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Synthesis and characterization of novel heteroannular benzoylferrocene polysiloxane monomers, oligomers, and polymers

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Abstract

Copoly[2,2′-bis[1,1′-ferrocene]benzoylylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (**III**) was synthesized by two approaches. High molecular weight **III** was obtained by an acid catalyzed equilibrium condensation of 1,1′-bis[1-(3′,3′,5′,5′-tetramethyl-4-oxa-3,5-disilahexyl)benzoyl] ferrocene (**IV**), while lower molecular weight **III** was synthesized by the dihydridocarbonyltris(triphenylphosphine)ruthenium (**Ru**) catalyzed co-oligomerization of 1,1′-benzoylferrocene and 1,3-divinyltetramethyl-disiloxane. **Ru** catalyzed reaction of benzoylferrocene and 1,3-divinyltetramethyl-disiloxane gave 1-[2′-ferrocenoylphenethyl]-3-vinyltetramethyl-disiloxane (**II**), 1,3-bis[2′-ferrocenoyl phenethyl]tetramethyldisiloxane (**I**). The electrochemistry of **I**, **III**, and **IV** have been examined by cyclic voltammetry. These materials show a single reversible oxidation process. The products have been characterized by ^{1}H, ^{13}C, ^{29}Si NMR, IR, UV–Vis spectroscopy, as well as elemental analysis and/or high resolution mass spectrometry with peak matching. GPC, DSC and TGA of the copolymer and co-oligomer **III** have been determined.

Keywords: Benzoylferrocene; Disiloxane copolymer; Ruthenium catalysis

1. Introduction

1.1. Silicon polymers which contain ferrocene moieties

There has been considerable interest in silicon containing polymers which either incorporate ferrocene units heteroannularly or as pendant groups. Such materials exhibit novel electrical, electrochemical, and optical properties [1,2]. Applications of such polymers have included their use in the chemical modification of electrodes and in the construction of amperometric biosensors [2].

Platinum catalyzed hydrosilation polymerization has been used to prepare polymers which contain ferrocene and disiloxane units as well as polymers with ferrocene and carbosilane units in the polymer chain [3]. For example, treatment of 1,1′-bis(dimethylsilyl)ferrocene and 1,1′-bis(vinyldimethylsilyl)ferrocene with chloroplatinic acid yields the expected ferrocene containing poly(carbosilane) [4]. Both anionic and thermal ring opening of 1,1′-ferrocenyldimethylsilane yield high molecular weight copoly(1,1′-ferrocenylene/dimethylsilylene) [5–7]. On the other hand, attempts to prepare polymers which contain both ferrocene and disiloxane units by ring opening of 1,3(1,1′-ferrocenylene)tetramethyldisiloxane were unsuccessful [8]. Condensation polymerization by formation of amide bonds has been used to prepare polymers which contain ferrocene and either disiloxane or carbosilane units. For example, condensation of 1,3-bis[3′-aminopropyl]-1,1,3,3-tetramethyldisiloxane with 1,1′-bis(chlorocarbonyl)ferrocene yields the expected polyamide [2].

1.2. Ruthenium catalyzed Murai polymerizations

Acetophenone and a number of other aromatic ketones have been found to undergo dihydridocarbonyltris(triphenylphosphine)ruthenium (**Ru**) catalyzed copolymerization with α,ω-divinylsilanes [9–12]. These reactions involve the **Ru** catalyzed anti-Markovnikov addition of both of the *ortho* C–H bonds of the acetophenone across the C–C double bonds of the α,ω-divinylsilane. Ferrocene is often described as an organometallic aromatic compound [13,14]. We were interested to see whether this novel ruthenium catalyzed reaction would prove useful for the preparation of ferrocene containing polymers. We have found that **Ru** is unable to catalyze the copolymerization of acetylferrocene with 1,3-divinyltetramethyldisiloxane.

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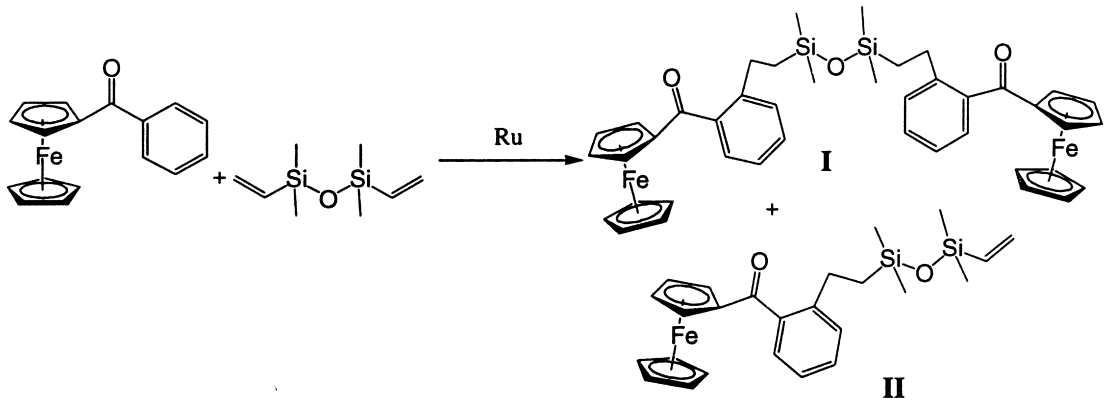

Fig. 1. Synthesis of model compounds by Ru catalyzed *ortho*-alkylation of benzoylferrocene by 1,3-divinyltetramethyldisiloxane.

