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Preparation of oligomers containing tetraphenylsilole, acetylene and aromatic groups in the main chain, and incorporation of iron carbonyl

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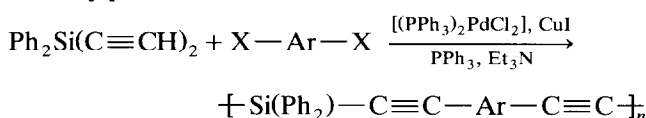
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Abstract

Polycarbosilanes with the structure $[-\text{SiR}_2-\text{C}\equiv\text{C}-\text{Z}-\text{C}\equiv\text{C}]_n$ ($\text{R}_2\text{Si} = 2,3,4,5\text{-tetraphenyl-1-sila-2,4-cyclopentadiene}$; $\text{Z} = 1,4\text{-benzene}$, $4,4'\text{-biphenyl}$, $9,10\text{-anthracene}$, $2,7\text{-fluorene}$, $2,5\text{-}$ and $2,6\text{-pyridine}$, $6,6'\text{-bipyridine}$, $2,5\text{-thiophene}$, $2,6\text{-}p\text{-dimethylaminonitrobenzene}$, $2,6\text{-}p\text{-nitroaniline}$, $2,6\text{-}p\text{-nitrophenol}$, and $2,7\text{-fluoren-9-one}$) were prepared by reaction of 1,1-diethynyl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene with the appropriate (hetero)aromatic dibromide or diiodide in the presence of $[(\text{PPh}_3)_2\text{PdCl}_2]$ and CuI . Exo- and endotherms observed in the initial DSC scans were absent in repeat scans. The oligomer where $\text{Z} = p\text{-C}_6\text{H}_4$ reacted with $[\text{Fe}(\text{CO})_5]$ under UV irradiation to give an oligomer containing iron carbonyl fragments attached to ca. 30% of the silole groups.

1. Introduction

As part of our continuing investigations into polycarbosilanes containing unsaturated groups in the backbone [1], we have previously described the preparation of polycarbosilanes with main chain acetylene and (hetero)aromatic groups by using the following palladium-catalyzed cross-coupling polymerization reaction [2].



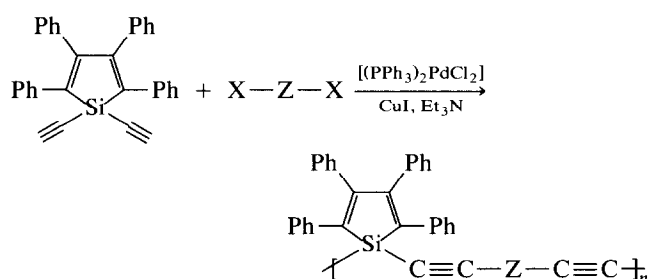
We have found that, depending on the substituents at silicon and on the nature of the Ar group, the polymers can become semi-conducting on being doped with FeCl_3 [3]. This suggests electron delocalization through the silicon atoms involving $(p-d)\pi$ bonding or $\sigma^*-\pi$ hyperconjugation [4]. When Ar is a donor-acceptor aromatic group, the polymer exhibits substantial and stable $\chi^{(2)}$ NLO effects [5].

We report here the preparation of the analogous series of oligomers containing the tetraphenylsilole group using the same palladium-catalyzed cross-cou-

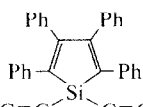
pling route. Since silole groups exhibit some aromatic character [6], we wished to investigate the effect of the electron-rich tetraphenylsilole group on properties related to main-chain conjugation. Additionally, silole groups are well known to form complexes with a wide variety of transition metals [7], and so we intended to use the polymer silole groups to bond metals. Indeed, the incorporation of several different metals could be envisaged since the polycarbosilanes contain other potential ligands (acetylenic, aromatic).

2. Results and discussion

The polycarbosilanes **I–XII** (Table 1) were synthesized in high yield by the following palladium-catalyzed polymerization between 1,1-diethynyl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene and the respective (hetero)aromatic dihalide.



