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# Synthesis and characterization of poly[(silylene)arylene] statistical copolymers

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New poly[(silylene)arylene] statistical copolymers with $\sigma$-conjugated silicon and $\pi$-conjugated carbon main-chain units are reported. They are synthesized in single-stage reactions by the Wurtz-type co-condensation of a dichlorosilylene and a dibromoaryl. Soluble polymers have been prepared with symmetrically and asymmetrically substituted silicon atoms, and several different arylene groups have been introduced into the polymer chains. The composition of the copolymers can be varied in a controlled way by altering the stoichiometry of the reaction mixture. The u.v.-visible spectra of the copolymers correlate with the degree of silicon catenation. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: poly[(silylene)arylene]s; copolymers; polyorganosilylenes)**

## *Introduction*

Among the extensive recent research into silicon-based polymers[1-3], there have been many reports of polymers containing $\sigma$-conjugated silicon and $\pi$-conjugated aromatic carbon units in the main chain. These poly[(silylene)arylene] polymers have potential for application as electronic or photosensitive materials, and as ceramic precursors[4,5].

Poly[(silylene)arylene]s have previously been synthesized by methods such as: Wurtz coupling of chlorosilyl-substituted aryls[4,6,7]; reaction of dichlorosilylenes with lithium aryls[5,8] or dibromoaryl Grignard reagents[9,10]; reaction of phenylenebis(silandiyl triflate)s with nucleophiles or dibromoaryl Grignard reagents[11]; nickel-catalysed dehalogenative cross-coupling of bis(bromophenyl)silylene Grignard reagents with dibromoaryls[7]; dehydropolymerization of bis(silyl)arenes[12]; and ring-opening polymerization of cyclic disilabenzo compounds[13]. All these methods give polymers with regular alternating arrangements of silylene and arylene units in the polymer chain. The silylene/arylene ratio can be varied only by the use of specially synthesized monomers[7,8]. Additionally, some of the polymer molecular weights that have been reported are very low.

We now report the preparation of new poly[(silylene)-arylene] statistical copolymers. They contain silylene and arylene units in random sequences of single units and short blocks. Soluble statistical copolymers containing a wide range of silylene and arylene structural units can be synthesized in single-stage reactions from readily available dichlorosilylene and dibromoaryl monomers. By altering the stoichiometry of the reaction mixture, the composition of the copolymers can be continuously varied in a controlled way between the extremes of pure poly(silylene) and pure poly(arylene). This permits detailed study of the variation of the electronic and optical properties of the copolymers with chain composition.

## *Experimental*

Statistical copolymers were prepared by Wurtz-type co-condensation of dichlorosilylenes and dibromoaryls with sodium metal in refluxing toluene:

$$m(\mathrm{R_1R_2SiCl_2}) + n(\mathrm{Br-Ar-Br}) + 2(m+n)\mathrm{Na} \rightarrow$$
$$-[-\mathrm{R_1R_2Si}-]_m[-\mathrm{Ar}-]_n- + 2m\,\mathrm{NaCl} + 2n\,\mathrm{NaBr}$$
$$\text{(a)}\ \mathrm{R_1 = Ph,\ R_2 = Me;\ (b)\ R_1 = R_2 = Ph;}$$
$$\text{(c)}\ \mathrm{R_1 = R_2 = Me}$$

All reactions were carried out using Schlenk-tube techniques under a dinitrogen or argon atmosphere. Typically, 2.45 ml (2.88 g, 15.1 mmol) of dichloromethylphenylsilylene and 3.56 g (15.1 mmol) of 1,4-dibromobenzene were refluxed with 1.53 g (66.4 mmol, a 10% excess) of small, freshly cut sodium pieces and 1.32 ml (1.46 g, 6.6 mmol) of 15-crown-5 in 40 ml of toluene with rapid stirring for 3 h. The blue colour characteristic of Wurtz reactions[14,15] was observed, except in cases where it was masked by the colour of the copolymer products. After cooling, 15 ml of methanol was added to quench the reaction and then 40 ml of water was added to remove ionic sodium halide products. The copolymer was precipitated by adding the organic layer to 200 ml of methanol, and collected by filtration. Oligomeric products were removed by extraction with hexane.

