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Synthesis and photodegradation of poly[2,5-bis(dimethylsilyl)thiophene]

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SUMMARY

Poly[2,5-bis(dimethylsilyl)thiophene] (I), a copolymer with alternating thiophene and disilyl units, has been prepared by the Wurtz coupling of 2,5-bis(dimethylchlorosilyl)thiophene (IV) with sodium metal in toluene. I has been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, UV, GPC, TGA and elemental analysis. The photolysis of I in benzene/methanol solution results in degradation of the polymer. The structure of the photoproducts and possible mechanisms for their formation are discussed.

INTRODUCTION

We should like to report the preparation and properties of poly[2,5-bis(dimethylsilyl)thiophene] (I). We were interested in this polymer for a number of reasons. Perhaps most important no alternate co-polymer of this type, whose properties might be expected to be determined by the interaction of the heteroaromatic system with the adjacent disilane units, has been previously prepared. Silicon-silicon sigma bonds have a number of properties which are analogous to those of C-C double bonds.[1-3] For example, linear polysilanes absorb light in the ultraviolet region of the spectrum. The wavelength of this absorption increases with the length of the polysilane chain in much the same way that the ultraviolet absorption of conjugated polyenes moves to longer wavelength with increasing length of the conjugated system.[4,5] On this basis, I might be expected to have properties like those of poly(vinylene thiophene) which has been shown to be an extended conjugated system which can be rendered highly electrically conducting by oxidative doping.[6] Further, I might be expected to undergo rapid photo-degradation on photolysis at 254 nm on the basis of its similarity to poly[1,4-bis(dimethylsilyl)benzene].[7] This might make I a useful material for photolithographic applications.[8,9]

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EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained on a Jeol FX-90Q spectrometer operating in the Fourier Tranform (FT) mode. ^{29}Si NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer operating in the FT mode. ^{13}C NMR spectra were run with broad band proton decoupling. Five to ten percent solutions in chloroform-d were used to obtain these spectra. Chloroform was used as an internal standard for ^1H and ^{13}C NMR. All chemical shifts reported were externally referenced to TMS. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least two methyl groups bonded to them.[10]

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra of monomers were taken on neat films on NaCl plates. Spectra of polymers were taken in KBr pellets. UV spectra were recorded on a Shimadzu UV-260 spectrometer. Spectra quality hexane was used to prepare solutions for UV spectra. Low resolution mass spectra of monomers were recorded on a Finnigan MAT Incos 50 GCMS instrument at an ionizing voltage of 70 eV.

GPC analysis of the molecular weight distribution of the polymers was performed on a Perkin-Elmer series 10 liquid chromatography equipped with an LC-25 refractive index detector (maintained at 25°C), a 3600 data station and a 660 printer. A 32 cm x 77 mm Perkin-Elmer PL 10 m particle size, mixed pore size crosslinked polystyrene gel column was used for the separation. The eluant was THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 3,600,000, 194,000, 28,000, 7,600 and 2,550 whose M_w/M_n are less than 1.09. The TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cc/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 5°C/min to 750°C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

All reactions were carried out under a dry nitrogen atmosphere. All glassware was flame dried under a nitrogen atmosphere.

THF was distilled from a blue solution of sodium benzophenone ketyl immediate prior to use.

Toluene was distilled from molten sodium immediately before use.

While the monomers are known compounds complete spectral data has not been reported. For this reason, we have included this information.

Preparation of 2,5-bis(Dimethylsilyl)thiophene (III)

A 100 mL three neck rb flask was fitted with a reflux condenser, a 0.5" ultrasonic probe which was connected to a Tekmar 500 W, 20 kHz high intensity ultrasonic generator and a rubber septum. Magnesium chips (0.73 g, 30 mmol) and 50 mL of THF were placed in the flask. II (1.1 mL, 10 mmol) and dimethyldichlorosilane (2.4 mL, 22 mmol) were injected into the flask through the rubber spectum. The reaction mixture was sonicated for 20 min at 30% energy output. As soon as the sonication began, the temperature inside the flask began to increase. A temperature between 30-40°C was maintained by cooling the flask in an ice water bath. As the reaction proceeds most of the magnesium is consumed. After completion of the reaction, the reaction mixture was extracted with a 50 mL portion of methylene chloride. The combined organic phase was washed three times with an equal volume of water, dried over anhydrous magnesium sulfate and filtered. The product was purified by fractional distillation through a 10 cm vacuum jacketed Vigreux column. A fraction bp 74- 75°C/4.2 mm, 1.66 g (83%) was obtained. When this reaction was conducted on a larger scale (0.1 mol of II) we have obtained a 90% yield. III had the following spectral properties. ^{1}H NMR δ: 0.39(d,12H, J = 3.4 Hz), 4.58(sept.,2H, J = 3.4 Hz), 7.38(s,2H). ^{13}C NMR δ: -2.69, 136.21, 142.77. ^{29}Si δ: - 23.56. IR ν: 3065, 2960, 2900, 2120, 1488, 1408, 1260, 1010, 810 cm^{-1}. UV: λ_{max} 243.8 nm, ε = 12,030. GCMS m/e (rel. intensity): 200(16.8) $M^{+\cdot}$, 199(7.5) $M-1^{+}$, 185(100.0) $M-15^{+}$, 141(28.7), 83(19.2), 59(20.7). ^{1}H NMR and IR are in agreement with those previously reported.[22]

