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Synthesis of Copoly[arylene-1,2-dioxy/oligodimethylsiloxanylene]s by Ruthenium-Catalyzed Dehydrogenative Silylation Copolymerization of *o*-Quinones with α,ω-Dihydridooligodimethylsiloxanes

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ABSTRACT: Activated dihydridocarbonyltris(triphenylphosphine)ruthenium (**Ru**) catalyzes the dehydrogenative silylation condensation copolymerization of *o*-quinones with α,ω-dihydridooligodimethylsiloxanes to give high molecular weight copoly(arylene-1,2-dioxy/oligodimethylsiloxanylene)s in good chemical yield. These copolymers have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as IR and UV. Their molecular weight distributions (M_w/M_n) have been determined by GPC. Their thermal stability was measured by TGA, and their glass transition temperatures (T_gs) were determined by DSC. The photoluminescence properties of the copolymers were studied along with those of two model compounds. The decrease in T_gs with increase in siloxane chain length as well as fluorescence spectra will be discussed. A mechanism of the copolymerization is proposed, in which, for these substrates, β-hydride elimination is favored over reductive elimination.

Introduction

The backbones of poly(silyl ether)s contain Si−O−C bond linkages. Copoly(siloxane/silyl ether)s may contain oligodimethylsiloxane (ODMS) units. The instability of poly(silyl ether)s with respect to hydrolysis,[1] and the biocompatibility of poly(dimethylsiloxane) (PDMS),[2] may make these copolymers attractive candidates for the controlled release of drugs or as materials whose degradation will limit their long-term environmental impact.[3] Regular copolymers, which incorporate ODMS units, may have T_gs similar to that of PDMS but no longer exhibit detectable melting points (T_ms).[4] There is also interest in the possible utility of poly(silyl ether)s as elastomers,[5] sensor materials,[6] and polymer membranes.[7]

Symmetrical poly(silyl ether)s have been prepared by equilibration polymerization of dialkoxysilanes and α,ω-diols.[8−10] Asymmetric poly(silyl ether)s have been synthesized by ring-opening polymerization of 2-sila-1-oxacyclopentanes.[11] Poly(silyl ether)s containing pendant chloromethyl groups have been obtained by quaternary ammonium chloride catalyzed ring-opening polymerization of bis(oxetane)s or bis(epoxide)s with dichlorosilanes.[12−15]

There is considerable interest in the application of transition-metal catalysis in organic and polymer synthesis.[16,17] Rh-catalyzed hydrosilylation of the C−O double bonds of ketones and aldehydes to form silyl ethers is well-known.[18−22] Likewise, transition-metal-catalyzed dehydrogenative silylation of ketones to yield silyl enol ethers has been reported.[23,24]

High molecular weight poly(silyl ether)s have been obtained by Rh- or Pd-catalyzed cross-dehydrocoupling condensation of α,ω-dihydridosilanes with diols.[25−28] Poly(silyl ether)s have been produced by Pd-catalyzed condensation copolymerization of α,ω-dihydridosilanes and *p*-quinones.[29] We have previously reported the Ru-catalyzed hydrosilylation addition polymerization of
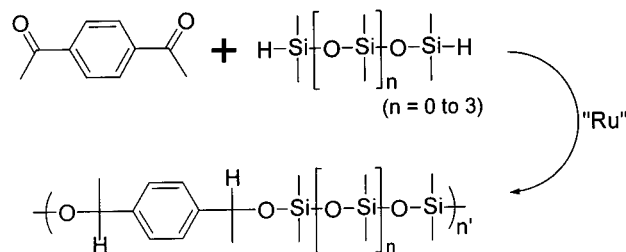

Figure 1. Ru-catalyzed hydrosilylation copolymerization.

aromatic α,ω-diketones and α,ω-dihydrido-oligodimethylsiloxanes to yield high molecular weight materials (Figure 1).[30,31]

Poly(silyl enol ether)s have been produced by radical ring-opening polymerization of trimethylsiloxy-substituted vinylcyclopropanes and by radical copolymerization of 2-trimethylsiloxy-1,3-butadiene with vinyl monomers.[32−35] In these polymers, while the C−C double bond of the silyl enol ether is an integral part of the polymer backbone, the trimethylsiloxy group is pendant.

