Macromolecules **2002,** *35,* 3369−3373

Ruthenium-Catalyzed Chemical Modification of Poly(vinylmethylsiloxane) with 9-Acetylphenanthrene

Shashi Kant Gupta and William P. Weber*

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

Received November 13, 2001; Revised Manuscript Received February 1, 2002

ABSTRACT: Poly[2-(9′-acetyl-10′-phenanthrenyl)ethylmethylsiloxane] (**I**) has been prepared by the activated dihydridocarbonyltris(triphenylphosphine)ruthenium (**Ru**)-catalyzed regioselective anti-Markovnikov addition of the 10-C−H bond of 9-acetylphenanthrene across the C−C double bonds of poly(vinylmethylsiloxane) (PVMS). This chemical modification of PVMS is highly efficient. The UV absorption, excitation, and emission spectral properties as well as the thermal properties of **I** have been studied. For comparison, the monomeric model systems tetrakis[2-(9′-acetyl-10′-phenanthrenyl)ethyldimethylsiloxy]silane (**II**), 2,3,4-tris[2-(9′-acetyl-10′-phenanthrenyl)ethyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane (**III**), and 9-acetyl-10-[2′-(trimethylsiloxydimethylsilyl)ethyl]phenanthrene (**IV**) were prepared by **Ru**-catalyzed reactions of 9-acetylphenanthrene with tetrakis[vinyldimethylsilyloxy]silane, 2,3,4-trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane, and vinylpentamethyldisiloxane, respectively.

Introduction

There is considerable interest in the application of transition-metal catalysis in organic[1,2] and polymer synthesis.[3] Murai reported a highly efficient dihydridocarbonyltris(triphenylphosphine)ruthenium (**Ru**)-catalyzed regioselective anti-Markovnikov addition of the ortho C−H bonds of aromatic ketones across the C−C double bond of vinylsilanes.[4−6] We have applied this **Ru**-catalyzed reaction to the copolymerization of α,ω-divinylsilanes or α,ω-divinyldisiloxanes with aromatic ketones such as acetophenone.[7−10]

Chemical modification of polymers has received much recent interest.[11−13] In this regard, we have utilized the Murai reaction to chemically modify copoly[dimethylsiloxane/vinylmethylsiloxane (8%)] by **Ru**-catalyzed addition of the ortho C−H bond of 2-methylacetophenone across the C−C double bonds of the Si−vinyl groups of the copolymer.[14] Recently, we reported the chemical modification of the pendant vinyl groups of copoly[dimethylsiloxane/vinylmethylsiloxane (1%)] by addition of the ortho C−H bonds of benzoylferrocene, 2,4,6-trimethylbenzophenone, or benzophenone.[15]

Modified siloxane polymers that incorporate aromatic ketone chromophore units may exhibit photoluminescent properties.[16,17] Phenanthrene and its derivatives are known to form excimers[18] and fluoresce.[19] Phenanthrene complexes have also been used for the preparation of electroluminescent devices.[20] We have previously reported the preparation and fluorescence spectra of copolymers in which 9,10-dioxyphenanthrene units are part of the copolymer backbone.[21] Interfacial nonradiative energy transfer in shell latex particles that have a phenanthrene donor and an anthracene acceptor has been measured. These have been prepared by a two-stage (seed and feed) free radical copolymerization of *N*-isopropylacrylamide and 9-phenanthrenylmethyl methacrylate or 9-anthracenyl methacrylate.[22] Interdiffusion vs cross-linking rates have been determined by photophysical studies of latex films that contain a small number of pendant phenanthrene chromophores. These have been also prepared by copolymerization of butyl acrylate and methyl methacrylate with 9-methylphenanthrenyl methacrylate or 9-vinylphenanthrene.[23]

Treatment of **Ru** with an equivalent (molar) amount of styrene at 135 °C for a few minutes yields ethylbenzene and a coordinatively unsaturated, activated, ruthenium catalyst [“Ru(CO)(PPh$_3$)$_2$”], in which the hydride bonded to the ruthenium center has been lost.[7] The regiochemistry of the C−H insertion is apparently determined by the initial coordination of the ruthenium center to the oxygen atom of the carbonyl group.[6]

Herein, we report the chemical modification of poly[vinylmethylsiloxane] (PVMS)[24] by the activated **Ru**-catalyzed anti-Markovnikov addition of the 10-C−H bond of 9-acetylphenanthrene across the C−C double bonds of the pendant vinyl groups of PVMS to yield poly[2-(9′-acetyl-10′-phenanthrenyl)ethylmethylsiloxane] (**I**). PVMS was prepared by anionic ring-opening polymerization (AROP)[25] of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane with methyllithium (Figure 1). For comparison, monomeric model systems, tetrakis[2-(9′-acetyl-10′-phenanthrenyl)ethyldimethylsiloxy]silane (**II**), 2,3,4-tris[2-(9′-acetyl-10′-phenanthrenyl)ethyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane (**III**), and 9-acetyl-10-[2′-(trimethylsiloxydimethylsilyl)ethyl]phenanthrene (**IV**), were prepared by similar activated **Ru**-catalyzed reactions of 9-acetylphenanthrene with tetrakis(vinyldimethylsilyloxy)silane, 2,3,4-trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane,[26] and vinylpentamethyldisiloxane, respectively (Figure 2).