A small forerun of 2-chloro-5-dimethylsilylthiophene was obtained. ^{1}H NMR δ: 0.36(d,6H, J = 3.9 Hz), 4.50(sept.,1H, J = 3.9 Hz), 6.95(d,1H, J = 3.4 Hz), 7.05(d,1H, J = 3.4 Hz). ^{13}C NMR δ: - 3.01, 127.54, 134.21, 134.53, 139.42. GCMS m/e (rel. intensity): 178 (7.4), 176(17.8) $M^{+\cdot}$, 163(44.0), 161(100.0) $M-15^{+}$, 137(10.6), 135(25.3).

Preparation of 2,5-bis(Dimethylchlorosilyl)thiophene (IV)

In a 50 mL three neck rb flask fitted with a thermometer, a reflux condenser and a rubber septum was placed a mixture of III (1.4 g, 7 mmol), benozyl peroxide (0.24 g, 1 mmol) and carbon tetrachloride (14 mL, 0.2 mol). The mixture was heated to reflux for 24 h. After cooling to rt, carbon tetrachloride and chloroform were removed by evaporation under reduced pressure. The residue was distilled through a 10 cm vacuum jacketed Vigreux column. A fraction bp 76-78°C/0.2 mm 1.73 g (92% yield) was obtained. Lit. bp 114-115°C/14 mm.[12] ^{1}H NMR δ:

0.74(s,12H), 7.50(s,2H). ^{13}C NMR δ: 3.27, 136.65, 143.26. ^{29}Si NMR δ: 14.81. GCMS m/e (rel. intensity): 272(1.5), 270(6.2), 268(8.1) $M^{+\cdot}$, 257 (9.7), 255(26.8), 253(36.3) $M\text{-}15^+$, 177(9.6), 149(41.8), 93 (31.6), 71(100.0), 42(90.4).

Preparation of Poly[2,5-bis(dimethylsilyl)thiophene] (I)

In a 50 mL three neck rb flask fitted with a thermometer, a reflux condenser, an a presure equalizing dropping funnel was placed a Teflon covered magnetic stirring bar, sodium (0.18 g, 8 mmol) and 4 mL of toluene. The contents of the flask were stirred and heated to reflux. To this was added dropwise a solution of IV (0.81 g, 3 mmol) in 10 mL of toluene. After the addition was complete, the reaction mixture was heated at 100°C overnight. It was cooled to rt and 20 mL of methylene chloride was added. Unreacted sodium and sodium chloride salts were removed by filtration. The filtrate was washed with water, dried over anhydrous magnesium sulfate and filtered. The solvents were removed by evaporation under reduced pressure. Crude I, 0.48 g, 81% yield, was obtained. It was dissolved in methylene chloride and purified by precipitation with methanol. In this way, 0.35 g of a colorless white powder mp 140-143°C was obtained. ^1H NMR δ: 0.37(s,12H), 7.18(s,2H). ^{13}C NMR δ: -2.58, 135.56, 143.85. ^{29}Si NMR δ: -24.76. IR : 2990, 2920, 1505, 1425, 1285, 1265, 1220, 1025, 850, 805 cm^{-1}. UV: λ_{max} 267.8 nm, ε = 10,336 per unit. GPC M_w/M_n = 17,900/8,200. Elemental Anal. Calcd. for $C_8H_{14}SSi_2$: C, 48.42; H, 7.11; S, 16.16. Found: C, 48.66; H, 7.01; S, 15.94.

