Polymer 41 (2000) 4423–4428

polymer

Synthesis of poly(silyl ethers) by Ru-catalyzed hydrosilylation

J.M. Mabry, J.K. Paulasaari, W.P. Weber*

K.B. and D.P. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

Received 16 April 1999; received in revised form 12 August 1999; accepted 13 September 1999

Abstract

Dihydridocarbonyltris(triphenylphosphine)ruthenium, activated with a stoichiometric amount of styrene, catalyzes the hydrosilylation polymerization of dimethylsilyloxyaryl ketones or aldehydes as well as the copolymerization of aromatic α,ω-diketones and oligo-α,ω-dihydridodimethylsiloxanes to yield poly(silyl ethers). The ruthenium catalyzed addition of Si–H bonds across C–O double bonds to form CH–O–Si bonds is key to the polymerizations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ruthenium catalyzed; Hydrosilylation polymerization; Poly(silyl ethers)

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1. Introduction

Symmetrical poly(silyl ethers) have been prepared by equilibration polymerization between dialkoxysilanes and α,ω-diols [1–3]. Unfortunately, the reaction of α,ω-diols with dichlorosilanes is not efficient, because the HCl released catalyzes the hydrolysis of Si–O–C ether linkages. Reaction of dichlorosilanes with bis-glycidyl ethers catalyzed by quarternary alkyl ammonium or phosphonium salts give symmetrical poly(silyl ethers) [4–6]. Ring opening polymerization of 2-sila-1-oxacyclopentanes yield unsymmetrical poly(silyl ethers) [7].

Reactive Si–O–C bonds in poly(silyl ethers) are known to be hydrolytically less stable than siloxanes which contain Si–O–Si bonds [8]. Either acid or base can catalyze the hydrolysis of silyl ethers. They are generally more susceptible to acid catalyzed hydrolysis and methanolysis than to basic hydrolysis. The hydrolytic stability of silyl ethers depends on the substituents bonded to both the silicon and carbon centers. Thus, if the carbon of the Si–O–C bond is secondary, the silyl ether is considerably more resistant to hydrolysis than if it is primary [9]. The hydrolytic instability of poly(silyl ethers) may make them attractive in a number of applications, such as, controlled release of drugs or as materials whose degradation will limit their long-term environmental impact. Related work on poly(silyl esters) has appeared [10,11].

Here, we report our work on the ruthenium-catalyzed hydrosilylation polymerization of dimethylsilyloxy-aryl ketones or aldehydes as well as the ruthenium-catalyzed hydrosilylation copolymerization of α,ω-diketones with oligo-α,ω-dihydridodimethylsiloxanes (Figs. 1 and 2). A few examples of this reaction were recently reported [12]. The Pt catalyzed hydrosilylation reaction, in which an Si–H bond adds across a C–C double bond [13], has been used to prepare poly(carbo-silanes) [14–16]. Similar reactions between *sym*-tetramethyldisiloxane and α,ω-dienes give copoly(carbosilane/siloxanes) [17–19]. While $(Ph_3P)_3RhCl$- and $(Ph_3P)_3RuCl_2$-catalyzed hydrosilylation reactions between ketones or aldehydes and silanes to yield silyl ether monomers are known [20–24], such reactions have not been applied to polymer synthesis.

2. Results

Hydrosilylation polymerization of 4-dimethylsiloxyacetophenone catalyzed by dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru), activated with a stoichiometric amount of styrene, gives a quantitative yield of high molecular weight *alt*-copoly(1,4-phenylene/2,2,4-trimethyl-1,3-dioxa-2-silabutanylene). Likewise, Ru catalyzed reaction of 4-dimethylsilyloxybenzaldehyde gives *alt*-copoly(1,4-phenylene/2,2-dimethyl-1,3-dioxa-2-silabutanylene) and 4-dimethylsiloxybenzophenone yields *alt*-copoly(1,4-phenylene/2,2-dimethyl-1,3-dioxa-4-phenyl-2-silabutanylene) (Fig. 1). The Ru catalyzed hydrosilylation copolymerizations of 1,4-diacetylbenzene (I) or 4,4′-diacetyldiphenylether (II) with sym-tetramethyldisiloxane (III) have been reported [12]. We should like to report analogous reactions of I or II with 1,1,3,3,5,5-hexamethyltrisiloxane (IV),

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* Corresponding author. Tel.: +1-213-740-5961; fax: +1-213-740-6679.
E-mail address: wpweber@bcf.usc.edu (W.P. Weber).

PII: S0032-3861(99)00683-7

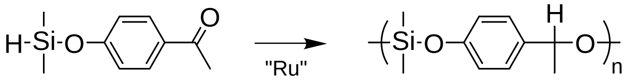

Fig. 1. Polymerization of 4-dimethylsiloxyacetophenone.

