Incorporation of cobalt carbonyl into poly(carbosilane)s containing main chain acetylene and aromatic groups

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The polymers $\text{-}\!\!\left(\text{SiR}^1\text{R}^2\text{–C}{\equiv}\text{C–(4,4'–C}_6\text{H}_4\text{C}_6\text{H}_4\text{)–C}{\equiv}\text{C}\right)\!\!\text{-}_n$ (where $R^1R^2 = Ph_2$ or MeOct^n) react with dicobalt octacarbonyl to give the corresponding polymers containing either all or half the acetylenes complexed by $Co_2(CO)_6$ groups depending on the reactant proportions. These polymers of different stoichiometry can be distinguished by ^{13}C and ^{29}Si n.m.r. spectroscopy.

(Keywords: poly(carbosilane)s; acetylene; cobalt)

We have recently developed the following new route to poly(carbosilane)s containing main chain acetylene and aromatic groups[1]:

$$R^1R^2Si(C{\equiv}CH)_2 + X\text{–}Ar\text{–}X \xrightarrow[\text{CuI, Et}_3\text{N}]{(\text{PPh}_3)_2\text{PdCl}_2} \text{-}\!\!\left[R^1R^2Si\text{–}C{\equiv}C\text{–}Ar\text{–}C{\equiv}C\right]\!\!\text{-}_n$$

Depending on the R^1R^2Si and Ar groups, some of these polymers become semiconducting[2] on being doped with $FeCl_3$. Also, when Ar is a donor–acceptor group, the polymers exhibit high and stable non-linear optical (n.l.o.) $\chi^{(2)}$ effects[3].

By using the various potential ligand groups (acetylene, aromatic, silole) present in the polymers, we are at present introducing metals into the polymers with a view to studying how their presence affects the electrical conductivity and n.l.o. properties. Here we report the synthesis of poly(carbosilane)s of the above type with cobalt carbonyl moieties attached to the backbone acetylene groups.

Following previous work in our laboratory on the preparation of silyl acetylene–cobalt carbonyl complexes[4,5], we have prepared the cobalt-carbonyl-containing poly(carbosilane)s **IA**, **IIA**, **IB** and **IIB** by stirring 1 equiv. of the appropriate starting polymer with dicobalt octacarbonyl (**IA**, **IIA**: 1 equiv.; **IB**, **IIB**: 2 equiv.) in CH_2Cl_2 for 24 h at room temperature (*Scheme 1*). The polymers were precipitated from CH_2Cl_2 solution by addition of pentane, and washed with pentane to remove traces of unreacted dicobalt octacarbonyl (the latter exhibiting a bridging ν(CO) i.r. absorbance which is absent for the cobalt-containing polymers). For the starting polymers, typical values of M_w (by s.e.c. with respect to polystyrene standards) were 57 000 for **I** and 9000 for **II**; the respective polydispersities were 3.1 and 1.4. The molecular weight properties were found by s.e.c. to be essentially unchanged following introduction of the cobalt carbonyl groups.

Because of ceramic formation, elemental analysis is often found to be unreliable for poly(carbosilane)s; this was the case here both for the starting polymers[1] and the cobalt-containing polymers [e.g. **IIA**: found (calcd) C 57.99 (61.09), H 3.38 (2.71), Si 4.80 (4.20), Co 15.17 (17.63)]. However, the analytical data for cobalt (*Table 1*) support the structures given in *Scheme 1*, half the acetylene groups being complexed in the cases of **IA** and **IIA**, and all the acetylene groups for **IB** and **IIB**. The i.r. spectra show the expected $\nu(C{\equiv}O)$ absorbances[4,5] (*Table 1*). There are also $\nu(C{\equiv}C)$ bands for **IA** and **IIA** which are absent in the cases of **IB** and **IIB**, since in the latter two polymers all the acetylene groups are complexed by $Co_2(CO)_6$ groups.

As previously observed for dialkynylsilanes[6], the ^{29}Si n.m.r. resonance is shifted downfield as the proportion of the acetylene groups which are complexed by $Co_2(CO)_6$ groups increases. Thus, for the uncomplexed polymer where $R^1R^2 = $ MeOct^n (**I**) the chemical shift[7] is −36.9 ppm, whereas when the silicon is adjacent to one uncomplexed and one complexed acetylene group the value of δ is −17.9 ppm (**IA**), and when all the acetylene groups are complexed the chemical shift is −5.5 ppm (**IB**). In the case of **IB**, a second minor resonance at −17.5 ppm is also observed arising from the presence of a small proportion of silicon sites adjacent to one complexed and one uncomplexed acetylene group. The same order of decreasing chemical shift is observed for the $R^1R^2 = Ph_2$ series of polymers, the value of δ being −48.0 ppm for the uncoordinated polymer **II**[1], −28.7 ppm for **IIA** where each silicon is adjacent to one complexed and one uncomplexed acetylene group, and −17.6 ppm for **IIB** in which all the acetylene groups are complexed. Since only a single resonance is observed for the partly complexed polymers **IA** and **IIA**, all the silicons must be equivalent, each being adjacent to one complexed and one uncomplexed acetylene group. These polymers are therefore regular.