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra of CDCl$_3$ solutions were obtained on a Bruker AMX-500 MHz spectrometer, operating in the FT mode. ^{13}C NMR spectra were obtained with broadband proton decoupling. ^{1}H and ^{13}C spectra were internally referenced to residual CHCl$_3$. ^{29}Si NMR spectra were referenced to TMS. A NONOE pulse sequence was used to acquire the ^{29}Si NMR spectra.[27,28] 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$_2$Cl$_2$ solutions were run on a Shimadzu UV-260

---

* Corresponding author. E-mail: wpweber@usc.edu.

10.1021/ma0119878 CCC: $22.00

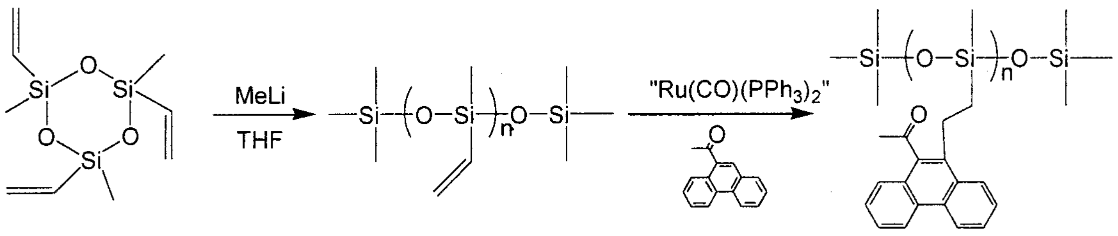

Figure 1. Synthesis of **I**.

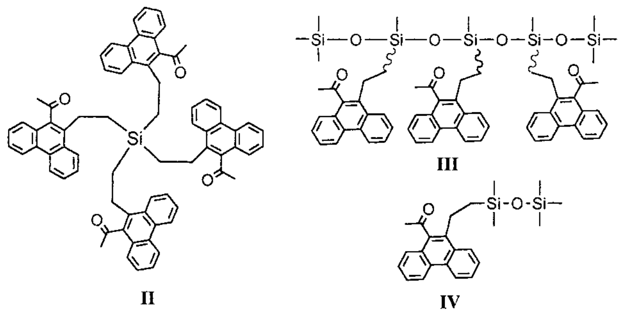

Figure 2. Structure of **II**, **III**, and **IV**.

spectrometer. Fluorescence spectra of degassed $CHCl_3$ solutions were obtained on a PTI instrument, equipped with a model A1010 Xe/Hg lamp and a model 710 photomultiplier defraction detector.

TGA of **I** and PVMS were carried out on a Shimadzu TGA-50 instrument, with argon or air at a flow rate of 40 cm^3/min. The temperature was increased by 4 °C/min, from 25 to 800 °C. The T_g was determined on a Perkin-Elmer DSC-7 instrument. The DSC was calibrated for high-temperature measurements (30−250 °C) from the melting point of indium (156.6 °C) and triphenylphosphine (79 °C) or for low-temperature (−150 to −50 °C) measurements from the thermal transition (−87.06 °C) and melting point (6.54 °C) of cyclohexane.[29] In either case, the temperature was increased by 10 °C/min.

GPC analysis of the molecular weight distribution of the polymers was performed on a Waters system comprised of a U6K injector, a 510 HPLC pump, a R401 RI detector, and a Millenium 2.15 session manager control system. Two 7.8 mm × 300 mm Styragel columns packed with <5 μm divinylbenzene cross-linked polystyrene (HR5E and HR3) in series were used for analysis. HPLC grade THF was used as the eluting solvent at a flow rate of 0.3 mL/min. The retention times were calibrated against those of monodispersed polystyrene standards: 929 000, 114 200, 13 700, and 794 ($M_w/M_n < 1.09$).

GC-MS was performed on a Hewlett-Packard (HP) 5890 GLPC equipped with an HP 5971 mass selective quadrupole detector and a 30 m DB-5 capillary column. High-resolution MS was run at the University of California Riverside Mass Spectroscopy Facility on either a VG-7070 EHF or DE-STR instrument. The exact mass of **IV** was determined on the VG-7070 instrument by peak matching against known masses of perfluorokerosene. Ammonia was employed as the chemical ionization agent. The exact mass of **III** was determined on the DE-STR instrument. High-resolution MALDI was carried out. Ionization was produced by adduction of sodium ions.

All reactions were run in flame-dried round-bottom (rb) flasks or Ace pressure tubes equipped with a Teflon-covered magnetic stir bar under argon.