Similarly, acetylferrocene does not undergo **Ru** catalyzed *ortho*-alkylation reaction with vinyltrimethylsilane [15].

In this paper we report the synthesis, characterization, and redox behavior of model compounds, oligomers and polymer, which contains both heteroannular ferrocenyl and siloxane units in the backbone. The model compounds were prepared by **Ru** catalyzed *ortho*-alkylation of benzoylferrocene by 1,3-divinyltetramethyldisiloxane (Fig. 1).

The oligomers are similarly prepared by **Ru** catalyzed *ortho*-alkylation of 1,1′-benzoyl-ferrocene by 1,3-divinyltetramethyldisiloxane (Fig. 2). Finally, a high molecular weight polymer was prepared by an acid catalyzed equilibrium condensation polymerization of a 1,1′-dibenzoylferrocene disiloxane derivative, which yields polymer and hexamethyldisiloxane. The reaction is driven to yield high molecular weight polymer by the removal of volatile hexamethyldisiloxane (Fig. 2).

2. Experimental

2.1. Spectroscopy

Before the NMR spectra of the ferrocene containing compounds were obtained, the materials were taken up in diethyl ether, extracted with an aqueous stannous chloride solution, dried over anhydrous magnesium sulfate, filtered, and then the volatile solvents were removed by evaporation under vacuum [16]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer operating in FT mode. ^{29}Si NMR spectra were obtained on a IBM Bruker WP-270-SY spectrometer. Five percent w/v solutions in acetone-d_6 or benzene-d_6 were used to obtain the NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. Residual acetone or chloroform was used as an internal standard to calculate ^{1}H and ^{13}C NMR spectra. A heteronuclear gated decoupled pulsed sequence (NONOE) with a 20 s delay was used to acquire ^{29}Si spectra [17]. These were externally referenced to TMS. IR of neat films or Nujol mulls on NaCl plates were recorded on a Perkin Elmer 2000 FT-IR spectrometer. UV spectra of methylene chloride solutions were acquired on a Shimadzu UV-260 ultra-violet visible spectrometer.

2.2. Molecular weight distribution

Gel permeation chromatography (GPC) analysis of the molecular weight distribution of these polymers was performed on a Waters system comprised of a U6K injector, a

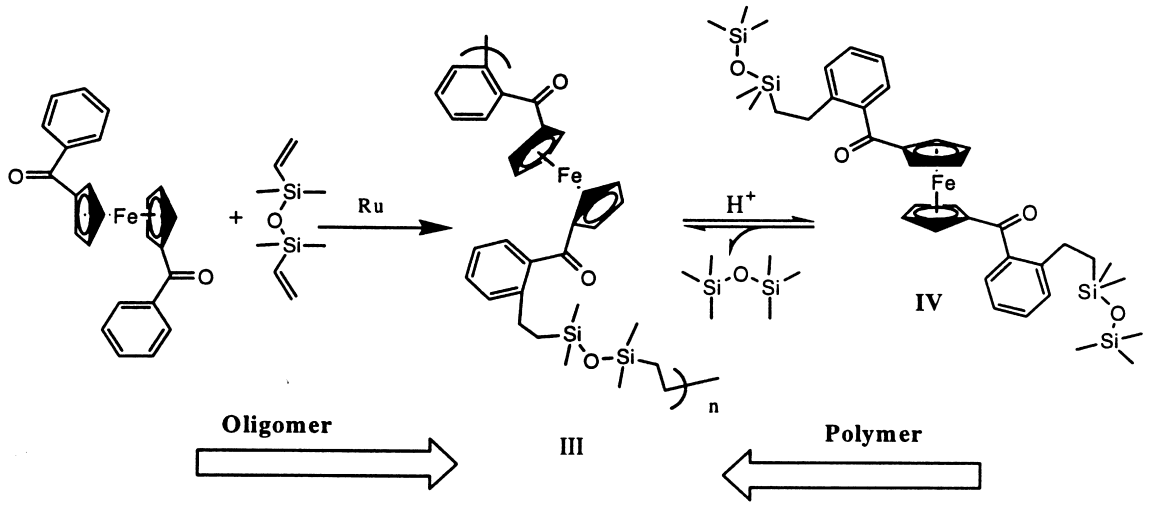

Fig. 2. Synthetic routes to oligomer and polymer **III**.

510 HPLC pump, and a R401 refractive index detector. The eluting solvents were either HPLC grade toluene at a flow rate of 0.4 mL/min or THF at a flow rates of 0.8 mL/min. The retention times were calibrated against known monodispersed polystyrene standards: 929 000; 114 200; 47 500; 18 700; 2200 Da whose M_w/M_n ratios are less than 1.09.

2.3. Thermal analysis

Thermogravimetric analysis of the polymers was carried out on a Shimadzu TGA-50 instrument with a nitrogen flow rate of 40 cc/min. The temperature program for the analysis was begun at 50°C. The temperature was then increased at a rate of 5.0°C/min up to 750°C.