The product from the 1/1 stoichiometric reaction mixture of dichloromethylphenylsilylene and 1,4-dibromobenzene described above was characterized as follows. Yield: 1.13 g (38%) of yellow solid; m.p. 126–146°C. $^1$H n.m.r. ($\mathrm{CD_2Cl_2}$, 270 MHz): $\delta$ – 0.87 to 1.19 (broad, $\mathrm{CH_3}$-Si), 6.01–8.75 (broad, aromatic H), together with 3.19–3.79 (weak, O-$\mathrm{CH_3}$ endcapping groups). Relative integrals of aliphatic/aromatic protons

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**Table 1** Representative results of copolymer syntheses with dichloromethylphenylsilylene and dibromoaryls in 1/1 stoichiometry in refluxing toluene. Syntheses with 15-crown-5 additive used it in 10% molar ratio to the sodium

| Silylene | Dibromoaryl | 15-Crown-5 | Yield (%) | $M_w$ | $M_n$ |
|---|---|---|---|---|---|
| $PhMeSiCl_2$ | 1,4-Dibromobenzene | Yes | 38 | 46 000 | 3500 |
| $PhMeSiCl_2$ | 1,4-Dibromobenzene | No | $6^a$ | | |
| $PhMeSiCl_2$ | 1,3-Dibromobenzene | Yes | 18 | 19 500 | 3300 |
| $PhMeSiCl_2$ | 1,3-Dibromobenzene | No | $6^b$ | 6600 | 1950 |
| $PhMeSiCl_2$ | 1,2-Dibromobenzene | Yes | 16 | 3500 | 1550 |
| $PhMeSiCl_2$ | 1,2-Dibromobenzene | No | 20 | 8200 | 1200 |
| $PhMeSiCl_2$ | 9,10-Dibromoanthracene | No | $30^b$ | 21 700 | 1350 |
| $PhMeSiCl_2$ | 4,4′-Dibromobiphenyl | Yes | $10^b$ | 13 700 | 3000 |
| $PhMeSiCl_2$ | 2,5-Dibromothiophene | No | 38 | 19 500 | 5600 |
| $PhMeSiCl_2$ | 2,6-Dibromopyridine | No | $57^b$ | | |

[a] Denotes an almost completely insoluble product
[b] Denotes the presence of a less soluble fraction

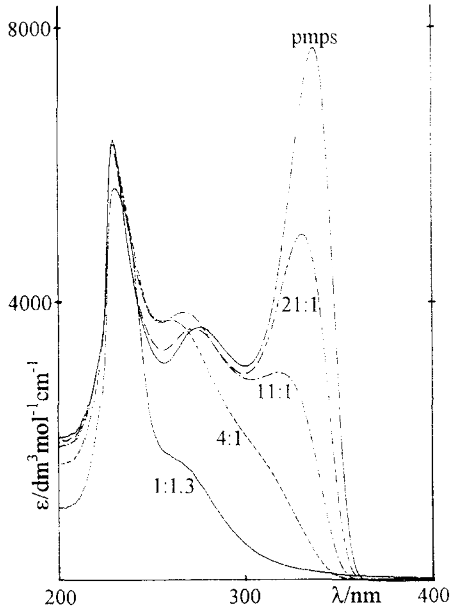

**Figure 1** U.v. spectra in dichloromethane solution of poly(methylphenylsilylene) (pmps) and poly(methylphenylsilylene-*co*-(*p*-phenylene) polymers of different silylene/phenylene compositions *m/n*. Values of the molar extinction coefficient $\epsilon$ are normalized to the concentrations of chain units

(ideal ratio for 1/1 copolymer 3/9) were 3/10.2, corresponding to a polymer—$[PhMeSi]_m[C_6H_4]_n$—with silylene/phenylene ratio $m/n$ of 1/1.3. $^{13}C$ n.m.r. ($CDCl_3$): $\delta$ – 3.45 ($CH_3$-Si), 124.24, 126.54, 127.80, 128.63, 129.36, 134.50, 135.23, 135.75 and 137.14 (phenyl and phenylene). $^{29}Si$ n.m.r. ($CDCl_3$): −11.20 (*s*) with additional minor peaks at −0.87 (*s*), −8.50 (*s*) and −23.20 (*s*). U.v.–vis. $\lambda_{max}$ 230 and 275 nm (shoulder). Anal. (calculated for $m/n$ 1/1.3 C 81.11%, H 6.07%); found C 78.36%, H 6.43%. Size exclusion chromatography: $M_w$ 46 000; $M_n$ 3500, relative to polystyrene standards.

## *Results and discussion*

In the first instance, statistical copolymers containing asymmetrically substituted silicon atoms were prepared (*Table 1*) by reaction of dichloromethylphenylsilylene with a range of dibromoaryls in a 1/1 stoichiometric ratio. The dibromoaryls successfully used to give copolymers included *ortho*-, *meta*- and *para*-substituted isomers of dibromobenzene, systems containing more than one aromatic ring, and examples containing a sulfur or nitrogen heteroatom. Except in one case, the copolymers showed good solubility in solvents such as tetrahydrofuran (THF) and $CH_2Cl_2$, although some products contained a less soluble fraction. Though most of the molecular weight distributions were monomodal, in many cases there was a high molecular weight tail extending beyond 100 000 Da and it is this that is responsible for the high polydispersities.