1,3,5-Trivinyl-1,3,5-trimethylcyclotrisiloxane, hexamethyldisiloxane, vinylpentamethyldisiloxane, trimethylchlorosilane, and tetrakis(vinyldimethylsiloxy)silane were purchased from Gelest. Methyllithium (1.4 M), 9-acetylphenanthrene, triethylamine, and triflic acid were obtained from Aldrich. **Ru** was prepared from ruthenium trichloride hydrate.[30]

Activation of Catalyst.[7] **Ru** (27.5 mg, 30 μmol), styrene (3.12 mg, 3.45 μL, 30.0 μmol), and 0.5 mL of toluene were placed in a 10.0 mL Ace pressure tube. The tube was sealed with a rubber O-ring and threaded Teflon seal and heated at 125−135 °C for 10 min. The solution turned red and was cooled to room temperature (rt).

Synthesis of PVMS by AROP. Methyllithium (56 μL) was added to a dry THF solution of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (1.0 g) in a 25 mL rb flask. The reaction mixture was stirred for 10 h. It was then quenched by sequential addition of triethylamine (100 μL) and trimethylchlorosilane (100 μL). Diethyl ether (20 mL) was added. The ether layer was washed with water, separated, dried over anhydrous $MgSO_4$, and filtered. The ether was removed by evaporation under reduced pressure. In this way, a clear viscous liquid, 810 mg, 81% yield, $M_w/M_n = 18\,600/11\,200$, $T_g = -130$ °C, was obtained. ^1H NMR δ: 0.129, 0.132 (s, 3H); 5.72−6.05 (m, 3H). ^{13}C NMR δ: −0.585; 133.089, 136.69, 136.71, 136.74. ^{29}Si NMR δ: −35.063, −35.037.

Ru-Catalyzed Reaction of PVMS with 9-Acetylphenanthrene To Produce I. Activated **Ru** (27.5 mg) was added to a toluene (0.5 mL) solution of PVMS (0.23 g, 2.50 mmol) and 9-acetylphenanthrene (0.60 g, 2.73 mmol) in a 10 mL Ace pressure tube. The tube was sealed as above, and the reaction mixture was stirred at 125−130 °C for 60 h. After cooling to room temperature, the polymer was precipitated into 50 mL of methanol and collected by centrifugation. A white solid (**I**) 0.75 g, 98.5% yield, was obtained, $M_w/M_n = 20\,900/12{,}300$, $T_g = 88$ °C. ^1H NMR δ: 0.26 (br s, 3H), 0.99 (br s, 2H), 2.14 (br s, 3H), 2.85 (br s, 2H), 7.01−7.35, 7.79, 8.15−8.29 (br m, 8H). ^{13}C NMR δ: −0.28, 19.79, 23.7, 32.76, 122.62, 122.70, 124.35, 124.59, 125.84, 126.37, 126.50, 126.86, 127.41, 128.94, 129.28, 130.17, 133.05, 136.64, 207.22. ^{29}Si NMR δ: −22.58, −22.44, −22.29. IR ν: 3072, 2955, 2896, 1698 (C=O), 1493, 1351, 1258, 1186, 1087, 1010, 808, 754 cm^{-1}. UV λ_{max} nm (ϵ): 350 (1.1×10^3), 302 (1.89×10^4), 290 (1.85×10^4), 256 (8.53×10^4). When irradiated at 325 nm, fluorescence was observed at 390 ± 5 nm.

Synthesis of Tetrakis[2-(9′-acetyl-10′-phenanthrenyl)-ethyldimethylsiloxy]silane (II). In a 10 mL Ace pressure tube was placed tetrakis(vinyldimethylsiloxy)silane (0.25 g, 0.577 mmol), 9-acetylphenanthrene (0.50 g, 2.27 mmol), and 0.5 mL of toluene. To this was added 27.5 mg of activated **Ru**. The tube was sealed. The reaction mixture was stirred at 120−130 °C for 45 h and cooled to room temperature, and the volatiles were removed by evaporation under reduced pressure. The resulting material was purified on a Cyclograph centrifugal chromatography system (6 mm silica gel rotor), using hexane/ethyl acetate as solvent.[31]

A white solid (**II**), 0.365 g, 97% yield, was obtained. ^1H NMR δ: 0.3 (s, 24H), 1.03−1.10 (m, 8H), 2.48 (s, 12H), 2.89−2.96 (m, 8H), 7.23 (t, 4H, $J = 7.4$ Hz), 7.28 (t, 4H, $J = 7.4$ Hz), 7.37 (t, 4H, $J = 7.9$ Hz), 7.40 (t, 4H, $J = 7.9$ Hz), 7.46 (t, 4H, $J = 7.4$ Hz), 7.82 (d, 4H, $J = 8.1$ Hz), 8.41 (d, 4H, $J = 8.1$ Hz), 8.46 (d, 4H, $J = 8.1$ Hz). ^{13}C NMR δ: 0.0, 20.27, 23.93, 33.16, 122.86, 123.02, 124.55, 124.72, 126.23, 126.68, 126.93, 126.97, 127.53, 129.43, 129.5, 130.5, 133.37, 136.65, 208.2. ^{29}Si NMR δ: −103.44 (1Si), 9.15 (4Si). IR ν: 3075, 2957, 1697 (C=O), 1494, 1446, 1352, 1252, 1189, 1058, 840, 781, 753, 723 cm^{-1}. UV λ_{max} nm (ϵ): 350 (3.3×10^3), 302 (1.1×10^5), 290 (1.06×10^5), 256 (5.25×10^5). When irradiated at 325 nm, fluorescence was observed at 380 ± 5 nm. High-resolution MS: Calcd for $MNa^{\bullet+}$, [$C_{80}H_{84}O_5Si_8$]: 1335.4910. Found: 1335.4966.

