Polymer Bulletin 22, 363–369 (1989)

Polymer Bulletin

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

Harry Hai Hong and William P. Weber*

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

SUMMARY

Poly[2,5-bis(dimethylsilyl)furan] (V), a copolymer with alternating furan and disilyl units, has been prepared by the Wurtz coupling of 2,5-bis(dimethylchlorosilyl)furan (II) with sodium metal dispersion in toluene. Lower molecular weight poly[2,5-bis(dimethylsilyl)furan] (IV) has been prepared by a similar condensation reaction with 2,5-bis(dimethylfluorosilyl)furan (III). IV and V have been characterized by ^{1}H, ^{13}C and ^{29}Si NMR, IR, and UV spectroscopy as well as by GPC, TGA and elemental analysis. Photolysis of V in a benzene/methanol solution results in degradation of the polymer.

INTRODUCTION

We should like to report the preparation and properties of poly[2,5-bis(dimethylsilyl)furan] (IV and V). We were interested in these polymers for a number of reasons. While monomeric silyl substituted furans have been extensively studied, polymer systems have not.[1] Only one alternate co-polymer of this type, whose properties are expected to be determined by the interaction of the heteroaromatic system with the adjacent disilane units has been previously prepared.[2] Silicon-silicon sigma bonds have a number of properties which are analogous to those of C-C double bonds.[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, IV and V might be expected to have properties like those of poly(N- methylpyrrole-2,5-diylvinylene-1,4-phenylenevinylene)[6] or poly(vinylene thiophene)[7] which has been shown to be an extended conjugated system that can be rendered highly electrically conducting by oxidative doping. Further, IV and V might be expected to undergo rapid photodegradation on photolysis at 254 nm on the basis of their similarity to poly[1,4-bis(dimethylsilyl)benzene].[8] This might make IV and V useful materials for photolithographic applications.

---

*To whom offprint requests should be sent

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on a Jeol FX-90Q spectrometer operating in the FT mode. ^{29}Si NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra.[9] This was effective since all the silicon atoms have at least two methyl groups bonded to them. ^{19}F NMR spectra were run on a Brucker AM-360 spectrometer. Ten to fifteen percent solutions in chloroform-d were used to obtain ^{13}C and ^{29}Si spectra, whereas 5% solutions were used for ^{1}H. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. Acetone-d_6 was used as solvent and $CFCl_3$ as an external standard for ^{19}F spectra. All chemical shifts reported were externally referenced to TMS.

IR spectra were recorded on an IBM FT-IR/30S spectrometer.

Spectra were taken on NaCl plates. UV spectra of spectro-quality hexane solutions were recorded on a Shimadzu UV-260 spectrometer. Low resolution mass spectra of monomers were recorded on a Finnigan MAT Incos 50 GCMS instrument, equipped with a Varian 3400 gas liquid phase chromatograph with a 30 m x 0.25 mm DB-5 capillary column as the inlet, at an ionizing voltage of 70 eV. High resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG 7070 EHF mass spectrometer at an ionizing voltage of 70 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

Gel permeation chromatographic (GPC) of the molecular weight distribution of the polymers was performed on a Waters system. This was comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector and a Model 820 Maxima Control System. A Waters 7.8 mm x 30 cm Ultrastyragel 10 μm particle size mixed pore size crosslinked polystyrene gel column maintained at 20°C was used for the separation. The eluant was 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 1,350 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis (TGA) of the polymer 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 5 min followed by an increase of 4°C/min to 650°C.

Elemental analysis was performed by Galbraith Laboratories Knoxville, TN.

All reactions were carried out under an atmosphere of dry nitrogen in flame dried glassware. Solvents were distilled immediately prior to use. Carbon tetrachloride was distilled from phosphorous pentoxide, toluene from molten sodium, and dimethoxyethane (DME) from a deep blue solution of sodium benzophenone ketyl and then from lithium aluminum hydride.

