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Synthesis and photodegradation of poly[1,4-*bis*(dimethylsilyl)naphthalene]

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SUMMARY

Poly[1,4-*bis*(dimethylsilyl)naphthalene](I), a copolymer with alternating 1,4-naphthalene and disilyl units, has been prepared by the Wurtz coupling of 1,4-*bis*(dimethylchlorosilyl)naphthalene (II) or 1,4- *bis*(dimethylfluorosilyl)naphthalene (III) with sodium metal dispersion in toluene. The molecular weight distribution of I prepared from III is significantly higher than when I is prepared from II. I has been characterized by ^{1}H, ^{13}C and ^{29}Si NMR, IR, UV, GPC, TGA and elemental analysis. Photolysis of I in benzene/methanol solution results in rapid degradation of I.

INTRODUCTION

We should like to report the preparation and properties of (I). We were interested in this polymer for a number of reasons. Perhaps most important only a few alternate co-polymers of this type, whose properties might be expected to be determined by the interaction of the aromatic system with the adjacent disilane units have been previously prepared.[1,2] Si-Si sigma bonds have a number of properties which are analogous to those of C-C double bonds.[3-5] For example, linear polysilanes absorb light in the ultraviolet (UV) region of the spectrum. The wavelength of this absorption increases with the length of the polysilane chain in much the same way that the UV absorption of conjugated polyenes moves to longer wavelength with increasing length of the conjugated system.[6,7] On this basis, I might be expected to have properties like those of poly(arylene vinylene)s which have been shown to be extended conjugated systems.[8-11] Further, I might be expected to undergo photo-degradation on the basis of its similarity to poly[1,4-*bis*(dimethylsilyl)benzene].[1] This might make I a useful material for photolithographic applications.[12,13]

EXPERIMENTAL

^{1}H, ^{13}C, ^{29}Si and ^{19}F NMR spectra were recorded on an IBM-Brucker WP-270-SY spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broad band proton decoupling. Ten to fifteen percent solutions in chloroform-d were used to obtain ^{29}Si spectra, whereas five percent solutions were used for ^{1}H, ^{13}C and ^{19}F NMR spectra.

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Chloroform was utilized as an internal standard for ^1H and ^{13}C NMR spectra. ^{19}F NMR spectra were externally referenced to $CFCl_3$. ^{29}Si NMR spectra 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 one methyl group bonded to them.[14] IR spectra of $CDCl_3$ solutions on NaCl plates were recorded either on an IBM FT- IR/30S, DTGS/CSI spectrometer or on a Perkin Elmer PE-281 spectrometer. UV spectra were recorded on a Shimadzu UV-260 spectrophotometer. Spectra quality hexane was used as the solvent to prepare solutions for UV analysis. Low resolution mass spectra were recorded on a Finnigan MAT Incos 50 GC-MS instrument at an ionizing voltage of 70 eV. A Varian 3400 GLPC equipped with a 0.25 mm x 30 M, DB-5 capillary column served as the inlet.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers was performed on a Waters system comprised on a U6K injector, 510 HPLC solvent delivery system, R401 refractive index detector, and a model 820 Maxima Control System. A Waters 7.8 mm x 30 cm, 10 µm particle size, mixed pore size, crosslinked polystyrene gel column was used for the separation. The eluting solvent was reagent THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 1,850,000, 170,000, 110,000, 20,400 and 1350 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis (TGA) of I was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 5°C/min to 600°C.

Elemental analysis was performed by Galbraith Laboratories Knoxville, TN.

THF was distilled from a deep blue solution of sodium benzophenone ketyl immediately prior to use. 1,2-Dimethoxyethane (DME) was distilled from a deep blue solution of sodium benzophenone ketyl and then from lithium aluminum hydride prior to use.

All reactions were carried out under an atmosphere of purified nitrogen in flame dried glassware.