Synthesis of 2,3,4-Trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane.[32] In a 100 mL rb flask were placed 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (5.0 g, 19.4 mmol) and hexamethyldisiloxane (16.0 g, 97.0 mmol). The reaction flask

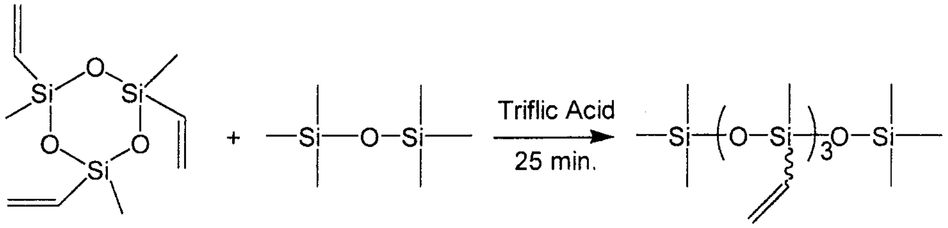

Figure 3. Synthesis of 2,3,4-trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane.

was cooled to 0 °C. Triflic acid (300 μL) was added, and the reaction mixture was stirred for 20 min. It was quenched with 1.0 mL of hexamethyldisilazane. The resulting mixture was fractionally distilled through a l5 cm vacuum jacketed Vigreux column. A fraction (6.1 g, 74.4%), bp 94−96 °C/1.5 mm, was obtained. ^{1}H NMR δ: 0.09 (s, 18H), 0.13 (s, 6H), 0.16 (s, 3H), 5.71−6.07 (m, 9H). ^{13}C NMR δ: −0.59, −0.53, 1.84, 132.74, 132.94, 136.94, 137.27. ^{29}Si NMR δ: −35.50 (s, 1Si), −35.07 (s, 2Si), 8.15 (s, 2Si). GC-MS: *m*/*e* (rel intensity): 405 (28) [M − 15]$^+$, 305 (91), 293 (100), 281 (33), 251 (26), 159 (65), 85 (63), 73 (74).

Ru-Catalyzed Reaction of 2,3,4-Trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane with 9-Acetylphenanthrene To Produce III. In a 10 mL Ace pressure tube were placed 2,3,4-trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane (0.212 g, 0.505 mmol), 9-acetylphenanthrene (0.50 g, 2.27 mmol), and 0.5 mL of toluene. To this was added 27.5 mg of activated **Ru**, and the tube was sealed as above. After heating at 130−135 °C for 70 h, the reaction mixture was cooled to rt, and the volatiles were removed by evaporation under reduced pressure. The resulting material was purified on the Cyclograph centrifugal chromatography system as above.

A highly viscous material (**III**) (0.286 g, 88.5%) was obtained. ^{1}H NMR δ: 0.30, 0.31, 0.32, 0.322 (18H); 0.43, 0.44 (6H); 0.52 (3H); 1.13−1.21 (m, 4H), 1.25−1.29 (2H); 2.64−2.73 (m, 9H); 3.11−3.19 (m, 4H), 3.20−3.24 (m, 2H); 7.53−7.69 (m, 15H), 8.14−8.28 (m, 3H), 8.55−8.63 (m, 6H). ^{13}C NMR δ: −0.342, −0.33, −0.30, −0.29, 1.93, 19.75, 23.79, 33.05, 33.06, 33.11, 122.78, 122.81, 123.03, 123.12, 124.56, 124.61, 124.66, 126.12, 126.18, 126.68, 126.81, 126.88, 127.02, 127.51, 127.54, 129.39, 129.43, 129.74, 130.41, 130.53, 130.58, 131.76, 133.32, 134.43, 136.78, 136.91, 207.57, 207.67. ^{29}Si NMR δ: −23.37, −23.35, −23.30, −23.28, −23.26, −23.08, −23.06, 8.56, 8.58, 8.59. IR ν: 3068, 2956, 2895, 2949, 1704 (C═O), 1699, 1694, 1683, 1678, 1673, 1668, 1612, 1528, 1493, 1445, 1348, 1249, 1186, 1092, 1016, 915, 839, 806, 745 cm^{-1}. UV $\lambda_{\max}$ nm (ϵ): 301 (2.34×10^4), 289 (2.05×10^4), 256 (1.01×10^5). When irradiated at 335 nm, fluorescence was observed at 380 ± 5 nm. High-resolution MS. Calcd for $C_{63}H_{72}O_7Si_5Na$: 1103.401 67. Found: 1103.399 04.