Herein, we report the Ru-catalyzed dehydrogenative silylation condensation copolymerization of *o*-quinones with α,ω-dihydridooligodimethylsiloxanes to yield *alt*-copoly(arylene-1,2-dioxy/oligodimethylsiloxanylene)s. These copolymers have been characterized spectroscopically by ^{1}H, ^{13}C, and ^{29}Si NMR as well as by IR and UV. Their molecular weight distributions have been determined by GPC, their thermal stability evaluated by TGA, and their T_gs measured by DSC. Model compounds have also been prepared, and their luminescence properties have been compared with those of the copolymers.

Results

Activated dihydridocarbonyltris(triphenylphosphine)-ruthenium (**Ru**) catalyzes the dehydrogenative silylation condensation copolymerizations of 9,10-phenanthrenequinone (**I**) or 1,2-acenaphthenequinone (**II**) with 1,11-dihydridododecamethylhexasiloxane (**III**) to yield

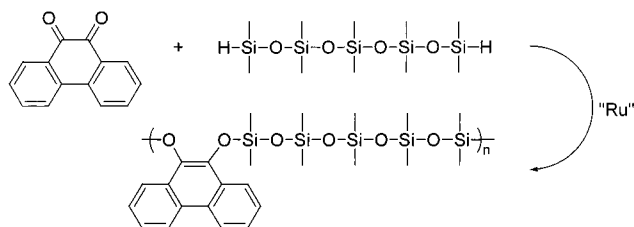* Corresponding author. E-mail: wpweber@usc.edu.
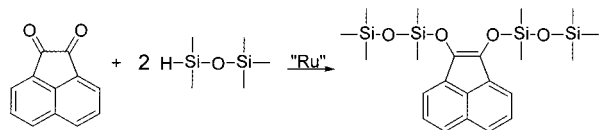
Figure 2. Ru-catalyzed synthesis of **VIII**.

Figure 3. Ru-catalyzed synthesis of **XIV**.

alt-copoly[phenanthrene-9,10-dioxy/1,1,3,3,5,5,7,7,9,9, 11,11-dodecamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10-pentaoxa-1,11-undecanylene] or *alt*-copoly[acenaphthalene-1,2-dioxy/1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-1,3,5,7,9, 11-hexasila-2,4,6,8,10-pentaoxa-1,11-dodecanylene], respectively. Similar reactions of **I** or **II** with 1,9-dihydridodecamethylpentasiloxane (**IV**) or 1,7-dihydridooctamethyltetrasiloxane (**V**) yield the expected copolymers. Reaction of **I** and **IV** is shown in Figure 2. **Ru**-catalyzed reaction of **I** or **II** with pentamethyldisiloxane (**VI**) yields model compounds 9,10-bis(pentamethyldisiloxanoxy)-phenanthrene (**XIII**) or 1,2-bis(pentamethyldisiloxanoxy)acenaphthene (**XIV**), respectively. Reaction of **II** and **VI** is shown in Figure 3.

Experimental Section

¹H, ¹³C, and ²⁹Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer operating in the FT mode. ¹H and ¹³C NMR spectra of 5% w/v CDCl₃ solutions were obtained. ²⁹Si NMR spectra of 25% w/v CDCl₃ solutions were acquired. ¹³C 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 ²⁹Si NMR spectra. Residual CHCl₃ was used as an internal standard for ¹H and ¹³C NMR. ²⁹Si NMR spectra were referenced to an internal TMS standard. IR spectra of neat films on NaCl plates were recorded using a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. UV spectra of CH₂Cl₂ solutions were obtained on a Shimadzu UV-260 spectrometer. Fluorescence spectra were taken on a PTI fluorimeter. Spectra were obtained of CH₂Cl₂ solutions, which had been degassed by bubbling argon through them for 10 min.

GPC analyses of the molecular weight distributions (M_w/M_n) of the polymers were performed on a Waters system equipped with a 401 refractive index detector. Two 7.8 × 300 mm Styragel columns packed with <5 μm divinylbenzene cross-linked 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 cm³ of nitrogen/min. The temperature was increased 4 °C/min from 25 to 800 °C. The T_gs of the polymers were determined on a Perkin-Elmer DSC-7. The DSC was calibrated using the thermal transition temperature (−87.06 °C) and melting point (6.54 °C) of cyclohexane.[36] The temperature was increased 10 °C/min from −150 to 25 °C.

