

Synthesis and characterization of copolymers with alternating 1,4-*bis*(5'-acetyl-2'-thienyl)benzene or 1,3-*bis*(5'-acetyl-2'-thienyl)benzene chromophore and disiloxane units

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Summary

Activated $(\text{Ph}_3\text{P})_3\text{RuH}_2\text{CO}$ (Ru) catalyzed copolymerization of 1,4-*bis*(5'-acetyl-2'-thienyl)benzene (I) and 1,3-divinyltetramethyldisiloxane (II) yields *alt*-copoly[3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2',2''-diacetyl-5',5''-(1,4-benzene)-3',3''-*bis*(thiophenylene)] (III). On the other hand, Ru catalyzed copolymerization of 1,3-*bis*(5'-acetyl-2'-thienyl)benzene (IV) and II fails. Nevertheless, Ru catalyzed reaction of IV with excess vinylpentamethyldisiloxane (V) yields 1,3-*bis*(4'-pentamethyldisiloxy-ethyl-5'-acetyl-2'-thienyl)benzene (VI). VI undergoes acid catalyzed siloxane equilibration polymerization to give *alt*-copoly[3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2',2''-diacetyl-5',5''-(1,3-benzene)-3',3''-*bis*(thiophenylene)] (VII) and hexamethyldisiloxane. Copolymers III and VII have been characterized.

Introduction

Murai reported the $(\text{Ph}_3\text{P})_3\text{RuH}_2\text{CO}$ catalyzed *ortho* alkylation reaction of aromatic ketones, such as acetophenone, with vinylsilanes (1,2). This catalytic C-H activation reaction involves the addition of an *ortho* C-H bond of the aromatic ketone across the C-C double bond of the vinyl silane in an anti-Markovnikov manner. The reaction is successful with a variety of aromatic ketones such as 2- or 3-acetylthiophene (2). This is significant because sulfur-containing compounds often poison noble metal catalysts.

We have shown that acetophenone, as well as other aromatic ketones, undergo activated Ru catalyzed copolymerization with α,ω -divinylsiloxanes to yield *alt*-copoly-(carbosilane/siloxane)s (3-7). Treatment of $(\text{Ph}_3\text{P})_3\text{RuH}_2\text{CO}$ with a stoichiometric amount of styrene gives ethylbenzene and an activated Ru catalyst (5). Loss of hydrogen from the Ru center creates a site of coordinate unsaturation.

The photophysical, photobiological and photochemical properties of monomeric thiophene derivatives have been studied (8-11). For example, 1,4-*bis*(2'-thienyl)benzene (VIII) and 1,3-*bis*(2'-thienyl)benzene (IX) can act as photosensitizers to generate singlet oxygen (12). While considerable work has been done on poly(thiophene), a conducting polymer (13), *alt*-copoly(carbosilane/siloxane)s which incorporate VIII or IX have not been previously reported. While chromophores VIII and IX are isomeric, they are

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significantly different. Thus, the thiophene rings of VIII are part of an extended conjugated π -system. On the other hand, the electronic interaction of the thiophene rings of IX with one another is decreased due to cross conjugation. Representative resonance structures of VIII and IX are shown in Fig. 1.

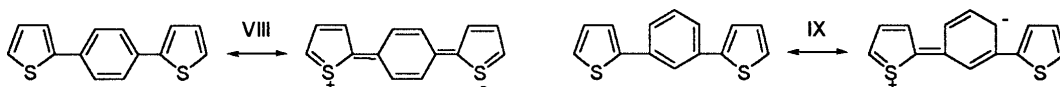


Figure 1. Resonance structures of VIII and IX.