1,2-Dichloro-1,1,2,2-tetramethyldisilane (V)

V was prepared from hexamethyldisilane (Petrarch) by reaction with trimethylchlorosilane and anhydrous aluminum chloride in 88% yield.[13]

Preparation of Oligomers of I

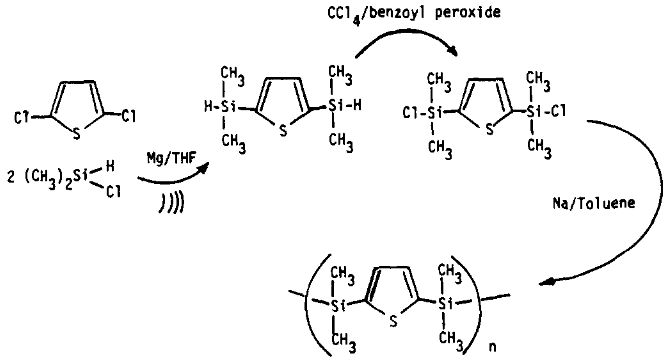
In a 100 mL three neck rb flask equipped with an ultrasound horn as above was placed V (1.87 g, 10 mmol), II (1.06 mL, 10 mmol), magnesium turnings (0.60 g, 25 mmol) and 50 mL of THF. The mixture was sonicated for 4 h. After work up, a yellow solid 2.24 g was obtained. It was recrystallized from THF/methanol to yield a white solid mp 93-112°C. Its IR and UV spectra were in agreement with I prepared by the Wurtz coupling above. On the other hand, resonances resulting from terminal thiophene groups were observed in the ^1H and ^{13}C NMR spectra.

Photodegradation of (I)

A solution of I M_w/M_n = 17,900/8,200 (100 mg, 0.5 mmol), methanol (5 mmol) and benzene (3 mL) was placed in a 0.8 x 15 mm quartz tube. Argon was bubbled through the solution for 10 min. The tube was sealed with a rubber septum. It was placed adjacent to a quartz photolysis well which contained a 550 W Hanovia medium pressure mercury lamp. The photolysis reaction was cooled to 25°C in a water bath. Photolysis for 5 h resulted in a polymer with M_w/M_n = 4,400/2,600, while photolysis for 16 h gave material in which both M_w and M_n were less than 1,000. After photolysis, the solvents were removed by evaporation under reduced pressure. The residue had the following spectral properties. ^{1}H NMR δ: 0.04–0.52(m,60H), 3.33(s,9H), 3.71(s,3H), 4.64(sept.,1H, J = 4.1 Hz), 7.24-7.85(m,10H). ^{13}C NMR δ: 1.06, 1.83, 135.60, 142.82. ^{29}Si NMR δ: -8.19, -9.42, -20.21, -21.84, -22.90. IR ν: 3400, 2962, 2125, 1641, 1632, 1384, 1258, 1040, 827, 799.6 cm^{-1}. UV: λ_{max} 236.2 nm, ε = 22,380.

RESULTS AND DISCUSSION

We have prepared I in three steps starting from commercially available 2,5-dichlorothiophene (II). While it is difficult to prepare a di-Grignard reagent from II under normal conditions, we have found that it is quite easy to carry out in-situ generation and coupling of this species with dimethylchlorosilane under ultrasound activation.[14-18] In this way, we have been able to prepare 2,5-bis(dimethylsilyl)-thiophene (III) in greater than 90% isolated yield. In a second step, III has been converted to 2,5-bis(dimethylchlorosilyl)thiophene (IV) by a benzoyl peroxide initiated free radical chlorination reaction.[19,29] Finally we have utilized a Wurtz type coupling reaction of IV with sodium dispersion in toluene to produce I with M_w/M_n = 17,900/8,200 (see Scheme 1).