I, **II**, toluene, and styrene were obtained from Aldrich. Hexamethylcyclotrisiloxane (D₃), octamethylcyclotetrasiloxane (D₄), 1,3-dihydridotetramethyldisiloxane, **V**, and **VI** were purchased from Gelest. **I** and **II** were recrystallized prior to use. 1,3-Dihydridotetramethyldisiloxane, **V**, and **VI** were distilled prior to use.

All reactions were conducted in flame-dried glassware under argon.

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) was prepared from ruthenium trichloride hydrate.[37] **Ru** (0.04 g, 43.6 μmol), styrene (5.0 μL, 43.6 μmol), and toluene (0.25 mL) were placed in a 20 mL Ace pressure tube. The tube and its contents were sealed and heated at 125 °C for 3 min to activate **Ru**. The color of the activated catalyst solution is red.[38]

1,11-Dihydridododecamethylhexasiloxane (III) was prepared by the triflic acid-catalyzed reaction of D₄ with 1,3-dihydridotetramethyldisiloxane.[39]

1,9-Dihydridodecamethylpentasiloxane (IV) was prepared by the triflic acid-catalyzed reaction of D₃ with 1,3-dihydridotetramethyldisiloxane.[31]

alt-**Copoly[phenanthrene-9,10-dioxy/1,1,3,3,5,5,7,7,9,9, 11,11-dodecamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10-pentaoxa-1,11-undecanylene] (VII).** **I** (0.30 g, 1.4 mmol), **III** (0.50 g, 1.4 mmol), and activated **Ru** catalyst (0.04 g, 43.6 μmol) as above were placed in a 25 mL round-bottom flask with a Teflon-covered magnetic stir bar. The flask was purged with argon and heated to 125 °C. After 5 min, the solution was brown. After 18 h at 125 °C, the reaction was stopped. The polymer was dissolved in a minimum amount of THF and precipitated from methanol three times. In this way, 0.64 g, 80.0% yield of material, M_w/M_n = 11 150/5970, T_g = −68 °C was obtained. ¹H NMR δ: 0.05 (s, 36H), 7.54 (m, 4H), 8.25 (d, 2H, J = 7.5 Hz), 8.59 (d, 2H, J = 7.5 Hz). ¹³C NMR δ: 0.24, 1.05, 1.23, 122.41, 123.52, 125.07, 126.38, 127.91, 129.94, 136.85. ²⁹Si NMR δ: −21.86 (s, 2Si), −21.13 (s, 2Si), −11.28 (s, 2Si). IR ν: 3076, 3032, 2961, 2904, 1618, 1602, 1525, 1490, 1455, 1413, 1374, 1354, 1341, 1262, 1183, 1088, 1029, 932, 860, 800, 756, 723 cm⁻¹. UV λ_{max} nm (ϵ): 309 (2907), 297 (2693), 257 (13 733). When irradiated at 308 nm, fluorescence was observed at 396 ± 5 nm. TGA: **VII** is stable in N₂ to 200 °C. Between 200 and 650 °C, catastropic decomposition occurs. 80% of the initial weight is lost. Between 650 and 800 °C, no additional weight is lost. **VII** is stable in air to 150 °C. Between 150 and 550 °C, 61% of the initial sample weight is lost. To 800 °C, no additional weight is lost.