The glass transition temperature (T_g) of the polymers was determined on a Perkin-Elmer DSC-7 instrument. The analysis program for the lower molecular weight material was −10°C for 20 min followed by an increase in temperature of 20°C/min to 150°C. The analysis program for the higher molecular weight material was −60°C for 20 min followed by an increase in temperature of 5°C/min to 500°C.

2.4. Elemental analysis and mass spectroscopy

Oneida Research Services Inc., Whitesboro, NY, performed elemental analysis. High resolution mass spectra were run at the UCR 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.

2.5. Electrochemistry

The solution electrochemical behavior of the ferrocenyl monomers, oligomers, and polymer in methylene chloride solutions was determined by cyclic voltammetry. Cyclic voltammograms were obtained on an EG&G Potentiostat/Galvanostat model 283 using a copper or platinum working electrode, and a platinum counter electrode which was referenced to a silver chloride electrode (0.222 V). A 0.1 M solution of tetrabutylammonium hexafluorophosphate was used as the electrolyte. The samples were scanned from 0 to 1.5 V using a scan rate of 0.1 V/s.

2.6. Method and materials

All reactions were carried out in flame dried glassware under atmosphere of purified argon. Ferrocene, benzoylferrocene, styrene, aluminum chloride, *p*-benzoyl chloride, and silica gel 60–200 mesh were obtained from Aldrich. Vinylpentamethyl-disiloxane and 1,3-divinyltetramethyldisiloxane was acquired from Gelest. **Ru** catalyst was prepared from ruthenium trichloride hydrate [18]. 1,1′-Dibenzoyl ferrocene was prepared by an aluminum chloride catalyzed Friedel–Crafts reaction between *p*-benzoyl chloride, ferrocene and aluminum chloride [19]. Benzene, pentane, tetrahydrofuran, hexane, and toluene was purchased from Fisher and distilled from sodium prior to use.

2.7. Reaction of benzoylferrocene and 1,3-divinyltetramethyldisiloxane

Ru (69.6 mg, 0.068 mmol), 0.25 mL of toluene, styrene (7.8 mL, 0.068 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube. The tube and its contents were heated at 135°C for 3 min. This served to activate the catalyst [11]. After rapid cooling to room temperature, the tube was opened and benzoylferrocene (0.95 g, 2.7 mmol) and 1,3-divinyltetramethyldisiloxane (0.597 g, 1.35 mmol) were added. The tube was sealed and heated for 24 h at 135°C. After cooling to room temperature, 5 mL of toluene were added. Silica gel (9 g) was added to the solution and the volatile solvents removed by evaporation under reduced pressure. The silica gel, which contained adsorbed reaction products, was placed at the top of a chromatography column, 25 cm in length and about 4.5 cm in diameter, filled with a hexane slurry of silica gel. The reaction products were separated by elution with a hexane/ether (4:1) mixture. The R_f of 1-[2′-ferrocenoyl phenethyl]-3-vinyl tetramethyl-disiloxane was 0.2 while that of 1,3-bis[2′-ferrocenoyl phenethyl] tetramethyldisiloxane was 0.4.

2.8. 1,3-bis[2′-Ferrocenoyl phenethyl]tetramethyldisiloxane (**I**)

Yield 0.75 g, 72.5% yield of a red oil was obtained. ^{1}H NMR δ: −0.09(s,12H), 0.72–0.80(br. m, 4H), 2.50–2.64(br.m, 4H), 4.12(s, 10H), 4.40(s, 4H), 4.61(s, 4H), 7.13(t, 2H, J = 7.5 Hz), 7.20(d, 2H, J = 7.0 Hz), 7.26(dd, 2H, J = 15.0 and 7.3 Hz), 7.42(d, 2H, J = 7.3 Hz). ^{13}C NMR δ: 0.29, 20.89, 26.78, 69.95, 71.15, 72.40, 79.64, 124.83, 127.29, 129.25, 129.79, 139.59, 143.03, 202.63. ^{29}Si NMR δ: 7.19. IR ν: 3070, 3062, 3018, 2956, 2886, 1645, 1599, 1483, 1468, 1442, 1412, 1397, 1375, 1339, 1291, 1275, 1255, 1176, 1107, 1047, 955, 909, 839, 786, 759, 737 cm^{-1}. UV λ_{max} nm (ϵ): 232 (7.14×10^4), 256 (4.16×10^4), 353 (5.93×10^3), 466 (2.90×10^3). High resolution mass spectra calc. for $[C_{42}H_{46}O_3Fe_2Si_2]^+\cdot$: 766.1674. Observed: 766.1683.