Results and discussion

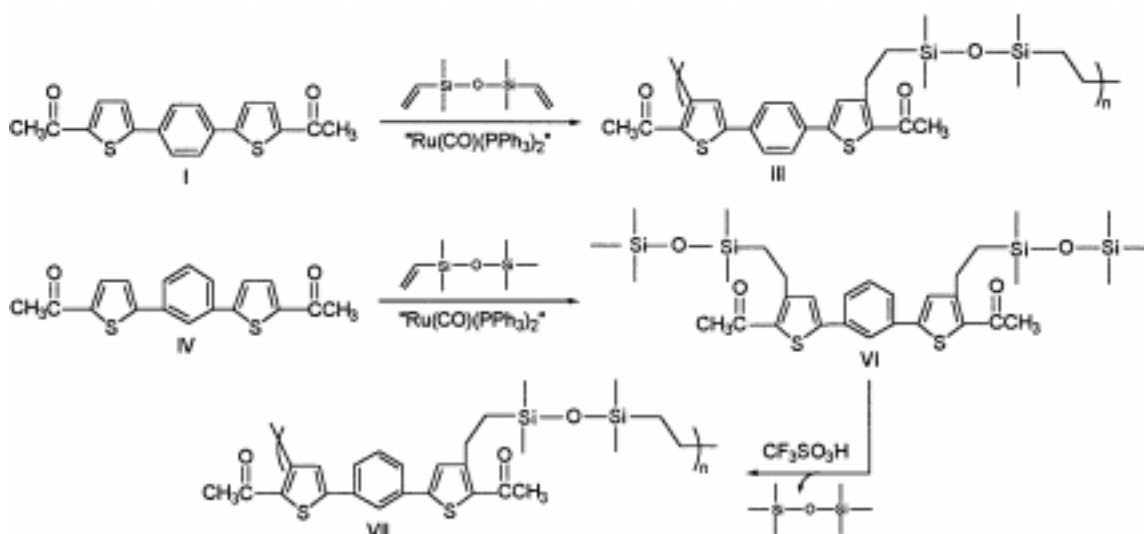
Monomer synthesis

VIII and IX were prepared by Suzuki coupling of 2-thienylboronic acid with 1,4- and 1,3-diiodobenzene respectively (14). Friedel-Crafts acetylation of VIII with acetic anhydride/ HClO_4 yields I. A similar reaction of IX gives IV (15).

Polymer synthesis

No copoly(carbosilane/siloxane) was obtained from the Ru catalyzed reaction of 3-acetylthiophene and II. Reaction only occurred at the 2-position (16). Apparently, Ru catalyzed reaction, like electrophilic substitution, occurs at the 2-position of thiophene in preference to the 4-position. Activated Ru catalyzed copolymerization of II with I or IV requires the C-H at the 4-position of each thiophene ring to react.

Activated Ru catalyzed reaction of I with II yields III. High molecular weight was achieved despite the low solubility of I. As the reaction proceeds, the initial heterogeneous mixture became homogeneous and viscous. On the other hand, similar reaction of IV and II gave only low molecular weight oligomers. Nevertheless, IV undergoes a Ru catalyzed reaction with an excess of V to afford VI. Triflic acid catalyzed siloxane equilibration polymerization of VI at rt yields VII and hexamethyldisiloxane (Scheme1). The siloxane equilibrium is driven to form high molecular weight VII by continuous removal of hexamethyldisiloxane.



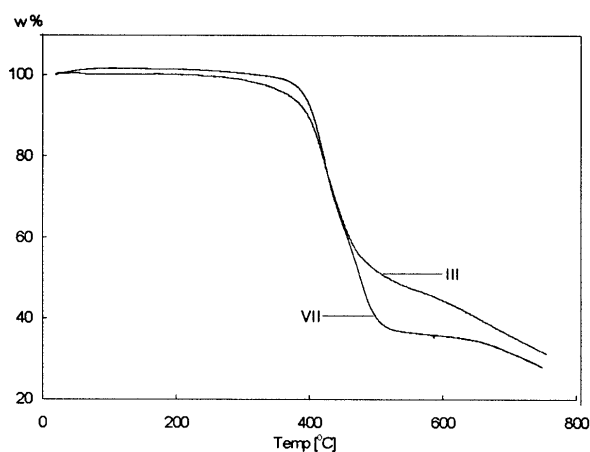
Scheme 1. Polymer synthesis.