alt-**Copoly[phenanthrene-9,10-dioxy/1,1,3,3,5,5,7,7,9,9-decamethyl-1,3,5,7,9-pentasila-2,4,6,8,10-tetraoxa-1,9-nonanylene] (VIII)** was prepared from **I** (1.24 g, 6.0 mmol) and **IV** (2.13 g, 6.0 mmol) as above. In this way, 3.0 g, 88.8% yield, of material, M_w/M_n = 26 070/16 860, T_g = −38 °C, was obtained. ¹H NMR δ: −0.011 (s, 12H), 0.013 (s, 6H), 0.322 (s, 12H), 7.59 (m, 6H), 8.30 (d, 2H, J = 7.5 Hz), 8.64 (d, 2H, J = 7.5 Hz). ¹³C NMR δ: 0.09, 0.86, 1.05, 122.24, 123.33, 124.90, 126.20, 127.76, 129.77, 136.68. ²⁹Si NMR δ: −21.77 (s, 1Si), −21.04 (s, 2Si), −11.22 (s, 2Si). IR ν: 3074, 3028, 2962, 2901, 1617, 1602, 1574, 1524, 1491, 1455, 1422, 1374, 1354, 1341, 1260, 1181, 1111, 1065, 1027, 931, 857, 842 cm⁻¹. UV λ_{max} nm (ϵ): 309 (20 830), 297 (19 240), 272 (34 650), 258 (92 930). When irradiated at 312 nm, fluorescence was observed at 394 ± 5 nm. TGA: **VIII** is stable in N₂ to 200 °C. Between 200 and 650 °C, catastropic decomposition occurs. 90% of the initial weight is lost. Between 650 and 800 °C, no additional weight is lost. **VIII** is stable in air to 150 °C. Between 150 and 550 °C, 69% of the initial sample weight is lost. To 800 °C, no additional weight is lost.

alt-**Copoly[phenanthrene-9,10-dioxy/1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasila-2,4,6-trioxa-1,7-heptanylene] (IX)** was prepared from **I** (1.04 g, 5 mmol) and **V** (1.41 g, 5 mmol) as above. 2.1 g, 85.6% yield, M_w/M_n = 12 900/8,800, T_g = −35 °C, was obtained. ¹H NMR δ: −0.10 (s, 12H), 0.25 (s, 12H), 7.55 (m, 4H), 8.24 (t, 2H, J = 7 Hz), 8.60 (t, 2H, J = 7 Hz). ¹³C NMR δ: 0.05, 0.80, 122.21, 123.27, 124.89, 126.19, 127.68, 129.68, 136.61. ²⁹Si NMR δ: −21.09 (s, 2Si), −11.22 (s, 2Si). IR ν: 3072, 3027, 2958, 2898, 1602, 1451, 1419, 1375, 1352, 1343, 1283, 1259, 1236, 1182, 1157, 1090, 1068, 1041, 930, 871, 843, 796, 754, 725 cm⁻¹. UV λ_{max} nm (ϵ): 310 (5473), 298 (5120), 273 (9445), 258 (23 846). When irradiated at 310 nm, fluorescence was observed at 396 ± 5 nm. TGA: **IX** is stable

in N_2 to 225 °C. Between 225 and 675 °C, catastrophic decomposition occurs and 89% of the initial weight is lost. To 800 °C, no additional weight is lost. **IX** is stable in air to 225 °C. Between 225 and 575 °C, 59% of the initial weight is lost. No additional weight is lost to 800 °C.

alt-Copoly[acenaphthalene-1,2-dioxy/1,1,3,3,5,5,7,7,9,9, 11,11-dodecamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10-pentaoxa-1,11-dodecanylene] (X) was prepared from **II** (0.26 g, 1.4 mmol) and **III** (0.50 g, 1.4 mmol) as above. In this way, 0.52 g, 68.4% yield of material, $M_w/M_n = 41\,300/17\,230$, $T_g = -93$ °C, was obtained. ¹H NMR δ: 0.07 (s, 36H), 5.62 (s, 0.4), 7.50 (m, 6H). ¹³C NMR δ: 0.05, 1.24, 74.50, 84.04, 120.17, 121.22, 124.59, 126.19, 127.40, 128.14, 134.60. ²⁹Si NMR δ: −21.86 (s, 2Si), −20.62 (s, 2Si), −11.46 (s, 2Si). IR v: 3045, 2961, 2902, 1592, 1479, 1462, 1437, 1412, 1380, 1338, 1261, 1185, 1089, 1043, 953, 915, 882, 800 cm⁻¹. UV λ_{max} nm (ϵ): 289 (3309), 231 (17 626). When irradiated at 338 nm, fluorescence was observed at 373 ± 5 nm. TGA: **X** is stable in N_2 to 200 °C. Between 200 and 650 °C, catastropic decomposition occurs. 90% of the initial weight is lost. Between 650 and 800 °C, no additional weight is lost. **X** is stable in air to 180 °C. Between 180 and 550 °C, 79% of the initial sample weight is lost. No additional weight is lost to 800 °C.