Ru-Catalyzed Reaction of Vinylpentamethyldisiloxane with 9-Acetylphenanthrene To Produce IV. In a 10 mL Ace pressure tube were placed vinylpentamethyldisiloxane (2.61 g, 15.0 mmol), 9-acetylphenanthrene (1.32 g, 6.0 mmol), and 0.5 mL of toluene. To this was added 27.5 mg of **Ru**, and the tube was sealed. The mixture was stirred at 120−130 °C for 50 h and cooled to room temperature, and the volatiles were removed by evaporation under reduced pressure. The product was purified on the Cyclograph centrifugal chromatography system as above.

A white solid (**IV**) (2.25 g, 95.2% yield) was obtained. ^{1}H NMR δ: 0.28 (s, 9H), 0.31 (s, 6H), 1.09−1.125 (m, 2H), 2.76 (s, 3H), 3.08−3.10 (m, 2H), 7.62−7.75 (m, 5H), 8.17−8.19 (m, 1H), 8.71−8.73 (m, 1H), 8.74−8.76 (m, 1H). ^{13}C NMR δ: 0.19, 2.02, 20.47, 23.96, 33.28, 122.92, 123.21, 124.7, 124.8, 126.26, 126.77, 126.95, 127.02, 127.61, 129.46, 129.77, 130.67, 133.76, 136.71, 208.28. ^{29}Si NMR δ: 6.735, 8.21. IR ν: 3076, 2956, 2896, 2362, 1943, 1700 (C═O), 1496, 1448, 1419, 1352, 1253, 1190, 1148, 1057, 916, 843, 814, 782, 754, 690 cm^{-1}. UV $\lambda_{\max}$ nm (ϵ): 350 (1.9×10^2), 301 (7.62×10^3), 289 (7.23×10^3), 256 (3.49×10^4). When irradiated at 335 nm, fluorescence was observed at 380 ± 5 nm. High-resolution MS: Calcd for M$^{\bullet+}$, [$C_{23}H_{30}O_2Si_2$]: 394.1779. Found: 394.1784.

Results and Discussion

Polymer **I** has been synthesized in high yield by the activated **Ru**-catalyzed reaction of PVMS with 9-acetylphenanthrene. Apparently all of the vinyl groups of PVMS react, since no evidence of residual unreacted vinyl groups was observed in either the ^{1}H or ^{13}C NMR spectra of **I**. Nevertheless, the molecular weights of PVMS ($M_w/M_n = 18\,600/11\,200$) and **I** ($M_w/M_n = 20\,900/12\,300$) by GPC do not differ appreciably. This is surprising since the molecular weight of **I** compared to that of PVMS is expected to be in a ratio of 3.6:1. Possibly, interaction of adjacent phenanthrene units by $\pi-\pi$ stacking causes **I** to adopt a conformation that has a lower hydrodynamic volume than a flexible linear polymer such as PVMS. We have neither UV nor fluorescence spectroscopic evidence to support such $\pi-\pi$ interaction. A referee has suggested that possibly, due to proximity, secondary intrachain reaction occurs at the 8-C−H bond of bound 9-acetylphenanthrene with unreacted vinyl groups within a polymer chain. This would create a rigid linkage within the polymer, which would decrease the polymer hydrodynamic radius. We do not favor this explanation since no evidence for such **Ru**-catalyzed reaction at the 8-C−H bond of 9-acetylphenanthrene or 1-acetyl naphthalene has been observed.[6] Thus, the reason for the small change in M_w/M_n cannot be satisfactorily explained at this time.

The T_g of **I** (88 °C) is much higher than that of PVMS (−130 °C). This difference (~220 °C) is remarkable. By comparison, chemical modification of poly(divinylsiloxane)[33] ($T_g = -134$ °C) or poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane)[34] ($T_g = -128$ °C) by Pt-catalyzed hydrosilylation with 3,3,3-trifluoropropyldimethylsilane gives modified polymers whose T_gs' are −34 and −81 °C, respectively. We suggest that this difference may result from the planar nature of phenanthrene units that can interact with one another in the solid phase. This may modify the highly flexible nature of the siloxane backbone of **I**.

Model compounds **II**, **III**, and **IV** were prepared in a similar manner in high yield by activated **Ru**-catalyzed reaction of 9-acetylphenanthrene with tetrakis(vinyldimethylsiloxy)silane, 2,3,4-trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane, and vinylpentamethylsiloxane, respectively. 2,3,4-Trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane was obtained by triflic acid-catalyzed reaction of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane with hexamethyldisiloxane (Figure 3).

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of model compounds **II** and **IV** are quite simple.

As expected, the ^{13}C NMR of **IV** has two signals due to Si−methyl groups at 0.19 and 2.02 ppm. Likewise, two resonances due to the nonequivalent methylene carbons and one due to the acetyl methyl group are detected at 20.47, 23.96, and 33.28 ppm, respectively. Fourteen nonequivalent resonances in the aromatic region due to the unsymmetrical phenanthrene nucleus are observed. Finally, a signal due to the carbonyl carbon at 208.28 ppm is seen. As expected, two signals are detected in the ^{29}Si NMR spectrum of **IV** at 6.74 and 8.21 ppm.

