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Preliminary communication

Polymeric Organosilicon Systems

VI. Synthesis and properties of *trans*-poly[(disilanylene)ethenylene]

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Abstract

The reaction of *trans*-bis(chloromethylphenylsilyl)ethene with sodium dispersion in benzene gave *trans*-poly[(1,2-dimethyldiphenyldisilanylene)ethenylene] (II) which is soluble in common organic solvents. Treatment of the film prepared from II with SbF_5 vapor produced a highly conducting film.

As part of a study on the preparation of organosilicon polymers that can be used as functional material [1–3], we have synthesized a polymer in which the regular alternating arrangement of a disilanylene unit and an ethenylene group is found in the polymer backbone, and have investigated its photochemical and conducting properties.

The reaction of *trans*-1,2-bis(chloromethylphenylsilyl)ethene (I) prepared from platinum-catalyzed hydrosilylation of chloroethynylmethylphenylsilane with chloromethylphenylsilane [4], with sodium dispersion in benzene under ultrasound afforded a white solid, *trans*-poly[(1,2-dimethyldiphenyldisilanylene)ethenylene] (II) in 61% yield, as shown in Scheme 1. The polymer II thus obtained melts at 60–64 °C without decomposition and is soluble in common organic solvents such as benzene, toluene, ethers and chlorocarbons. Polymer II can be cast into a film. The molecular weight ($\overline{Mw}$) of II was found to be 39800, relative to the polystyrene standard.

* For part V see ref. 6.

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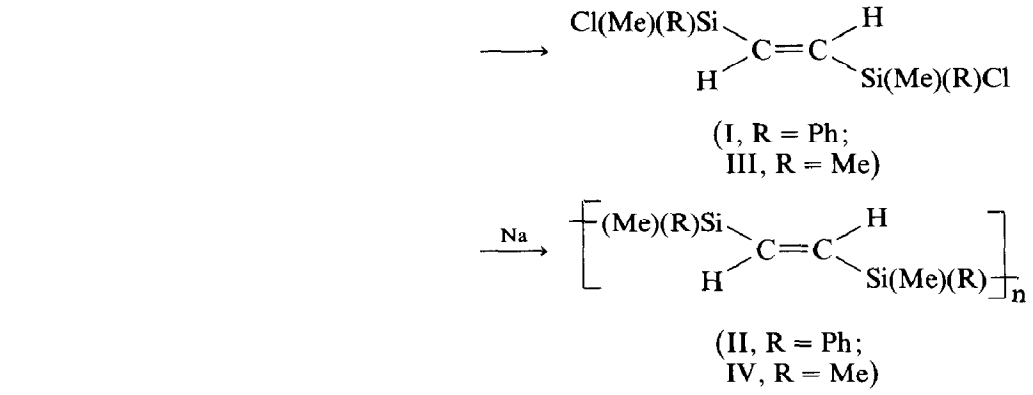

Scheme 1

Treatment of *trans*-1,2-bis(chlorodimethylsilyl)ethene (III) with sodium metal under the same conditions gave *trans*-poly[(tetramethyldisilanylene)ethenylene] (IV). However, the polymer IV thus obtained did not melt below 300 °C, and was scarcely soluble in common organic solvents.

The structure of II was confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopy, as well as by elemental analysis. The ^{1}H NMR spectrum of II shows resonances at 0.29(3H, s, MeSi), 0.32(3H, s, MeSi), 6.69(2H, s, HC=CH), and 6.85–7.68 ppm(10H, m, PhSi). The ^{13}C NMR spectrum * indicates a single resonance at 149.4 ppm, which is attributed to the olefinic carbons.

Characteristic of the polymer II is a strong absorption at 260 nm in the ultraviolet region. As expected, the polymer II is highly photoactive. Thus, irradiation of the thin film of II in air with a low-pressure mercury lamp led to disappearance of the absorption at 260 nm, indicating that homolytic scission of silicon–silicon bonds in the polymer backbone had occurred, as observed in the photolysis of poly[*p*-(1,2-dimethyldiphenyldisilanylene)phenylene] [1,2].

To our surprise, when the thin film of II with thickness of 6700 Å was treated with SbF_5 vapor, a highly conducting film whose conductivity was found to be 0.47 $S \cdot cm^{-1}$ was obtained.

Further studies on the silicon-containing polymer conductors are now in progress.

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* ^{13}C NMR spectrum of II (δ ppm in $CDCl_3$) −5.45 (MeSi), 127.7, 128.6, 134.5, 136.7 (phenyl ring carbons), 149.4 (olefinic carbons).

* For a conducting polysilane: see ref. 5.

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