1,4-Dibromonaphthalene (IV)

The *p*-dioxane bromine complex was prepared by slow addition of bromine (102 g, 0.64 mol) to *p*-dioxane (60.0 g, 0.63 mol) in a 500 mL rb flask. The complex was added with stirring to naphthalene (40.3 g, 0.315 mol) in a 500 mL three neck rb flask. The reaction mixture was allowed to react overnight and was neutralized with 10% NaOH. The white crystalline residue was purified by recrystallization from absolute ethanol. The yield of IV was 73 g, mp 81°C, Lit. mp 83-83.5°C,[15] 81% yield, was obtained. ^1H NMR δ: 7.56(s,2H), 7.58(d of d,2H, J = 6.3 and 3.4 Hz), 8.19(d of d,2H, J = 6.3 and 3.4 Hz). ^{13}C NMR δ: 122.40, 127.60, 127.98, 129.87 and 132.75.

1,4-*bis*(Dimethylsilyl)naphthalene (V)

In a 500 mL three neck rb flask equipped with a reflux condenser, a pressure equalizing addition funnel and a Teflon covered magnetic stirring bar was placed 200 mL of THF and (4.95 g, 0.2 mol) of magnesium turnings. To this was slowly added IV (28.4 g, 99 mmol) dissolved in 50 mL of THF. The reaction flask was cooled in a water bath to control the vigorous reaction. After the magnesium had been consumed, the solution was refluxed for 1 h. Dimethylchlorosilane (23.7 g, 0.25 mmol) dissolved in 20 mL of THF was then added dropwise to the THF solution of 1,4- diGrignard reagent. The solution was refluxed for 6 h and then poured into a 2 L Erlenmeyer flask which was half filled with ice. The phases were separated and the aqueous phase was extracted twice with ether. The combined organic phases were washed with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was distilled through a 22 cm vacuum jacketed Vigreux column. V, bp 110-113°C/0.1 mm, 11.17 g, 46% yield was obtained. ^{1}H NMR δ: 0.49(d,12H, J = 3.9 Hz), 4.86 (septet,2H, J = 3.9 Hz), 7.53(d of d,2H, J = 6.3 and 3.4 Hz), 7.70(s,2H), 8.15(d of d,2H, J = 6.3 and 3.4 Hz). ^{13}C NMR δ: -3.23, 125.65, 128.63, 132.91, 136.15, 137.84. ^{29}Si NMR δ: -19.13. IR ν: 3080, 3040, 2965, 2124 (s), 1510, 1455, 1430, 1255 (s), 900 (s), 840 (s), 773 (s) cm^{-1}. UV λ nm (ε): 219.2(23,170); 279.6(10,420); 289.4(12,880); 299.6(8,970); 316.0(1,020). GC-MS m/e (rel. intensity): 246(1.23), 245(3.25), 244(13.09) M$^{+\cdot}$, 243(1.59) M-1$^+$, 187(4.81), 186(16.71), 185(100.00) M-59$^+$, 170(4.36), 169(14.98), 168(2.44), 155(5.96), 73(9.51), 59(11.64), 43(7.42). Elemental Anal. Calcd. for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.24. Found: C, 67.91; H, 8.07.

1-Dimethylsilylnaphthalene

A fraction bp 82-85°C/0.1 mm, 3.68 g, 20% yield was obtained. It had the following spectral properties. ^{1}H NMR δ: 0.183(d,6H, J = 3.8 Hz), 4.86(septet,1H, J = 3.8 Hz), 7.43-7.55(m,3H) 7.72(d of d,1H, J = 6.8 and 1.2 Hz), 7.82-7.89(m,2H), 8.11(d of d,1H, J = 7.0 and 2.0 Hz). ^{13}C NMR δ: -3.22, 127.63, 127.75, 127.88, 128.99, 130.03, 130.18, 133.37, 133.65, 135.69, 137.11. ^{29}Si NMR δ: -19.37. IR ν: 3062, 2970, 2913, 2128 (s), 1596, 1510, 1431, 1332, 1257, 1150, 1092, 1029, 990, 900 (s), 842, 800, 782 (s) cm^{-1}. UV λ nm (ε): 220.6(25,890); 271.8 (8,841); 281.8(10,360); 292.8(6,885); 313.2(531). GC-MS m/e (rel. intensity): 188(3.00), 187(11.68), 186(63.36) M$^{+\cdot}$, 185(20.47) M-1$^+$, 173(4.79) 172(17.06), 171(100.00) M-15$^+$, 169(15.74), 167 (13.67), 155(15.90), 129(12.22), 128(15.77), 58(32.25), 43 (28.50).