Preparation of 2,5-bis(Dimethylsilyl)furan (I)

In a 500 mL three neck rb flask equipped with a dry-ice/acetone cold finger condenser, a pressure equalizing addition funnel and a Teflon covered magnetic stirring bar was placed furan (8 mL, 0.11 mol) and n-butyllithium 1.6 M in hexane (Aldrich) (172 mL, 0.27 mol). The mixture was refluxed for 0.5 h. During this time it turned dark red in color. Dimethylchlorosilane (27 mL, 0.27 mol) was then added dropwise with stirring at a rate to maintain a gentle reflux. After the addition was complete, the mixture was refluxed for 0.5 h. The reaction mixture was cooled, and washed with water several times. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed by evaporation under reduced pressure. The residue was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column. I, a colorless liquid, 5.78 g (29%), bp 84°C/37 mm was obtained. ^{1}H NMR δ: 0.34 (d,12H, J = 3.7 Hz), 4.46 (septet,2H, J = 3.7 Hz), 6.71(s,2H). ^{13}C NMR δ: -4.53, 120.72, 162.11. ^{29}Si NMR δ: -20.58. IR ν: 2963, 2134(s), 1251, 867 cm^{-1}. UV λ_{max} 227 nm (ϵ = 1.2 x 10^4). GCMS m/e (rel. intensity): 186(2.05), 185(4.58), 184(24.74) $M^{+\cdot}$, 171(2.35), 170(5.09), 169(29.12) M-15$^+$, 145(8.15), 144(15.26), 143(100.00), 121(5.80), 120(10.08), 119(76.65). High resolution mass spectrum m/e: Calcd. for $C_8H_{16}OSi_2$: 184.0740. Found: 184.0739.

Preparation of 2,5-bis(dimethylchlorosilyl)furan (II)

In a 100 mL rb flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar was placed I (4.3 g, 23.4 mmol), benzoyl peroxide (1.6 g, 6.7 mmol) and 63 mL of carbon tetrachloride. The mixture was heated to 85°C for 24 h. The solvent was removed by evaporation under reduced pressure. The residue was distilled as above to give 2.65 g (45%) of II, a colorless liquid, bp 85°C/1.6 mm. ^{1}H NMR δ: 0.71(s,12H), 6.87(s,2H). ^{13}C NMR δ: 1.65, 121.53, 161.13. ^{29}Si NMR δ: 9.61. GCMS m/e (rel. intensity): 256(4.47), 255(3.77), 254(20.63), 253(5.53), 252(31.39) $M^{+\cdot}$, 240(2.73), 239(16.67), 238(4.43), 237(24.75) M-15$^+$, 189(76.38), 188(17.02), 187(100.00). High resolution mass spectra m/e Calcd. for $C_8H_{14}OCl_2Si_2$: 251.9960. Found: 251.9974.

Preparation of 2,5-bis(Dimethylfluorosilyl)furan (III)

In a 100 mL rb flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar was placed II (2.2 g, 8.73 mmol), ammonium hexafluorosilicate (3.1 g, 17.6 mmol) and DME (69 mL). The reaction was heated to 85°C for 10 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was distilled as above. A central fraction, 1.15 g (60%) bp 86°C/38 mm was obtained. ^{1}H NMR δ: 0.52(d,12H, J = 7.3 Hz), 6.85 (s,2H). ^{13}C NMR δ: -1.74(d, J = 16 Hz), 121.37, 161.11(d, J = 21 Hz). ^{29}Si NMR δ: 11.80(d, J = 276 Hz). ^{19}F NMR δ: -157.34. IR ν: 2968, 1260, 826, 735 cm^{-1}. UV: λ_{max}227.4 nm (ϵ = 1.1 x 10^4). GCMS m/e (rel. intensity): 223(0.24), 222(1.76), 221(4.05), 220(21.84) $M^{+\cdot}$, 207(0.33), 206(0.69), 205(3.86), M-15$^+$, 167(0.70), 166(1.23), 165(8.74), 157(7.58), 156(13.73), 155(100.00). High resolution mass spectra Calcd. for $C_8H_{14}OF_2Si_2$: 220.0551. Found 220.0543.

