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Preparation of diphenylsilylene polymers containing main-chain acetylene and (hetero)aromatic groups: $\chi^{(2)}$ non-linear optical and other properties

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Abstract

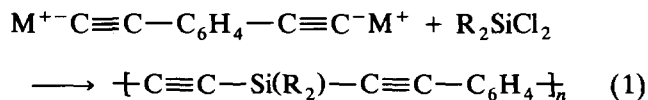
Polymers having the structure $\text{-(C}\equiv\text{CSi(Ph)}_2\text{C}\equiv\text{C-Z)}_n$ (Z = 1,4-benzene, 4,4'-biphenyl, 9,10-anthracene, 2,7-fluorene, 6,6'-bipyridine, 2,5 and 2,6-pyridine, 2,5-thiophene, 2,6-*p*-dimethylaminonitrobenzene, 2,6-*p*-nitroaniline, 2,6-*p*-nitrophenol, 2,6-*p*-cyanophenol, *p*-tetrafluorobenzene and 2,7-fluoren-9-one) were prepared by reaction of diethynyldiphenylsilane with the appropriate (hetero)aromatic dibromide or diiodide in the presence of $[(\text{PPh}_3)_2\text{PdCl}_2]$, CuI and PPh_3 , the solvent being either triethylamine or triethylamine with toluene. Depending on the Z group and the solvent system, the weight-average molecular weight as determined by SEC ranged from 2600 for 2,6-pyridine to 34,000 for 1,4-benzene. The UV/visible spectra show absorption maxima in the region 250–400 nm. The polymer with 2,6-*p*-dimethylaminonitrobenzene groups was $\chi^{(2)}$ active, the value of r_{33} being 0.8 pm V^{-1} following fixed electrode poling at $17.5 \text{ V } \mu\text{m}^{-1}$. The polymers did not melt below the decomposition temperature, and all transitions shown in the DSC thermogram to 300°C were found to be absent on repeat scans. Thermogravimetric and thermal dynamic analysis of the polymer where Z = 1,4-benzene showed decomposition commencing at 290°C and continuing up to ca. 750°C . The residue was composed of α -SiC and amorphous carbon. Treatment of the same polymer with BH_3/SMe_2 gave rise to an insoluble polymer containing boron. The polymer where Z = 6,6'-bipyridine reacted with copper(II) trifluoromethanesulfonate to give a copper(II)-containing polymer, hydrazine reduction of which afforded the corresponding Cu^{I} -containing polymer.

1. Introduction

There is current interest in polycarbosilanes containing main-chain acetylene and other unsaturated groups [1–3], in particular since some of the properties are consistent with electron delocalization through the silicon atoms suggesting $d_{\pi}\text{-}p_{\pi}$ backbonding or $\sigma^*\text{-}\pi$ hyperconjugation [4].

Polycarbosilanes of the type described here with both acetylene and aromatic groups in the backbone have been prepared in the past by reaction of the

disodium or dilithium salt of *p*-diethynylbenzene with a dialkyl- or diaryldichlorosilane [5–8]:



As we have reported recently in a preliminary communication [2], such polycarbosilanes may also be obtained by using the palladium-catalyzed cross-coupling of aryl halides with acetylenic reagents [9–11], a reaction previously employed by us for the preparation of acetylene-terminated monomers and oligomers [12]. We describe here in detail the preparation and some properties of a series of polymers prepared from diethynyl-

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TABLE 1. Preparative details for $\text{-(C}\equiv\text{C-SiPh}_2\text{-C}\equiv\text{C-Z)}_n\text{-}$ polycarbosilanes

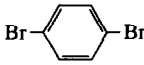
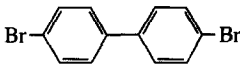
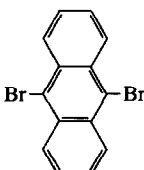
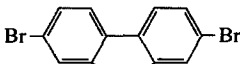
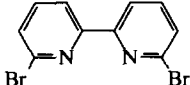
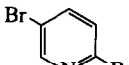
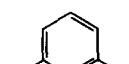

