Synthesis and Electrochemistry of Copoly(dimethylanthraquinonylene/ 3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylenes)

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ABSTRACT: Copoly(dimethylanthraquinonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylenes) have been prepared by direct Ru-catalyzed reaction of 1,4-, 1,5-, and 1,8-dimethylanthraquinones with 1,3-divinyltetramethyldisiloxane. Alternatively, these dimethylanthraquinones can undergo a Ru-catalyzed reaction with vinylpentamethyldisiloxane to yield the corresponding bis(2′-trimethylsiloxydimethylsiloxy)-ethyldimethylanthraquinones. Their acid-catalyzed siloxane equilibration polymerization yields copolymers whose molecular weights are two to three times higher than similar copolymers obtained by direct Ru-catalyzed reaction. These higher molecular weight copolymers have higher T_g's and thermal stabilities. The monomers show two reduction potentials, whereas the copolymers show a single broad reversible reduction potential at approximately the average of the two reduction potentials of the corresponding monomers.

Introduction

There has been a considerable recent interest in polymers that contain anthraquinone units either as pendant groups or as part of the polymer backbone. For example, 2-hydroxymethylanthraquinone has been attached as a pendant group to a poly(glycidyl ether) via ester formation.[1] Electrochemical oxidative polymerization of the pyrrole ring of *N*-(1-anthraquinone)-6-(1-pyrrol)hexamide yields a poly(pyrrole) film, which has pendant anthraquinone units, whose electrochemistry has been studied.[2] Low molecular weight poly(2-acrylamidoanthraquinone), prepared by free radical polymerization of 2-acrylamidoanthraquinone (Figure 1), has been used as a photosensitizer for cross-linking Nylon 6,6 fiber and film.[3] Recently, 2-anthraquinonylalanine, a nonnatural amino acid, has been incorporated into strepavidin by in vitro protein synthesis.[4]

Anthraquinone units constitute the main chain of π-unsaturated polymers which have been prepared by dehalogenation-condensation of 1,4-dichloro- or 1,5-dichloroanthraquinones using Ni(0) complexes in DMF (Figure 2). The redox chemistry of these polymers has been studied.[5,6,7] Poly(anthraquinone imines) were synthesized by a $TiCl_4$-facilitated dehydration reaction of anthraquinone with various aromatic diamines.[8] Copolymers, both those with extended conjugation and those in which each anthraquinone imine unit is electronically isolated, have been prepared by appropriate selection of the aromatic diamine. For example, reaction of anthraquinone with *p*-phenylenediamine gave a copolymer with an extended π-conjugated backbone (Figure 3). On the other hand, use of 4,4′-methylenedianiline gives copolymer in which the anthraquninone bis(*N*-phenylimine) units are electronically isolated.

Murai et al., have reported that dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) catalyzes the *anti*-Markonikov's addition of the *ortho* C−H bonds of aromatic ketones across the C−C double bonds of vinylsilanes to yield *ortho* alkyl-substituted aromatic ketones.[9,10] We have modified this reaction and applied it to achieve step-growth copolymerization of aromatic ketones such as anthrone, fluoren-9-one, xanthone,[11] thioxanthen-9-one,[12] and benzophenone[13] with 1,3-divinyltetramethyldisiloxane.

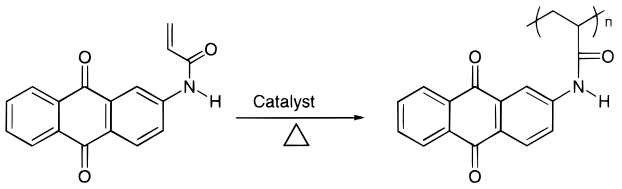

Figure 1. Synthesis of poly(2-acrylamidoanthraquinone).

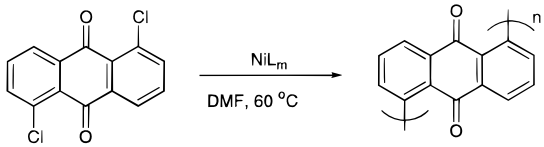

Figure 2. Ni/Zn dehalogenation−condensation of 1,5-dichloroanthraquinone.

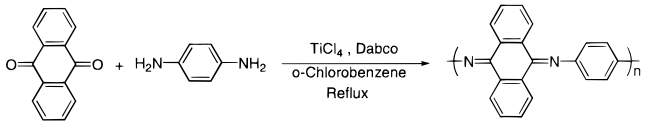

Figure 3. Synthesis of poly(anthraquinone imine).

The Ru-catalyzed reaction of 9,10-anthraquinone with 1,3-divinyltetramethyldisiloxane gave a complex mixture of low molecular weight oligomers. Analysis by ^1H and ^{13}C NMR suggested that all four of the C−H bonds *ortho* to the carbonyl groups can react.[14] For this reason, we have chosen to study the Ru-catalyzed reaction of anthraquinones in which two of the reactive *ortho* C−H bonds are replaced by methyl groups. Specifically, we have studied the Ru-catalyzed reactions of 1,4-, 1,5-, and 1,8-dimethylanthraquinones with 1,3-divinyltetramethyldisiloxane and vinylpentamethyldisiloxane.

The Ru-catalyzed reaction of 1,4-, 1,5-, and 1,8-dimethylanthraquinones with 1,3-divinyltetramethyl-

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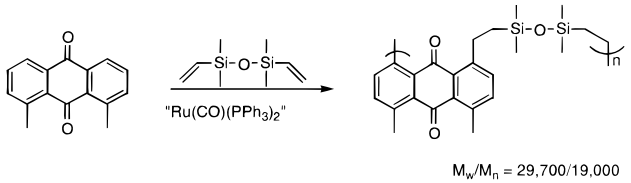


Figure 4. Ru-catalyzed direct synthesis of copoly[1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene].