The NMR spectra of **II** are quite similar to **I**. In the ^{13}C NMR, the signal at 0.0 ppm is assigned to the Si−methyl groups, while the resonances at 20.27 and 23.93 ppm are consistent with the unsymmetrical methylene carbons and the signal at 33 ppm is due to the acetyl methyl group. As expected, 14 resonances in the aromatic region due to the unsymmetrical phenanthrene nucleus are observed. Finally, a signal at 208.2 ppm due to the carbonyl carbon is detected. In the ^{29}Si NMR spectrum a resonance at −103.4 ppm due to the central silicate silicon is found in addition to a signal at 9.15 ppm, which is assigned to the four $O-Si(CH_3)_2-CH_2-CH_2-$ silicon atoms. This chemical shift (9.15 ppm) is similar to that typically observed for trimethylsiloxy groups. Comparison of the integration of the two silicon resonances gives a value of 1:4 as expected. A longer pulse was used to obtain this since the central silicate silicon has no adjacent methyl groups, and so its dipolar relaxation is expected to be slower.

PVMS, **I,** 2,3,4-trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane, and **III**, by comparison, all have chiral silicon centers. Adjacent chiral silyl centers of PVMS affect one another. On the basis of a triad analysis, these can have the following relationship to one another: R**R**R or S**S**S; R**R**S or S**S**R; S**R**S or R**S**R, respectively. Consistent with this interpretation, three resonances due to the vinyl carbon bonded to silicon are observed in the ^{13}C NMR spectrum of PVMS. However, neither the Si−methyl nor the remote vinyl carbons are affected. This difference in the carbons directly bonded to silicon may be due to their different bond lengths. The Si−C bond in which the carbon is sp^2 hybridized is shorter than a Si−C sp^3 hybridized bond. In the ^{1}H NMR spectrum, two resonances due to Si−methyl groups are observed rather than the anticipated three. Similarly, in the ^{29}Si NMR two resonances are detected rather than the three expected. Apparently, two of the resonances fortuitously overlap.

Similarly, the chirality of adjacent silyl centers only affects the ^{29}Si NMR of **I**. Three resonances are detected in the ^{29}Si NMR as expected on the basis of triad analysis. By comparison, the ^{1}H and ^{13}C NMR spectra of **I** are quite simple. Thus, in the ^{13}C NMR one resonance due to Si−methyl at −0.28 ppm, two signals at 19.79 and 23.7 ppm due to the nonequivalent methylene carbons, a single resonance at 32.76 ppm due to the acetyl methyl group, 14 signals in the aromatic region (122−137 ppm) due to the unsymmetrical phenanthrene unit, and finally a single carbonyl carbon signal at 207.22 ppm are detected.

In the case of 2,3,4-trivinyl-1,1,1,2,3,4,5,5,5-nonamethylpentasiloxane, the ^{1}H, ^{13}C, and ^{29}Si NMR spectra are quite simple. No effect of the chiral silyl centers is observed. Specifically, two resonances in a 2:1 intensity ratio are observed in the ^{1}H NMR spectrum for the methyl groups of the vinylmethylsiloxane units. In the ^{13}C NMR spectrum, a total of seven resonances are detected. One of these at 1.84 ppm is due to the methyl groups of the terminal trimethylsiloxy groups. Two signals are detected at −0.59 and −0.53 ppm for the Si−methyl carbons. One is due to the Si−methyl carbon that is bonded to the central 3-Si silicon while the other is due to the two Si−methyl carbons that are bonded to the equivalent 2-Si and 4-Si silicon centers. Similarly, one vinyl group is bonded to 3-Si and two vinyl groups are bonded to 2-Si and 4-Si. This leads to four vinyl carbon signals. Finally, three resonances are observed in the ^{29}Si NMR. The one at −35.5 ppm is due to the central silicon (3-Si), while the one at −35.07 ppm is due to 2-Si and 4-Si. Finally, the resonance at 8.15 ppm is due to the silicon atoms of the two terminal trimethylsiloxy groups.

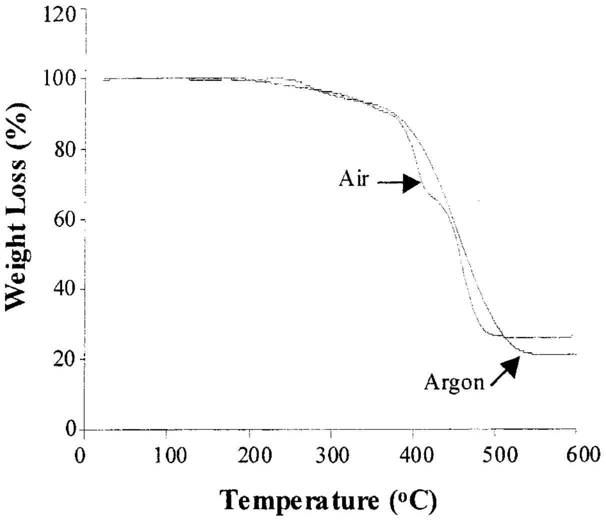

Figure 4. TGA of **I** in argon and air.

