

Synthesis and conducting properties of poly[(disilanylene)butenyne-1,4-diyls] and poly[(disilanylene)ethynylenes]

Mitsuo Ishikawa

Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Higashi-Hiroshima 724, Japan

Abstract - The reaction of 1,2-diethynyldisilanes with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) in toluene at room temperature afforded poly[(disilanylene)butenyne-1,4-diyls]. Treatment of 1,2,5,6-tetrasilacyclo-octa-3,7-diyne with a catalytic amount of *n*-butyllithium in THF at room temperature led to ring-opening polymerization to give poly[(disilanylene)ethynylenes]. When the films of poly[(disilanylene)butenyne-1,4-diyls] and poly[(disilanylene)ethynylenes] were treated with antimony pentafluoride vapor, the highly conducting films were obtained.

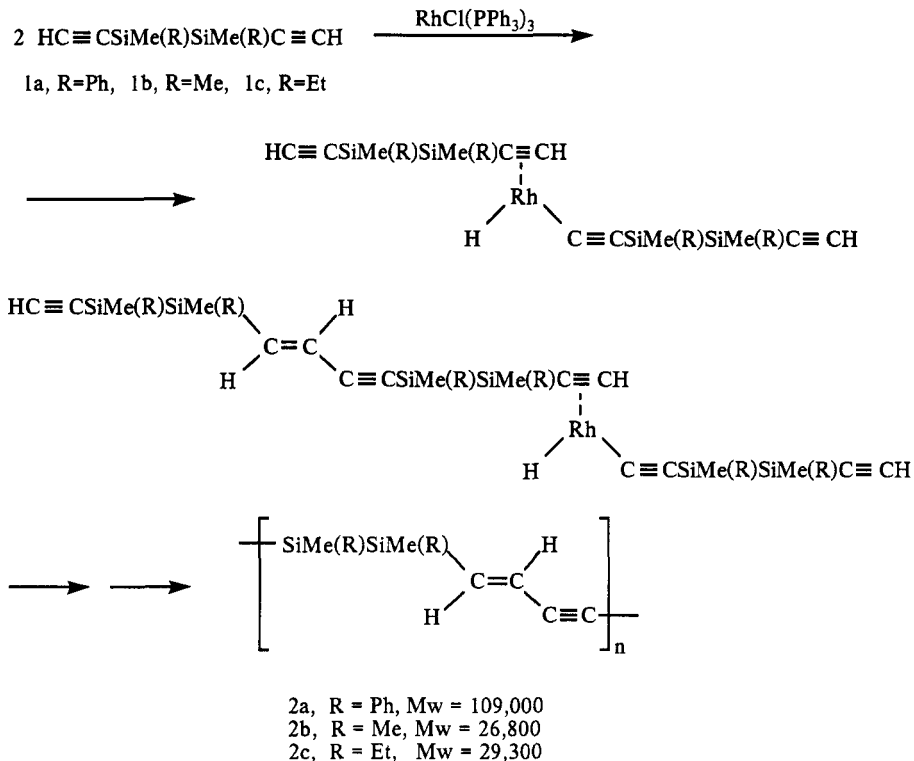
INTRODUCTION

There has been a considerable interest in the synthesis of polymers that can be used as functional material. We have demonstrated that the polymers in which the regular alternating arrangement of a disilanyl unit and the π -electron system is found in the polymer backbone can readily be synthesized by the sodium condensation reaction of compounds having two chlorosilyl groups attached to a π -electron system (ref. 1-3). We have also found that these polymers are photoactive and show conducting properties when the polymers are doped by exposure to antimony pentafluoride vapor. In this paper, we report the synthesis of poly[(disilanylene)butenyne-1,4-diyls] and poly[(disilanylene)ethynylenes], in which no alkaline metal condensation is involved in all processes, and conducting properties of the polymers obtained.

POLY [(DISILANYLENE) BUTENYNE-1,4-DIYLS]

During the course of our investigation on the C-H bond activation of ethynylsilanes by a transition metal complex (ref. 4), we have found that treatment of 1,2-diethynyldisilanes with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) readily affords a new type of polymers, poly[(disilanylene)butenyne-1,4-diyls], in which the alternate arrangement of a disilanylene unit and an enyne group is found regularly in the polymer backbone (ref. 5). Thus, the reaction of 1,2-diethynyl-1,2-dimethyldiphenyldisilane (1a) with a 2 mol percent of chlorotris(triphenylphosphine)rhodium(I) in toluene under an argon atmosphere at room temperature gave a light yellow solid polymer, poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (2a) in 73% yield, after reprecipitation from benzene-ethanol (Scheme 1). The polymer 2a is soluble in common organic solvents such as benzene, halocarbons and ethers and melts at 90-95°C without decomposition. Molecular weight of 2a which showed broad monomodal molecular weight distribution in the gel permeation chromatogram was determined to be 117,000 relative polystyrene standards ($M_w/M_n = 6.1$). The structure of 2a was confirmed by its ^{13}C NMR spectrum. Thus, the ^{13}C NMR spectrum of 2a shows resonances at δ 91.2, 91.3, 91.5, 91.6, 109.81, 109.84, 109.9 ppm and 125.8, 125.9, 142.5, 142.8 ppm, due to ethynylic and ethylenic carbons, respectively. These chemical shifts are consistent with those of (E)-1,4-bis(methyldiphenylsilyl)-1-buten-3-yne obtained from the head-to-head dimerization reaction of ethynylmethyl-diphenylsilane with a rhodium(I) catalyst. Similar reaction of 1,2-diethynyltetramethyldisilane (1b) with a rhodium catalyst afforded