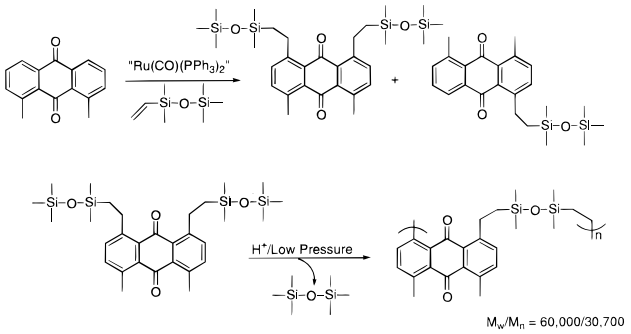


Figure 5. Acid-catalyzed siloxane equilibration polymerization of 1,8-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,5-dimethylanthraquinone to yield copoly[1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene].

disiloxane permits the direct synthesis respectively of the desired copoly[1,4-(5,8-dimethylanthraquinonylene)/-, 1,5-(4,8-dimethylanthraquinonylene)/-, and 1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-1,3-disila-1,7-heptanylenes] (Figure 4). However, the molecular weights of these copolymers are fairly low. Alternatively, these copolymers can also be prepared by a two-step process described below. While this is less direct, the molecular weights of the copolymers produced are significantly higher. These copolymers, synthesized by a two-step process have high molecular weights, high T_g's, and improved thermal stabilities as compared to the copolymers synthesized by direct Ru-catalyzed reaction.

The ruthenium catalyzed Murai reaction between 1,4-, 1,5-, and 1,8-dimethyl anthraquinones and vinylpentamethyldisiloxane yields a mixture of α-mono- and α,α′-bis(2′-trimethylsiloxydimethylsiloxy)ethyldimethylanthraquinones. Use of a large excess of vinylpentamethyldisiloxane favors the formation of the bis products. The reaction gives reasonable yields with the 1,5- and 1,8-dimethylanthraquinones, but very low yields with the 1,4-dimethylanthraquinone. After purification, treatment of α,α′-bis-1,8-(2′-trimethylsiloxydimethylsiloxy)ethyl-4,5-dimethylanthraquinone with a catalytic amount of triflic acid results in siloxane equilibration with the formation of hexamethyldisiloxane and the desired copoly[1,8-(4,5-dimethylanthraquinonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. This equilibration reaction can be driven to high molecular weight copolymer by removal of the hexamethyldisiloxane under vacuum, as it is formed, (Figure 5).

We have previously utilized an acid-catalyzed siloxane equilibration reaction to polymerize α,α′-bis(trimethylsiloxydimethylsiloxy)thioxanthen-9-one,[12] and α,α′-bis(trimethylsiloxydimethylsiloxy)-1,1′-dibenzoylferrocene[15] to obtain high molecular weight copolymers.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-250 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were run in $CDCl_3$ and were internally referenced to residual $CHCl_3$. ^{13}C spectra were obtained with broad-band proton decoupling. ^{29}Si NMR spectra were acquired on a Bruker AMX-500 MHz spectrometer. A heteronuclear gated decoupling pulse sequence (NONOE), with a 60 s delay (for monomers) and a 30 s delay (for polymers), was used to acquire the ^{29}Si NMR spectra, which were referenced to an external TMS standard.

IR spectra of neat films on NaCl plates for liquids and KBr pellets for solids were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer.

UV spectra of CH_2Cl_2 solutions were run 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 R401 refractive index detector. Two 7.8 mm × 300 mm Styragel columns packed with <5 μm divinylbenzene cross-linked polystyrene (HR2 and HR4) in series were used for analysis. THF was used as the elutant, at a flow rate of 0.3 mL/min. The retention times of the polymers were calibrated against those of known polystyrene standards.

GPC/MALLS was performed with a Wyatt Dawn-DSP MALLS detector, inserted between the GPC columns and RI detector. Data were analyzed with a Wyatt ASTRA system. The DN/DC of the polymers is not known, so an assumption of 100% mass recovery of the polymer was used to determine the molecular weights.

Thermogravimetric analysis of the polymers was carried out on a Shimadzu TGA-50 instrument, at a flow rate of 40 cm^3 of nitrogen per min. The temperature was increased at the rate 5 °C per min, from 25 to 750 °C.

The glass transition temperature (T_g) of the polymer was determined by DSC, on a Perkin-Elmer DSC-7. The DSC was calibrated against the melting point of indium (156.6 °C), triphenylphosphine (79 °C), and water (0 °C). The temperature program for the analysis was begun at −50 °C and was increased at the rate of 10 °C/min to 250 °C.

High-resolution mass spectra were run at the University of California, Riverside, Mass Spectroscopy Facility on a VG-7070 EHF instrument. Exact masses were determined by peak matching against known masses of perfluorokerosene. Ammonia was employed as the chemical ionization agent.

GC-MS was performed on a Hewlett-Packard 5890 Series II gas chromatograph connected to a Hewlett-Packard 5971 Series mass selective detector.

Cyclic voltamograms were obtained on an EG&G, PAR model 283 potentiostat/galvanostat, using a Au working electrode, a Pt counter electrode, and a Ag/Ag$^+$ reference electrode (0.222 V). Tetrabutylammonium hexafluorophosphate (0.1 M) was used as electrolyte. Nitrogen-purged, acetonitrile solutions of monomers (0.02 M) were scanned at a rate of 0.5 V/s. from 0.0 to −1.8 V. Nitrogen purged, benzonitrile solutions of polymers (2.0 mM) were scanned at a rate of 2.0 mV/s.

Vinylpentamethyldisiloxane and 1,3-divinyltetramethyldisiloxane were purchased from Gelest. All other reagents were purchased from Aldrich.

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) catalyst was prepared from ruthenium trichloride hydrate.[16]

1,5- and 1,8-Dimethylanthraquinone were prepared by a Diels−Alder reaction of 1,3-pentadiene and benzoquinone, following the literature.[17]

1,4-Dimethylanthraquinone was synthesized from phthalic anhydride and *p*-xylene following the literature.[18]

All reactions were carried out in flame-dried glassware under an atmosphere of argon. Reactions were stirred with Teflon-covered magnetic stir bars.

Melting points were measured on a Electrothermal melting point apparatus.

Elemental analyses were performed by Oneida Research Services Inc., Whitesboro, NY.