Physical properties

While polythiophene has poor solubility, III and VII are soluble in a variety of organic solvents. This may be due to the flexible siloxane units in the copolymer backbone.

Both III and VII are thermally stable by TGA (Fig. 2). While most siloxane polymers and copolymers have T_g s below rt, the T_g of III is 114 °C and the T_g of VII is 53 °C.

Figure 2. TGAs of III and VII.



The UV-Vis absorption spectrum of III in solution has a λ_{max} at 371 nm, while the excitation spectrum ($\lambda_{\text{em}} = 438$ nm) shows a λ_{max} at 410 nm as well as a smaller peak at 318 nm (17). When irradiated at 410 nm, a blue luminescence is detected at 438 nm ($\Phi = 0.073$). However, when irradiated at 318 nm the luminescence at 438 nm is orders of magnitude lower. This behavior has precedent in poly(phenylene/vinylene) systems where the maximum emission comes from a wavelength of lower energy relative to the

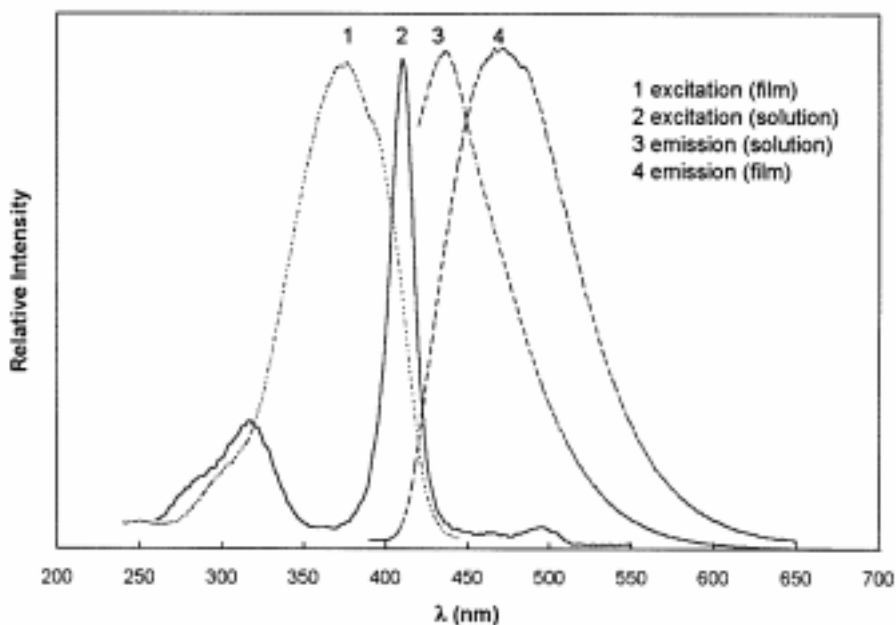


Figure 3. Excitation scan and fluorescence emission of III.

λ_{\max} of the absorption (18). A thin film of II luminesces at 472 nm ($\lambda_{\text{ex}} = 376$ nm). This is consistent with emission from an excimer which is expected in the solid state. (Fig. 3)

The UV-Vis absorption (λ_{\max} at 370 nm) and fluorescence emission (λ_{\max} at 430 nm) of monomer I are quite similar to those of copolymer III. However, the quantum yield of I is higher ($\Phi = 0.30$). The maximum UV-VIS absorption of monomers IV and VI as well as copolymer VII all occur at about 328 nm with extinction coefficients between 34,000 and 43,000. When excited at 375 nm, they all give very weak fluorescence at about 440 nm.

Experimental

General procedures and reagents

Reactions were carried out in flame-dried rb flasks or Ace pressure tubes. They were stirred with Teflon covered magnetic stirring bars under an atmosphere of argon. II and V were purchased from Gelest. Other reagents were obtained from Aldrich. Compounds 1 (14), VIII (12) and IX (15) were synthesized following literature procedures. $(\text{Ph}_3\text{P})_3\text{RuH}_2\text{CO}$ (Ru) was prepared from RuCl_3 hydrate (19).