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TABLE 1. Data for $\text{[C}\equiv\text{C-Si(C}_6\text{H}_5)_4\text{-C}\equiv\text{C-Z]}_n$ polycarbosilanes ^a

Oligomer	Aromatic dihalide X-Z-X	Polymer colour	Yield (%)	$\nu(\text{C}\equiv\text{C})$ (cm^{-1})	λ_{max} ^b (nm)	M_w ^c	M_w/M_n ^c	n ^d
I		yellow	68	2147	—	5180	2.49	10
II		yellow	77	2157	300	5690	2.10	10
III		red	77	2131	380, 402 426, 455	10 190	3.15	19
IV		yellow	80	2146	328, 347	6010	2.69	10
V		brown	71	2140	—	1950	1.60	3
VI		yellow	78	2158	—	3860	2.43	7
VII		brown	65	2140	—	2990	1.64	6
VIII		orange	74	2136	—	4760	2.27	9
IX		yellow	95	2148	390	4300	1.68	7
X		yellow	61	2147	370	1610	1.42	3

XIII by the existence of more than one conformation and the effect of silole complexes at and near the ends of the oligomer chains. Elemental analysis showed that iron carbonyl had been introduced at *ca.* 30% of the silole sites.

We have found that other metals can be attached to the acetylene groups and also to the aromatic groups (*e.g.* bispyridine) in the main chain for the diphenyl- and methyl(*n*-octyl)-silylene series of polymers [8]. We are currently investigating the attachment of several different metals in a given polymer using the various potential ligands (silole, acetylene, aromatic)

compound by reaction with $\text{HC}\equiv\text{CMgBr}$ in THF under the conditions previously described for the preparation of diethynylsilanes [14,15]. Removal of the reaction solvent *in vacuo* afforded the crude product which was recrystallized by addition of pentane to a toluene solution thus giving the pure compound in 75% yield (m.p. 203–204°C; lit. [16] 170–172°C). IR $\nu(\text{C}\equiv\text{C})$ 2037, $\nu(\text{H}-\text{C}\equiv)$ 3250 cm^{-1} (lit. [16] 2040, 3275 cm^{-1}). ^1H NMR (CDCl_3): δ 2.6 (s, 2H, $\text{HC}\equiv\text{C}$), 6.5–7.3 (m, 20H, aromatic). ^{13}C NMR (CDCl_3) (principal resonances); δ 140.5, 136.0, 131.9, 130.5, 129.9, 128.8, 100.2, 83.5. ^{29}Si NMR (CDCl_3): δ -46.5. Anal. Found: C 88.22, H

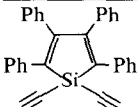
The reactions were carried out in triethylamine, except in the case of **V** and **VII** where toluene was used as cosolvent to retain the incipient polymer in solution and thus to increase the molecular weight. The progress of polymerization, which was complete after 16 h, was followed by the disappearance of the $\nu(\equiv\text{CH})$ band at 3250 cm^{-1} and the $\nu(\text{C}\equiv\text{C})$ band at 2037 cm^{-1} of the starting monomer, and the appearance of the $\nu(\text{C}\equiv\text{C})$ absorbance for the oligomer at *ca.* 2150 cm^{-1} (Table 1). The $\nu(\text{C}\equiv\text{C})$ band for the anthracene-containing oligomer **III** occurs at a lower frequency as we have observed for the diphenylsilylene [2] and methyl(*n*-octyl)silylene [8] series of polymers. Likewise, $\nu(\text{C}\equiv\text{C})$ for the thiophene-containing oligomer **VIII** occurs at a relatively low frequency in the present silole series. This suggests some degree of conjugation between the aromatic and acetylene groups for **III** and **VIII** perhaps also involving the silane moieties.

The crude reaction products containing different amounts of amine salt complexed to the oligomer were purified either by (a) filtering a solution in toluene through diatomaceous earth and then precipitating the oligomer by addition of pentane, or by (b) extracting a solution of the oligomer in THF and diethyl ether with 3% HCl(aq) followed by precipitation of the oligomer from the ether solution by addition of pentane. Both methods gave rise to a reduction in molecular weight and polydispersity (see Experimental section).

The UV/visible spectrum for **III** shows a long wavelength absorption at 455 nm which corresponds to a band-gap of 2.72 eV [9]. This value is similar to those observed for the corresponding polymers in the diphenyl- and methyl(*n*-octyl)-silylene series [8]. However, in the present series several of the other oligomers (**IV**, **IX**, **X** and **XII**) also exhibit absorbances at fairly long wavelength, and the band-gap is therefore also moderate in these cases. The oligomers are all electrically non-conducting in the absence of doping. When doped with FeCl_3 , **III** has a conductivity of 10^{-6} S cm^{-1} [3], much lower than the value for the corresponding polymer with an anthracene group in the diphenylsilylene series, suggesting that conjugation through the silole group in **III** is less extensive. Hyperconjugation [4] may be involved since the conductivity of doped acetylene-containing polycarbosilanes with at least one phenyl substituent at silicon is substantially greater than when there are only alkyl substituents [3,10].