alt-Copoly[acenaphthalene-1,2-dioxy/1,1,3,3,5,5,7,7,9,9-decamethyl-1,3,5,7,9-pentasila-2,4,6,8-tetraoxa-1,9-nonanylene] (XI) was prepared from **II** (0.49 g, 2.7 mmol) and **IV** (0.96 g, 2.7 mmol) as above. In this way, 1.2 g, 82.8% yield, $M_w/M_n = 8620/3750$, $T_g = -54$ °C, was obtained. ¹H NMR δ: 0.11 (s, 18H), 0.320 (s, 12H), 7.41 (d, 2H, $J = 6.5$ Hz), 7.50 (t, 2H, $J = 6.5$ Hz), 7.61 (d, 2H, $J = 6.5$ Hz). ¹³C NMR δ: −0.14, 1.05, 79.13, 119.97, 126.02, 127.20, 127.40, 127.55, 129.51, 134.35. ²⁹Si NMR δ: −21.90 (s, 1Si), −20.60 (s, 2Si), −11.49 (s, 2Si). IR v: 3064, 3048, 2962, 2901, 1772, 1739, 1589, 1478, 1460, 1437, 1407, 1382, 1339, 1288, 1260, 1230, 1199, 1187, 1090, 1024, 953, 913, 860, 839 cm⁻¹. UV λ_{max} nm (ϵ): 327 (17 523), 239 (19 958). When irradiated at 348 nm, fluorescence was observed at 373 ± 5 nm. TGA: **XI** is stable in N_2 to 150 °C. Between 150 and 400 °C, 10% of the initial weight is lost. Between 400 and 625 °C, an additional 80% of the initial weight is lost. **XI** is stable in air to 125 °C. Between 125 and 550 °C, 72% of the initial weight is lost. No additional weight is lost to 800 °C.

alt-Copoly[acenaphthalene-1,2-dioxy/1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasila-2,4,6-trioxa-1,7-heptanylene] (XII) was prepared from **II** (1.00 g, 5.5 mmol) and **V** (1.55 g, 5.5 mmol) as above. In this way, 2.1 g, 82.3% yield, $M_w/M_n = 20\,300/12\,600$, $T_g = -43$ °C, was obtained. ¹H NMR δ: 0.08 (s, 12H), 0.30 (s, 12H), 5.62 (d, 0.2H, $J = 8.5$ Hz), 7.38 (t, 2H, $J = 7.5$ Hz), 7.48 (d, 2H, $J = 7.5$ Hz), 7.59 (d, 2H, $J = 7.5$ Hz). ¹³C NMR δ: −0.14, 1.03, 74.51, 84.03, 93.73, 119.97, 120.98, 126.03, 126.65, 127.20, 134.33, 136.79. ²⁹Si NMR δ: −20.47 (s, 2Si), −11.42 (s, 2Si). IR v: 3062, 3047, 2963, 2903, 1627, 1590, 1479, 1461, 1437, 1412, 1380, 1338, 1288, 1261, 1197, 1187, 1123, 1073, 1044, 952, 915, 838, 799, 769 cm⁻¹. UV λ_{max} nm (ϵ): 315 (4142), 241 (5705). When irradiated at 344 nm, fluorescence was observed at 374 ± 5 nm. TGA: **XII** is stable in N_2 to 225 °C. Between 225 and 600 °C, catastrophic decomposition occurs, and 90% of the initial sample weight is lost. To 800 °C, an additional 5% of the initial weight is lost. **XII** is stable in air to 200 °C. Between 200 and 550 °C, 80% of the initial sample weight is lost. No additional weight is lost to 800 °C.