Spectroscopic characterization

^1H and ^{13}C NMR spectra were obtained on a Bruker AC-250 or 360 spectrometer operating in the FT mode. ^{29}Si NMR spectrum was recorded on a Bruker AMX-500 MHz spectrometer. Five percent w/v solutions in CDCl_3 or $\text{DMSO}-d_6$ were used to obtain NMR spectra. ^{13}C NMR was run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 30 sec delay was used to acquire ^{29}Si NMR spectra (20). UV-Vis spectra of CH_2Cl_2 solutions were acquired on a Shimadzu UV-260 spectrometer. IR spectra of neat films on NaCl plates were recorded on a Perkin Elmer Spectrum 2000 FT-IR spectrometer. Photoluminescence spectra were measured on a PTI instrument, equipped with a model A1010 Xenon/Mercury lamp and a model 710 photomultiplier diffraction detector. Spectra were obtained from CH_2Cl_2 or acetonitrile solutions which had been degassed by bubbling argon for at least five min. Quantum yields were determined using 7-diethylamino-4-methylcoumarin ($\lambda_{\max} = 430$ nm, $\Phi = 1.03$) as standard (21). Thin film was spin-cast on quartz slide from CHCl_3 solution.

Copolymer characterization

GPC analysis of M_w/M_n of the copolymers was performed on a Waters system equipped with a R401 RI detector. Two 7.8 mm x 300 mm Styragel columns HR4 and HR2 in series were used for the analysis with THF as eluant at a flow rate of 0.8 mL/min. The retention times were calibrated against monodisperse polystyrene standards. TGAs of the copolymers were determined on a Shimadzu TGA-50 instrument at a nitrogen flow rate of 40 mL per min. The temperature was increased at 4 °C per min, from 25 to 750 °C. The T_g s of the copolymers were determined on a Perkin-Elmer DSC-7 instrument which was calibrated against triphenylphosphine (79.0 °C) and indium (156.6 °C) as standards. The temperature was increased at 10 °C per min from 25 to 200 °C.

Elemental analysis and mass spectroscopy

Elemental analysis was carried out by Oneida Research Services, Inc., Whitesboro, NY. High resolution mass spectra (HRMS) were run at the University of California Riverside Mass Spectroscopy Facility on a VG-7070 EHF instrument. Exact mass was determined by peak matching against known masses of perfluorokerosene.

alt-Copoly III: Ru. (8.44 mg, 9.2 μmol), toluene (0.5 mL), and styrene (1.05 μL , 9.2 μmol) were heated at 135 $^{\circ}\text{C}$ for 3 min to activate the catalyst (5). After cooling to rt, I (0.15 g, 0.46 mmol) and II (106 μL , 0.46 mmol) were added. The reaction mixture was heated at 135 $^{\circ}\text{C}$ for 24 h. After removing the solvent, the residue was dissolved in THF and the copolymer was precipitated with methanol and collected by centrifugation. III, 0.16 g, $M_w/M_n = 44,860/15,400$, $T_g = 114$ $^{\circ}\text{C}$, was obtained in 68% yield. ^1H NMR δ : 0.16 (s, 12H), 0.94 (m, 4H), 2.51 (s, 6H), 3.02 (m, 4H), 7.26 (s, 2H), 7.61 (s, 4H). ^{13}C NMR δ : 0.26, 19.28, 24.32, 29.54, 126.51, 127.44, 133.52, 134.17, 146.92, 154.12, 190.67. ^{29}Si NMR δ : 6.9. IR ν : 1659 (C=O), 1048 (Si-O) cm^{-1} . UV λ_{max} (ϵ): 228 (12,990), 250 (11,240), 299 (10,400), 371 (40,480). When irradiated at either 318 or 410 nm (λ_{max} excitation), fluorescence was observed at 438 nm. Elemental Anal. Calc. for $\text{C}_{26}\text{H}_{32}\text{O}_3\text{S}_2\text{Si}_2$: C, 60.89%; H, 6.29%. Found C, 59.91%; H, 6.70%.