The ^{1}H and ^{13}C NMR spectra of 2,3,4-[2-(9′-acetyl-10′-phenanthrenyl)ethyl]-1,1,1,2,3,4−5,5,5-nonamethylpentasiloxane can be similarly understood. The chirality of adjacent silyl centers affects signals due to the Si−methyl groups in the ^{1}H and ^{13}C NMR spectra. The ^{29}Si NMR spectrum is also affected. In the ^{13}C NMR, 26 resonances in the aromatic region are detected. There are two nonequivalent types of phenanthrene units. One of these is bonded to the central 3-Si, while the other two are bonded to the 2-Si and 4-Si centers. On the basis of this, we expect a total of 28 unique aromatic ^{13}C NMR signals. Apparently two of these fortuitously overlap. Similarly, two unique carbonyl carbon signals are observed at 207.57 and 207.67 ppm. A single resonance at 1.93 is seen for the carbons of the trimethylsiloxy groups, and two signals at 19.75 and 23.79 ppm are detected for the nonequivalent methylene carbons. On the other hand, three carbon resonances due to the acetyl methyl group are seen at 33.05, 33.06, and 33.11 ppm. Similarly, four signals due to the Si−methyl groups bonded to 2-Si, 3-Si, and 4-Si centers are detected. If we assume that the chemical shifts of the 2-Si, 3-Si, and 4-Si silicon atoms are affected by their nearest neighbors, there are two possible environments for 2-Si or 4-Si. These can be R**R**-OTMS, S**S**-OTMS or S**R**-OTMS, R**S**-OTMS. For the central silicon Si-3, a similar analysis predicts three stereochemically unique environments R**R**R, S**S**S or R**R**S, S**S**R and finally S**R**S, R**S**R. Thus, there should be a total of five ^{13}C NMR resonances for the Si−methyl groups. In fact, only four signals are detected. Apparently, one of the signals is not observed due to fortuitous overlap.

Thermogravimetric Analysis. In argon, **I** is stable to 245 °C. A weight loss of 8.5% occurs between 245 and 370 °C. A further 69% weight loss occurs on heating to 550 °C. Above this temperature, no additional weight is lost (Figure 4). In air, **I** is stable to 200 °C. Between 200 and 380 °C there is a 10% loss of weight. Between 380 and 400 °C a rapid 20% weight loss is observed. Between 400 and 500 °C, there is an additional 40% weight loss. To 600 °C, there is no further loss of weight.

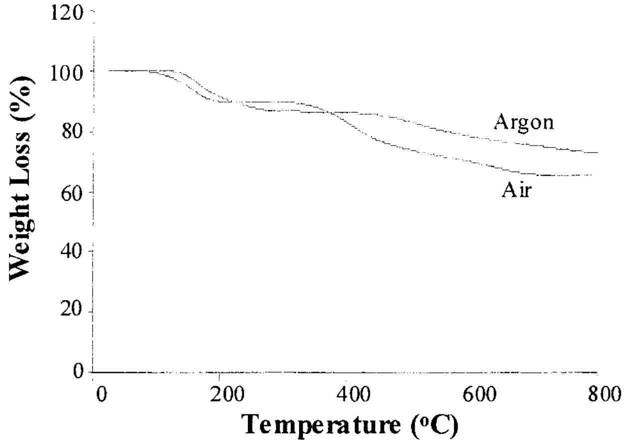

Figure 5. TGA of PVMS in argon and air.

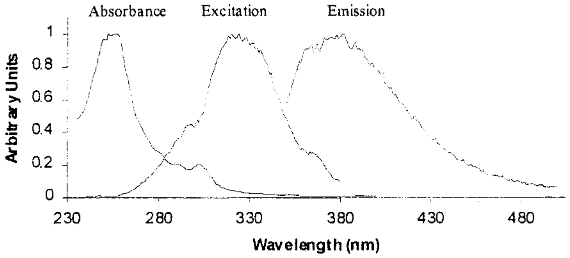

Figure 6. Absorption, excitation, and emission spectra of **I**.

A char yield greater than 20% is formed in either air or argon.

On the other hand, PVMS begins to decompose at 150 °C in either air or argon (Figure 5). In argon, between 150 and 250 °C, a 10% weight loss is observed. No further weight loss occurs until 450 °C. Above this temperature, an additional 20% weight loss is observed. Similarly in air, between 150 and 350 °C a 10% weight loss occurs. Above 350 °C an additional 25% weight loss is detected. PVMS does not undergo catastrophic decomposition in either air or argon. In both, a high (∼75%) char yield is formed. Formation of high char yields has also been observed with vinyl-substituted poly(carbosilane)s.[35]

Photoluminescence. Polymer **I** and model compounds **II**, **III**, and **IV** all have similar UV absorption spectra.

The most intense absorption occurs at 256 nm. Lower extinction coefficient absorption peaks at 290, 301, and 350 nm are also observed. When these materials are irradiated between 325 and 335 nm, the maximum of their excitation spectra, intense fluorescence between 380 and 390 nm is detected. There is considerable interest in materials that fluorescence in this region of the spectrum.