9,10-Bis(pentamethyldisiloxanoxy)phenanthrene (XIII) was prepared from **I** (0.72 g, 3.5 mmol) and **VI** (1.48 g, 10 mmol) as above. Volatiles were removed under reduced pressure. In this way, 1.7 g, 96.6% yield, of **XIII** was obtained. ¹H NMR δ: 0.21 (s, 18H), 0.51 (s, 12H), 7.70 (t, 2H, $J = 8$ Hz), 7.76 (t, 2H, $J = 8$ Hz), 8.51 (d, 2H, $J = 8$ Hz), 8.76 (d, 2H, $J = 8$ Hz). ¹³C NMR δ: 0.38, 1.80, 122.43, 123.50, 125.06, 126.29, 127.90, 129.98, 136.89. ²⁹Si NMR δ: −11.04 (s, 2Si), 8.72 (s, 2Si). IR v: 3078, 3031, 2957, 2900, 1683, 1617, 1600, 1574, 1526, 1491, 1452, 1435, 1422, 1376, 1354, 1341, 1283, 1257, 1233, 1183, 1154, 1113, 1063, 1035, 931, 839, 813, 798, 754, 724 cm⁻¹. UV λ_{max} nm (ϵ): 309 (5056), 298 (4889), 258 (25 556).
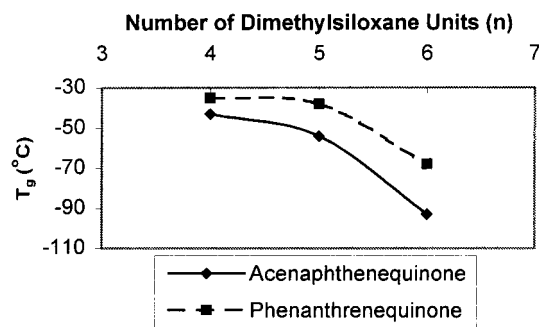

Figure 4. Chart of T_g vs number of dimethylsiloxane units.
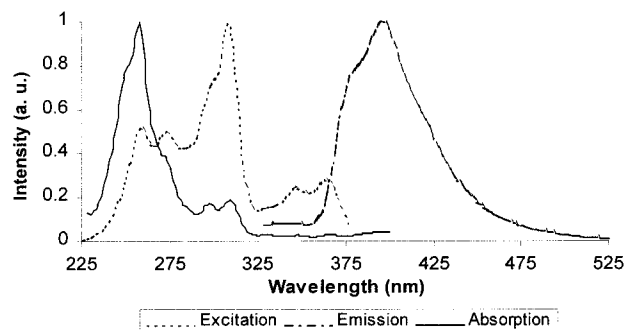

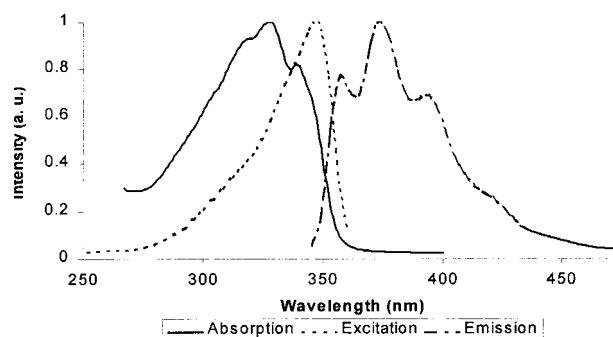**Figure 5.** Luminescence spectra of **VII**.

Figure 6. Luminescence spectra of **XI**.

When irradiated at 308 nm, fluorescence was observed at 396 ± 5 nm.

1,2-Bis(pentamethyldisiloxanoxy)acenaphthene (XIV) was prepared from **II** (1.82 g, 10 mmol) and **VI** (4.45 g, 30 mmol) as above. Volatiles were removed under reduced pressure. The product was further purified by sublimation. In this way, 2.1 g, 44.0% yield, of **XIV** was obtained. ¹H NMR δ: 0.14 (s, 18H), 0.31 (s, 12H), 5.63 (s, 0.2), 7.42 (t, 2H, $J = 7.5$ Hz), 7.50 (d, 2H, $J = 7.5$ Hz), 7.62 (d, 2H, $J = 7.5$ Hz). ¹³C NMR δ: 0.20, 1.97, 74.47, 74.72, 84.03, 120.12, 121.11, 124.57, 125.22, 126.17, 127.35, 128.10. ²⁹Si NMR δ: −11.15 (s, 2Si), 9.22 (s, 2Si). IR v: 3051, 2955, 2897, 1625, 1590, 1494, 1477, 1461, 1438, 1411, 1380, 1338, 1286, 1257, 1196, 1186, 1144, 1124, 1057, 949, 913, 840, 813, 797, 782, 770, 753 cm⁻¹. UV λ_{max} nm (ϵ): 316 (5031), 230 (27 987). When irradiated at 340 nm, fluorescence was observed at 374 ± 5 nm.