1,4-*bis*(Chlorodimethylsilyl)naphthalene (II)

In a 250 mL rb flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar was placed V (10.0 g, 40.9 mmol), 120 mL of carbon tetrachloride and benzoyl peroxide (0.74 g, 1.53 mmol). The solution was refluxed for 12 h. The solvent was removed by evaporation under reduced pressure. The residue was fractionally distilled through a 22 cm vacuum jacketed Vigreux column. II, bp 141-143°C/0.3 mm, 11.4 g, 89% yield was obtained. ^{1}H NMR δ: 0.99(s,12H), 7.71(d of d,2H, J = 6.3 and 3.2 Hz), 7.97(s,2H), 8.44(d of d,2H, J = 6.3 and 3.2 Hz). ^{13}C NMR δ: 3.52, 126.12, 128.91, 132.66, 135.89, 137.26. ^{29}Si NMR δ: 20.81. IR ν: 3076, 3037, 2965, 2904, 1695, 1509, 1452, 1407, 1286, 1257 (s), 1231, 1002 (s), 839 (s), 810 (s), 791 (s) cm^{-1}. UV λ nm (ε): 222.4(53,270); 282.4(20,048); 291.6(23,530); 321(2,880).

1,4-*bis*(Fluorodimethylsilyl)naphthalene (III)

In a 250 mL rb flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar was placed DME (60 mL), $(NH_4)_2SiF_6$ (3.36 g, 19 mmol) and II (2.9 g, 9.26 mmol). The reaction mixture was refluxed overnight. The solution was cooled, and then filtered to remove salts. The solvent was removed by evaporation under reduced pressure. The residue was purified by distillation. III, bp 83-84°C/0.05 mm, 1.97 g, 76% yield was obtained. ^{1}H NMR δ: 0.75(d,12H, J = 7.5 Hz), 7.66(d of d,2H, J = 6.4 and 3.3 Hz), 7.88(s,2H), 8.26(d of d of d,2H, J = 6.4, 3.3 and 1.2 Hz). ^{13}C NMR δ: 0.18(d, J = 14.6 Hz), 126.19, 128.76(d, J =

3.7 Hz), 132.20(d, J = 4.9 Hz), 136.05, 137.73 (d, J = 14.6 Hz). ^{29}Si NMR δ: 22.57(d, J = 278.3 Hz). ^{19}F NMR δ: -157.90. IR ν: 3080, 3045, 2975, 1700, 1512, 1455, 1410, 1260 (s), 1220, 1008, 870 (s), 830 (s), 794 (s) cm^{-1}. UV λ nm (ε): 222.2(36,080); 280.0 (9,570); 289.2(11,320); 300.0(8,380); 320.8(1,235). GC-MS m/e (rel. intensity): 282(8.61), 281(22.30), 280(86.41) $M^{+\cdot}$, 267(4.72), 266(12.08), 265(50.37) M-15^{+}, 183(7.33), 171(5.03), 170(17.17), 169(100.00), 155(4.68), 141(5.56), 125(5.03), 115 (6.22), 77(47.81), 49(12.83), 47(17.79). Elemental Anal. Calcd. for $C_{14}H_{18}Si_2F_2$: C, 59.96; H, 6.47. Found: C, 60.24; H, 6.54.