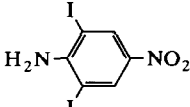
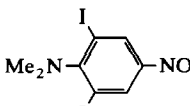
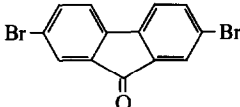
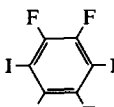
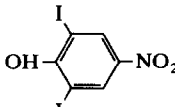
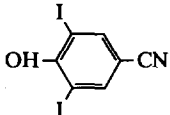
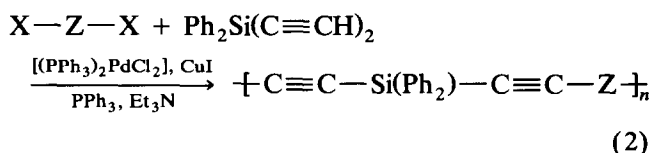
Polymer	Aromatic dihalide X-Z-X	Reactant proportions ^a	Catalyst proportions ^b	Solvent ^c	Reaction time (h)	Polymer colour	Yield (%)
I		A	L	S	16	Light brown	87
II		B	L	T	16	Beige	81
III		A	L	T	16	Dark red	66
IV		A	L	S	16	Cream	89
V		A	L	T	16	Dark brown	86
VI		B	L	S	16	Dark brown	89
VII		C	L	S	16	Brown	75
VIII		C	M	U	16	Dark brown	85
IX		A	L	T	2.5	Orange	70
X		A	N	S	2.0	Brown	80
XI		A	N	T	16	Brown	82
XII		A	N	T	16	Dark brown	79
XIII		C	L	T	16	Brown	87

TABLE 1. (continued)

Polymer	Aromatic dihalide X-Z-X	Reactant proportions ^a	Catalyst proportions ^b	Solvent ^c	Reaction time (h)	Polymer colour	Yield (%)
XIV		C	L	T	16	Yellow	58

^a In all cases, quantities relate to 1 mmol of aromatic dihalide. Amount of $\text{Ph}_2\text{Si}(\text{C}\equiv\text{CH})_2$: (A) 1.00 mmol; (B) 1.05 mmol; (C) 1.10 mmol. ^b L, $(\text{PPh}_3)_2\text{PdCl}_2$ (0.001 g, 1.4×10^{-3} mmol), CuI (0.0043 g, 2.25×10^{-2} mmol), PPh_3 (0.01 g, 3.81×10^{-2} mmol); M, $(\text{PPh}_3)_2\text{PdCl}_2$ (0.007 g, 9.8×10^{-3} mmol), CuI (0.0057 g, 2.98×10^{-2} mmol); N, $(\text{PPh}_3)_2\text{PdCl}_2$ (0.014 g, 19.6×10^{-3} mmol), CuI (0.0057 g, 2.98×10^{-2} mmol). ^c S, 6 ml of Et_3N ; T, 3 ml of Et_3N , 3 ml of PhMe; U, 0.5 ml of Et_3N , 5.5 ml of PhMe.

diphenylsilylene and dihaloarenes [$\text{X} = \text{Br}$ or I ; $\text{Z} =$ (hetero)aromatic group]:



This Pd-catalyzed cross-coupling route is of wide scope because of the extensive range of Z groups,

including those that are heteroaromatic [13–18], which may be incorporated into the polymers.

Since submission of our initial communication describing this work [2], the same route to the polymers has been described by other workers [19]. We have previously reported that doping certain of the polymers with FeCl_3 renders them semiconducting [20].

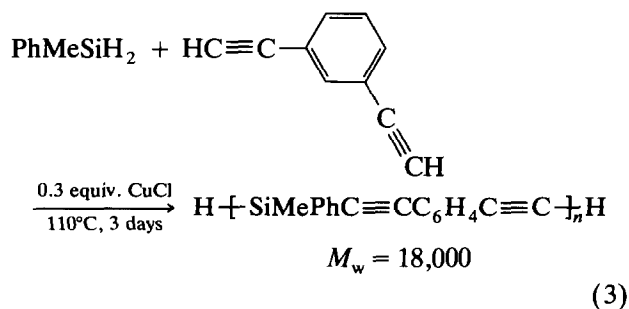
Recently, a novel route to polymers of the type reported in the present work has been described, involving copper(I) chloride-catalyzed dehydrocoupling