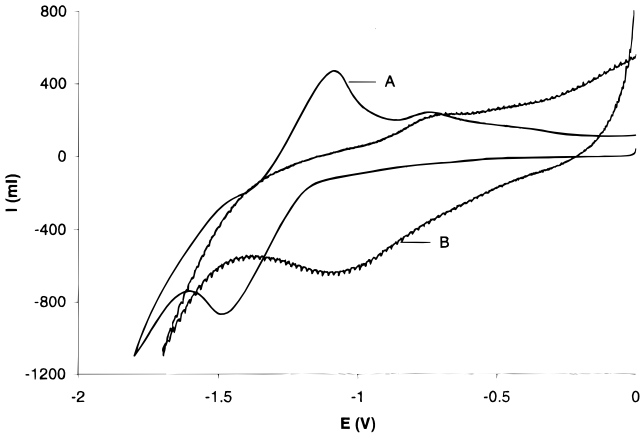


Figure 6. Cyclic voltamograms: (A) 1,5-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,8-dimethylanthraquinone; (B) copoly[1,5-(4,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene].

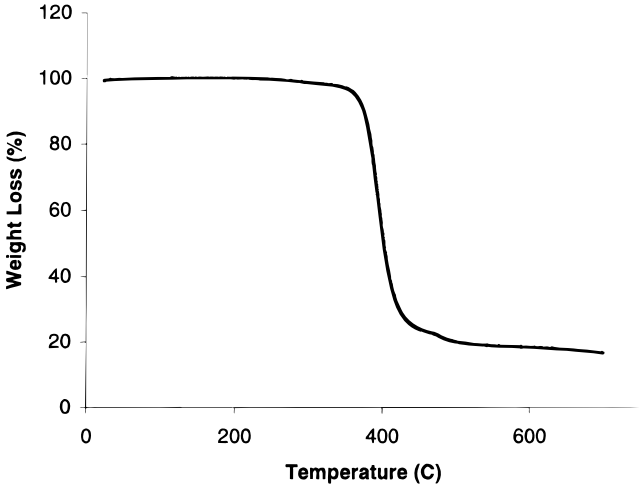


Figure 7. TGA of copoly[1,5-(4,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. M_w/M_n = 130 400/57 020.

Ru-Catalyzed Reaction of 1,5-Dimethylanthraquinone with Vinylpentamethyldisiloxane. Ru (45.85 mg, 50 μmol), 1,5-dimethylanthraquinone (1.06 g, 4.5 mmol), and vinylpentamethyldisiloxane (4.4 g, 25.3 mmol) were placed in an Ace pressure tube. The tube was sealed and heated at 125−130 °C for 72 h. The initial red color of the solution indicates catalyst activation.[19] After the reaction was cooled to room temperature, the volatiles were removed by evaporation under reduced pressure. The reaction products were separated by column chromatography on silica gel with hexane−ethyl acetate (80:20).

1,5-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,8-dimethylanthraquinone. A yellow viscous liquid, 1.45 g, 55% yield was obtained. ^{1}H NMR, δ: 0.14 (s, 18H), 0.20 (s, 12H), 0.95−1.02 (m, 4H), 2.67 (s, 6H), 3.00−3.06 (m, 4H), 7.33 (d, 2H, J = 8.0 Hz), 7.38 (d, 2H, J = 8.0 Hz). ^{13}C NMR, δ: 0.43, 2.03, 21.00, 21.69, 27.70, 131.58, 134.18, 134.44, 135.65, 136.44, 144.18, 190.07. ^{29}Si NMR, δ: 11.10, 11.23. IR ν: 1669 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 350 (10 600), 251 (34 300). High-resolution mass spectrum: calculated for $C_{30}H_{48}O_4Si_4$ $M^{+\bullet}$, 584.2629; found, 584.2660. Reduction potentials: −0.66 and −1.47 V (Figure 6).

Acid-Catalyzed Equilibration Polymerization of 1,5-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,8-dimethylanthraquinone. In a 5 mL round-bottom flask were placed 1,5-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,8-dimethylanthraquinone (70 mg, 0.11 mmol), mesitylene (0.2 mL), and concentrated sulfuric acid (10 μL). The reaction mixture was stirred at room temperature, while hexamethyldisiloxane was removed under vacuum (5−10 mm of Hg). After 10 h. the reaction mixture was taken up in 20 mL of diethyl ether, washed with saturated aqueous K_2CO_3, separated, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed by evaporation under reduced pressure. The residue was dissolved in 1.0 mL of THF. The polymer was precipitated by addition of 20 mL of methanol and collected by centrifugation.

Copoly[1,5-(4,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. A viscous, yellow material, 50.10 mg and 71.6% yield, was obtained; M_w/M_n = 130 400/57 020; T_g = 178 °C. ^{1}H NMR, δ: 0.16 (s, 12H), 0.91−0.97 (m, 4H), 2.59 (s, 6H), 2.91−2.97 (m, 4H), 7.22 (d, 2H, J = 8.3 Hz), 7.27 (d, 2H, J = 8.3 Hz). ^{13}C NMR, δ: 0.58, 21.08, 21.75, 27.80, 125.57, 134.18, 134.42, 135.72, 136.50, 144.13, 190.08. ^{29}Si NMR, δ: 7.35. IR ν: 1666 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 349 (5750), 255 (11 560). Anal. Calcd for $C_{24}H_{30}O_3Si_2$: C, 68.20; H, 7.15. Found: C, 67.62; H, 7.33. Reduction potential: −1.04 V, (Figure 6). TGA, (Figure 7).

Ru-Catalyzed Direct Synthesis of Copoly[1,5-(4,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. Ru (27.5 mg, 30.0 μmol), styrene (3.12 mg, 3.45 μL, 30.0 μmol) and 0.5 mL of toluene were placed in an Ace pressure tube. The tube was sealed with a rubber O-ring and a threaded Teflon seal and heated at 130−140 °C for 5 min to activate the Ru catalyst. The solution in the tube turned red.[19] The tube was then cooled to room temperature. 1,5-Dimethylanthraquinone (0.345 g, 1.460 mmol) and 1,3-divinyltetramethyldisiloxane (0.27 g, 1.46 mmol) were added. The tube was resealed and heated at 130−140 °C for 72 h. After the reaction was allowed to cool, the volatiles were removed by evaporation under reduced pressure. The residue was dissolved in 1.0 mL of THF, and 10 mL of methanol was added dropwise. The polymer was precipitated and collected by centrifugation. A hexane solution of the polymer was passed through a column (25 cm long and 0.5 cm diameter) packed with silica gel (60−200 mesh, 70 Å) to remove residual Ru catalyst. Hexane was removed by evaporation under reduced pressure, and the polymer was dried. In this way, 212 mg, 34.4% yield, M_w/M_n = 19 910/13 340, T_g = 55 °C, T_m = 90 °C, of copoly[1,5-(4,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] was obtained. Spectral properties are identical with those above. TGA: copoly-[1,5-(4,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] prepared by direct reaction begins decomposing about 75 °C lower than that prepared by acid-catalyzed siloxane equilibration polymerization of 1,5-bis-[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,8-dimethylanthraquinone.