2.9. 1-[2′-Ferrocenoylphenethyl]-3-vinyltetramethyldisiloxane (II)

Yield 0.15 g, 13.6% yield of red oil was obtained. ^{1}H NMR δ: 0.06(s, 6H), 0.13(s, 6H), 0.87–0.92(br. m, 2H), 2.70–2.75(br. m, 2H), 4.28(s, 5H), 4.61(s, 2H), 4.67(s, 2H), 5.74(dd, 1H, J = 20 and 3.6 Hz), 5.92(dd, 1H, J = 15.1 and 3.6 Hz), 6.14(dd, 1H, J = 20 and 15.1 Hz), 7.31(dd, 1H, J = 7.5 and 6.7 Hz), 7.37(d, 1H, J = 7.2 Hz), 7.42(dd, 1H, J = 7.2 and 7.1 Hz), 7.59(d, 1H,

Hz). ^{13}C NMR δ: 0.12, 0.34, 20.82, 26.70, 69.89, 71.10, 72.32, 79.59, 124.79, 127.25, 129.12, 129.71, 131.50, 139.50, 139.55, 143.00, 202.55. ^{29}Si NMR δ: −9.12, 2.53. IR ν: 3098, 3051, 3015, 2957, 2900, 1648, 1598, 1573, 1483, 1443, 1408, 1376, 1354, 1340, 1291, 1276, 1254, 1176, 1108, 1048, 955, 909, 839, 786, 759, 741, 706 cm^{-1}. UV λ_{max} nm (ε): 233 (4.38×10^4), 254 (2.49×10^4), 352 (3.69×10^3), 468 (1.84×10^3). High resolution mass spectra calc. for $[C_{25}H_{32}O_2FeSi_2]^{+}\cdot$: 476.1281. Found: 476.1314.

2.10. Reaction of 1,1′-dibenzoylferrocene with 1,3-divinyltetramethyldisiloxane

Ru (69.6 mg, 0.068 mmol), 0.8 mL of toluene, styrene (7.8 mL, 0.068 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube as above. After activation of the catalyst as described above, 1,1′-dibenzoylferrocene (1.21 g, 3.07 mmol) and 1,3-divinyltetramethyldisiloxane (0.57 g, 3.07 mmol) were added. The tube was resealed and heated for 24 h at 135°C. The oligomeric product was isolated by addition of the red colored reaction solution to 20 mL of methanol. This caused a red/black colored oil to separate. The viscous oil was separated by decantation. It was redissolved in a minimum amount of THF and reprecipitated by addition of methanol. This process was repeated. Silica gel (3 g) was then added to the oil. The silica gel/reaction product mixture was added to the top of a chromatography column (18 cm × 1 cm) which was packed with a hexane slurry of silica gel. The product was eluted with ether.

2.11. Co-oligo[2,2′-bis[1,1′-ferrocene]benzoylylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (**III**)

Yield 0.38 g, 21% yield, M_w/M_n = 3400/2200 was obtained. ^{1}H δ: −0.04(s, 12H), 0.74–0.82(m, 4H), 2.51–2.58(m, 4H) 4.55(t, 4H, J = 1.71 Hz), 4.73(t, 4H, J = 1.66 Hz), 7.20(dd, 2H, J = 7.06 Hz and 7.48 Hz), 7.38(dd, 2H, J = 7.34 Hz and 9.11 Hz), 7.53(d, 1H, J = 7.68 Hz), 7.79(d, 1H, J = 6.59 Hz). ^{13}C NMR δ: 0.47, 21.62, 27.44, 72.96, 75.04, 82.00, 125.84, 128.29, 130.18, 130.82, 139.90, 143.93, 200.73. ^{29}Si NMR δ: 7.33. IR ν: 3063, 3019, 2955, 2927, 2884, 1700, 1654, 1649, 1643, 1637, 1448, 1443, 1374, 1289, 1273, 1254, 1048, 840, 781, 759 cm^{-1}. UV λ_{max} nm (ε): 260(2.0×10^5), 278(1.74×10^5), 350(3.1×10^4), 470(1.0×10^4). Elemental Anal. Calc. for $C_{32}H_{36}O_3Si_2Fe$: C, 66.19%; H, 6.25%. Found: C, 64.82%; H, 6.62%.

2.12. Reaction of 1,1′-dibenzoylferrocene with vinylpentamethyldisiloxane

Ru (0.100 g, 0.0978 mmol), 4.5 mL of toluene, and styrene (11.2 μl, 0.068 mmol) and a Teflon covered stirring bar were placed in a 20 mL Ace pressure tube and the catalyst activated as described above. 1,1′-Dibenzoylferrocene (2.00 g, 5.07 mmol) and vinylpentamethyldisiloxane (2.05 g, 11.76 mmol),) were added. The tube was then purged again with argon, sealed and heated for 20 h at 135°C. The tube was cooled to room temperature and 10 mL of silica gel was added to the dark red viscous solution. The solvent and excess vinylpentamethyldisiloxane were removed by evaporation under vacuum. The absorbed product was added to the top of a column of silica gel in hexane packed in a 20 cm × 2.8 in. column. Hexane was used as a mobile phase. The first fraction eluted, 0.09 g, was yellow in color, and according to ^{1}H-NMR contains no ferrocene units. The mobile phase was changed to hexane/THF (98%/2%), and three additional peaks were eluted. Fraction two, R_f = 0.5, 1.13 g, a red viscous oil shows ^{1}H-NMR consistent with 1,1′-bis[1-(3′,3′,5′,5′-tetramethyl-4-oxa-3,5-disilahexyl)benzoyl]ferrocene (**IV**). Fraction three, R_f = 0.18, 2.8 g, red viscous oil, shows a ^{1}H NMR consistent with a mixture of **IV** and 1(-1-(3′,3′,5′,5′-tetramethyl-4-oxa-3, 5-disilahexyl)benzoyl)-1′-benzoylferrocene. The third fraction which is deep purple in color, R_f = 0.09, was 1,1′-dibenzoylferrocene.