Sodium Dispersion

In one neck of a two neck 100 mL rb flask equipped with a reflux condenser was placed a 1/2" ultrasound probe which was connected to a Tekmar 500 W, 20 kHz high intensity ultrasonic generator. A rubber septum was used to seal the probe to the flask. Toluene (30 mL) and freshly cut sodium metal (240 mg, 10 mmol) was added to the flask. The solution was heated to 100°C by use of an oil bath. At this point, the ultrasound generator was turned on at 30% continuous energy output. As soon as the sonication began, the toluene solvent began to reflux and the sodium metal was finely dispersed. The oil bath was removed and the sonication continued until the flask had cooled to 70°C. The ultrasound probe was removed.

Preparation of Polymer I from II

A Teflon covered magnetic stirring bar was added to the 100 mL two neck rb flask containing freshly prepared sodium dispersion (83 mg, 3.61 mmol) as above. A pressure equalizing addition funnel was inserted into one neck of the flask. A solution of II (0.55 g, 1.76 mmol) in 10 mL of toluene was placed in the pressure equalizing addition funnel and was slowly added to a well stirred refluxing toluene solution of sodium dispersion. After 60 h, I was obtained by precipitation from the toluene solution by addition of methanol. After centrifugation, the solution was decanted and the polymer was redissolved in toluene. The toluene solution was extracted with water. Methanol was added to reprecipitate the white powdery polymer, mp = 128-130°C, 179 mg, 42% yield M_w/M_n = 12,750/10,840. ^{1}H NMR δ: 0.40(s,12H), 7.08(d of d,2H, J = 6.3 and 3.1 Hz), 7.50(s,2H), 7.79(d of d, 2H, J = 6.2 and 3.3 Hz). ^{13}C NMR δ: -1.54, 124.57, 129.49, 132.74, 136.97, 139.13. ^{29}Si NMR δ: -20.98. IR ν: 3070, 2952, 2895, 1505, 1450, 1251, 1210, 1149, 1033, 996, 833, 788, 768, 688, 663 cm^{-1}. UV λ nm (ε): 229.2(31,160), 302.2(10,270); 319.4 (7,060); 331.0 (1,570). Elemental Anal. Calcd. for $C_{14}H_{18}Si_2$: C, 69.35; H, 7.48. Found: C, 70.01; H, 7.68.

Preparation of Polymer I from III.

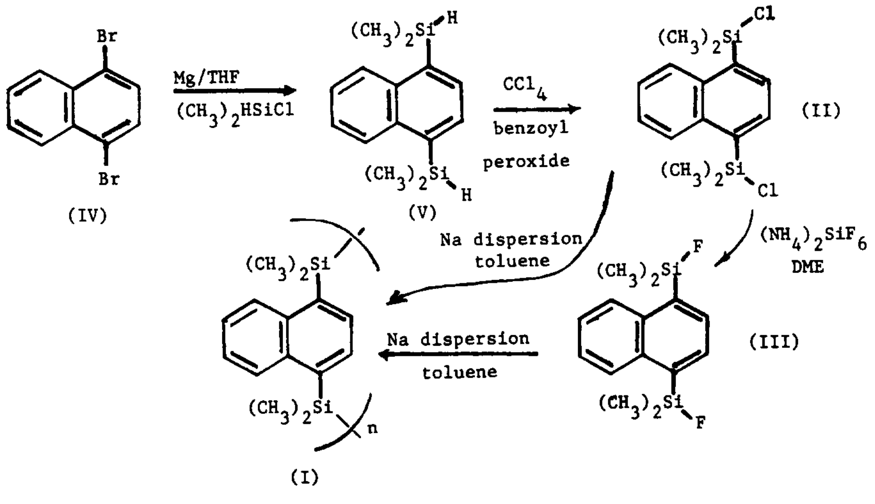
III (703 mg, 2.51 mmol) was slowly added to a refluxing solution of sodium dispersion (0.12 g, 5.15 mmol) in 40 mL toluene as above. After 17 h, I was obtained by precipitation from the toluene solution by addition of methanol. I was redissolved in toluene and reprecipitated from methanol. In this way, 361 mg, 59% yield of I was obtained. Its spectral properties were in complete agreement with I prepared from II. However, the molecular weight distribution of I was significantly higher M_w/M_n = 28,900/15,760.