Discussion

The **Ru**-catalyzed dehydrogenative silylation condensation copolymerization of *o*-quinones with α,ω-dihydridooligodimethylsiloxanes gives *alt*-copoly(arylene-1,2-dioxy/oligodimethylsiloxanylene)s in good yield. The incorporation of aromatics units into a polymer backbone increases the thermal stability. Some of these copolymers show only a 10% weight loss to 400 °C.
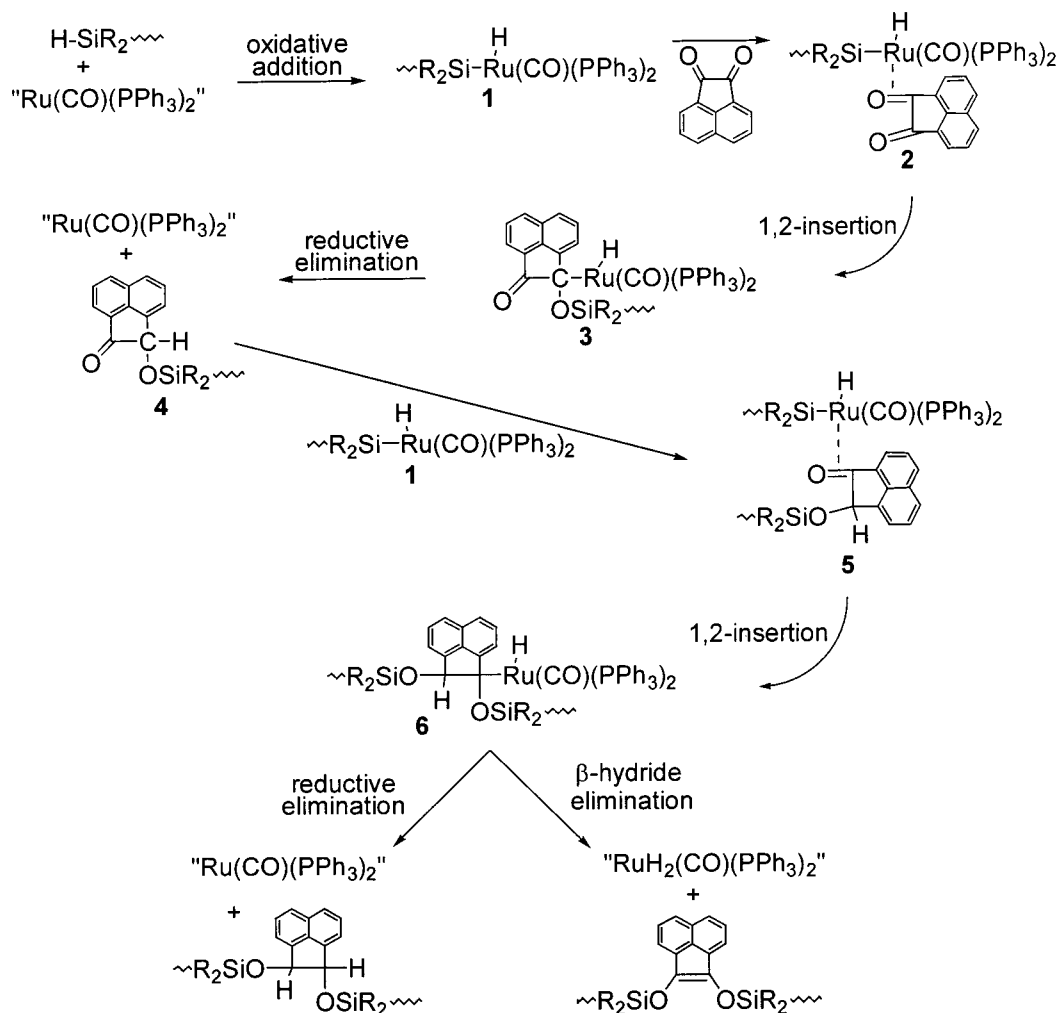
H-SiR$_2$〰 + "Ru(CO)(PPh$_3$)$_2$" —oxidative addition→ 〰R$_2$Si–Ru(CO)(PPh$_3$)$_2$ (H) **1**