TABLE 2. Spectral and molecular weight data for $\text{-(C}\equiv\text{C)-SiPh}_2\text{-C}\equiv\text{C-Z-}_n$ polycarbosilanes

Polymer ^a	IR $\nu(\text{C}\equiv\text{C})$ (cm^{-1})	UV/visible λ_{max} (nm) ^b	NMR δ (ppm) ^c			M_w ^c	M_w/M_n ^c	n ^f	
			¹ H	²⁹ Si	¹³ C ^d				
					C_α				C_β
I	2145	284, 302	6.9–7.4 7.7–8.2	–48.0	90.4	108.4	34 047	3.54	109
II	2145	304	6.8–8.4	–48.0	89.1	108.9	8972	1.44	23
III	2110	266, 420 450	7.5–8.1 8.4–8.8 9.0–9.5	–47.4	102.2	106.1	23 543	3.15	56
IV	2135	322, 340	3.2 s (2H) 7.0–8.4 (16H)	–48.1	88.5	109.8	10 963	2.67	26
V	2150	298	6.6–7.4 (10H) 7.4–8.8 (6H)	–47.1	87.8	107.7	8077	2.50	20
VI	2155	268, 300	6.7–7.4 7.6–8.0	–47.4	90.1 94.0	105.2 107.0	6632	1.73	20
VII	2165	296	6.9–8.0				2635	1.39	8
VIII	2137	304	6.9–7.9				10 119	3.23	32
IX	2150	355	3.3 (2H) 6.3–8.4 (12H)	–47.8	96.2	106.2	4741	1.45	13
X	2150	386	3.0 (6H) 7.0–8.2 (12H)	–47.8	94.9	106.5	8974	2.42	21
XI	2157	285, 325 340, 420	6.9–8.0				9766	2.95	23
XII	2174	269, 283	6.6–7.8				6628	2.20	17
XIII	2137	256	7.0–8.0				2641	1.92	7
XIV	2153		7.0–8.0				3120	2.02	8

^a See Table 1. ^b In CH_2Cl_2 solution. ^c Reference, $\text{Si}(\text{CH}_3)_4$; solvent, CDCl_3 or C_6D_6 . ^d $\text{Si}-\text{C}_\alpha=\text{C}_\beta-\text{Ar}$. ^e Determined by SEC, with reference to polystyrene standards. ^f Calculated from the value of M_w , neglecting end-groups.

polymerization of phenylmethylsilane with *m*-diethynylbenzene for several days at 110°C in the presence of an amine [3].



2. Results and discussion

Polycarbosilanes I–XIV were prepared by the cross-coupling reaction (2). The specific reaction conditions for each polymer are given in Table 1. Diethynyldiphenylsilane and the appropriate aromatic dihalide were heated in triethylamine, alone or with toluene, under reflux in the presence of dichlorobis(triphenylphosphine)palladium and copper(I) iodide, and in some cases triphenylphosphine. Except for IX and X, for which much shorter reaction times were used (Table 1), the reaction was complete after 16 h as monitored by the disappearance of the IR diethynyldiphenylsilane $\nu(\text{C}\equiv\text{C})$ absorbance at 2040 cm^{-1} and appearance of that arising from the polymer (see Table 2). In some cases, ethynyltrimethylsilane was added as a potential chain terminating agent. However, this was unsuccessful since the IR and NMR spectra showed no evidence of Me_3Si groups. On completion of the reaction (as shown by IR, normally after 16 h), the solvent was removed under vacuum, the polymer was taken up in THF, and the solution filtered through diatomaceous earth. Addition of pentane precipitated the polymer. In spite of the amine salt $[\text{Et}_3\text{NH}]\text{X}$ being practically insoluble in THF, ^1H and ^{13}C NMR spectra showed contamination by amine salt in some cases. However, the polymers could be purified by repeated precipitation from THF by addition of pentane. Various other methods of purification were tried unsuccessfully as described previously [2]; namely, extraction with methanol (which led to cleavage of the Si–alkynyl bond), and elimination of traces of $[\text{Et}_3\text{NH}]\text{X}$ by sublimation under high vacuum. In addition, removal of the salt by stirring the crude polymer in dichloromethane in the presence of the anion exchange resin [Bio-Rad AG1X8(HCO_3^-)] was carried out [21]. However, this resulted in a greatly reduced molecular weight, in the case of I M_w decreasing from 29,630 to 2695.