Preparation of Poly[2,5-bis(Dimethylsilyl)furan] (IV)

In a 50 mL three neck rb flask equipped with a reflux condenser, a rubber septum and a 0.5" ultrasound probe which was connected to a Tekmar 500 W 20 kHz high intensity ultrasonic generator, was placed sodium (80 mg, 3.45 mmol) and 15 mL of toluene. The reaction flask was heated to 110°C in an oil bath. The ultrasound generator was turned on to produce a fine sodium dispersion. The ultrasound probe was removed and a Teflon covered magnetic stirring bar was added. III (311 mg, 1.41 mmol) was added dropwise via a syringe to the sodium dispersion which was maintained at 110°C. The reaction mixture was stirred at 110°C for 24 h. The reaction mixture was allowed to settle. The clear supernatant was carefully decanted from the black residue and was added to methanol. Methylene chloride was added. The organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered and most of the solvent removed by evaporation under reduced pressure. Methanol was added. The organic solvents were decanted from an oil which separated. In this way IV, 80 mg (31%) was obtained. ^{1}H NMR δ: 0.30(s,12H), 6.53(s,2H). ^{13}C NMR δ: -4.20, 120.00, 163.41. ^{29}Si NMR δ: -29.24. IR ν: 2961, 1255, 909, 736 cm^{-1}. UV: λ_{max} 244.6 nm (ϵ = 1.2×10^4). GPC M_w/M_n = 7100/5300. Elemental Anal. Calcd. for $C_8H_{14}OSi_2$: C, 52.68; H, 7.74. Found: C, 52.26; H, 7.84.

Preparation of poly[2,5-bis(Dimethylsilyl)furan] (V)

V was prepared from II by a similar procedure, M_w/M_n = 11,900/7,600. The spectral properties of IV and V were identical with the exception of the UV: λ_{max} 250.6 nm (ϵ = 1.5×10^4).

Photodegradation of V

A solution of V (18 mg, 0.01 mmol) in methanol (32 L, 0.8 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 then 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 maintained at rt in a water bath. After irradiation for specific time intervals 30 μL aliquots were withdrawn by syringe. These were analyzed by GPC and UV (See Table 1). After photolysis for 4 h, the polymer (VI) had the following spectral properties. ^{1}H NMR δ: 0.00-0.35(m), 3.40(s), 6.45-6.70(m). IR ν: 2961, 1259, 1045, 799 cm^{-1}.

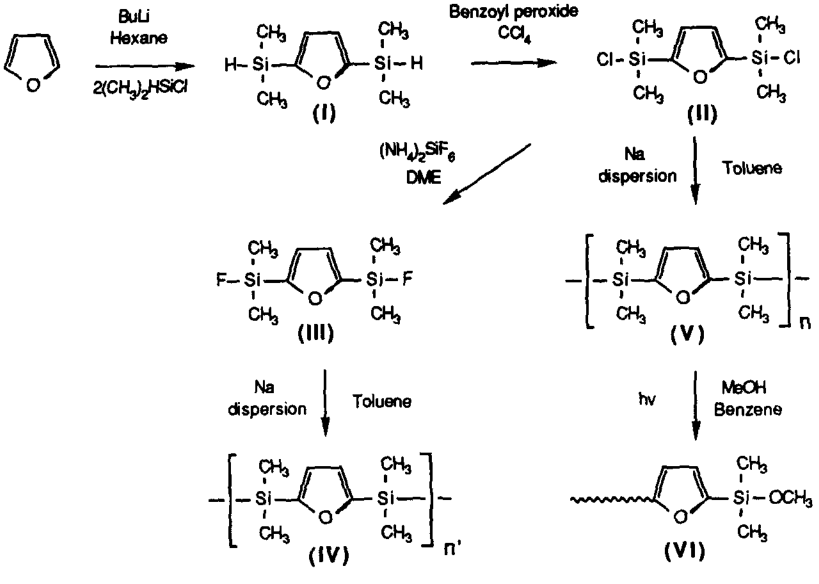
Table 1. Photodegradation of V in Benzene/Methanol.