Ru-Catalyzed Reaction of 1,8-Dimethylanthraquinone with Vinylpentamethyldisiloxane. Ru (45.85 mg, 0.05 mmol), 1,8-dimethylanthraquinone (1.06 g, 4.5 mmol) and vinylpentamethyldisiloxane (4.4 g, 25.3 mmol) were placed in an Ace pressure tube. The tube was sealed and the contents heated at 125−130 °C for 72 h. After the reaction was allowed to cool, the volatiles were removed by evaporation under reduced pressure. The reaction product was dissolved in minimum amount of hexane. The hexane solution was passed through a silica gel (60−200 mesh, 70 Å) column (25 cm long and 0.5 cm diameter), to remove the Ru catalyst. The reaction mixture was then purified on a Cyclograph Centrifugal Chromatography System, equipped with a 4000 μm silica gel rotor, with hexane−ethyl acetate (90:10).

1-[2′-(Trimethylsiloxydimethylsiloxy)ethyl]-4,5-dimethylanthraquinone. A yellow solid, 0.10 g, 5.6% yield, mp = 46−47 °C, was obtained. ^{1}H NMR, δ: 0.12 (s, 9H), 0.17 (s, 6H), 0.89−0.96 (m, 2H), 2.73 (s, 3H), 2.74 (s, 3H), 3.04−3.11 (m, 2H), 7.35 (d, 1H, J = 7.6 Hz), 7.42 (d, 1H, J = 7.6 Hz), 7.48 (dd, 1H, J = 1.2 and 7.6 Hz), 7.54 (t, 1H, J = 7.5 Hz), 7.99 (dd, 1H, J = 1.2 and 7.5 Hz). ^{13}C NMR, δ: 0.34, 2.03, 21.15, 21.72, 23.03, 28.56, 124.74, 132.06, 132.28, 133.47, 134.06, 134.87, 135.61, 136.34, 136.63, 138.66, 139.24, 145.83, 186.84, 189.21. ^{29}Si NMR, δ: 7.20, 7.56. IR ν: 1668 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 349 (5540), 255 (32 400). GC−MS: calculated for $C_{30}H_{48}O_4Si_4$ $M^{+\bullet}$, 410.0; found, 410.0.

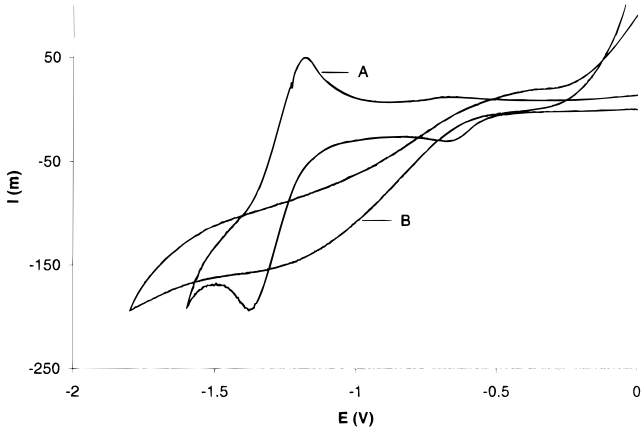


Figure 8. Cyclic voltamograms: (A) 1,8-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,5-dimethylanthraquinone; (B) copoly[1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene].

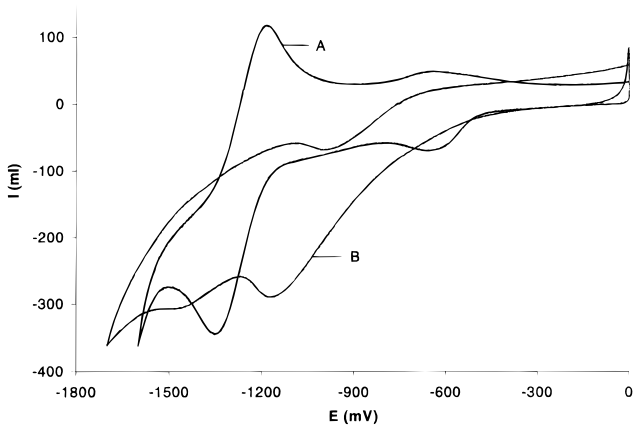


Figure 9. Cyclic voltamograms: (A) 1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-5,8-dimethylanthraquinone; (B) copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene].

1,8-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,5-dimethylanthraquinone. A yellow solid, 1.31 g, 90.6% yield, mp 68−72 °C, was obtained. ^{1}H NMR, δ: 0.12 (s, 18H), 0.17 (s, 12H), 0.87−0.94 (m, 4H), 2.65 (s, 6H), 3.00−3.07 (m, 4H), 7.33 (s, 4H). ^{13}C NMR, δ: 0.30, 2.01, 21.32, 21.36, 27.68, 132.03, 134.04, 134.93, 135.59, 136.17, 144.28, 190.31. ^{29}Si NMR, δ: 7.15, 7.54. IR, ν: 1664 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 350 (10 600), 252 (30 000). High-resolution mass spectra calculated for $C_{30}H_{48}O_4Si_4$ $M^{+\bullet}$, 584.2629; found, 584.2610**.** Reduction potentials: −0.67 and −1.34 V, (Figure 8).

Acid-Catalyzed Equilibration Polymerization of 1,8-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,5-dimethylanthraquinone. 1,8-Bis[2′-(trimethylsiloxydimethylsiloxy)-ethyl]-4,5-dimethylanthraquinone (200 mg, 0.34 mmol) and 5 μL of concentrated sulfuric acid were placed in a 5 mL pear-shaped flask. The reaction mixture was stirred at 70−75 °C while hexamethyldisiloxane was removed under vacuum (5−10 mm of Hg). The temperature was increased to 140 °C over 24 h. The reaction mixture was neutralized with 20 μL of hexamethyldisilazane. It was then taken up in 15 mL of diethyl ether, washed with water, separated, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed by evaporation under reduced pressure. The residue was dissolved in 1.5 mL of THF and the polymer was precipitated into 30 mL of methanol and collected by centrifugation.

