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Preliminary communication

Polymeric organosilicon system

VIII *. Synthesis of poly[(disilanylene)diethynylene] with highly conducting properties

Mitsuo Ishikawa *, Yutaka Hasegawa ** and Atsutaka Kunai
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724 (Japan)

Toru Yamanaka
Mitsui Petrochemical Industries Ltd., Nagaura, Sodegaura, Chiba 299 (Japan)

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Abstract

The reaction of bis(trimethylsilyl)butadiyne with 2 equiv. of methyllithium, followed by 1,2-dichloro-1,2-dimethyldiphenyl- or 1,2-dichloro-1,2-diethyldimethyldisilane gives poly[(1,2-dimethyldiphenyldisilanylene)diethynylene] (II) or poly[(1,2-diethyldimethyldisilanylene)diethynylene] (III), respectively. Films of II and III become conducting when treated with SbF_5 vapor.

We have designed and made silicon containing polymers which have a regular, alternating arrangement of disilanylene unit and π electron system in the polymer backbone. The polymers are photoactive and are conducting when doped with antimony pentafluoride vapor [1–4]. Here we report the first synthesis of poly[(disilanylene)diethynylenes] which is highly conducting.

The reaction of hexachlorobutadiene with chlorotrimethylsilane and magnesium in THF readily gives bis(trimethylsilyl)butadiyne (I), which as the starting material was treated with 2 equiv. of methyllithium to give 1,4-dilithiobutadiyne for the condensation with 1,2-dichlorodisilane.

In a typical experiment, 53.3 ml (0.08 mol) of a methyllithium/diethylether solution was added to 7.76 g (0.04 mol) of I dissolved in 150 ml of diethyl ether with

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* For part VII see ref. 7.

** Present address: Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., 6 Kitahara, Tukuba, Ibaraki 300-32, Japan.

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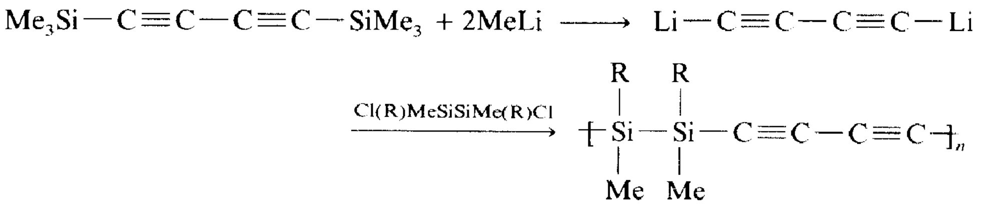

$$Me_3Si-C\equiv C-C\equiv C-SiMe_3 + 2MeLi \longrightarrow Li-C\equiv C-C\equiv C-Li \xrightarrow{Cl(R)MeSiSiMe(R)Cl} \left[\overset{R}{\underset{Me}{Si}}-\overset{R}{\underset{Me}{Si}}-C\equiv C-C\equiv C \right]_n$$

II, R = Ph
III, R = Et

Scheme 1

ice-cooling for 1 h. After addition of 50 ml of dry THF with ice-cooling [6], the mixture was stirred for 4 h at the same temperature, then a small aliquot of the mixture was extracted and hydrolyzed with water. Gas chromatographic analysis of the organic layer showed that neither the starting compound I nor trimethylsilylbutadiyne was detected, which indicates that compound I was completely transformed into 1,4-dilithiobutadiene. To the mixture was added 12.45 g (0.04 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane in 10 ml of THF. The mixture was stirred for 15 h at room temperature and then hydrolyzed with 0.5 *N* hydrochloric acid. The organic layer was separated off, washed with water, and filtered to remove insoluble material. The filtrate was concentrated and the resulting solid was reprecipitated twice from benzene/ethanol, and benzene/isopropyl alcohol to give 2.2 g (19% yield) of poly[(1,2-dimethyldiphenyldisilanylene)diethynylene] (II) as shown in Scheme 1.

The polymer II, a light brown solid decomposes at 110–125 °C without melting, is soluble in common organic solvents such as a benzene, ethers and chlorocarbons, and can be cast into a thin film. The molecular weight ($\overline{M}_w$) of II was found to be 44,400, relative to the polystyrene standards ($\overline{M}_w/\overline{M}_n = 9.27$).

The structure of II was confirmed by IR, ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of II reveals broad resonances at 0.1–0.8 (6H, br m, MeSi) and 6.9–7.8 ppm (10 H, br m, phenyl ring protons). The ^{13}C NMR spectrum [-3.7 (MeSi), 83.9 and 93.9 (*sp* carbons), 129.5, 131.2, 133.7 and 135.8 ppm (phenyl ring carbons)] and also IR spectrum [$\nu(C\equiv C)$ 2062 cm^{-1}] clearly indicate the presence of diyne units in the polymer backbone.

Similar treatment of I with methyllithium, followed by 1,2-dichloro-1,2-diethyldimethyldisilane gives a pale yellow solid, poly[(1,2-diethyldimethyldisilanylene)diethynylene] (III) [IR, $\nu(C\equiv C)$ 2059; ^1H NMR 0.33 (6H, s, MeSi), 0.7–1.23 ppm (10H, m, CH_3CH_2Si); ^{13}C NMR, -5.2 and -5.1 (MeSi), 6.1 and 8.0 (CH_3CH_2Si), 83.4 and 91.3 ppm (*sp* carbons)] in 56% yield.

Polymer III is soluble in common organic solvents, and decomposes at 180 °C without melting. The molecular weight of III was found to be 4,800 ($\overline{M}_w/\overline{M}_n = 2.75$).

Solid films of II and III show characteristic absorptions in the ultraviolet region. Polymer II shows a strong absorption at 235 nm, together with weak absorptions at 264 (sh), 280 and 299 nm, whereas III shows strong absorptions at 245, 262 (sh), and weak ones at 280 and 298 nm. As expected, polymers II and III are photoactive. Thus, irradiation of thin solid films with a low-pressure mercury lamp causes a rapid decrease of these absorptions, which indicates the homolytic scission of silicon–silicon bonds in the polymer backbone.

When thin films of II and III were treated with antimony pentafluoride vapor, they became conducting with conductivities close to those for metals. The conductivity measured by the four-probe method was 1.04 S cm^{-1} for II and 0.38 S cm^{-1} for III.

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