Spectroscopy and solubility properties showed the products to be true copolymers and not mixtures of polymers and copolymers with different main-chain compositions. The characteristic u.v. band of poly(methylphenylsilylene) at 337 nm was not observed in any of the products in *Table 1*, and any polyarylenes formed would be intractable solids. In every case, Soxhlet extraction of the products with a range of solvents gave separate high and low molecular weight fractions with u.v.–vis. $\lambda_{max}$ and molar absorption coefficient $\epsilon$ identical to those of the original product.

The main-chain compositions of the copolymers, while close to the 1/1 stoichiometry of dichloromethylphenylsilylene to dibromoaryl, did not correspond exactly to this ratio. Integrations of aliphatic and aromatic regions of $^1H$ n.m.r. spectra showed that 1/1 monomer feeds gave poly(methylphenylsilylene)-*co*-(*p*-phenylene) with a silylene/phenylene ratio of 1/1.3, and poly(methylphenylsilylene)-*co*-(2,5-thiophenylene) with a silylene/thiophenylene ratio of 1/1.2. U.v.–vis. spectra of the other copolymers obtained using 1/1 monomer feeds closely resembled that shown in *Figure 1* for the 1/1.3 poly(methylphenylsilylene)-*co*-(*p*-phenylene), showing them to have similar compositions.

The yields of the new copolymers were comparable with those obtained in the Wurtz synthesis of poly(silylene)s under the same conditions[15]. However, significant differences were found between these syntheses. Yields in poly(silylene) syntheses can be improved by carrying out the reaction in refluxing diethyl ether at 35°C, with the addition of a crown ether[16]. In contrast, to achieve reasonable yields of poly[(silylene)arylene] copolymers, synthesis at the temperature of refluxing toluene (111°C) was necessary. Additionally, the beneficial effect of crown ether on polymer yield was not clear in the copolymer syntheses.

Copolymer syntheses were also attempted with dichloroaryls, but these did not give satisfactory results, because of their low reactivity. The dibromoaryls have similar reactivity to the dichlorosilylenes. Attempts to synthesize copolymers containing aliphatic carbon main-chain units, by reacting dichloromethylphenylsilylene with linear and branched dibromoalkyls, were also unsuccessful. This can be attributed to the aliphatic monomers being unable to sustain the stable anionic reaction intermediate required in the Wurtz reaction[15].

*Table 2* shows representative results of copolymerizations of the symmetrically substituted silylenes, dichlorodimethylsilylene and dichlorodiphenylsilylene, with dibromoaryls in a 1/1 stoichiometric ratio. These copolymers also showed good solubility. This is noteworthy, as the symmetrically substituted poly(silylene)s, poly(diphenylsilylene) and poly(dimethylsilylene)[1], and the other end member of this composition series, poly(*p*-phenylene)[17], are all intractable solids. In the copolymers, the potential for close molecular association

**Table 2** Representative results of copolymer syntheses with symmetrically substituted dichlorosilylenes and dibromoaryls in 1/1 stoichiometry in refluxing toluene. Syntheses with 15-crown-5 additive used it in 10% molar ratio to the sodium

| Silylene | Dibromoaryl | 15-Crown-5 | Yield (%) | $M_w$ | $M_n$ |
|---|---|---|---|---|---|
| $Me_2SiCl_2$ | 1,4-Dibromobenzene | No | 20 | 6750 | 1900 |
| $Me_2SiCl_2$ | 1,3-Dibromobenzene | Yes | 3 | 8500 | 2500 |
| $Me_2SiCl_2$ | 1,2-Dibromobenzene | Yes | 11 | 12 700 | 3800 |
| $Ph_2SiCl_2$ | 1,4-Dibromobenzene | Yes | 23 | 26 100 | 2500 |
| $Ph_2SiCl_2$ | 2,5-Dibromo-*p*-xylene | Yes | 16[a] | 3550 | 1000 |
| $Ph_2SiCl_2$ | $\alpha,\alpha'$-Dibromo-*p*-xylene | Yes | 67[a] | 27 900 | 1950 |