Copoly[1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. A yellow solid, 0.13 g, 65% yield, was obtained, with M_w/M_n = 60 000/30 700 and T_g = 196 °C. ^{1}H NMR, δ: 0.24 (s, 12H), 0.92−0.99 (m, 4H), 2.62 (s, 6H), 3.03−3.1 (m, 4H), 7.27 (d, 2H, J = 8.1), 7.33 (d, 2H, J = 8.1). ^{13}C NMR, δ: 0.73, 21.70, 28.07, 131.95, 134.03, 134.84, 135.55, 136.13, 144.22, 190.20. ^{29}Si NMR, δ: 7.42. IR, ν: 1670 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 350 (11 700), 250 (33 000). Anal. Calcd for $C_{24}H_{30}O_3Si_2$: C, 68.20; H, 7.15. Found: C, 67.56; H, 7.35. Reduction potential −1.17 V (Figure 8). TGA, of this copolymer, is similar to that of copoly[1,5-(4,8-dimethylanthraquinonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (Figure 7), and this copolymer is more stable by 50 °C.

Direct Ru-Catalyzed Synthesis of Copoly[1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. Ru (27.5 mg, 30.0 μmol), styrene (3.12 mg, 3.45 μL, 30.0 μmol), and 0.5 mL of toluene were placed in an Ace pressure tube. The tube was sealed with a rubber O-ring and threaded Teflon seal and heated at 130−135 °C for 5 min, to activate the catalyst. The solution in the tube turned red.[19] The tube was then cooled to room temperature, and 1,8-dimethylanthraquinone (0.405 g, 1.715 mmol) and 1,3-divinyltetramethyldisiloxane (0.0.320 g, 1.715 mmol) were added to the tube. The tube was sealed and the contents stirred at 130−135 °C for 27 h. The reaction mixture was cooled and transferred to a 25 mL round-bottom flask, and the volatiles were removed by evaporation under reduced pressure. The residue was dissolved in hexane and run through a silica gel (60−200 mesh, 70 Å) column (25 cm long and 0.5 cm diameter) to remove residual Ru catalyst. Hexane was removed by evaporation under reduced pressure. The residue was dissolved in 1 mL of THF and added to 10 mL of methanol dropwise. The polymer was precipitated and collected by centrifugation. A yellow viscous polymer copoly[1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene], 0.43 g, 59.5% yield, was obtained, with M_w/M_n = 29 700/19 000. T_g = 112 °C; T_m = 124 °C. Spectral properties are as reported above. TGA: copoly[1,8-(4,5-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] prepared by direct reaction begins decomposing about 25 °C lower than that prepared by acid-catalyzed siloxane equilibration polymerization of 1,8-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]4,5-dimethylanthraquinone.

Ru-Catalyzed Reaction of 1,4-Dimethylanthraquinone with Vinylpentamethyldisiloxane. Ru (45.85 mg, 50 μmol), 1,4-dimethylanthraquinone (1.2 g, 5.08 mmol), and vinylpentamethyldisiloxane (4.42 g, 25.4 mmol) were placed in an Ace pressure tube. The tube was sealed and heated at 125−130 °C for 100 h. The initial color of the solution was red.[19] After the reaction was allowed to cool to room temperature, the volatiles were removed by evaporation under reduced pressure. The reaction products were separated by column chromatography on silica gel with hexane−ethyl acetate (96:04).

1-[2′-(Trimethylsiloxydimethylsiloxy)ethyl]-5,8-Dimethylanthraquinone. A yellow viscous liquid, 120 mg, 8.08% yield was obtained. ^{1}H NMR, δ: 0.13 (s, 9H), 0.19 (s, 6H), 0.90−0.97(m, 2H), 2.70 (s, 3H), 2.73 (s, 3H), 3.10−3.17 (m, 2H), 7.34 (d, 1H, J = 7.9 Hz), 7.37 (d, 1H, J = 7.9 Hz), 7.51 (dd, 1H, J = 2.2 and 7.8 Hz), 7.56 (t, 1H, J = 7.5 Hz), 7.99 (dd, 1H, J = 2.2 and 7.3 Hz). ^{13}C NMR, δ: 0.30, 2.01, 21.00, 22.35, 22.86, 28.07, 124.61, 128.77, 130.83, 132.01, 132.28, 135.58, 135.40, 135.93, 136.70, 137.95, 138.73, 147.08, 186.73, 189.03. ^{29}Si NMR, δ: 7.25, 7.52. IR ν: 1668 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 348 (5470), 253 (28 200). GC−MS: calculated for $C_{30}H_{48}O_4Si_4M^{+\bullet}$, 410.0; found, 410.0.

1,4-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-5,8-dimethylanthraquinone. A yellow viscous liquid, 70 mg, 4.72% yield, was obtained. ^{1}H NMR, δ: 0.12 (s, 18H), 0.17 (s, 12H), 0.89−0.94 (m, 4H), 2.64 (s, 6H), 3.01−3.06 (m, 4H), 7.29 (s, 2H), 7.35 (s, 2H). ^{13}C NMR, δ: 0.30. 2.01, 21.17, 21.35, 27.78, 134.18, 134.38, 134.80, 135.27, 136.28, 144.12, 190.32. ^{29}Si NMR, δ: 7.14, 7.53. IR ν: 1671 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 350 (11 130), 255 (55 000). High-resolution mass spectra calculated for $C_{30}H_{48}O_4Si_4$ $M^{+\bullet}$, 584.2629; found, 584.2609. Reduction potentials: −0.65 and −1.36 V (Figure 9).

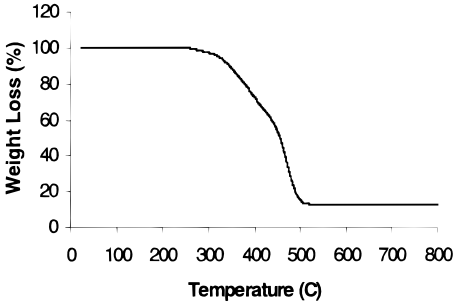


Figure 10. TGA of copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. M_w/M_n = 18 900/14 300.

The acid-catalyzed siloxane equilibration polymerization of 1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-5,8-dimethylanthraquinone was not attempted.