1,1,3,3,5,5,7,7-octamethyltetra-siloxane (V), or 1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane (VI). These reactions produce the expected poly(silyl ether)s. Thus, Ru catalyzed copolymerization of I and IV yields *alt*-copoly[1,4-phenylene/1,3,3,5,5,7,7,9-octamethyl-2,4,6,8-tetraoxa-3,5,7-trisilanonanylene], while reaction of II and IV gives *alt*-copoly[4,4′diphenyletherylene/-1,3,3,5,5,7,7,9-octamethyl-2,4,6,8-tetraoxa-3,5,7-trisilanonanylene]. Reaction of I and V gives *alt*-copoly[1,4-phenylene/1,3,3,5,5,7,7,9,9,11-decamethyl-2,4,6,8,10-pentaoxa-3,5,7,9-tetrasilaundecanylene], while reaction of II and V yields *alt*-copoly[4,4′diphenyletherylene/1,3,3,5,5,7,7,9,9,11-decamethyl-2,4,6,8,10-pentaoxa-3,5,7,9-tetrasila-undecanylene]. Finally, Ru catalyzed reaction of I and VI gives *alt*-copoly[1,4-phenylene/1,3,3,5,5,7,7,9,9,11,11,13-dodecamethyl-2,4,6,8,10,12-hexaoxa-3,5,7,9,11-pentasilatridecanylene], while reaction of II and VI produces *alt*-copoly[4,4′diphenyletherylene/1,3,3,5,5,7,7,9,9,11,11,13-dodeca-methyl-2,4,6,8,10,12-hexaoxa-3,5,7,9,11-pentasilatridecanylene] (Fig. 2).

Siloxanes are known to undergo equilibration under either acid or base catalysis, nevertheless the Ru catalyst does not cause siloxane equilibration.

The oligo-α,ω-dihydridodimethylsiloxanes (III–V) are commercially available whereas VI is not. VI was prepared in high yield by a triflic acid catalyzed reaction of III and hexamethylcyclotrisiloxane (D_3). This reaction may be related to the ring opening reaction of D_3 with dimethylchlorosilane, water, and inorganic salts to produce oligo α,ω-difunctional dimethylsiloxanes [25].

3. Experimental

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz, AM-360 MHz, or AC-250 MHz spectrometer operating in the FT mode. ^{1}H and ^{13}C NMR spectra were run on 5% (w/v) chloroform-d solutions. ^{29}Si NMR spectra were obtained in 25% (w/v) acetone-d_6 solutions. ^{13}C NMR spectra were obtained with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60 s delay was used to acquire ^{29}Si NMR spectra. Residual chloroform was used as an internal standard for ^{1}H and ^{13}C NMR. ^{29}Si NMR spectra were referenced to an external TMS standard. IR spectra of neat films on NaCl plates were recorded using a Perkin–Elmer Spectrum 2000 FT-IR spectrometer. UV spectra were run in CH_2Cl_2 or c-C_6H_{12} solutions on a Shimadzu UV-260 spectrometer.

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 columns packed with < 5 μ divinylbenzene crosslinked polystyrene HR4 and HR2 in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.3 ml/min. The retention times were calibrated against known monodisperse polystyrene standards: (929,000; 212,400; 47,400; 13,700; and 794).

TGA of the polymers was measured on a Shimadzu TGA-50 instrument at a flow rate of 40 cc of nitrogen per min. The temperature program was 4°C/min from 25 to 750°C. The T_g of the polymers was determined on a Perkin–Elmer DSC-7. The DSC was calibrated using the melting point of indium (156.6°C) and the thermal transition temperature of cyclohexane (−87.06°C). The temperature for the analysis was initially −100°C. It was increased at a rate of 10°C/min to 50°C.

1,4-Diacetylbenzene, diphenyl ether, 4-hydroxybenzaldehyde, 4-hydroxyacetophenone, 4-hydroxybenzophenone and styrene was obtained from Aldrich. D_3, dimethylchlorosilane, hexamethyldisilazane, and III–V were purchased from Gelest.

All reactions were conducted in flame dried glassware under argon.

Dihydridocarbonyltris(triphenylphosphine) ruthenium (Ru) was prepared from ruthenium trichloride hydrate [26]. Ru was activated as follows: Ru (65 μmol, 0.06 g), toluene (1.0 ml), and styrene (7.5 μl, 65 μmol, 6.8 mg) were placed in a 20 ml Ace pressure tube. The tube and its contents were sealed and heated at 135°C for 3 min. The color of the activated catalyst solution is red [27].

4,4′-Diacetyldiphenyl ether was prepared from diphenyl ether, mp 100–101°C [28].