Time (h)	M_w/M_n	UV λ_{max} (nm)
0.0	11,700/7,900	250.6
0.5	6,800/3,700	243.2
1.0	3,900/2,400	241.0
2.0	2,500/1,900	239.2
3.0	2,300/1,800	238.2
4.0	2,100/1,700	238.0

RESULTS AND DISCUSSION

We have prepared V in three steps and IV in four steps starting from furan. Metallation of furan with n-butyllithium gave 2,5-dilithiofuran which was reacted with dimethylchlorosilane to yield 2,5-bis(dimethylsilyl)furan (I).[10,11] In a second step, I has been converted to 2,5-bis(dimethylchlorosilyl)thiophene (II) by a benzoyl peroxide initiated free radical chlorination reaction.[12,13] Finally a Wurtz type condensation reaction of II with sodium dispersion in toluene to give V with M_w/M_n = 11,900/7,600. Alternatively, II was converted to 2,5-bis(dimethylfluorosilyl)furan (III) by treatment with ammonium hexafluorosilicate in dry DME.[14,15] Wurtz coupling of III gave IV with M_w/M_n = 7,100/5,300 (Scheme 1). This type of Si-Si bond forming reaction has been previously utilized to prepare various polysilanes.[16] All spectral properties of IV and V are identical with the exception of the position of their maximum absorption in the UV. The properties of low molecular weight polymers often vary with molecular weight. The ultraviolet absorption maxima for both IV and V are significantly shifted to longer wavelength compared to those of monomeric model compounds: I λ_{max} 227 nm, $\epsilon = 1.2 \times 10^4$; III λ_{max} 227.4 nm, $\epsilon = 1.1 \times 10^4$; IV λ_{max} 244.6 nm, $\epsilon = 1.2 \times 10^4$; V λ_{max} 250.6 nm, $\epsilon = 1.5 \times 10^4$.

Scheme 1



Photolysis of a benzene/methanol solution of V results in photodegradation of the polymer. The decrease in the molecular weight depends on the length of time of photolysis (Figure 1). The λ_{max} of the UV absorption of V moves to shorter wavelength as its molecular weight decreases (See Table 1). The molecular weight of V after photolysis for 0.5 h is virtually the same as the molecular weight of IV. As expected, the wavelength of their UV absorption maxima are almost identical. Analysis of the resi due (VI) after photolysis of V for 4 h by ^{1}H NMR and IR spectroscopy shows no indication of products containing Si-H NMR bonds. This is surprising.[2,8] The signal at 3.4 ppm in the ^{1}H NMR as well as the strong broad signal in the IR at 1045 cm^{-1} are consistent with the presence of CH_3O-Si groups.

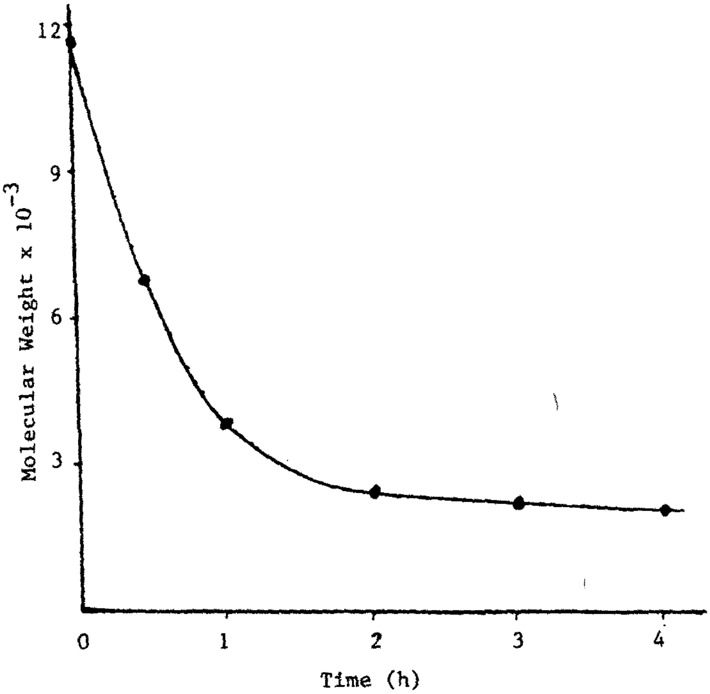


Figure 1. Molecular weight of V vs. Time of Irradiation.