Ru-Catalyzed Direct Synthesis of Copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. In an Ace pressure tube were placed Ru (27.5 mg, 30 μmol), styrene (3.12 mg, 3.45 μL, 30.0 μmol), and 0.2 mL of toluene. The tube was sealed with a rubber O-ring and threaded Teflon seal and heated at 130−140 °C for 5 min to activate the catalyst. The solution in the tube turned red.[19] After the reaction was allowed to cool to room temperature, the tube was opened, and 1,4-dimethylanthraquinone (0.422 g, 1.788 mmol) and 1,3-divinyltetramethyldisiloxane (0.333 g, 1.788 mmol) were added. The tube was sealed and the contents stirred at 130−140 °C for 100 h. The reaction mixture was cooled and transferred to a 25 mL round-bottom flask, and the volatiles were removed by evaporation under reduced pressure. The residue was dissolved in 1.0 of mL THF, and 10 mL of methanol was added to precipitate the polymer, which was collected by centrifugation.

Copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. A yellow solid, 0.31 g, 41% yield, was obtained, with M_w/M_n = 18 900/14 300 (GPC), M_w = 6140 (MALLS) and M_n = 5740 (^{1}H NMR end group analysis), T_g = 24.6 °C, and T_m = 47.8 °C. ^{1}H NMR, δ: 0.20 (s, 12H), 0.90−0.95 (m, 4H), 2.55 (s, 6H), 3.00−3.05 (m, 4H), 7.20 (s, 2H), 7.32 (s, 2H). ^{13}C NMR, δ: 0.41, 21.19, 21.35, 27.83, 134.13, 134.40, 134.68, 135.23, 136.25, 144.10, 190.24. ^{29}Si NMR, δ: 7.38. IR ν: 1668 (C═O) cm^{-1}. UV λ_{max} nm (ϵ): 349 (5520), 253 (28 220). Anal. Calcd for $C_{24}H_{30}O_3Si_2$: C, 68.2; H, 7.15. Found: C, 67.47; H, 7.32. Reduction potentials: −1.18 and −1.48 V (Figure 9). TGA (Figure 10).

Ru-Catalyzed Reaction of 2,3-Dimethylanthraquinone with Vinylpentamethyldisiloxane. Ru (45.85 mg, 50 μmol), 2,3-dimethylanthraquinone (1.0 g, 4.23 mmol), and vinylpentamethyldisiloxane (2.64 g, 15 mmol) were placed in an Ace pressure tube. The tube was sealed and heated at 110−120 °C for 12 h. After cooling to room temperature, the reaction mixture was transferred to a 25 mL round-bottom flask, and the volatiles were removed under reduced pressure. The reaction mixture was purified, repeatedly, on a Cyclograph Centrifugal Chromatography System, equipped with a 4000 μm silica gel rotor, with hexane−ethyl acetate mixtures.

1-[2′-(Trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone. A yellow solid, 0.22 g, 12.7% yield, mp = 62−63 °C, was obtained. ^{1}H NMR, δ: 0.16 (s, 9H), 0.22 (s, 6H), 0.91−0.94 (m, 2H), 2.33 (s, 3H), 2.34 (s, 3H), 3.18−3.22 (m, 2H), 7.52 (dd, 1H, J = 2.0 and 7.5 Hz), 7.58 (t, 1H, J = 7.2 and 7.5 Hz), 7.85 (s, 1H), 7.88 (s, 1H), 8.13 (dd, 1H, J = 2.0 and 7.2 Hz). ^{13}C NMR, δ: 0.27, 1.99, 19.89, 19.90, 20.04, 29.23, 125.58, 127.22, 127.98, 130.23, 130.42, 132.72, 132.79, 135.16, 136.47, 142.82, 143.63, 149.11, 183.25, 184.41. ^{29}Si NMR, δ: 7.47, 7.49. IR ν: 1667 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 342 (6195), 263 (41 470). GC−MS calculated for $C_{30}H_{48}O_4Si_4$ M$^{+\bullet}$, 410.0; found, 410.0.

1,4-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone. A yellow solid, 0.43 g, 17.8% yield, mp = 63−64 °C, was obtained. ^{1}H NMR, δ: 0.11 (s, 18H), 0.18 (s, 12H), 0.89−0.96 (m, 4H), 2.40 (s, 6H), 3.13−3.20 (m, 4H), 7.44 (s, 2H), 7.90 (s, 2H). ^{13}C NMR, δ: 0.34, 2.06, 20.10, 20.20, 29.60, 127.31, 132.40, 132.58, 136.13, 143.00, 147.15, 186.08. ^{29}Si NMR, δ: 7.45, 7.53. IR, ν: 1667 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 352 (5540), 264 (40 390). High-resolution mass spectra calculated for $C_{30}H_{48}O_4Si_4$ M$^{+\bullet}$, 584.2629; found, 584.2633. Reduction potentials: −0.65 and −1.19 V (Figure 11).

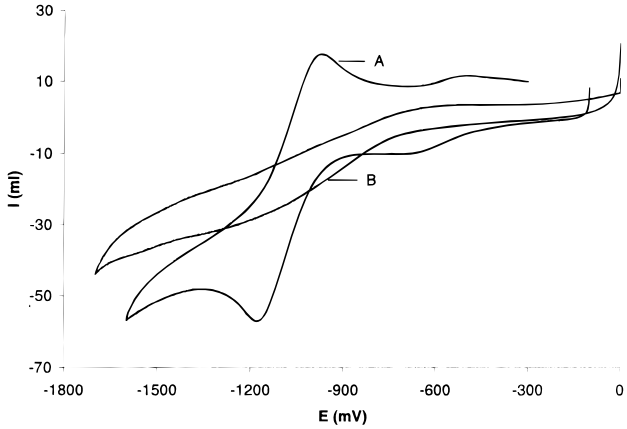


Figure 11. Cyclic voltamograms: (A) 1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone; (B) copoly[1,4-(6,7-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene].