1,1,3,3,5,5,7,7,9,9-Decamethylpentasiloxane [25] was prepared by a triflic acid catalyzed reaction of D_3 (150 mmol, 33.37 g) and III (375 mmol, 50.37 g) in a 150 ml rb flask equipped with a Teflon covered magnetic stirring bar. The flask was cooled to 0°C. After 15 min, the acid was neutralized by addition of hexamethyldisilazane. The contents of the flask were fractionally distilled. A fraction bp 72–73°C/3 mm, 39.51 g, 79% yield was obtained. ^{1}H NMR δ: −0.08 (s, 6H), −0.01 (s, 12H), 0.10 (d, 12H,

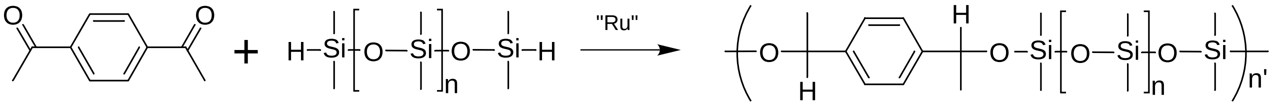

Fig. 2. Copolymerization of I and α,ω-dihydrido-oligodimethylsiloxanes.

$J = 2.5$ Hz), 4.68 (m, 2H, $J = 2.5$ Hz). ^{13}C NMR δ: 0.77, 0.90, 1.06. ^{29}Si NMR δ: -22.16 (s, 1Si), -20.34 (s, 2Si), -7.29(s, 2Si). IR ν: 2128 (Si–H), 1041(br) (Si–O–C) cm^{-1}.

Dimethylsilyloxyacetophenone was prepared by reaction of dimethylchlorosilane (11.4 g, 121 mmol) with 4-hydroxyacetophenone (12.7 g, 93 mmol) and triethyl-amine (11.5 g, 114 mmol) in THF (120 ml). After a non-aqueous work-up, the product was purified by fractional distillation. A fraction bp 75°C/0.1 mm, 15 g, 82% yield was obtained. ^{1}H NMR δ(0.37 (d, 6H, $J = 3$ Hz), 2.48 (s, 3H), 5.00 (sept. 1H, $J = 3$ Hz), 6.94 (dt, 2H, $J = 9$ and 2.5 Hz), 7.91 (dt, 2H, $J = 9$ and 2.5 Hz). ^{13}C NMR δ: -1.63, 26.17, 119.32, 130.90, 131.67, 159.97, 195.53. ^{29}Si NMR δ: 6.16. IR ν: 2139 (Si–H), 1683 (C=O) cm^{-1}. UV c-C_6H_{12} λ_{max} nm (ϵ): 258 (300). Elemental Anal. Calc. for $C_{10}H_{14}O_2Si$: C, 61.81%; H, 7.26%. Found: C, 61.62%; H, 7.14%.

4-Dimethylsilyloxybenzophenone was prepared by reaction of dimethylchlorosilane (7 g, 74 mmol) with 4-hydroxybenzophenone (11.3 g, 57 mmol) and triethyl-amine (11.5 g, 114 mmol). After filtration, the product was purified by fractional distillation. A fraction, 12 g, bp 141°C/0.2 mm, 80% yield was isolated. ^{1}H NMR δ: 0.36 (d, 6H, $J = 3$ Hz), 5.02 (sept. 1H, $J = 3$ Hz), 6.99 (dt, 2H, $J = 9$ and 2.5 Hz), 7.41 (tt, 2H, $J = 7.5$ and 1.5 Hz), 7.50 (tt, 1H, $J = 7.5$ and 1.5 Hz), 7.73 (dt, 2H, $J = 7$ and 1.7 Hz), 7.77 (dt, 2H, $J = 9$ and 2.5 Hz). ^{13}C NMR δ: -1.63, 119.15, 128.51, 129.83, 131.29, 132.13, 132.65, 138.44, 159.67, 194.34. ^{29}Si NMR δ: 6.33. IR ν: 2139 (Si–H), 1656 (C=O) cm^{-1}. UV c-C_6H_{12} λ_{max} nm (ϵ): 269 (1430). Elemental Anal. Calc. for $C_{15}H_{16}O_2Si$: C, 70.27%; H, 6.29%. Found: C, 70.15%; H, 6.17%.

