Synthesis and characterization of poly[2,5-thiophenediyl(dimethylsilylene)]

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A polycarbosilane is prepared by condensation between dichlorodimethylsilane and dianionic species of thiophene. The structure of the polycarbosilane is characterized by spectroscopic methods, gel permeation chromatography and thermal analysis. This polymer shows strong u.v. absorption at $\lambda_{\max}$, as found for thiophene itself, which indicates that the σ–π interaction through the polymer backbone is not significant. The polymer is also found to be photodegradable upon illumination with u.v. light.

(Keywords: polycarbosilane; synthesis; characterization)

Introduction

Recently, considerable attention has been paid to polysilanes and polycarbosilanes because of their potential use as positive u.v. photoresist materials and silicon carbide preceramic polymers[1]. Unlike paraffins, long chain polysilanes display strong low-energy u.v. absorption in the 300 nm region due to delocalized $\sigma_{\mathrm{Si-Si}}$ bonding orbitals. It is also well known[2–4] that σ–π interaction (σ(Si)–π(C)) exists in π-electron-system-substituted polysilanes, which causes a bathochromic shift so that $\lambda_{\max}$ of phenyl-substituted polysilane reaches 350 nm. Such σ delocalization breaks down in linear saturated polycarbosilanes so that they only absorb in vacuum u.v. ($\lambda_{\max} < 210$ nm). Therefore it is of interest whether such σ–π interaction prevails for polycarbosilanes having π-electron systems in the polymer backbone. Recently Tanaka *et al.*[5] reported a molecular orbital calculation result for the structure of $-[\mathrm{SiH_2(CH{=}CH)}_x]_n-$ showing that such a σ–π interaction exists but becomes weaker with an increase in x. Also poly[*p*-(disilanylene)arylene] derivatives have been investigated and show $\lambda_{\max}$ at 260–270 nm, which is close to the $\lambda_{\max}$ of aryl groups, thus they do not exhibit evidence of σ–π interaction through the polymer backbone[6–9]. The synthesis of polysilarylenes having backbone structures of alternating silicon and aromatic π-electron system, such as poly(silphenylene)[10] and poly(silbiphenylene)[11], has been reported previously, but their physical properties have not been treated in detail.

In this paper, we report the synthesis and some physical properties of a new polysilarylene, i.e. poly[2,5-thiophenediyl(dimethylsilylene)] by condensation between dichlorodimethylsilane and dilithiothiophene. This polymer was characterized by various spectroscopic methods and gel permeation chromatography. Some thermal and photochemical properties of the polymer are also reported.

Experimental

All the reactions were carried out on a dual manifold providing vacuum and dry argon. The chemicals used were all reagent grade and were further purified by standard methods: hexane was distilled from a pot containing $\mathrm{LiAlH_4}$ prior to use. Dichlorodimethylsilane was degassed by the freeze–thaw method under vacuum after distillation. Thiophene and tetramethylethylenediamine (TMEDA) were distilled after refluxing for 3 h with sodium and stored under argon with molecular sieves.

The u.v. spectrum in chloroform solution was recorded on a Hewlett–Packard 8452 A diode array spectrophotometer. ^{1}H and ^{13}C n.m.r. spectra were obtained in $\mathrm{CDCl_3}$ solutions on a Bruker Aspect 300 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane but were measured relative to the residual ^{1}H in the solvent.

Molecular weights of the polycarbosilane relative to polystyrene standards were measured by gel permeation chromatography (g.p.c.) (LDC Analytical) with chloroform as the eluent. Thermal properties of the polymer were examined by thermal gravimetric analysis (t.g.a.) (Perkin–Elmer TGA-7) and differential scanning calorimetry (d.s.c.) (Perkin–Elmer DSC-7) under $\mathrm{N_2}$ atmosphere.

Photochemical behaviour of the polycarbosilane was investigated by irradiating u.v. to the chloroform solution with a 12 W medium-pressure mercury-vapour discharge lamp. A cut-off filter (WG280) was used to prevent photodegradation of chloroform. After exposure for certain periods, a small aliquot of the solution was sampled and analysed by g.p.c. for the change of molecular weight.