Attempts were made to synthesize the polymers by using immobilized amines on inert supports in place of

triethylamine. The heterogeneous reagents were pre-dried by Soxhlet extraction with triethylamine, the latter being distilled over powdered potassium hydroxide. With 3-aminopropyltriethylsilane-treated glass beads (Petrarch), low oligomers were obtained (SEC, IR) after reaction for many hours in toluene. With Amberlyst A21 resin (Aldrich) also in toluene, the extent of polymerization was slightly greater, but still much less than in the presence of triethylamine.

Various catalysts and solvents have been used previously for coupling reactions of this type, as we have already discussed [2]. With diethylamine or piperidine in place of triethylamine, we found no significant differences in the product yield and molecular weight characteristics. The main factor influencing molecular weight is the co-solvent. Thus, in the case of III, the value of M_w decreased to 6800 when the polymerization was performed in neat triethylamine, and it was only slightly greater when a 1:2 v/v mixture of $\text{Et}_3\text{N}/\text{PhMe}$ was used. The addition of the required amount of toluene increases the solubility of the incipient polymer, so increasing the molecular weight. In the case of the thiophene-containing polymer VIII, optimum molecular weight properties were obtained with a 1:11 v/v $\text{Et}_3\text{N}/\text{PhMe}$ solvent mixture.

Equimolar proportions of the two reactants were generally used. In some cases, a small excess of diethynyldiphenylsilane was employed but this did not affect the molecular weight characteristics. Various proportions of dichlorobis(triphenylphosphine)palladium in the catalyst mixture were used (see Table 1); at the higher levels, triphenylphosphine was omitted since its presence was without effect.

In the case of polymers IX and X, the reaction times were very short. Longer times resulted in lower molecular weights, presumably because of side reactions.

The UV/visible absorbances of the polymers (Table 2) include high wavelength bands for III and XI containing anthracene and fluorenone groups, respectively. These wavelengths correspond to a band gap of 2.75 eV for III and 2.95 eV for XI [22]. Indeed, the polymers are all electrically non-conducting when not doped [20].

The ^{13}C NMR spectra show the expected two acetylene carbon resonances, C_α and C_β . In the particular case of VI containing 2,5-pyridine groups, two C_α and two C_β resonances are observed, each acetylene-pyridine linkage being in either the 2- or 5-pyridine position.

The polymers do not melt below their decomposition temperature, the latter being in excess of 200°C. Differential scanning calorimetric (DSC) thermograms for a selection of the polymers were run from 10°C to 300°C (Table 3). Various exotherms were observed in

TABLE 3. DSC results for polymers I–III, IX and X ^a

Polymer ^b	Exotherm peak temperature (°C) ^c	
	Major	Minor
I	235, > 300	90, 150
II	235, 280	100
III	–	150, 260
IX	200	75
X	200, > 300	100 (<i>endo</i>)

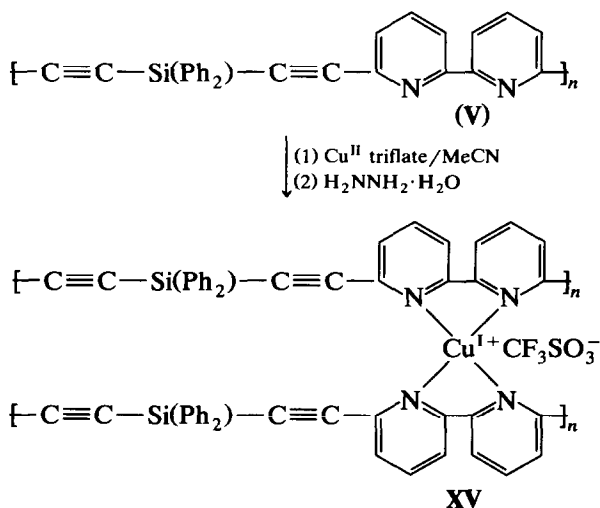
^a From 25°C to 300°C at heating rate of 20°C min⁻¹. ^b See Table 1.