4-Dimethylsilyloxybenzaldehyde was prepared by reaction of 4-hydroxybenzaldehyde (15 g, 123 mmol) with dimethylchlorosilane (145.7 g, 155 mmol) and triethylamine (17.3 g, 171 mmol). After filtration, the product was purified by fractional distillation. A fraction, bp 61°C/0.1 mm, 18.4 g, 83% yield was collected. ^{1}H NMR δ: 0.38 (d, 6H, $J = 3$ Hz), 5.01 (sept. 1H, $J = 3$ Hz), 7.02 (d, 2H, $J = 7$ Hz), 7.83 (d, 2H, $J = 7$ Hz), 9.92 (s, 1H). ^{13}C NMR δ: -1.70, 119.88, 131.30, 132.06, 161.09, 190.26. ^{29}Si NMR δ: 6.51. IR ν: 2141 (Si–H), 1698 (C=O) cm^{-1}. UV c-C_6H_{12} λ_{max} nm (ϵ): 263 (190). Elemental Anal. Calc. for $C_9H_{12}O_2Si$: C, 59.96%; H, 6.71%. Found: C, 59.91%; H, 6.82%.

***alt*-Copoly(1,4-phenylene/1,3-dioxa-2,2,4-trimethyl-2-silabutanylene** was prepared by an activated Ru catalyzed reaction of 4-dimethylsilyloxyacetophenone (3.0 g, 15 mmol) following procedures described in reference [12]. $M_w/M_n = 119,000/57,800$, $T_g = -10$°C. ^{1}H NMR δ: 0.12 (s, 3H), 0.21 (s, 3H), 1.41 (d, 3H, $J = 6$ Hz), 5.07 (q, 1H, $J = 6$ Hz), 6.83 (d, 2H, $J = 8$ Hz), 7.21 (d, 2H, $J = 8$ Hz). ^{13}C NMR δ: -2.41, -1.94, 26.82, 71.05, 119.91, 127.01, 139.37, 154.12. ^{29}Si NMR δ: -5.67. IR ν: 1087 and 1033 (Si–O–C) cm^{-1}. Elemental Anal. Calc. for $C_{10}H_{14}O_2Si$: C, 61.81%; H, 7.26%. Found: C, 61.94%; H, 7.32%.

***alt*-Copoly(1,4-phenylene/1,3-dioxa-2,2-dimethyl-4-phenyl-2-silabutanylene)** was prepared as above by reaction of 4-dimethylsilyloxybenzophenone (3.0 g, 12 mmol). M_w/M_n 94,200/66,400, $T_g = 25$°C. ^{1}H NMR δ: -0.14 (s, 6H), 6.02 (s(1H), 6.76 (d, 2H, $J = 8$ Hz), 7.11 (t, 1H, $J = 7$ Hz), 7.19 (d, 4H, $J = 7$ Hz), 7.35 (d, l2H, $J = 7$ Hz). ^{13}C NMR δ: -2.00, -1.98, 76.63, 120.06, 126.73, 127.52, 128.17, 128.64, 138.22, 145.00, 154.13. ^{29}Si NMR δ: -4.15. IR ν: 1083, and 1064 (Si–O–C) cm^{-1}. Elemental Anal. Calc. for $C_{15}H_{16}O_2Si$: C, 70.27%; H, 6.29%. Found: C, 69.99%; H, 6.35%.

***alt*-Copoly(1,4-phenylene/1,3-dioxa-2,2-dimethyl-2-silabutanylene)** was prepared as above by reaction of 4-dimethylsilyloxybenzaldehyde. $M_w/M_n = 83,000/39,200$, $T_g = -26$°C. ^{1}H NMR δ: 0.24 (s, 6H), 4.79 (s, 1H), 6.89 (d, 2H, $J = 8$ Hz), 7.22 (d, 2H, $J = 8$ Hz). ^{13}C NMR δ: -2.53, 64.76, 120.14, 128.79, 134.28, 154.42. ^{29}Si NMR δ: -3.73. IR ν: 1107 and 1083 (Si–O–C) cm^{-1}. Elemental Anal. Calc. for $C_9H_{12}O\ _2Si$: C, 59.96%; H, 6.71%. Found: C, 59.46%; H, 6.82%.

***alt*-Copoly[1,4-phenylene/1,3,3,5,5,7-hexamethyl-2,4,6-trioxa-3,5-disila-1,7-heptanylene]** $M_w/M_n = 46,200/19,650$, $T_g = -55$°C. For preparation, spectral data and analysis, see Ref. [12].

***alt*-Copoly[4,4′diphenyletherylene/1,3,3,5,5,7-hexamethyl-2,4,6-trioxa-3,5-disila-1,7-heptanylene]** $M_w/M_n = 49,700/26,970$, $T_g = -18$°C. For preparation, spectral data and analysis, see Ref. [12].