Photodegradation of I

The photolysis was done using a 550 W medium pressure Hanovia Hg lamp. The samples of I (24 mg, 0.1 mmol) dissolved in benzene (3 mL) and methanol (30 L, 0.8 mmol) were placed in Pyrex test tubes 10 mm x 75 mm. The photolysis solutions were degassed by slowly bubbling Argon through them for ten minutes. The tubes were then sealed with rubber septa. After irradiation for definite time intervals, 20 µL aliquots were withdrawn by syringe. These were analyzed by GPC.

RESULTS AND DISCUSSION

We have prepared I in four or five steps starting from naphthalene. Use of the bromine complex of *p*-dioxane permits selective bromination of naphthalene to give IV.[15] IV was converted to a diGrignard reagent in THF which was reacted with dimethylchlorosilane to give V. V which converted to II by a benzoyl peroxide initiated free radical chlorination reaction.[16,17] A Wurtz type coupling reaction of II with sodium dispersion in toluene produced I with M_w/M_n = 12,750/10,840. This type of Si-Si bond forming reaction has been utilized to prepare numerous polysilane as well as to synthesize monomeric compounds possessing Si-Si bonds.[18,19] Alternatively, we have converted II to III by treatment with $(NH_4)_2SiF_6$ in DME.[20,21] III, likewise, undergoes Wurtz coupling on treatment with sodium dispersion to yield I (Scheme 1). This is the first time that Si-Si bonds have been formed by Wurtz type coupling of silyl fluorides. A major difference between these two procedures is that the molecular weight distribution of I prepared from III is significantly higher than I prepared from II. This may result from the fact that silyl fluorides are less prone to undergo hydrolysis than silyl chlorides. Experiments to determine the generality of this finding are in progress.



The UV spectrum of I is shifted to longer wavelength compared to model monomeric compounds: I, 331 nm (1,570); II, 321 nm (2,880); III, 320.8 nm (1,235) and I, 316 nm (1,020). The long wavelength absorption of I was selectively photolyzed through Pyrex. Photolysis of a benzene/methanol or benzene solution of I results in photodegradation of I. The decrease in the molecular weight of I depends on the length of the photolysis (Figure 1). Analysis of photodegraded I by ^{1}H or IR spectroscopy shows no indication products containing Si-H bonds. This is unexpected since photolysis of monomeric pentamethyl-1-naphthyldisilane is reported to give high yields of 1-dimethylsilyl-2-trimethylsilyl naphthalene.[22] On the other hand, signals at 3.4 ppm in the ^{1}H NMR due to CH_3-O groups as well as strong Si-O vibrations in the IR spectrum of photodegraded I are seen. The reason for this difference is under investigation.