The ^{13}C n.m.r. spectra (*Table 1*) for the fully complexed polymers **IB** and **IIB** show a single acetylene C_β resonance

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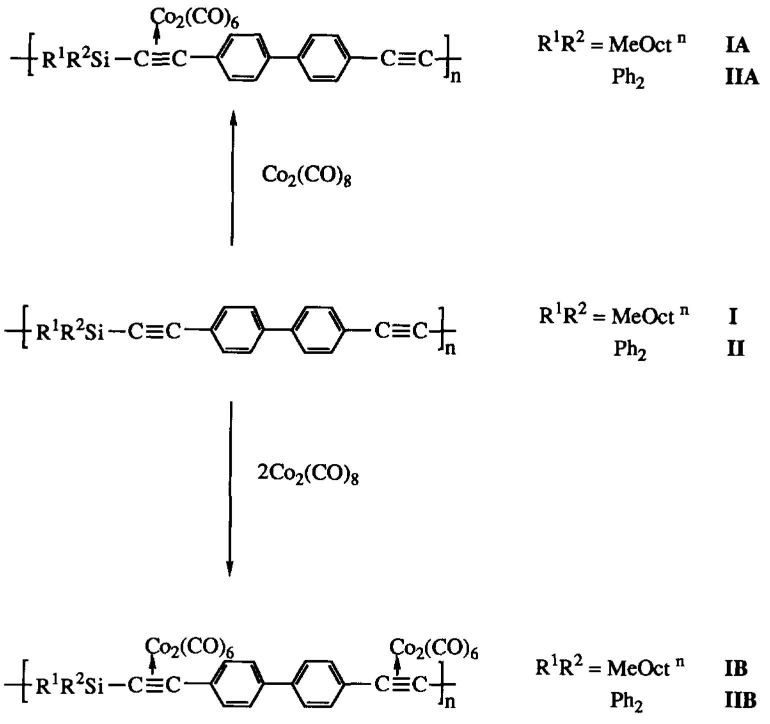

Scheme 1

Table 1 Analytical, i.r. and n.m.r. data

Polymer	Co found (%) (calcd)	$\nu(C\equiv O)$ (cm^{-1})^a	$\nu(C\equiv C)$ (cm^{-1})^a	^{29}Si δ (ppm)^b	^{13}C δ (ppm)^b	
					C_α	C_β
I	-	-	2157	−36.9	91.6	106.4
IA	17.05	2088	2157	−17.9	76.0	105.0
	(18.35)	2054			92.5	107.5
		2026				
IB	26.29	2086	-	−5.5	-	106.0
	(25.39)	2056		(−17.5)		
		2025				
II	-	-	2145	−48.0	89.1	108.9
IIA	15.17	2090	2160	−28.7	73, 74	105.4
	(17.63)	2057			90.3	109.8
		2029				
IIB	23.38	2086	-	−17.6	75.0	107.8
	(24.70)	2057				
		2026				

[a] In CCl_4

[b] In $CDCl_3$; $SiMe_4$ reference; $[Si]-C_\alpha\equiv C_\beta-$

at $\delta = 106.0$ and 107.8 ppm, respectively, these values being slightly upfield of those for the uncomplexed polymers **I** and **II** ($\delta = 106.4$ ppm[7] and 108.9 ppm[1], respectively). As previously observed[6], the upfield shift for the acetylene C_α is much greater; the resonance occurs at $\delta = 75$ ppm for **IIB** as compared to $\delta = 89.1$ ppm for the uncomplexed polymer **II**. However, no C_α resonance was recorded for **IB**, presumably because it was obscured by the solvent signal. In the case of the partly complexed polymers **IA** and **IIA**, acetylene C_α and C_β resonances are exhibited arising from both complexed and uncomplexed acetylene groups. For **IA**, only one complexed acetylene C_α resonance is observed at $\delta = 76$ ppm. Somewhat curiously, in the case of **IIA** two complexed acetylene C_α resonances are observed at $\delta = 73$ and 74 ppm in spite of the fact that **IIA** shows only a single ^{29}Si n.m.r. resonance, thus indicating that each silicon is adjacent to one complexed and one uncomplexed acetylene group and therefore all complexed acetylene groups are equivalent. The uncomplexed acetylene C_α resonance for **IA** occurs at $\delta = 92.5$ ppm and that for **IIA** at $\delta = 90.3$ ppm, these chemical shifts being similar to those for the starting polymers **I** and **II** ($\delta = 91.6$ and 89.1 ppm, respectively). Two acetylene C_β resonances are exhibited for each of **IA** and **IIA**, one upfield and one downfield of the C_β resonances for the uncomplexed polymers **I** and **II**. The upfield C_β resonances in **IA** and **IIA** presumably arise from complexed acetylene groups since in **IB** and **IIB**, where all the acetylene groups are complexed, the acetylene C_β resonances are shifted upfield with respect to those for **I** and **II**, respectively. Thus, for **IA** the uncomplexed acetylene C_β resonance is at $\delta = 107.5$ ppm, and that for **IIA** lies at $\delta = 109.8$ ppm (cf. $\delta = 106.4$ and 108.9 ppm for **I** and **II**, respectively), whilst the complexed acetylene C_β resonance for **IA** appears at $\delta = 105$ ppm and that for **IIA** at $\delta = 105.4$ ppm. The ^{13}C n.m.r. spectra also show the carbonyl carbon resonance at ca. $\delta = 200$ ppm for all four polymers.

In view of the recent report of fast third-order non-linearities for cobalt-carbonyl-containing polydiacetylenes[8], the n.l.o. properties of the present polymers should be of interest. We are currently extending this work to polymers with other R^1R^2 and Ar groups, and we are investigating the possibility of incorporating several different metals into a given poly(carbosilane).

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