〰R$_2$Si–Ru(CO)(PPh$_3$)$_2$ (H) **2**

1,2-insertion

〰R$_2$Si–Ru(CO)(PPh$_3$)$_2$ (H), OSiR$_2$〰 **3**

reductive elimination

"Ru(CO)(PPh$_3$)$_2$" + C–H, OSiR$_2$〰 **4**

〰R$_2$Si–Ru(CO)(PPh$_3$)$_2$ **1**

〰R$_2$Si–Ru(CO)(PPh$_3$)$_2$ (H), 〰R$_2$SiO (H) **5**

1,2-insertion

〰R$_2$SiO—C—Ru(CO)(PPh$_3$)$_2$ (H), OSiR$_2$〰 **6**

reductive elimination → "Ru(CO)(PPh$_3$)$_2$" + 〰R$_2$SiO–H, OSiR$_2$〰

β-hydride elimination → "RuH$_2$(CO)(PPh$_3$)$_2$" + 〰R$_2$SiO OSiR$_2$〰

Figure 7. Proposed mechanism.

Among the advantages of the **Ru** catalyst is that the reaction does not equilibrate the oligodimethylsiloxane units. Siloxane equilibration is observed in many cation or anion-catalyzed reactions of siloxanes.[40]

T_gs of the copolymers decrease as the number of ODMS units (*n*) increases as previously observed.[31] However, the steep decrease in T_g values at $n = 6$ is surprising (Figure 4). This may be due to the fact that the siloxane segment is significantly longer than the aromatic segment, and the $\pi-\pi$ stacking of the aromatic segments is less likely. This may allow copolymer flexibility to more rapidly approach that of PDMS, which has a T_g of -125 °C.[41]

The luminescence spectra of these copolymers, on the other hand, remain constant as the length of the oligodimethylsiloxane unit increases. Apparently, luminescence mainly depends on individual aromatic units. In the case of copolymers **VII–IX** as well as model compound **XIII**, excitation maxima are seen at 308 ± 5 nm, and fluorescence maxima are seen at 396 ± 5 nm. The absorption, excitation, and emission spectra are shown for **VII** (Figure 5).

Copolymers **X–XII** and model compound **XIV** have excitation maxima at 340 ± 8 nm and fluorescence maxima at 374 ± 5 nm. The absorption, excitation, and emission spectra are shown for **XI** (Figure 6). A large shift is seen between the excitation and emission maxima of **VII–IX** and **XIII** ($\sim$88 nm). A much smaller shift is observed between the excitation and emission maxima of **X–XII** and **XIV** ($\sim$34 nm).

The mechanism of this copolymerization reaction is interesting. The hydrogen lost during the copolymerization appears to come from the ends of the ODMS monomer. **Ru** reacts with styrene to form the active catalyst, "Ru(CO)(PPh$_3$)$_2$". In this process, styrene is hydrogenated to ethylbenzene and one triphenylphosphine ligand is lost.[38] The mechanism of the reaction begins with the oxidative addition of a silicon hydride to "Ru(CO)(PPh$_3$)$_2$" to yield **1** (Figure 7). Coordination of a carbonyl group of the *o*-quinone to **1** yields **2**. 1,2-Insertion of the carbonyl into the Ru–Si bond yields **3**. Reductive elimination produces an α-keto silyl ether (**4**) and regenerates the active catalyst. Coordination of the carbonyl group of **4** by **1** yields **5**. 1,2-Insertion of the carbonyl of **5** into the Ru–Si bond produces **6**, which has a hydrogen β to the Ru center. β-Hydride elimination from **6** yields a dehydrogenative silylation condensation product and generates "RuH$_2$(CO)(PPh$_3$)$_3$". Apparently, the reaction temperature is sufficient to cause the reductive elimination of hydrogen from this species and regenerates the active catalyst. On the other hand, **6** can reductively eliminate a hydrosilylation addition product and regenerate the active catalyst.

^{1}H and ^{13}C NMR spectra show trace amounts of reductive elimination products are formed in reactions with **II**. This may be due to competition between

reductive elimination and β-hydride elimination. No reductive elimination products are observed in products from reactions of **I**. In both systems, β-hydride elimination is favored.

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