The thermal stability of V was determined by TGA (Figure 2). V is stable to 200°C in a nitrogen atmosphere. Between 200 and 350°C the polymer loses 10% of its initial weight. Above 350°C rapid weight loss occurs. By 550°C 61% of the original weight of the sample has been lost. Between 550 and 650°C no further weight loss occurs. A black residue which amounts of thirty-seven percent of the initial sample weight remains.

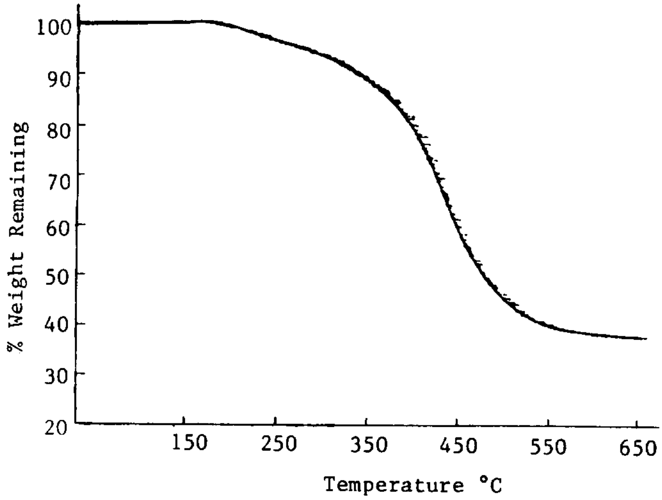


Figure 2. TGA of Polymer V.

Acknowledgement This work was supported in part by the Air Force Office of Scientific Research 89-0007.

REFERENCES

1. For a recent review see: Lukevics, E. Ya.; Pudova, O. A.; Erchak, N. P. "Organosilicon Derivatives of Furan and Thiophene" in Advances in Organosilicon Chemistry, ed. Voronkov, M. G., MIR Publishers, Moscow, **1985**. p 153-176.
2. Hu, S. S.; Weber, W. P. *Polymer Bull.*, **1989**, *21*, 133.
3. West, R. *Pure and Applied Chem.*, **1982**, *54*, 1041.
4. Boberski, W. G.; Allred, A. L. *J. Organometal. Chem.*, **1975**, *88*, 65.
5. Boberski, W. G.; Allred, A. L. *J. Organometal. Chem.*, **1974**, *71*, C27.
6. Jen, K. Y.; Cava, M. P.; Huang, W. S.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.*, **1983**, 1502.
7. Yamada, S.; Tokito, S. ; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.*, **1987**, 1449.
8. Nate, K.; Ishikawa, M.; Ni, J.; Watanabe, H; Saheki, Y. *Organometallics*, **1987**, *6*, 1673.
9. Pegg, D.T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.*, **1982**, *77*, 2745.
10. Benkeser, R. A.; Currie, R. B. *J. Am. Chem. Soc.*, **1948**, *70*, 1780.
11. Chadwick, D. J.; Willbe, C. *J. Chem. Soc. Perkin I*, **1977**, 887.
12. Sakurai, H.; Murakami, M.; Kumada, M. *J. Am. Chem. Soc.*, **1969**, *91*, 519.
13. Jung, I. N.; Weber, W. P. *J. Org. Chem.*, **1976**, *41*, 946.
14. Damrauer, R.; Simon, R. A. *Organometallics*, **1988**, *7*, 1161.
15. Damrauer, R.; Danahey, S. E. *Organometallics*, **1986**, *5*, 1490.
16. Zhang, X. H.; West, R. *J. Polym. Sci. Polym. Chem. Ed.*, **1984**, *22*, 159 and 225.

Accepted September 12, 1989 K