***alt*-Copoly[1,4-phenylene/1,3,3,5,5,7,7,9-octamethyl-2,4,6,8-tetraoxa-3,5,7-trisilanonanylene]** was prepared by an activated Ru catalyzed reaction of I (1.62 g, 10.0 mmol) and IV (2.09 g, 10.0 mmol) as described in reference [12] at 120°C for 12 h. After precipitation with methanol, 3.04 g, 82% yield, $M_w/M_n = 89,200/-40,100$, $T_g = -72$°C was obtained. ^{1}H NMR δ: -0.10 (s, 1.5H), -0.09 (s, 3H), -0.08 (s, 1.5H), 0.07 (s, 6H), 0.02 (s, 6H), 1.36 (d, 6H, 6.5 Hz), 4.90 (q, 2H, $J = 6.5$ Hz), 7.19 (s, 4H). ^{13}C NMR δ: -0.23, 0.95, 27.19, 70.48, 125.56, 145.46. ^{29}Si NMR δ: -14.03 (s, 2Si), -21.59 (s, 1Si). IR ν: 1088(br), and 1031(br) (Si–O–C) cm^{-1}. UV CH_2Cl_2 λ_{max} nm (ϵ): 254(1081), 227(1478). TGA: Polymer is stable to 275°C. Between 275 and 400°C, catastrophic decomposition occurs; 90% of initial weight is lost. Elemental Anal. Calc. for $C_{16}H_{30}O_4Si_3$: C, 51.85%; H, 8.16%. Found: C, 51.69%. H, 8.00%.

***alt*-Copoly[4,4′diphenyletherylene/1,3,3,5,5,7,7,9-octamethyl-2,4,6,8-tetraoxa-3,5,7-trisilanonanylene]** was prepared by an activated Ru catalyzed reaction of II (2.54 g, 10.0 mmol) and IV (2.09 g, 10.0 mmol) as above. After precipitation from methanol, 3.94 g, 85% yield, $M_w/M_n = 44,800/9,700$, $T_g = -46$°C was obtained. ^{1}H NMR δ: -0.10 (s, 1.5H), -0.09 (s, 3H), -0.08 (s, 7.5H), 0.00 (s, 6H), 1.34 (d, 6H, $J = 6$ Hz), 4.87 (q, 2H, $J = 6$ Hz), 6.82 (d, 4H, $J = 8.5$ Hz), 7.17 (d, 4H, $J = 8.5$ Hz). ^{13}C NMR δ: 1.59, 2.64, 28.88, 71.87, 120.50, 129.03, 143.61, 158.59. ^{29}Si NMR δ: -13.92 (s, 2Si), -21.52 (s, 1Si). IR ν:

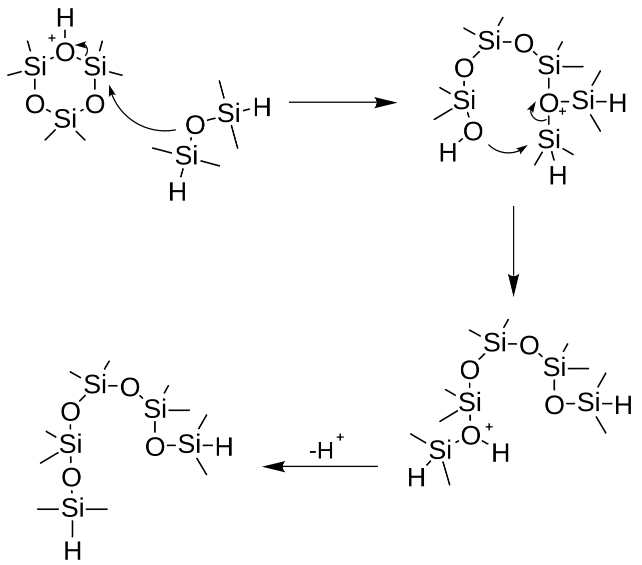

Fig. 3. Proposed mechanism for synthesis of VI.

1090(br), and 1033(br) (Si–O–C) cm^{-1}. UV CH_2Cl_2 λ_{max} nm (ϵ): 274(3442), 235(11,590). TGA: Polymer is stable to 275°C. Between 275 and 400°C, catastrophic decomposition occurs; 90% of initial weight is lost. Elemental Analysis: $C_{22}H_{34}O_5Si_3$: C, 57.10%; H, 7.41%. Found: C 57.04%; H, 7.25%.