^c All peaks exothermic except minor endothermic peak for X. In all cases, the initial peaks were absent in repeat scans.

the initial scans, but these were all absent in repeat scans. In the case of X, a minor endotherm at 100°C occurred in the initial run, but this also was absent in repeat scans. These transitions appear to correspond to realignment of the polymer chains. Similar processes can be observed under the polarizing microscope on physical deformation of the polymers.

The thermogravimetric analysis (TGA) trace for I heated under Ar from 30°C to 1200°C showed an overall weight loss of 21%, commencing at *ca.* 290°C and continuing up to *ca.* 750°C. The differential thermal analysis (DTA) trace showed no transition below 300°C. The black residue was found by X-ray diffraction to contain α -SiC as well as amorphous carbon.

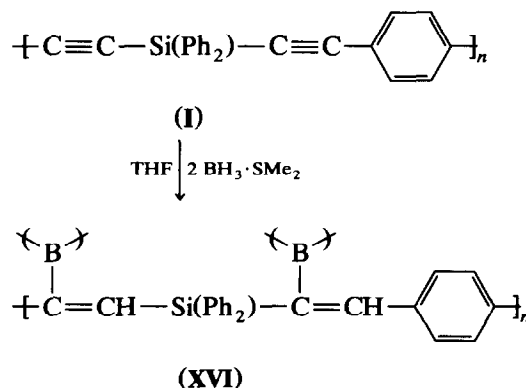
The insoluble copper(I)-containing polymer XV was prepared by reaction of V with 0.5 equiv. of copper(II) triflate in acetonitrile followed by reduction of the resulting Cu^{II} complex with hydrazine monohydrate.



Incorporation of Cu^I gives rise to a reduction in the IR $\nu(\text{C}\equiv\text{C})$ stretching frequency from 2150 cm⁻¹ to 2017 cm⁻¹. Two resonances were observed for XV in the solid state ²⁹Si NMR spectrum at chemical shifts of δ -34.8 ppm and δ -39.0 ppm whereas the parent polymer V exhibited a single resonance at δ -47.1

ppm. The presence of two ²⁹Si NMR resonances may result from Si adjacent to one or two Cu^I-bispyridine complexes. The acetylene ¹³C NMR resonances in the solid state spectrum were of too low intensity to be detectable, and the other resonances were very broad and unresolved. No resonances were detected in the solid state ⁶³Cu NMR spectrum. This may be because the coordination environment of the copper is severely distorted from tetrahedral [23]. Microanalysis suggested that copper had not been introduced at all the bispyridine sites (see Experimental section). However, elemental analysis in the case of polycarbosilanes is not generally a good indication of purity because of ceramic formation.

The insoluble boron-containing polymer XVI was prepared by treatment of I with 2 equiv. of BH₃·Me₂S in THF.



The presence of a $\nu(\text{C}\equiv\text{C})$ band at 2126 cm⁻¹ in the IR spectrum indicates that the highly crosslinked polymer also contains some unreacted acetylene groups. The solid state ¹¹B spectrum showed a main resonance at δ -0.5 ppm. The solid state ²⁹Si NMR spectrum exhibited a single broad resonance at δ -8.7 ppm whereas that for the parent polymer I occurs at δ -48.0 ppm. Microanalysis suggested that boron had not been introduced at all the acetylene sites (see Experimental section). However, as mentioned above, elemental analysis in the case of polycarbosilanes is often unreliable.