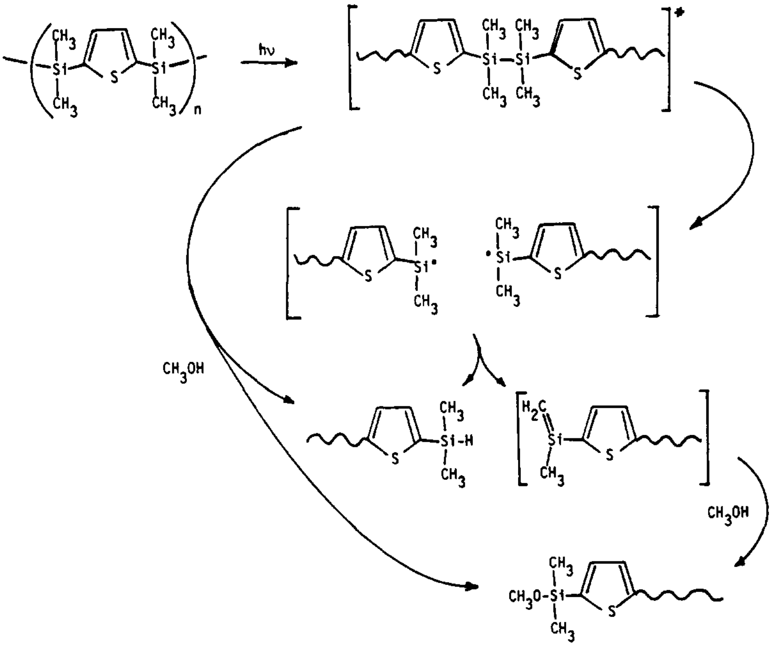


This type of Si-Si bond forming reaction has been utilized to prepare various polysilanes as well as to synthesize monomeric compounds possessing Si-Si bonds.[21,22]

We have also prepared oligomers of I, M_w/M_n = 1,000/880, by the ultrasound promoted reaction of 1,2-dichloro-1,1,2,2-tetramethyldisilane (V) with II and magensium. Failure of this approach to yield I may partially result from degradation of I by ultrasound. Thus the molecular weight of I, M_w/M_n = 17,900/8,200, rapidly (1 h) decreases on irradiation of a solution of I with ultrasound to M_w/M_n = 5,600/2,700. However, additional ultrasound causes no further degradation of I.

The ultraviolet absorption spectrum of I is significantly shifted to longer wavelength compared to those of monomeric model compounds: I λ_{max} 267.8 nm, ε = 10,340; III λ_{max} 243.8 nm, ε = 12,030; 1,2-bis(2'-thiophenyl)-1,1,2,2-tetramethyldisilane λ_{max} 244.0 nm, ε = 24.700.[24]

Photolysis of a benzene/methanol solution of I results in photodegradation of the polymer. The decrease in molecular weight depends on the length of the photolysis. This process may occur by homolytic scission of a photoexcited Si-Si bond to yield a pair of polymeric fragments which are terminated by silyl radical centers. These may undergo disproportionation to yield one polymer chain terminated by a dimethylsilyl group while the other polymer chain is terminated by a reactive Si-C double bond. Addition of methanol across the Si-C double bond will yield a polymer chain terminated by a methoxydimethylsilyl group.[23] Direct reaction of methanol with a photoexcited Si-Si bond of I will produce identical results (see Scheme 2).[24] Spectroscopic analysis of the oligomeric residue present after photolysis of I is consistent with the presence of Si-H and Si-OCH_3 functional groups.



The thermal stability of I was determined by TGA. The polymer is stable to 250°C. Between 250 and 350°C the polymer loses about four percent of its original weight. At temperatures above 350°C rapid weight loss occurs. By 550°C only 23 percent of the original weight of the sample remains. Virtually no further loss of weight occurs on increasing the temperature to 750°C (see Figure 1). At this point a black colored residue remains.

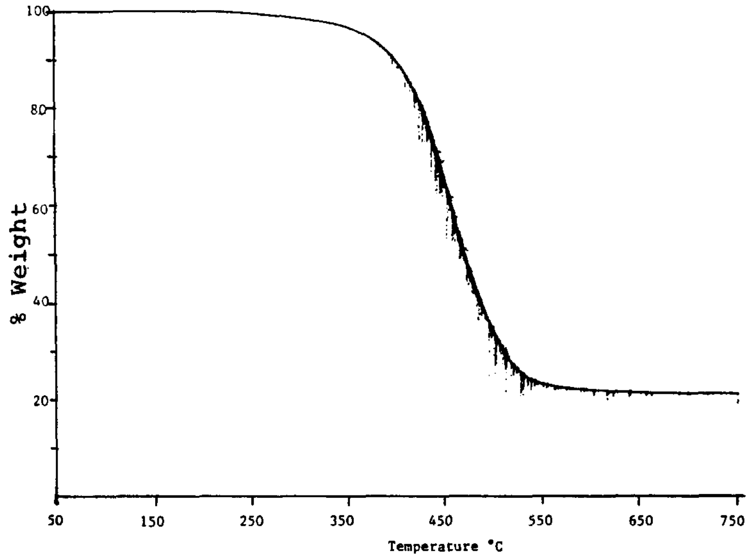


Figure 1. TGA of Polymer I.

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