***alt*-Copoly[1,4-phenylene/1,3,3,5,5,7,7,9,9,11-decamethyl-2,4,6,8,10-pentaoxa-3,5,7,9-tetrasila-undecanylene]** was prepared by an activated Ru catalyzed reaction of I (1.62 g, 10.0 mmol) and V (2.83 g, 10.0 mmol) as above. After precipitation with methanol, 3.57 g, 80% yield, $M_w/M_n = 168{,}000/75{,}700$, $T_g = -81$°C was obtained. ^{1}H NMR δ: −0.07 (s, 6H), −0.05 (s, 6H), −0.04 (s, 6H), −0.02 (s, 6H), 1.36 (d, 6H, $J = 6.5$ Hz), 4.90 (q, 2H, $J = 6.5$ Hz), 7.19 (s, 4H). ^{13}C NMR δ: −0.17, 1.11, 27.25, 70.59, 125.58, 145.57. ^{29}Si NMR δ: −14.07 (s, 2Si), −21.83 (s, 2Si). IR ν: 1090(br), and 1036(br) (Si–O–C) cm^{-1}. UV CH_2Cl_2 λ_{max} nm (ϵ): 255(399), 227(832). TGA: Polymer is stable to 300°C. Between 300 and 425°C, catastrophic decomposition occurs; 90% of initial weight is lost. Elemental Anal. Calc. for $C_{18}H_{36}O_5Si_4$: C, 48.60%; H, 8.16%. Found: C, 48.27%; H, 7.96%.

***alt*-Copoly[4,4′diphenyletherylene/1,3,3,5,5,7,7,9,9,11-decamethyl-2,4,6,8,10-pentaoxa-3,5,7,9-tetrasila-undecanylene]** was prepared by an activated Ru catalyzed reaction of II (2.54 g, 10.0 mmol) and V (2.83 g, 10.0 mmol) as above. After precipitation with methanol, 4.57 g, 85% yield $M_w/M_n = 14{,}700/4{,}300$, $T_g = -60$°C was obtained. ^{1}H NMR δ: −0.08 (s, 6H), −0.07 (s, 6H), −0.06 (s, 6H), −0.01 (s, 6H), 1.34 (d, 6H, $J = 6.5$ Hz), 4.87 (q, 2H, $J = 6.5$ Hz), 6.83 (d, 4H, $J = 9$ Hz), 7.18 (d, 4H, $J = 9$ Hz). ^{13}C NMR δ: 0.10, 1.16, 27.40, 70.40, 119.03, 127.55, 142.13, 157.12. ^{29}Si NMR δ: −13.93 (s, 2Si), −21.71 (s, 2Si). IR ν: 1095(br), and 1033(br) (Si–O–C) cm^{-1}. UV CH_2Cl_2 λ_{max} nm (ϵ): 273(6298), 233(12,473). TGA: Polymer is stable to 300°C. Between 300 and 425°C, catastrophic decomposition occurs; 90% of initial weight is lost. Elemental Anal. Calc. for $C_{24}H_{40}O_6Si_4$: C, 53.69%; H, 7.51%. Found: C, 53.81%; H, 7.43%.

***alt*-Copoly[1,4phenylene/1,3,3,5,5,7,7,9,9,11,11,13-dodecamethyl-2,4,6,8,10,12-hexaoxa-3,5,7,9,11-penta-silatridecanylene]** was prepared by an activated Ru catalyzed reaction of I (1.46 g, 9.0 mmol) and VI (3.21 g, 9.0 mmol) as above. After precipitation, 3.78 g, 81% yield, $M_w/M_n = 102{,}300/36{,}800$, $T_g = -84$°C was obtained. ^{1}H NMR δ: 0.02 (s, 6H) 0.05 (s, 6H), 0.06 (s, 6H), 0.096 (s, 6H), 0.097 (s, 6H), 1.42 (d, 6H, $J = 6$ Hz), 5.05 (q, 2H, $J = 6$ Hz), 7.30 (s, 4H). ^{13}C NMR δ: −0.35, 1.19, 27.18, 70.75, 125.73, 145.74. ^{29}Si NMR δ: −14.15 (s, 2Si), −21.84 (s, 2Si), −22.02 (s, 1Si). IR ν: 1094(br), and 1032(br) (Si–O–C) cm^{-1}. UV c-C_6H_{12} λ_{max} nm (ϵ): 248(1078), 224(3708). TGA: Polymer is stable to 300°C. Between 300 and 525°C,

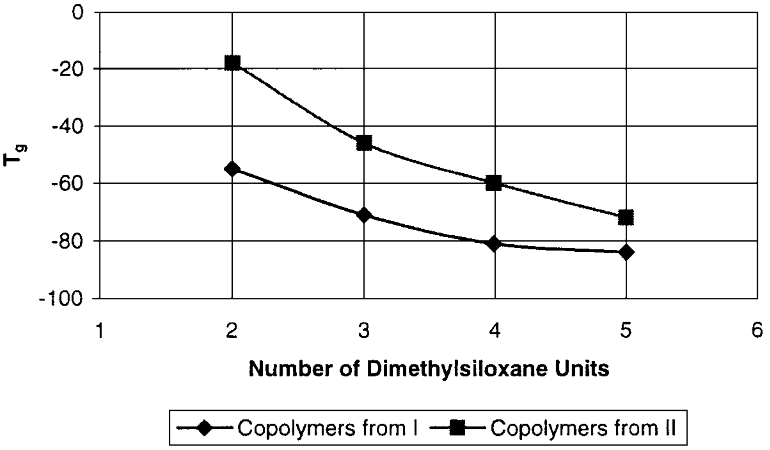

Fig. 4. Plot of T_g vs. number of dimethylsiloxane units in copolymers.