2.1. $\chi^{(2)}$ non-linear optical measurements

Polymer X, which contains a donor-acceptor group in the main chain, exhibits stable $\chi^{(2)}$ non-linear optical (NLO) effects [24]. Films of X were prepared by spin-coating solutions of the polymer in 1,2,3-trichloropropane. Fixed-electrode poling with a poling field of 11.7 V μm^{-1} for 10 min was carried out at various temperatures, and the electro-optic coefficient, r_{33} , was measured. The maximum poling response was at 85°C (Fig. 1). After fixed-electrode poling at 17.5 V μm^{-1} , the value of the electro-optic coefficient was 0.8 pm V⁻¹. The electro-optic response shows no measur-

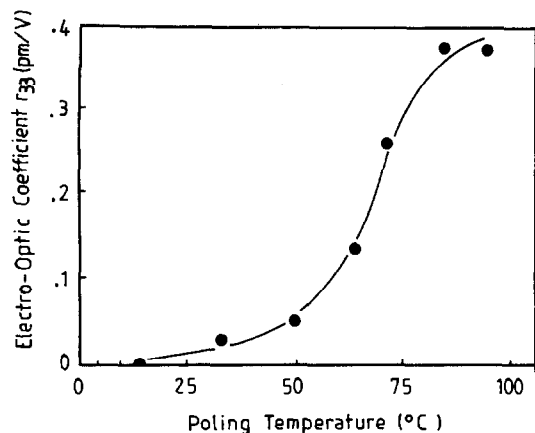
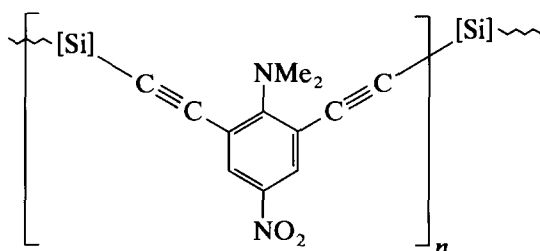


Fig. 1. Poling efficiency vs. temperature for a film of X.

able decay at room temperature over a period of at least 16 days. The NLO-active donor-acceptor group is contained in a segment in the polymer chain which adopts a rigid V conformation so restricting rotation of the group on application of the poling field.



The effective number density of NLO groups in the polymer is thus reduced to those at chain ends, these being the only ones free to re-orient. We aim to increase the magnitude of the effect by incorporating groups with a more favorable dipole orientation.

2.2. Conclusion

We have shown that polycarbosilanes with main chain arylene and acetylene groups can be prepared using a palladium-catalyzed cross-coupling reaction between dihaloarenes and diethynylsilanes. A wide variety of arene groups can be incorporated into the polycarbosilane backbone, and in the case of bispyridine groups, these can be used as ligands for copper. Boron-containing polymers may be prepared by hydroboration. Polymers with main chain donor-acceptor NLO active groups are readily obtainable. Owing to the rigidity of the polymer chain, the electro-optic response shows no decay over extended periods.

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. Molecular weights were determined by size-exclusion chromatography (SEC) using a Waters 510 system equipped with 100, 500, 1000 and 10000 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. TGA and DTA were carried out using a Netzsch STA 409 thermobalance. X-Ray analysis was performed by Rhône-Poulenc, and elemental analyses were done by the CNRS Service Central d'Analyse. Except for diethynyldiphenylsilane [25,26], 6,6'-dibromo-2,2'-bipyridyl [27], and 2,6-diiodo-4-nitro-*N,N*-dimethylamine (see below), the monomers and catalysts were commercial samples and used as received.

3.1. Preparation of 2,6-diiodo-4-nitro-*N,N*-dimethylaniline

Following the literature method for conversion of arylamines to *N,N*-dimethylarylamines with trimethyl phosphate [28], 2,6-diiodo-4-nitroaniline (25.0 g, 3.8 mmol) was heated under reflux in *ca.* 80 ml of (MeO)₃PO for 4 days. The reaction mixture was purified by flash chromatography on silica gel with pentane/diethyl ether (9:1 v/v) eluent. The desired product was eluted first as a yellow band. Recrystallization from hexane afforded the product as orange crystals in 50% yield (m.p. 50.2–50.6°C). ¹H NMR (CDCl₃): δ 8.65 (2H), 2.9 (6H) ppm.