[a] Denotes the presence of a less soluble polymer fraction

**Table 3** Representative results of copolymer syntheses with dichloromethylphenylsilylene and 1,4-dibromobenzene in different stoichiometries in refluxing toluene. All syntheses used 15-crown-5 additive in 10% molar ratio to the sodium

| Reagent mixture (silylene/phenylene) | Copolymer composition | Yield (%) | Colour | $M_w$ | $M_n$ |
|---|---|---|---|---|---|
| 20/1 | 21/1 | 35 | White | 5700 | 5000 |
| 10/1 | 11/1 | 35 | White | 4800 | 2700 |
| 5/1 | 4/1 | 42 | White | 6500 | 3300 |
| 2/1 | 1.6/1 | 30 | Pale yellow | 6800 | 2100 |
| 1/1 | 1/1.3 | 38 | Yellow | 46 000 | 3500 |
| 1/2 | — | 5 | Light brown | 5100 | 2600 |
| 1/4 | — | 23 | Brown, insoluble | — | — |

is destroyed without recourse to the introduction of long-chain alkyl substituents, which is the usual strategy to induce solubility in the homopolymers[1,17].

An important advantage offered by statistical copolymers is that their composition can be varied in a controlled way by varying the stoichiometry of the reaction mixture. This offers potential for controlling the properties of the polymers, which is not available to their ordered analogues. *Table 3* shows the results of syntheses with dichloromethylphenylsilylene and 1,4-dibromobenzene in various stoichiometries. These copolymers were soluble in solvents such as THF and $CH_2Cl_2$ over a wide range of composition. Only copolymers containing a high proportion of *p*-phenylene units were insoluble. The silylene/arylene ratios $m/n$ of the copolymers, determined from the relative integrals of the aliphatic and aromatic regions of the $^1H$ n.m.r. spectra, were broadly in line with the stoichiometry of the reaction mixtures, containing a slightly enhanced proportion of the *p*-phenylene units except at the highest silylene contents. From Fineman and Ross copolymer reactivity plots[18], reactivity ratios $r_{Si} = 1.1 \pm 0.1$ and $r_{Ar} = 2.0 \pm 0.3$ were derived, indicating a slight preference for arylene units to add another arylene unit and thus appear in short blocks. However, the $^{29}Si$ n.m.r. spectrum of the copolymer obtained from the 1/1 reaction mixture did not show the broad triad structure as found in poly(methylphenylsilylene)[19,20], but was dominated by a single sharp peak at $-11.26$ ppm, showing an absence of silicon catenation.

The effect of varying composition on the u.v. spectra of poly(methylphenylsilylene)-*co*-(*p*-phenylene) polymers in solution is shown in *Figure 1*. In poly(methylphenylsilylene) of similar $M_w$ to the copolymer samples, the absorption at 337 nm arises from the $\sigma \rightarrow \sigma^*$ transition of the catenated silicon atoms[1]. As the silylene/phenylene ratio $m/n$ in the copolymers was reduced, this absorption band moved to shorter wavelength, and its intensity decreased. These changes correlate with the statistical probability of silicon catenation. The secondary poly(methylphenylsilylene) absorption band at 273 nm moved to slightly shorter wavelength, and was lost at the lowest silylene content. However, the $\pi \rightarrow \pi^*$ band associated with the aromatic groups at about 230 nm remained almost unchanged in intensity. This is consistent with each repeat unit containing one aromatic ring, and indicates that any interaction of the $\pi$ system with the Si atoms[21,22] is unaffected by the location of the ring in either the polymer chain or as a substituent.

Poly(methylphenylsilylene), and statistical copolymers containing mainly silylene units, absorb only in the u.v. region, and are consequently white. As the proportion of phenylene units in the copolymer was increased, the u.v. spectra developed a long-wavelength tail extending beyond 400 nm into the visible region. This gave yellow colours to most of the statistical copolymers obtained from 1/1 stoichiometric reaction mixtures. In copolymers containing a higher proportion of phenylene units, this progressively darkened towards the brown of poly(*p*-phenylene) (*Table 3*).

Poly[(silylene)arylene] statistical copolymers can be expected to have interesting electrical properties, because of the presence of $\sigma$-conjugated silicon and $\pi$-conjugated aromatic carbon units in the main chain. There is also the possibility of $d_\pi - p_\pi$ interactions between empty silicon d-orbitals and full arylene $\pi$-orbitals. Preliminary electrical measurements have been carried out on a poly(methylphenylsilylene)-*co*-(*p*-phenylene) statistical copolymer with a silylene/phenylene ratio of 1/1.07 ($M_w/M_n$ 59 000/4000). A thin film of this polymer deposited from chloroform solution had a very high electrical resistance at room temperature under vacuum, showing an absence of mobile electrons in the conduction band. On treatment with iodine vapour, the conductivity increased by three orders of magnitude, showing the effect of p-doping. Further experiments are in progress to characterize the electrical properties of the new statistical copolymers, for comparison with their ordered analogues.

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