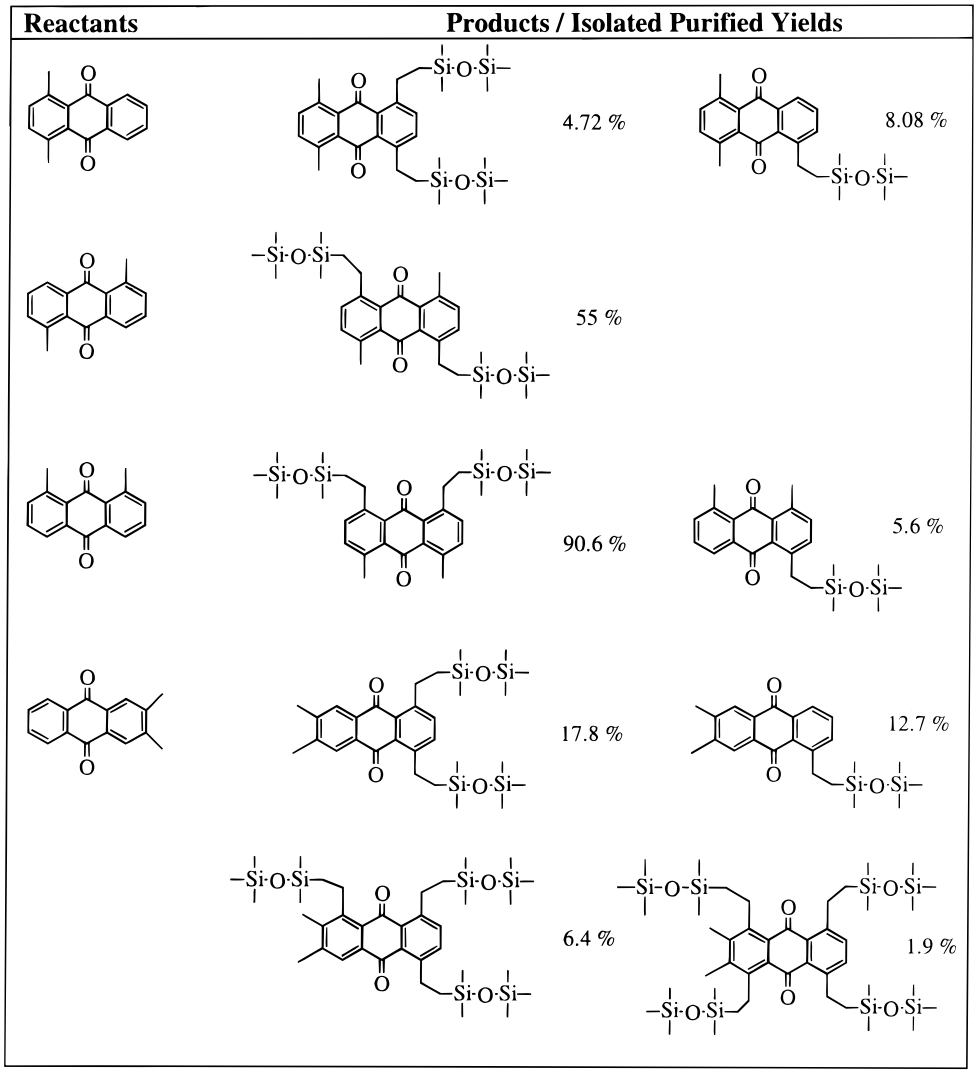
1,4,5-Tris[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone. A yellow viscous liquid, 0.20 g, 6.4% yield, was obtained. ^{1}H NMR, δ: 0.15 (s,9H), 0.16 (s, 9H), 0.17 (s, 9H), 0.21 (s, 6H), 0.22 (s, 6H), 0.27 (s, 6H), 0.95−1.05 (m, 6H), 2.36 (s, 3H), 2.44 (s, 3H), 3.06−3.09 (m, 4H), 3.13−3.17 (m, 2H), 7.40 (d, 1H, J = 8.0 Hz), 7.46 (d, 1H, 8.0 Hz), 7.80 (s, 1H). ^{13}C NMR, δ: 0.35, 0.43, 0.48, 2.05, 15.29, 19.37, 20.39, 20.92, 21.47, 23.90, 28.16, 28.76, 124.45, 131.52, 131.83, 133.51, 134.40, 135.28, 136.15, 141.42, 141.98, 144.33, 144.54, 145.53, 186.91, 190.27. ^{29}Si NMR, δ: 7.40, 7.44, 7.49, 7.52. IR, ν: 1670 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 351 (4450), 266 (25 550).

1,4,5,8-Tetrakis[2′-(trimethylsiloxydimethylsiloxy)-ethyl]-6,7-dimethylanthraquinone. A yellow viscous liquid, 0.08 g, 1.9% yield, was obtained. ^{1}H NMR, δ: 0.09 (s, 18H), 0.11 (s, 18H), 0.14 (s, 12H), 0.21 (s, 12H), 0.90−0.99 (m, 8H), 2.32 (s, 6H), 2.90−2.93 (m, 4H), 2.94−2.98 (m, 4H), 7.33 (s, 2H). ^{13}C NMR, δ: 0.44, 2.03, 16.25, 19.92, 20.92, 24.10, 27.11, 132.89, 133.48, 134.93, 140.72, 141.05, 142.74, 191.47. ^{29}Si NMR, δ: 7.31, 7.42. IR, ν: 1669 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 352 (4030), 273 (21 870).

Acid-Catalyzed Siloxane Equilibration Polymerization of 1,4-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone. 1,4-Bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone (70 mg, 0.12 mmol) and 1.0 mL of mesitylene were placed in a 5 mL round-bottom flask. To this was added 10 μL of concentrated sulfuric acid in 1.0 mL of mesitylene. The reaction mixture was stirred at room temperature, while hexamethyldisiloxane was removed under vacuum (5−10 mm of Hg). The reaction mixture was neutralized with 15 μL of hexamethyldisilazane. It was then taken up in 15 mL of diethyl ether, washed with water, separated, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed by evaporation under reduced pressure. The residue was dissolved in 1.0 mL of THF, and the polymer was precipitated into 30 mL of methanol and collected by centrifugation.