The ^{29}Si NMR spectra of the oligomers all show a singlet at *ca.* $\delta -46$, the same chemical shift as that for the monomer (Table 2). The ^{13}C NMR resonances for both the acetylene carbons are deshielded with respect to those for the monomer (Table 2) as previously observed in the diphenyl- [2] and methyl(*n*-

TABLE 2. ^{13}C and ^{29}Si NMR data ^a

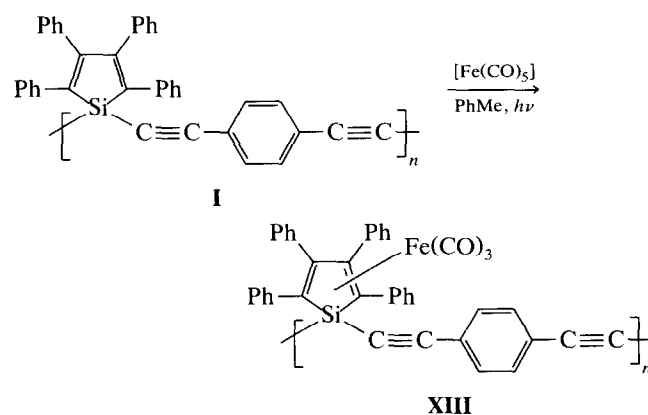
Monomer/Oligomer	^{29}Si δ (ppm)	^{13}C δ (ppm) ^b	
		C_α	C_β
	-46.5	83.5	100.2
I	-45.8	88.2	108.0
II	-45.9	90.9	106.2
III	-45.2	87.3	108.8
IV	-45.7	86.6	109.7

^a Reference, $\text{Si}(\text{CH}_3)_4$; solvent, CDCl_3 . ^b $[\text{Si}]-\text{C}_\alpha\equiv\text{C}_\beta-$.

octyl)-silylene [8] series. Additionally, numerous unassigned aromatic carbon resonances are observed. These extra resonances presumably arise from non-equivalent conformations, and also from the effect of residues at and near the ends of the oligomer chains.

DSC thermograms for a selection of the oligomers were run from 10°C to 300°C (Table 3). In the cases of **II** and **III**, only minor exotherms were observed in the initial run. For **IX**, both an exotherm and an endotherm were observed, whereas for **X** there was a single endotherm with a peak temperature of 120°C . All the above transitions were absent in repeat scans, and in view of their minor nature they probably arose from conformational relaxations. The start of the highly exothermic crosslinking process involving the acetylene groups was observed towards 300°C .

The iron-containing oligomer **XIII** was prepared by UV irradiation of **I** in the presence of $[\text{Fe}(\text{CO})_5]$ under the conditions previously described for the synthesis of tetraphenylsilole iron carbonyl complexes [11].



No bridging carbonyl IR absorbances are observed. Five $\nu(\text{C}\equiv\text{O})$ absorbances appear in the region for terminal carbonyl groups whereas there are only two or three $\nu(\text{C}\equiv\text{O})$ bands for the parent monomeric tetraphenylsilole iron carbonyl complexes [11]. As with the ^{13}C NMR spectra (see above), we explain the presence of the additional IR absorbances for oligomer

XIII by the existence of more than one conformation and the effect of silole complexes at and near the ends of the oligomer chains. Elemental analysis showed that iron carbonyl had been introduced at *ca.* 30% of the silole sites.

We have found that other metals can be attached to the acetylene groups and also to the aromatic groups (*e.g.* bispyridine) in the main chain for the diphenyl- and methyl(*n*-octyl)-silylene series of polymers [8]. We are currently investigating the attachment of several different metals in a given polymer using the various potential ligands (silole, acetylene, aromatic).

3. Experimental details

Reactions were carried out under dinitrogen using Schlenk tube techniques. Triethylamine was distilled over powdered KOH, and toluene was distilled from CaH₂. ¹H NMR spectra were run on a Bruker AW 60 spectrometer at 60 MHz, and ¹³C and ²⁹Si NMR spectra on a Bruker WP 200SY instrument operating at 50.327 MHz and 39.763 MHz, respectively. The SEC results were obtained using a Waters 510 system equipped with 100, 500, 1000 and 10,000 Å columns at a THF flow rate of 0.9 ml min⁻¹. UV/visible spectra were recorded on a Cary 118 instrument in CH₂Cl₂ solution, and IR spectra on a Perkin Elmer 1600 FTIR instrument in CCl₄ solution or as Nujol mulls. DSC scans were performed by using a Mettler TA 3000 system. Except for 6,6'-dibromo-2,2'-bipyridyl [12], 2,6-diiodo-4-nitro-*N,N*-dimethylaniline [8] and 1,1-diethynyl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene (see below), the monomers and catalysts were commercial samples and used as received.