In summary, we have shown that the **Ru**-catalyzed reaction provides an efficient method to completely modify the pendant vinyl groups of poly(vinylmethylsiloxane). This single step procedure proceeds in high yield. Ring-opening polymerization of cyclic siloxanes often involves ring/chain equilibrium. In such processes the presence of large groups bonded to silicon often favors formation of small cyclics. In 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane, the vinyl and methyl groups are both relatively small. Anionic polymerization of this monomer permits the preparation of high molecular weight PVMS. The activated **Ru**-catalyzed chemical modification of PVMS does not lead to polymer degradation.

Acknowledgment. This work was supported by the D. P. and K. B. Loker Hydrocarbon Research Institute. S.K.G. thanks the Harold and Lillian Moulton endowment for fellowship support. We thank Sudhakar Madhusoodhanan for assistance with fluorescence studies.

References and Notes

(1) Davies, S. G. *Organotransition Metal Chemistry: Application to Organic Synthesis;* Pergamon Press: Oxford, England, 1982.
(2) Negishi, E. L. *Organometallics in Organic Synthesis;* J. Wiley & Sons: New York, 1980.
(3) Boffa, L. S., Novak, B. M., Eds.; *Transition Metal Catalysis in Macromolecular Design;* ACS Symposium Series 760; American Chemical Society: Washington, DC, 2000.
(4) Murai, S.; Kaiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature (London)* **1993**, *366*, 529.
(5) Kakiuchi, F.; Tanaka, Y.; Sato, T.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 679.
(6) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sanod, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62.
(7) Guo, H.; Wang, G.; Tapsak, M. A.; Weber, W. P. *Macromolecules* **1995**, *28*, 5686.
(8) Kepler, C. L.; Londergan, T. M.; Lu, J.; Paulasaari, J.; Weber, W. P. *Polymer* **1998**, *40*, 765.
(9) Sargent, J. R.; Weber, W. P. *Polymer* **1999**, *40*, 3795.
(10) Gupta, S. K.; Weber, W. P. *Macromolecules* **2000**, *33*, 108.
(11) Carraher, C. E., Jr.; Moore, J. A. *Modification of Polymers*; Plenum Press: New York, 1983.
(12) Mathais, L. J.; Carraher, C. E., Jr. *Crown Ethers and Phase Transfer Catalysis in Polymer Science;* Plenum Press: New York, 1984.
(13) Benham, J. L.; Kinstle, J. F. *Chemical Reaction on Polymers;* ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988.
(14) Guo, H.; Tapsak, M. A.; Weber, W. P. *Polym. Bull. (Berlin)* **1994**, *33*, 417.
(15) Mabry, J. M.; Brooks, J.; Weber, W. P. *Polym. Prepr.* **2001**, *42* (2), 344.
(16) Gupta, S. K.; Weber, W. P. *Polym. Prepr.* **2001**, *42* (1), 204.
(17) Londergan, T. M.; You, Y.; Thompson, M. E.; Weber, W. P. *Macromolecules* **1998**, *31*, 2784.
(18) Chow, Y. L.; Wu, S. P.; Ouyang, X. *J. Org. Chem.* **1994**, *59*, 421.
(19) Morishima, Y.; Ohgi, H.; Kamachi, M. *Macromolecules* **1993**, *26*, 4293.
(20) Huang, D.; Jiang, X.; Phelan, G. D.; Londergan, T. M.; Jen, A. K.-Y.; Dalton, L. R. *Polym. Mater. Sci. Eng.* **2000**, *83*, 266.
(21) Mabry, J. M.; Runyon, M, K.; Weber, W. P. *Macromolecules* **2001**, *34*, 7264.
(22) Gan, D.; Lyon, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 8203.
(23) Liu, R.; Winnik, M. A.; DiStefano, F.; Vanketessan, J. *Macromolecules* **2001**, *34*, 7306.
(24) Poly(vinylmethylsiloxane) [CAS: 68037-87-6] is available from Gelest Inc. catalog p 490.
(25) Lee, C. L.; Fryer, C. L.; Johanson, O. K. *Polym. Prepr.* **1969**, *10* (2), 1361.
(26) Andrianov, K. A.; Kochet, K.; Khananashvili, L. M. *Zh. Obshch. Khim.* **1968**, *38*, 175.
(27) Freeman, F.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.* **1972**, *7*, 327.
(28) Marsmann, H. C. In *Silicon-29 NMR in Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; J. Wiley & Sons: New York, 1996; Vol. 7, p 4386.
(29) Aston, J. G.; Szabz, G. J.; Fink, H. L. *J. Am. Chem. Soc.* **1943**, *65*, 1135.
(30) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 2947.
(31) Gupta, S. K.; Sargent, J. R.; Weber, W. P. *Anal. Chem.* **2001**, *73*, 3781.
(32) Mabry, J. M.; Paulasaari, J. K.; Weber, W. P. *Polymer* **2000**, *41*, 4423.
(33) Cai, G.; Weber, W. P. *Polym. Prepr.* **2001**, *42* (2), 490.
(34) Cai, G.; Weber, W. P. *Polym. Prepr.* **2001**, *42* (2), 455.
(35) Liao, C. X.; Weber, W. P. *Macromolecules* **1992**, *25*, 1639.

MA0119878