Copoly[1,4-(6,7-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. A yellow solid, 0.04 g, 60% yield, was obtained, with M_w/M_n = 33 000/12 200, T_g = 46 °C, and T_m = 77.9 °C. ^{1}H NMR, δ: 0.24 (s, 12H), 0.95−1.01 (m, 4H), 2.28 (s, 6H), 3.17−3.23 (m, 4H), 7.44 (s, 2H), 7.72 (s, 2H). ^{13}C NMR, δ: 0.49, 20.00, 20.13, 29.63, 127.13, 132.19, 132.49, 136.06, 142.79, 147.12, 185.83. ^{29}Si NMR, δ: 7.53. IR, ν: 1664 (C═O) cm^{-1}. UV λ_{max}, nm (ϵ): 352 (4140), 264 (32 550). Anal. Calcd for $C_{24}H_{30}O_3Si_2$: C, 68.20;

Table 1. Ru-Catalyzed Murai Reaction of 1,4-, 1,5-, 1,8-, and 2,3-Dimethylanthraquinones with Vinylpentamethyldisiloxane



H, 7.15. Found: C, 67.58; H, 7.34. Reduction potential −1.18 V, (Figure 11). TGA, of this copolymer, is similar to that of copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (Figure 10), and this copolymer is more stable by 25 °C.

Results and Discussion

The synthesis of nonconjugated copolymers, incorporating dimethylanthraquinone units in the polymer backbone, has been achieved in two ways. The direct Ru-catalyzed reaction of 1,4-, 1,5-, and 1,8-dimethylanthraquinones with 1,3-divinyltetramethyldisiloxane is successful. However, the molecular weights of the copolymers are comparatively low. This results in lower T_g's and thermal stability. While the ruthenium-catalyzed Murai reaction of 1,5- and 1,8-dimethylanthraquinone with excess pentamethyldisiloxane gives preparatively useful quantities of the desired bis(2′-trimethylsiloxydimethylsiloxy)ethyldimethylanthraquinone monomers, the analogous reaction with 1,4-dimethylanthraquinone gives poor yields (Table 1). While, both the α-mono- and α,α′-bis(2′-trimethylsiloxydimethylsiloxy)ethyldimethylanthraquinones have been isolated and characterized, insufficient quantities were obtained to carry out the acid-catalyzed siloxane equilibration polymerization.

We have carried out the ruthenium catalyzed reaction of 2,3-dimethylanthraquinone with vinylpentamethyldisiloxane, in the hope that formation of 1,4-bis(2′-trimethylsiloxydimethylsiloxy)ethyl-6,7-dimethylanthraquinone would be favored. In fact a mixture of mono-, di-, tri-, and tetrasubstituted products was obtained. These have been separated and characterized. The major product is 1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone, 17.8% yield. This material undergoes successful acid-catalyzed siloxane equilibration to yield the desired copolymer. 1-[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone, 1,4,5-tris[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone, and 1,4,5,8-tetrakis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone are the other products formed (Table 1). In point of fact, neither 1-(2′-trimethylsiloxydimethylsiloxy)ethyl-2,3-dimethylanthraquinone nor 1,4-bis(2′-trimethylsiloxydimethylsiloxy)ethyl-2,3-dimethylanthraquinone is formed, as shown by ^{1}H NMR (Figure 12). The monosubstituted product obtained is the isomer where the substitution is on the ring without the methyl groups. Substitution has to occur on the ring with the methyl groups for the tri- and tetrasubstituted products. This shows that the methyl groups impart

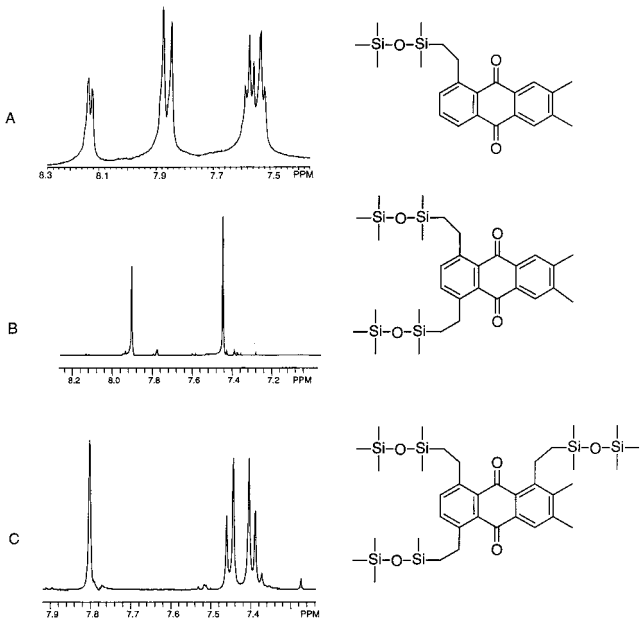


Figure 12. ^{1}H NMR spectra: (A) 1-[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone; (B) 1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone; (C) 1,4,5-tris[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone.

some steric hindrance but do not completely block the α-position. The peak heights for the two peaks in the aromatic region for 1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone are unequal; however, peak integration gives an equal value for both.

Molecular weights of the copolymers were obtained by GPC based on comparison to polystyrene standards. To get a more accurate estimate, the M_w and M_n obtained from GPC, MALLS, and ^{1}H NMR end group analysis were compared for copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]. From GPC, M_w/M_n was found to be 18 900/14 300 (polydispersity = 1.3), and MALLS gave $M_w = 6140$. In the proton spectra, anthraquinone units were observed as end groups. The methyl protons on the end group anthraquinone units were integrated against the intensity of the rest of the methyl protons in the polymer. The M_n found by the ^{1}H NMR end group analysis was 5740.

Ru-catalyzed direct synthesis gives copolymers with low molecular weights. This stems from the requirement that step−growth polymerization requires, for the direct synthesis, a 1:1 ratio of the two reagents and that the overall yield of the reaction be high or near quantitative. On the other hand once the monomer, on reaction with dimethylanthraquinone and vinylpentamethyldisiloxane, has been prepared and purified, the acid-catalyzed siloxane equilibration polymerization can be driven to near completion by removing the hexamethyldisiloxane formed. The properties of the higher molecular weight copolymers are markedly better than the ones prepared by direct synthesis.

In the study of electrochemistry of the monomers and copolymers, two reversible reduction potentials were observed for each monomer (1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-5,8-dimethylanthraquinone, 1,4-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-6,7-dimethylanthraquinone, 1,5-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,8-dimethylanthraquinone, and 1,8-bis[2′-(trimethylsiloxydimethylsiloxy)ethyl]-4,5-dimethylanthraquinone). For the copolymers only one broad peak was obtained, except in the case of copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene], for which two reduction potentials were observed. Both peaks are much narrower compared to the peaks observed for the isomeric copolymers. This difference could be attributed to the low molecular weight of the copoly[1,4-(5,8-dimethylanthraquinonylene)/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene].

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