3.1. Preparation of 1,1-diethynyl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene

Following the published procedure [13], 1,4-dilithio-1,2,3,4-tetraphenylbutadiene was prepared by shaking clean lithium shavings (2.50 g, 0.36 mol) with diphenylacetylene (65 g, 0.36 mol) in 400 ml diethyl ether at 0°C. Both the resulting suspension diluted with 400 ml diethyl ether and a solution of SiCl₄ (55.08 g, 0.324 mol) in 400 mls diethyl ether were added dropwise at the same rate and simultaneously to 600 ml diethyl ether over a period of 2–4 h at 20°C. The yellow solution was stirred for 3 d. The solvent was removed *in vacuo* and the residue was dissolved in toluene and filtered. Concentration of the filtrate afforded yellow-green 1,1-dichloro-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene which was recrystallized by addition of pentane to a solution in toluene (m.p. 201.7–202.7°C; 31% yield) This was converted into the required com-

pound by reaction with HC≡CMgBr in THF under the conditions previously described for the preparation of diethynylsilanes [14,15]. Removal of the reaction solvent *in vacuo* afforded the crude product which was recrystallized by addition of pentane to a toluene solution thus giving the pure compound in 75% yield (m.p. 203–204°C; lit. [16] 170–172°C). IR $\nu(\text{C}\equiv\text{C})$ 2037, $\nu(\text{H}-\text{C}\equiv)$ 3250 cm⁻¹ (lit. [16] 2040, 3275 cm⁻¹). ¹H NMR (CDCl₃); δ 2.6 (s, 2H, HC≡C), 6.5–7.3 (m, 20H, aromatic). ¹³C NMR (CDCl₃) (principal resonances); δ 140.5, 136.0, 131.9, 130.5, 129.9, 128.8, 100.2, 83.5. ²⁹Si NMR (CDCl₃); δ -46.5. Anal. Found: C, 88.22; H, 5.38; Si, 6.72. C₃₂H₂₂Si calc.: C, 88.43; H, 5.10; Si, 6.46%.

3.2. Preparation of oligomers I–XII

The experimental procedure previously described for the diphenylsilylene series of analogous polymers [2] was followed. The specific preparative conditions together with spectral and molecular weight data for the resulting oligomers are given in Tables 1 and 2. The products were purified in one of the two following ways: (a) by filtering a solution in toluene through diatomaceous earth and then precipitating the oligomer by adding pentane, or (b) by addition of diethyl ether to a solution of oligomer in THF followed by extraction with 3% HCl(aq), and precipitation of the oligomer from the ether solution (dried over MgSO₄) by addition of pentane. Both methods resulted in a reduction of molecular weight and polydispersity, *e.g.* oligomer **II**, method (a): before purification M_w, 25580; M_w/M_n, 3.93; *n*, 11; after purification M_w, 5690; M_w/M_n, 2.10; *n*, 5. oligomer **III**, method (b): before purification M_w, 23070; M_w/M_n, 5.52; *n*, 7; after purification M_w, 10190; M_w/M_n, 3.15; *n*, 6.

3.3. Preparation of XIII

A solution of oligomer **I** (2.3 g, 4.5 mmol) and [Fe(CO)₅] (3.0 g, 15.2 mmol) in 350 ml toluene was irradiated for 100 h in a Rayonet photochemical reactor equipped with 2537 Å lamps. After removal of the toluene *in vacuo*, the crude product was taken up in dichloromethane. Addition of pentane precipitated **XIII** in 50% yield. IR $\nu(\text{C}\equiv\text{O})$ 2159, 2118, 2036, 1993, 1976 cm⁻¹. Anal. Found: C, 71.08; H, 5.23; Si, 4.10; Fe, 2.90. C₄₁H₂₄FeO₃Si calc.: C, 75.93; H, 3.73; Si, 4.33; Fe, 8.61%.

3.4. DSC

Samples (5–10 mg) in sealed aluminium pans were heated from 10°C to 300°C at a heating rate of 20°C min⁻¹. The exo- and endo-therms observed are listed in Table 3. The samples were recooled to 10°C, and the

TABLE 3. DSC results for oligomers **II**, **III**, **IX** and **X**^a

Oligomer	Peak temperature (°C) ^b	
	Endothermic	Exothermic
II		150
III		90, 150, 215, 260
IX	170	150
X	120	

^a From 25°C to 300°C at heating rate of 20°C min⁻¹. ^b In all cases, the transitions were absent in repeat scans.

thermograms re-run. The transitions observed in the initial runs were absent in the repeat scans.

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