catastrophic decomposition occurs; 90% of initial weight is lost. Elemental Anal. Calc. for $C_{20}H_{42}O_6Si_5$: C, 46.29%; H, 8.16%. Found: C, 45.75%; H, 7.93%.

***alt*-Copoly[4,4′diphenyletherylene/1,3,3,5,5,7,7,9,9,11,11,13-dodecamethyl-2,4,6,8,10,12-hexaoxa-3,5,7,9,11-pentasilatridecanylene]** was prepared by an activated Ru catalyzed reaction of II (1.78 g, 7.0 mmol) and VI (2.50 g, 7.0 mmol) as above. After precipitation with methanol, 3.59 g, 84% yield, $M_w/M_n = 84,600/-50,800$, $T_g = -72$°C was obtained. ^{1}H NMR δ: 0.05 (s, 6H), 0.070 (s, 6H), 0.073 (s, 6H), 0.11 (s, 6H), 0.12 (s, 6H), 1.43 (d, 6H, $J = 6.5$ Hz), 5.07 (q, 2H, $J = 6.5$ Hz), 6.93 (d, 4H, $J = 8.5$ Hz), 7.35 (d, 4H, $J = 9$ Hz). ^{13}C NMR δ: -0.21, 0.85, 1.32, 27.32, 70.51, 119.23, 127.60, 142.24, 157.27. ^{29}Si NMR δ: -13.8 (s, 2Si), -21.63 (s, 2Si), -21.80 (s, 1Si). IR ν: 1094(br), and 1030(br) (Si–O–C) cm^{-1}. UV c-C_6H_{12} λ_{max} nm (ϵ): 268(2946), 233(12,756). TGA: Polymer is stable to 300°C. Between 300 and 550°C, catastrophic decomposition occurs; 90% of initial weight is lost. Elemental Anal. Calc. for $C_{26}H_{46}O_7Si_5$: C, 51.10%; H, 7.59%. Found: C, 51.01%; H, 7.52%.

4. Discussion

The high yield synthesis of VI by the triflic acid catalyzed ring-opening reaction of D_3 and III is unusual. One might expect D_3 to undergo ring-opening polymerization under these conditions. We believe that this reaction occurs by protonation of one of the oxygens of D_3 which may be more basic than the oxygens of III. Our expectation is based on analogy between siloxanes and ethers, since the basicities of siloxanes have not been determined. THF is well known to be more basic than alicyclic ethers [29]. Nucleophilic attack by the oxygen of III on one of the silyl centers adjacent to the protonated oxygen of D_3 leads to ring opening. Intramolecular nucleophilic attack by the terminal hydroxy group on a dimethylsilyl group followed by proton transfer gives VI (Fig. 3). This involves an eight-membered cyclic transition state. While this would be unusual in organic chemistry in which six-membered cyclic transition states are favored, in silicon chemistry, eight-membered cyclic siloxanes, such as, octamethylcyclotetrasiloxane are unstrained compared to D_3.

The Ru catalyzed hydrosilylation polymerization is unusual in that the completion of the reaction is often indicated by the return of the red color associated with the initial activated Ru catalyst. In this way, the reaction is comparable to a titration. The treatment of Ru with styrene activates the catalyst by creating a site of coordinate unsaturation by removal of hydrogen from the ruthenium center [27].

The T_gs for the copolymers decrease as the length of the oligo-dimethylsiloxane chain between the aromatic units increases. This is expected. The decrease in the T_gs asymptotically approach values higher than the T_g of poly (dimethylsiloxane) (-123°C) [30]. The nature of the aromatic unit in the copolymer also affects T_gs. The plot of the T_gs for the copolymers derived from II, while similar to that of those derived from I, has a much steeper slope (Fig. 4).