2.13. 1,1′ bis[1-(3′,3′,5′,5′-Tetramethyl-4-oxa-3,5-disilahexyl)benzoyl]ferrocene (**IV**)

Yield 1.13 g, 30%. ^{1}H NMR δ: 0.03(s, 18H), 0.06(s, 12H), 0.82–0.87(m, 4H), 2.61–2.66(m, 4H), 4.70(t, 4H, J = 1.9 Hz), 4.75(t, 4H, J = 1.8 Hz), 7.26(td, 2H, J = 7.6 and 1 Hz), 7.34(d, 2H, J = 7.6 Hz), 7.43(td, 2H, J = 7.2 and 1 Hz), 7.53(dd, 2H, J = 7.2, 1 Hz). ^{13}C NMR δ: 0.39, 2.12, 21.71, 27.46, 72.97, 74.80, 81.90, 125.93, 128.35, 130.15, 131.01, 139.90, 143.93, 200.89. ^{29}Si NMR δ: 7.03, 7.48. IR ν: 3282.9, 3092.4, 3064.4, 3019.6, 2947.9, 2481.7, 1949.6, 1930.0, 1725.8, 1655.9, 1650.3, 1597.2, 1572.0, 1482.5, 1440.5, 1398.6, 1409.7, 1398.6, 1370.6, 1342.6, 1286.7, 1253.1, 1177.6, 1121.6, 1046.1, 953.8, 909.0, 841.9, 800.0, 774.8, 755.2, 696., 682.5, 660.1, 626.5 cm^{-1} UV λ_{max} nm (ε): 241 (1.04×10^4), 277 (8.02×10^3), 360 (1.56×10^3), 474 (7.83×10^2). High resolution mass spectra calc. for $[C_{38}H_{54}O_4FeSi_4]^{+}\cdot$: 742.2449. Observed: 742.2447.

2.14. Acid catalyzed condensation equilibration polymerization of **IV**–copoly **III**

Diglyme (1.5 g) and concentrated sulfuric acid (four drops) were placed into a test tube and mixed with a stir rod. This mixture was then added to 0.5 g of **IV** in a 20 mL round-bottomed flask containing a Teflon covered magnetic stirring bar. The mixture was then placed under vacuum, 15 mmHg, and stirred at room temperature for a total of 144 h. Three additional drops of sulfuric acid dissolved in diglyme (1 mL) were added after 44 h. After 144 h, 0.25 g of potassium carbonate was added to the mixture followed by 10 mL of water. The organic mixture was taken up in benzene, 100 mL, and washed with three 100-mL portions of water. The organic layer was then separated and dried over anhydrous magnesium sulfate and filtered. The solvent

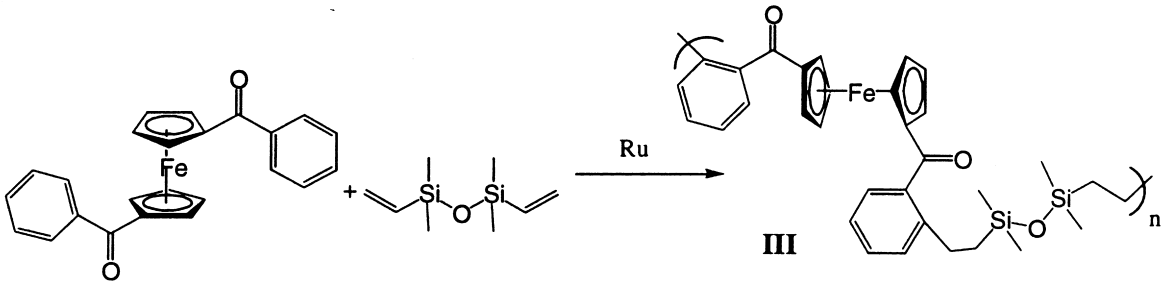

Fig. 3. Ru catalyzed co-oligomerization of 1,1′-dibenzoylferrocene and 1,3-divinyltetramethyldisiloxane.

was removed by evaporation under reduced pressure to a volume of 3 mL. The viscous oil was precipitated by addition of 200 mL of pentane. The resulting reddish black swollen polymer was rinsed two times with 20-mL portions of pentane, until the washings were clear. The product was dissolved in benzene (2 mL) and precipitated again with 100 mL of pentane. The precipitate was washed with 20 mL of pentane and then dried under high vacuum for 16 h to yield 0.26 g, 65.1% of a reddish black crystalline polymer. A similar reaction carried out with triflic acid in *ortho*-dichlorobenzene at 50°C gave similar results.

