copolymers. The T_gs of copolymers **VII**, **VIII**, and **IX** are -41, -36, and -34 °C, respectively. An increase in T_g of fluorinated copolymers **VIII** and **IX** is anticipated versus the non-fluorinated copolymer (**VII**) as a result of the electronic repulsion between adjacent CF$_n$ groups which leads to side chain rigidity [24].

4.5. Thermal analysis

Fluorosilicones typically have lower thermal stability than comparable siloxanes [34]. As expected, **VII** is the most thermally stable in nitrogen and air (Figs. 3 and 4). **VII** is stable up to approximately 300 °C in both nitrogen and in air. As the level of fluorination increases from 3′,3′,3′-trifluoropropyl groups (**VIII**) to 1′H,1′H,2′H,2′H-perfluoro-

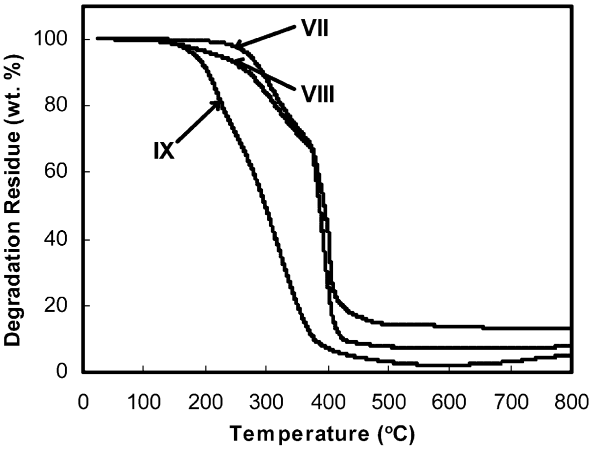

Fig. 4. TGA in air of **VII–IX**.

octyl groups (**IX**), thermal stability decreases. In both nitrogen and in air, **VIII** begins to degrade at approximately 250 °C, whereas **IX** is stable only to 200 °C. In nitrogen, catastrophic decomposition occurs with virtually no char residue remaining for **VII**–**IX**. As expected, the amount of residue remaining in air is greater than in nitrogen for **VII**–**IX**. In air, a maximum of 15% residue remains in the case of **VII**.

Acknowledgements

We thank the Office of Naval Research for support.

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