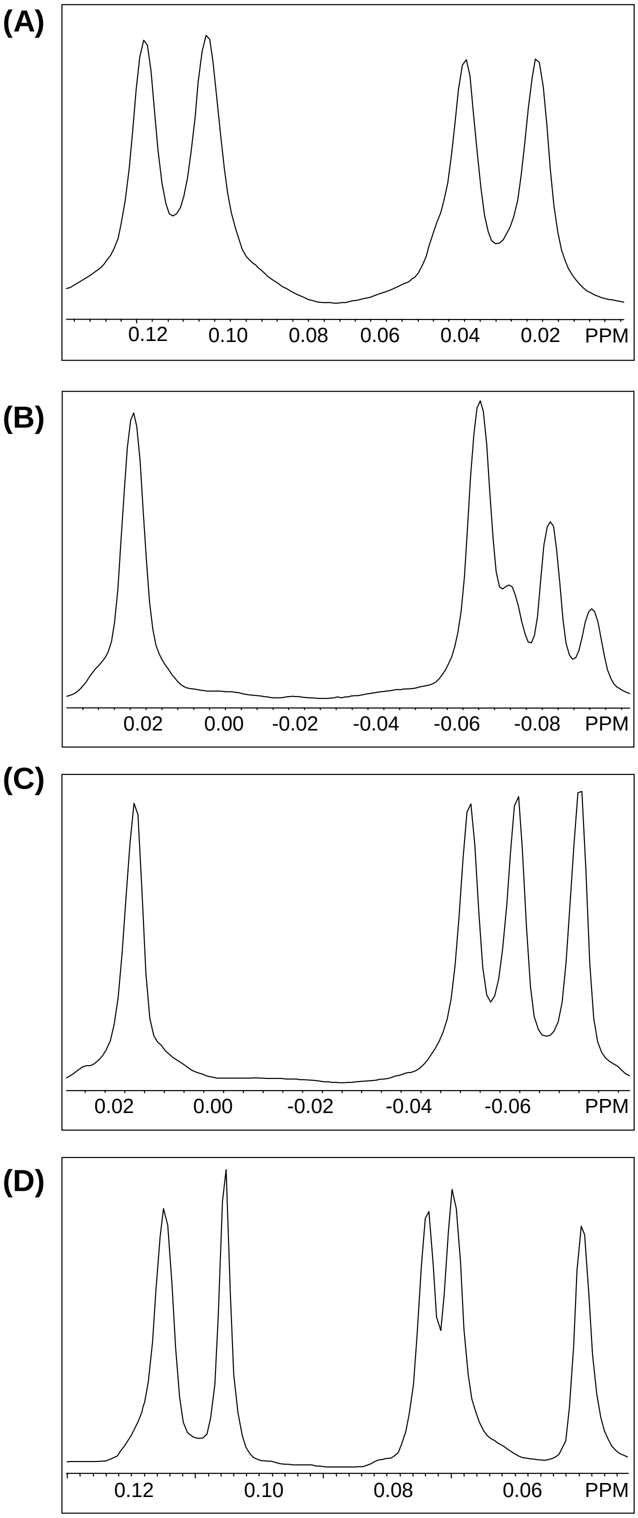

Fig. 5. ^{1}H NMR of Si–CH_3 groups in *alt*-copolymers of: II and III (A), I and IV (B), I and V (C), and II and VI (D).

The ^{1}H NMR spectra for these *alt* copolymers is rather interesting. The spectra are complicated by the presence of two chiral centers associated with each polymer unit. The spectra are similar for both series of copolymers (See Fig. 5). The Si-methyl protons of the disiloxane series of copolymers are equivalent. Each is affected by both chiral centers. This produces four diastereotopic environments: RR′, SS′, RS′ and R′S which are distinct. This results in four singlets of equal intensity.

In the case of the trisiloxane copolymers, each unit contains three silicons. Two of these are adjacent to a chiral center. Their diastereopic environments are only affected by this adjacent chiral center which can be either R or S. This results in two signals of equal intensity. The central silicon of the trisiloxane copolymer is affected by both chiral centers. This results in four diastereotopic environments: RR, SS, RS and SR. This leads to three resonances in a 1:2:1 ratio since RS and SR are meso.

The tetrasiloxane polymers contain four silicons, each of which is affected only by the nearest chiral center which can be either R or S. The difference between these environments is larger for the Si-methyl groups which are adjacent to chiral center than those which are further removed. This leads to four resonances of equal intensity.

The pentasiloxane copolymers have five Si-methyl groups. Those which are closest to the chiral center experience the largest difference in diastereotopic environments. The inner pair of Si-methyl groups experiences a smaller difference. Finally, the central Si-methyl groups are not affected by either chiral center because they are too remote. This results in five signals of equal intensity.

Among the advantages of the Ru catalyst is that the reaction does not equilibrate the oligodimethylsiloxane units. Siloxane equilibration is observed in many cation and anion catalyzed reactions [30]. The reaction also gives high molecular weight copolymers in excellent chemical yield.

Acknowledgements

We thank the National Science Foundation and Air Force Office of Scientific Research for support. J.K. Paulasaari thanks Neste Foundation for a fellowship.

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