*2.15. Copoly[2,2′-[1,1′-ferrocene]benzoylyene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (***III***)*

Yield 0.26 g, 65.1%. ^{1}H NMR δ: 0.01(s, 12H), 0.80–0.85(m, 4H), 2.63–2.58(m, 4H) 4.62(br. s, 4H), 4.70(br. s, 4H), 7.23(t, 2H, J = 7.6 Hz), 7.31–7.34(m, 2H), 7.38–7.40(m, 2H), 7.51(d, 2H, J = 6.5 Hz). ^{13}C NMR δ: 0.59, 21.80, 27.60, 73.10, 74.91, 82.09, 125.96, 128.44, 130.32, 130.96, 140.00, 144.09, 200.84. ^{29}Si NMR δ: 7.68. IR ν: 3097, 3028, 3013, 2954, 2917, 28431, 2365.3, 1723, 16574, 1648, 1642, 1598, 1481, 1440, 1407, 1370, 1341, 1330, 1289, 1256, 1179, 1135, 1042, 954, 943, 906, 880, 840,792, 755, 740, 700, 659 cm^{-1}. UV λ_{max} nm (ϵ): 256 (1.71×10^4), 276 (1.28×10^4), 360 (3.67×10^3), 496.6 (2.45×10^3). GPC $M_w/M_n = 28624/9135 = 3.13$. Elemental Anal. Calc. for $C_{32}H_{36}O_3Si_2Fe$: C, 66.19%; H, 6.25%; Si, 9.67%; Fe, 9.62%. Found: C, 65.65%; H, 6.46%; Si, 12.35%; Fe, 6.99% DSC was run but no T_g was detected.

3. Results and discussion

3.1. Synthetic approach

Based on previous work, it was anticipated that a **Ru** catalyzed reaction benzoyl ferrocene with 1,3-divinyltetramethyldisiloxane would lead to copoly[2-ferrocenoyl-1,3-phenylene/3,3,5,5-tetramethyl-4-oxa-3, 5-disila-1, 7-heptanylene]. The success of this reaction depends on the ability of the **Ru** to activate both of the *ortho*-hydrogens of the benzoyl ring [9–12]. In point of fact, monomeric 1-[2′-ferrocenoyl phenethyl]-3-vinyltetramethyldisiloxane, 1,3-bis[2′-ferrocenoyl phenethyl]tetramethyl-disiloxane and unreacted 1,3-divinyltetramethyldisiloxane are obtained from this reaction (Fig. 1). The formation of these products clearly indicates that, while one of the *ortho*-C–H bonds of the benzoyl group is reactive, the second is not.

Based on this analysis, the **Ru** catalyzed copolymerization reaction of 1,1′-dibenzoylferrocene and 1,3-divinyltetramethyldisiloxane was carried out. This reaction was successful; however, it gave only low molecular weight co-oligo[2,2′-[1,1′-ferrocene]benzoylyene/3, 3, 5, 5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (**III**) (Fig. 3).

A different synthetic approach was explored in an effort to synthesize a high molecular weight polymer copoly[2,2′-[1,1′-ferrocene]benzoylyene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] **III**. This involves the acid catalyzed equilibrium condensation of 1,1′ bis[1-(3′,3′,5′,5′-tetramethyl-4-oxa-3,5-disilahexyl)benzoyl] ferrocene (**IV**) to yield high molecular weight polymer and hexamethyldisiloxane. This method takes advantage of the acid catalyzed equilibrium of siloxane groups. By exploiting the boiling point differences between the hexamethyldisiloxane and polysiloxane containing benzoylferrocenyl moieties, the reaction can be driven to high molecular weight polymer **III**. The monomer **IV** was prepared via a **Ru** catalyzed mono *ortho*-alkylation reaction between both of the benzoyl groups of 1,1′-dibenzoylferrocene and two equivalents of vinylpentamethyldisiloxane (Fig. 4).

The polymerization of **IV** was carried out in a high boiling ether solvent, diglyme, under high vaccum using a

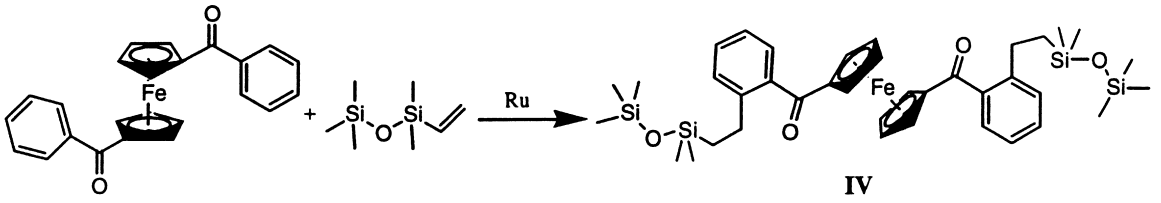

Fig. 4. Ru catalyzed *ortho*-alkylation of 1,1′-dibenzoylferrocene by vinylpentamethyldisiloxane.