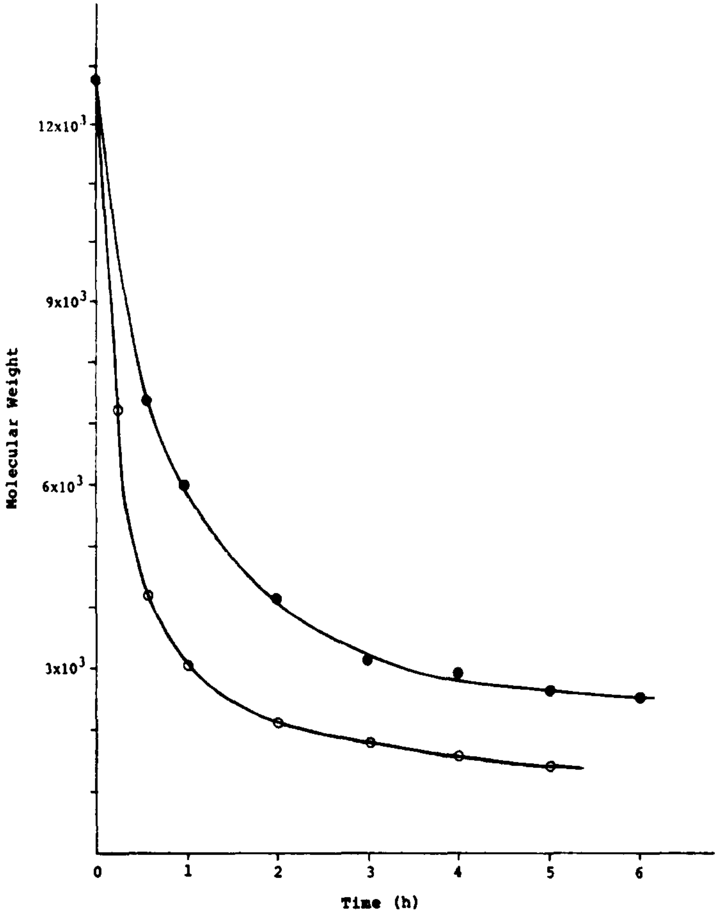


Figure 1. Plot of molecular weights of products vs. irradiation time for the photolysis of I: (●) irradition in benzene; (O) irradiation in the presence of methanol in benzene.

The thermal stability of I was determined by TGA in a nitrogen atmosphere. I was thermally stable to 100°C. Between 100°C and 210°C, I lost five percent of its intial weight. No further weight loss occurred between 210°C and 365°C. Between 385°C and 510°C rapid weight loss occurs. A black residue, which is stable to at least 600°C, equal to 33% of the initial sample weight remains (Figure 2).

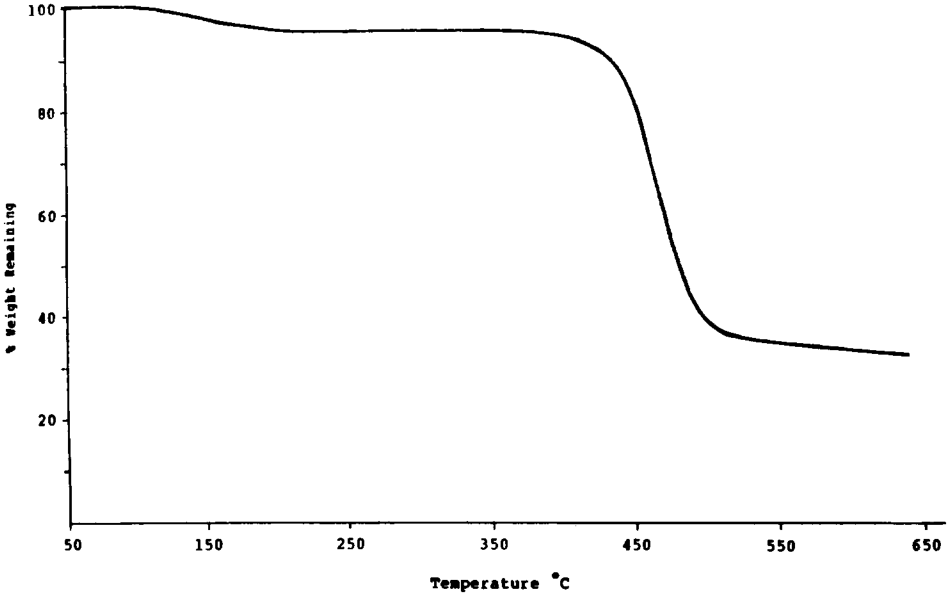


Figure 2. TGA of Polymer I.

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