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Electrical conductivity of $FeCl_3$-doped poly(alkynylsilane)s

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Abstract

The electrical conductivities of the poly(alkynylsilane)s $\left[C\equiv C-SiR^1R^2-C\equiv C-Z\right]_n$ (R^1R^2Si = Ph_2Si, ${}^nOct(Me)Si$, 2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentene; Z = (hetero)aromatic group) doped with $FeCl_3$ are found to lie in the range $10^{-9} < \sigma < 10^{-3}$ S cm^{-1}, whereas those of the undoped polymers are less than 10^{-10} S cm^{-1}. The presence of Ph groups on Si leads to increased conductivity.

We described recently [1] the synthesis of poly(alkynylsilane)s by means of the following Pd-catalyzed coupling reaction between diethynyldiphenylsilane and dihaloarenes (X = Br, I; Z = (hetero)aromatic group):

$$X-Z-X + Ph_2Si(C\equiv CH)_2 \xrightarrow[PPh_3,\ Et_3N]{(PPh_3)_2PdCl_2,\ CuI} \left[C\equiv C-SiPh_2-C\equiv C-Z\right]_n$$

We have now extended this reaction to other diethynylsilanes and dihaloarenes. Some of the resulting polymers are listed in Table 1 along with their electrical conductivities when doped with $FeCl_3$. Polymers containing acetylene [2] or heteroaromatic [3] groups along with Si residues in the backbone become electrically conducting when doped, suggesting possible $d\pi$-$p\pi$ conjugation. We show below that the same effect is observed for poly(alkynylsilane)s which contain both acetylene and (hetero)aromatic groups in the backbone.

For measurements of the electrical conductivities, 0.1 *M* solutions of the polymers in CH_2Cl_2 containing 0.3–0.5 mol $FeCl_3$ per mole-alkynyl group were stirred until the characteristic dark colour of the doped polymer had appeared. Thin films of the doped polymers were then formed these solutions by spin coating on to a glass substrate. The thickness of the films was measured with a Sylvac 25 thickness monitor. Electrical conductivities were determined by the four-point method [4].

In the undoped state, the polymers show conductivities of less than 10^{-10} S cm^{-1} but doping with $FeCl_3$ raises the values to as high as 10^{-3} S cm^{-1} in the case of II (Table 1). This is of the same order of magnitude as the value observed in our

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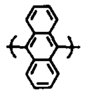
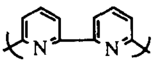
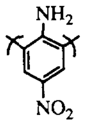
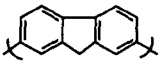
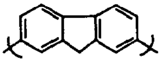
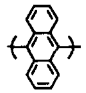
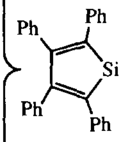
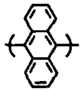
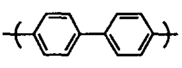
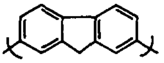
laboratories for doped $\left[\mathrm{Si(Ph_2)}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{C}\right]_n$ [2]. The conductivity of the present polymers is very dependent on both the arene group Z and the R^1R^2 substituents at Si as can be seen from Table 1. The dependence on the R^1R^2 substituents on Si is similar to that observed in the case of poly[(silanylene)diethynylene]s [2]. The

Table 1

Electrical conductivities [a] and molecular weights [b] of poly(alkynylsilane)s $\left[\mathrm{C}\equiv\mathrm{C}-\mathrm{SiR^1R^2}-\mathrm{C}\equiv\mathrm{C}-\mathrm{Z}\right]_n$

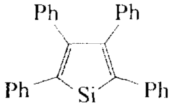
Polymer	SiR^1R^2	Z	M_w	M_w/M_n	n	σ (S cm^{-1})$^{(a)}$
I	$SiPh_2$		34000	3.54	31	10^{-8}
II			23500	3.15	18	10^{-3}
III			8000	2.5	8	10^{-5}
IV			4700	1.45	11	$<10^{-8}$
V			4000	1.45	10	10^{-4}
VI	MeSi(n-Octyl)		7800	1.93	11	5×10^{-9}
VII			15700	3.07	13	2×10^{-8}
VIII			10200	3.15	6	10^{-6}
IX			5700	2.10	5	5×10^{-9}
X			6000	2.69	4	10^{-7}

(a) doped with $FeCl_3$.

(b) determined by GPC, with reference to polystyrene standards.

highest conductivity is observed when there are two phenyl substituents; the presence of alkyl groups leads to a lower conductivity. Thus, for a given arene group Z in the polymer backbone, the electrical conductivity decreases in the order

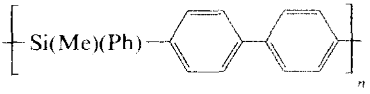
Ph_2Si >



> $^nOct(Me)Si$

(e.g. polymers II, VII, VIII or V, VI, X).

As regards the effect of the arene group Z in the polymer backbone, anthracene residues give rise to the highest conductivities, and fluorene groups are almost as effective (polymers II and V, VI and VII, VIII and X). The bis-pyridine group induces a somewhat lower conductivity (polymer III). However, the presence of either benzene or biphenylene residues gives rise to very low conductivities (polymers I and IX). We observed a similar low conductivity for $FeCl_3$-doped XI ($\sigma = 5 \times 10^{-9}$ S cm^{-1}), whereas $FeCl_3$-doped $\text{+}Si(Ph_2)-C{\equiv}C-C{\equiv}C\text{+}_n$ has a conductivity of 3×10^{-3} S cm^{-1} [2]. The presence of anthracene groups between the two acetylene residues thus has little effect on the conductivity (see II in Table 1), whereas that of the other (hetero)aromatic Z groups shown in Table 1 leads to lower conductivities.



(XI)

Although the molecular weights of the various polymers vary (Table 1), this should not appreciably affect the electrical conductivities since the band-gap energy for oligomers is almost the same as that for the parent polymers [5].

In conclusion, we have shown that poly(alkynylsilane)s $\text{+}C{\equiv}C-SiR^1R^2-C{\equiv}C-Z\text{+}_n$ containing both acetylene and (hetero)aromatic groups in the backbone become conducting on doping with $FeCl_3$. The magnitude of the effect depends on the SiR^1R^2 and Z groups.

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