Synthesis of poly[2,5-thiophenediyl(dimethylsilylene)]. To a solution of TMEDA (5.0 ml, 33 mmol) in 20 ml of hexane was added 33 mmol of n-BuLi (2.5 M in hexane 13.2 ml) at 25°C. After stirring for 30 min, 1.0 ml of thiophene (13 mmol) was added. The resulting mixture was heated to reflux for 3 h to yield a brown suspension and then 1.6 ml of dichlorodimethylsilane (13 mmol) was

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added dropwise to the suspension at $-78°C$. After the addition was completed the reaction mixture was warmed up slowly to 25°C, then transferred to a separating funnel which was filled with hexane and aqueous NH_4Cl solution. The solid above the aqueous layer was separated by filtration and washed with water, methanol and hexane. Removal of volatiles *in vacuo* gave a light brown solid (900 mg, 49%).

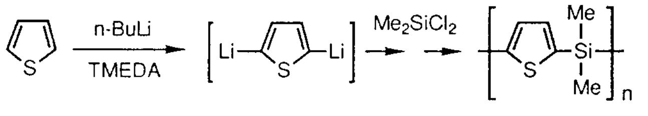
U.v.($CHCl_3$): $\lambda_{max} = 254$ nm ($\varepsilon = 1.0 \times 10^4$ M^{-1} cm^{-1}). I.r.(KBr): 2960(w), 1480(s), 1260(br s), 1200(s), 1010(s), 840–780(s) cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.35(s, 2H), δ 0.61(s, 6H).

Results and discussion

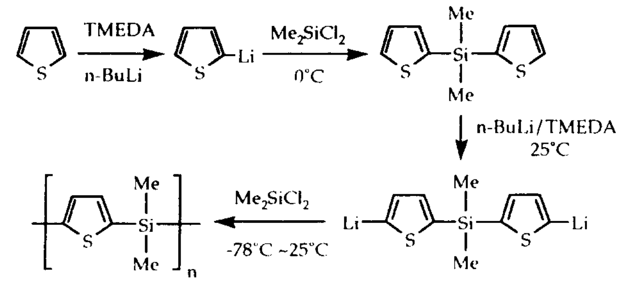
Poly[2,5-thiophenediyl(dimethylsilylene)] was obtained by condensation between dilithiothiophene and dichlorodimethylsilane in 49% yield. 2,5-Dilithiothiophene was generated by the treatment of thiophene with 2.5 equivalent of n-BuLi/TMEDA at 70°C (ref. 12). The reaction scheme is illustrated in *Scheme 1*.

The structure of the polycarbosilane was examined by i.r. and n.m.r. spectroscopic methods and the results were found to be consistent with the alternating thiophene and dimethylsilylene structure. The polymer is insoluble in common organic solvents such as aromatic and aliphatic hydrocarbons, alcohol and acetone but soluble in chloroform and dichloromethane. The polymer swells in tetrahydrofuran.

Molecular weights of the polycarbosilane relative to polystyrene are found to be fairly low and show broad unimodal molecular weight distribution. Efforts to adjust the stoichiometric ratio of reactants has not been successful in raising the molecular weight of the polymer: we obtained several results with M_n ranging from 1700 to 4100 and M_w/M_n around 2. The low molecular weight of the polymer is thought to be caused mainly by the incomplete dianionization of thiophene as well as the poor solubility of the polycarbosilane in hexane, the reaction medium. In order to improve the dianionization yield, we attempted to make dithiophenyldimethylsilane first by the synthetic route shown in *Scheme* 2. We found, however, that it did not help to increase the molecular weight. Furthermore, the n.m.r. spectrum of the resulting polymer shows the multiplet thiophenyl hydrogen peak, indicating that the dilithiation of the dithiophenyldimethylsilane took place not only at the desired 5 and 5′ positions but also at other positions. We are currently working on the detailed mechanism for the coupling reactions and on a method to improve the yield and molecular weight of the polymers.