IV: IX (1.43 g, 5.91 mmol), Ac_2O (115 mL) and 70% HClO_4 (2 drops) were stirred at rt for 1 h. After work-up, IV was recrystallized from cyclohexane. IV, 1.3 g, mp 147-149 $^{\circ}\text{C}$, was obtained in 67% yield. ^1H NMR δ : 2.55 (s, 6H), 7.54 (t, 1 H, $J = 8$ Hz), 7.77 (dd, 2H, $J = 8$ and 1.5 Hz), 7.82 (d, 2H, $J = 4$ Hz), 7.99 (d, 2H, $J = 4$ Hz), 8.11 (t, 1 H, $J = 1.5$ Hz). ^{13}C NMR δ : 26.21, 123.04, 125.98, 126.65, 130.40, 133.73, 135.13, 143.25, 150.30, 180.21. IR ν : 1646 (C=O) cm^{-1} . UV λ_{max} (ϵ): 230 (13,680), 329 (37,870). Elemental Anal. Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{S}_2$: C, 66.23%; H, 4.32%. Found C, 66.34%; H, 4.47%.

VI: IV (0.2 g, 0.61 mmol), V (1.4 mL, 6.1 mmol), Ru (22.5 mg, 0.025 mmol), and toluene (0.5 mL) were heated at 135 $^{\circ}\text{C}$ for 24 h. After work-up, the residue was purified by column chromatography (silica gel with 1:10 ethyl acetate and hexane). VI, 0.27 g, mp 95.5-97 $^{\circ}\text{C}$, was obtained in 65% yield. ^1H NMR δ : 0.09 (s, 18H), 0.12 (s, 12H), 0.92 (pent., 4H, $J = 4.5$ Hz), 2.54 (s, 6H), 3.00 (pent., 4H, $J = 4.5$ Hz), 7.27 (s, 2H), 7.42 (t, 1H, $J = 8$ Hz), 7.60 (d, 2H, $J = 7.5$ Hz), 7.85 (s, 1 H). ^{13}C NMR δ : 0.21, 1.97, 19.33, 24.27, 29.67, 123.58, 126.31, 127.63, 129.73, 134.18, 134.40, 147.01, 153.98, 190.56. ^{29}Si NMR δ : 7.20, 7.97. IR ν : 1634 (C=O), 1071 (Si-O) cm^{-1} . UV λ_{max} (ϵ): 240 (18,790), 327 (43,260). HRMS Calc. for $[\text{C}_{32}\text{H}_{50}\text{O}_4\text{S}_2\text{Si}_4]^+$: 674.2228. Found: 674.2220.

alt-Copoly VII: Triflic acid/mesitylene (v/v 1/100, 0.1 mL), VI (0.184 g, 0.27 mmol) and mesitylene (0.5 mL) were stirred at rt under a vacuum of 10 mm of Hg for 10 h. After work-up, the residue was dissolved in THF and the copolymer was precipitated with methanol and collected by centrifugation. The product, 0.1 g, $M_w/M_n = 53,160/19,620$, $T_g = 53$ $^{\circ}\text{C}$, was obtained in 70% yield. ^1H NMR δ : 0.16 (s, 12H), 0.94 (m, 4H), 2.50 (s, 6H), 3.02 (m, 4H), 7.27 (s, 2 H), 7.36 (t, 1H, $J = 7$ Hz), 7.55 (d, 2H, $J = 6.5$ Hz), 7.80 (s, 1H). ^{13}C NMR δ : 0.33, 19.33, 24.32, 29.69, 123.58, 126.27, 127.67, 129.69, 134.15, 134.30, 147.00, 154.00, 190.55. ^{29}Si NMR δ : 7.8. IR ν : 1661 (C=O), 1056 (Si-O) cm^{-1} .

UV λ_{\max} (ϵ): 240 (15,250), 327 (33,900). Elemental Anal. Calc. for $C_{26}H_{32}O_3S_2Si_2$: C, 60.89%; H, 6.29%; S, 12.50%. Found C, 60.76%; H, 6.38%; S, 12.07%.

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