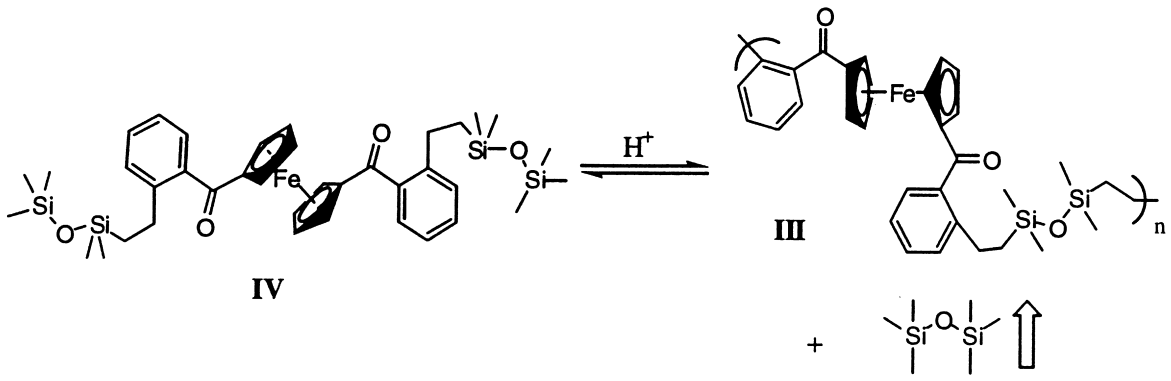

Fig. 5. Acid catalyzed equilibration polymerization of **IV**.

catalytic amount of concentrated sulfuric acid as the catalyst, or in *ortho*-dichlorobenzene with triflic acid catalysis (Fig. 5). High molecular weight **III** has been characterized by spectroscopic methods and elemental analysis, TGA, GPC, and DSC.

3.2. NMR spectra of ferrocene derivatives

It should be noted that it is quite easy to oxidize ferrocene compounds to the corresponding ferricinium derivatives, which are paramagnetic. Since traces of paramagnetic impurities can cause broadening of the NMR spectra, we have treated the ether solutions of the ferrocene derivatives prior to obtaining the NMR spectra with an aqueous solution of tin(II) chloride in order to reduce any ferricinium present to the corresponding ferrocene.

3.3. Elemental analysis—ferrocenyl siloxane derivatives problems

The percent carbon found for oligo and poly **III** is low. This, however, is not unusual. Low carbon values have been previously reported in the literature for polymers that contain both silicon and ferrocene. These results have been attributed to incomplete combustion of the compound, possibly due to the formation of ceramic products at elevated temperatures [2,20].

3.4. Electrochemistry

Both the mono and bis(ferrocenyl)siloxane derivatives examined undergo a single diffusion controlled reversible one-electron oxidation/reduction. These scans can be seen

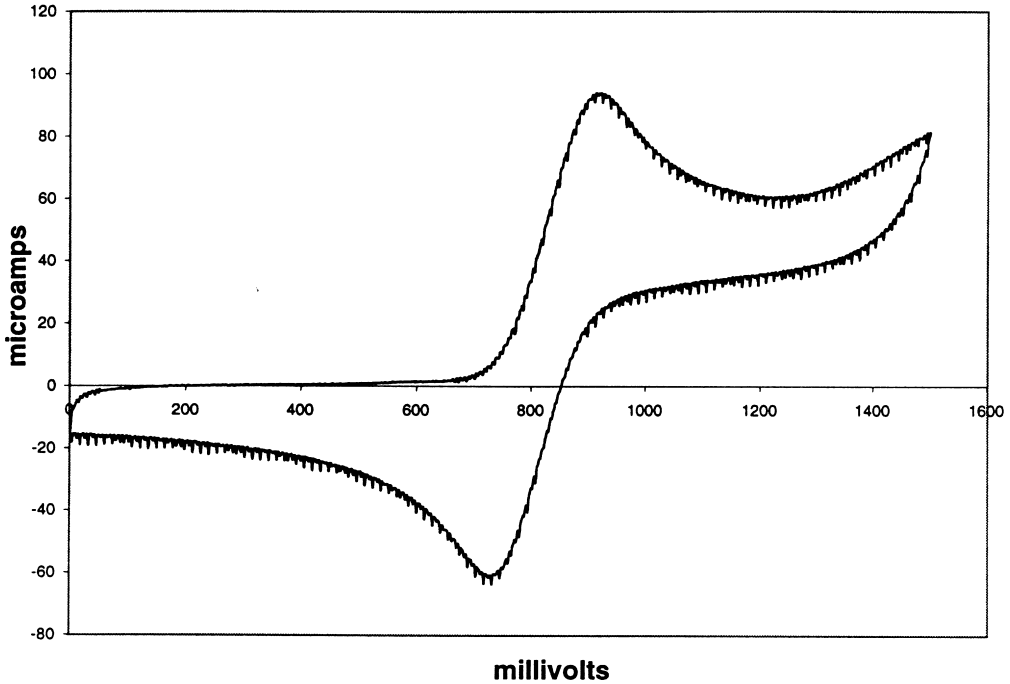

Fig. 6. Cyclic voltammogram of **I**.