3.2. Preparation of polymers I–XIV

The reactant and catalyst quantities are given in Table 1, as are the specific reaction conditions in each case. A mixture of diethynyldiphenylsilane, aromatic dihalide, dichlorobis(triphenylphosphine)palladium, copper(I) iodide (and in some cases triphenylphosphine) was stirred under N₂ in triethylamine (and sometimes also toluene) at 89°C. The reaction was monitored by following the evolution of the relative intensities of the ν(C≡C) IR absorbances for the starting diethynyldiphenylsilane (2040 cm⁻¹) and for the incipient polymer (see Table 2). On completion of the reaction (normally after 16 h), the solvent was removed under vacuum to give a solid which was extracted with THF (*ca.* 50 ml), in which the amine salt is practically insoluble. The resulting solution was filtered through diatomaceous earth, concentrated and the polymer

precipitated by addition of pentane. The spectral and other data for the polymers are given in Table 2.

3.3. Preparation of XV

Following the literature method for the formation of copper complexes of polymers containing bis(pyridine) moieties [29], copper(II) triflate (0.362 g, 1 mmol) in 10 ml acetonitrile was added at room temperature to V (0.80 g, 2.08 mmol) dissolved in 40 ml of dichloromethane. The blue-green solution of the Cu^{II} complex thus obtained was stirred for 10 min. Addition of an excess of hydrazine monohydrate (3 ml) gave rise to reduction of Cu^{II} to Cu^I with the concomitant change to red. After the reaction mixture had been stirred for 15 min, the solvent was removed and the residue was dissolved in dichloromethane (50 ml). The resulting solution was filtered and the product was obtained in quantitative yield on addition of pentane to the filtrate. IR: $\nu(\text{C} \equiv \text{C})$ 2017 cm⁻¹. ²⁹Si NMR (solid state): δ -34.8, -39.0 ppm. Anal. Found: Cu, 4.50. C₅₃H₃₂CuF₃N₄O₃SSi₂ calc.: Cu, 6.47%.

3.4. Preparation of XVI

A 2.0 M solution of BH₃ · SME₂ in THF (0.7 ml, 1.4 mmol) was added to I (0.21 g, 0.69 mmol) dissolved in THF (50 ml). After the reaction mixture had been stirred at room temperature for 16 h, the solvent was removed under vacuum thus affording the product in quantitative yield. ²⁹Si NMR (solid state): δ -8.7 ppm. ¹¹B NMR (solid state): δ -0.5 ppm. Anal. Found: B, 4.90. C₂₂H₁₆B₂Si calc.: B, 6.55%.

3.5. Differential scanning calorimetry

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 exotherms observed are listed in Table 3. The samples were cooled to 10°C, and the thermograms re-run. The exotherms observed in the initial runs were absent in the second runs.

3.6. Thermogravimetric analysis and differential thermal analysis

A sample of I (ca. 14 mg) was heated under Ar from 30°C to 1200°C at a heating rate of 10°C min⁻¹. Weight loss commenced at ca. 290°C and attained 21% at 1200°C. DTA showed no transitions below 300°C. The black residue was found by X-ray diffraction to contain α -SiC as well as amorphous carbon.

3.7. Non-linear optical measurements

Solutions of 17% w/w of X were prepared in 1,2,3-trichloropropane and were filtered through 0.5 μm Millipore disposable filters. Thin films of the polymer were prepared by spin coating at 1300 rev./min onto

indium tin oxide coated glass slides followed by drying under vacuum at 80°C for 1–2 h. Silver contacts were deposited onto the top surface, and were subsequently used as both electrode and mirror. Fixed-electrode poling with a poling field of 11.7 V μm^{-1} for 10 min was carried out at various temperatures, and the electro-optic coefficient, r_{33} , was measured. The maximum poling response was at 85°C. After fixed-electrode poling at 17.5 V μm^{-1} , the value of r_{33} was found to be 0.8 pm V⁻¹. The electro-optic response showed no measurable decay at room temperature over a period of at least 16 days.

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