Scheme 1



Scheme 2

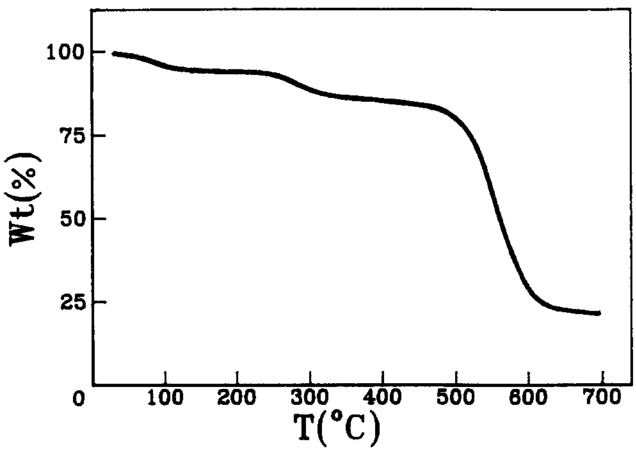


Figure 1 T.g.a. diagram of poly[2,5-thiophenediyl(dimethylsilylene)]

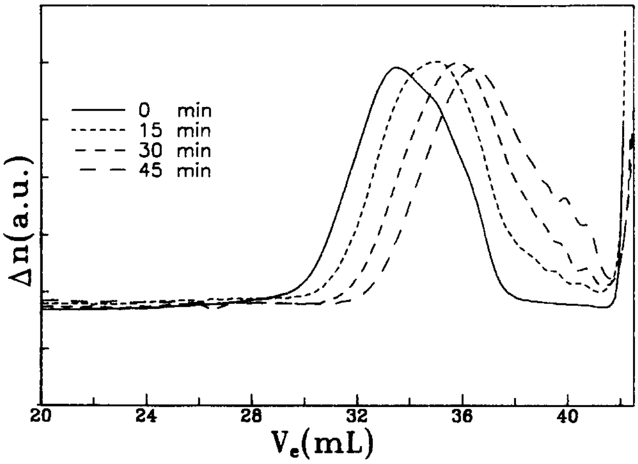


Figure 2 G.p.c. chromatograms, differential refractometer response (Δn) *versus* elution volume (V_e), of poly[2,5-thiophenediyl(dimethylsilylene)] at different exposure times with u.v. lamp. The increase of Δn at the end represents the solvent elution peaks

The polycarbosilane shows strong u.v. absorption bands at $\lambda_{max} = 254$ nm, which are not much different from thiophene itself. Also, λ_{max} does not change with molecular weight, although the molecular weight range tested was rather limited. This λ_{max} value is quite comparable to that of poly[(*p*-disilanylene)arylene]s which contain both Si–Si bonds and aromatic rings ($\lambda_{max} = 260$–270 nm)[6–9]. Therefore, we may conclude that the σ–π interaction through the backbone of these polymers is not significant.

The polycarbosilane is found to have some crystallinity from the melting endotherm in the d.s.c. thermogram at around 115°C as well as the X-ray powder pattern, while glass transition behaviour is not observed clearly between room temperature and the melting point. *Figure 1* shows the result of t.g.a. of the polymer under N_2 atmosphere. The polymer clearly shows a three-step mass loss. About 5% mass loss was observed at around 90°C and the second step of thermal degradation occurs near 280°C, amounting to about 10% mass loss. Between 500 and 600°C the third and major degradation occurs, leaving the final char content above 700°C at around 24%.

Upon exposure to u.v. light through the short wavelength cut-off filter, it was found that photodegradation of the polymers occurred. The evolution of g.p.c. profiles upon illumination with u.v. light on the chloroform solution of the polymer is displayed on *Figure 2*. It clearly shows the decrease of molecular weight with increase of exposure time, indicative of photochemically induced chain scission. The photodegradation mechanism has yet to be elucidated. Under this condition ($\lambda > 280$ nm), however, we confirmed that chloroform itself did not photodegrade. Without the cut-off filter we observed a rapid photodegradation of the polymer together with decomposition of the chloroform.

Acknowledgements

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