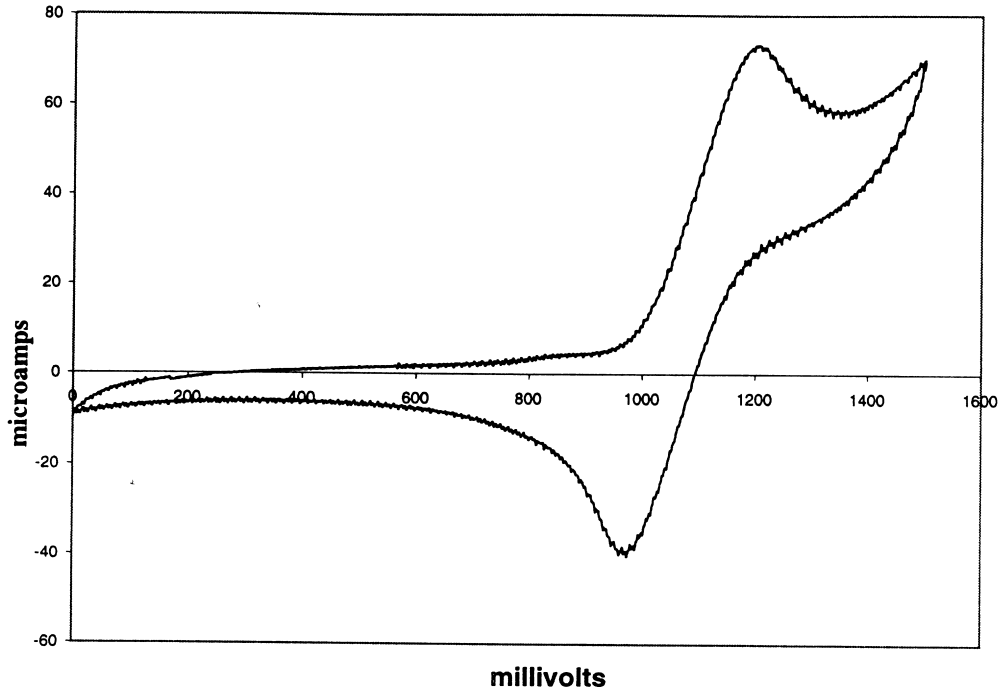

Fig. 7. Cyclic voltammogram of **IV**.

in Figs 6 and 7. Their $E_{1/2}$ values are summarized in Table 1. It has been shown that when two ferrocene units are closely joined by a spacer group, two oxidation potentials can result [7,21]. The separation between these potentials is thought to be due to an interaction between the iron sites and is proportional to the spacer length between the ferrocenyl units. At small separations, this interaction is large and yields two distinct oxidation potentials. For example, two reversible oxidation waves are reported for copoly(1,1′-ferrocenylene/dimethylsilylene). At large separation, this interaction is non-existent or undetectable and only a single oxidation potential results [21,22]. It should come as no surprise that bis(ferrocenyl)disiloxane derivative **I** shows only a single oxidation potential. Polymer **III** also undergoes diffusion controlled reversible one-electron oxidation/reductions with one potential (Fig. 8 and Table 1). Similar results have been seen for the condensation polymer of 1,3-bis[3′-aminopropyl]-1,1,3,3-tetramethyl-disiloxane with 1,1′-bis(chlorocarbonyl)ferrocene which shows a single reversible oxidation process [2].

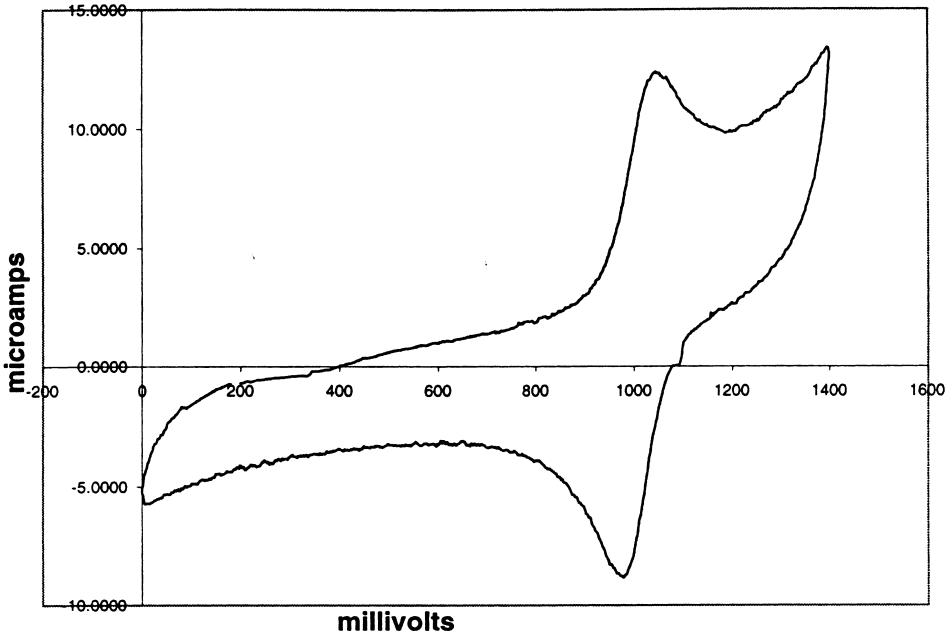

Fig. 8. Cyclic voltammogram of co-poly **III**.

Table 1
$E_{1/2}$ values vs. $AgCl_2$ electrode (0.222 V)

Compound	$E_{1/2}$ value (V)
I	0.79
IV	1.09
III	1.01

3.5. Thermal analysis

Copoly **III** is thermally stable to almost 300°C. Between 300 and 400°C, the sample loses 4% of its initial weight. Above 400°C rapid weight loss occurs. By 460°C only 65% of the initial sample weight remains. Between 500 and 750°C virtually no further weight loss is observed.

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