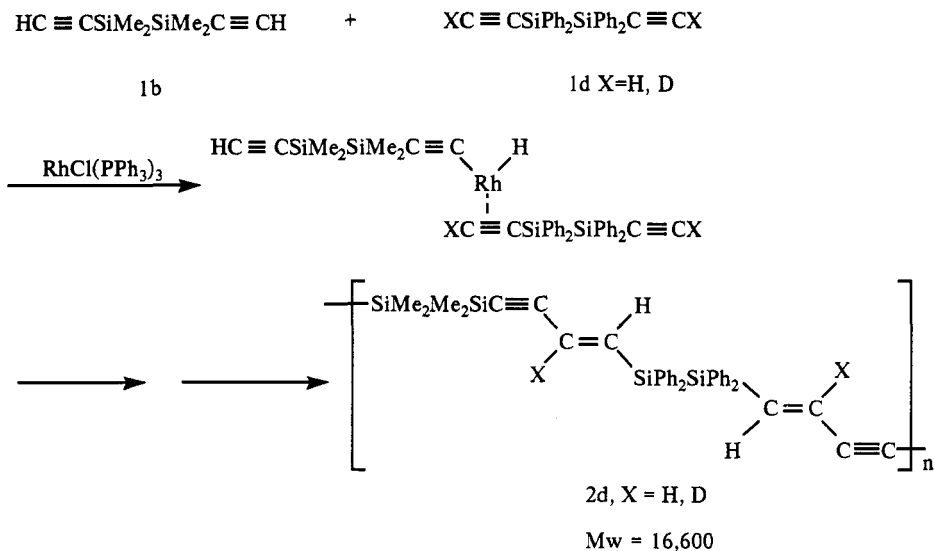
Scheme 1



poly[(tetramethyldisilanylene)butenyne-1,4-diy] (2b) in 52% yield, while 1,2-diethynyl-1,2-diethyldimethyldisilane (1c) produced poly[(1,2-diethyldimethyldisilanylene)butenyne-1,4-diy] (2c) in 47% yield. The molecular weight of 2b and 2c was calculated to be 26,800 and 29,300, respectively.

Treatment of 1,2-diethynyltetraphenyldisilane (1d) with the rhodium catalyst, however, gave no polymeric substances, but the starting compound 1d was recovered unchanged. Interestingly, when a 1:1 mixture of 1b and 1d was treated with the rhodium catalyst under the same conditions, an alternating copolymer (2d) was obtained in 49% yield (Scheme 2). Polymers 2a-2d can be

Scheme 2

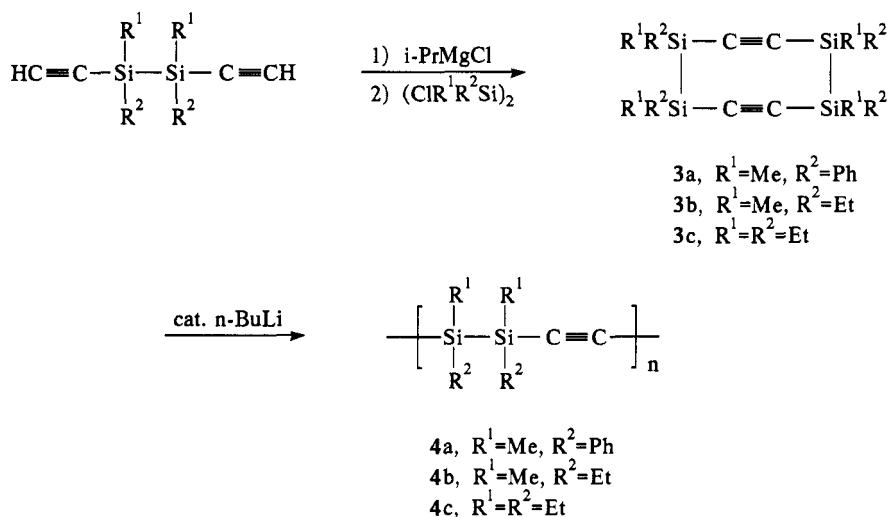


cast to a thin film by spin coating of their methylene chloride solution. The polymers exhibit strong absorption at near 290 nm and are photoactive in the ultraviolet. Irradiation of thin solid films of 2a-2d with a low-pressure mercury lamp in air led to the disappearance of the absorption at near 290 nm indicating that homolytic scission of silicon-silicon bonds in the polymer backbone occurred, as observed in the photolysis of poly[p-(disilanyl)-phenylenes] (ref. 2). When the films of 2a, 2b and 2d were doped by exposure to antimony pentafluoride vapor, the conducting films were obtained. The conductivity determined by the four-probe method was found to be $1.09 \text{ S}\cdot\text{cm}^{-1}$ for 2a, $0.02 \text{ S}\cdot\text{cm}^{-1}$ for 2b, and $0.04 \text{ S}\cdot\text{cm}^{-1}$ for 2d, respectively.

POLY [(DISILANYLENE) ETHYNYLENES]

Poly[(disilanyl)ethynylenes] can readily be obtained by the anionic polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes in the presence of a catalytic amount of alkyl lithium. The starting 1,2,5,6-tetrasilacycloocta-3,7-diynes could be prepared by the reaction of 1,2-diethynylsilanes with isopropylmagnesium chloride, followed by treatment of the resulting solution with 1,2-dichlorodisilanes (ref. 6). Thus, the reaction of the di-Grignard reagent prepared from 1,2-diethynyl-1,2-dimethyldiphenyldisilane and isopropylmagnesium chloride with 1,2-dichloro-1,2-dimethyldiphenyldisilane afforded two isomers of 1,2,5,6-tetramethyltetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (3a) in 41% yield (Scheme 3). Compound 3a could

Scheme 3



readily be isolated from the reaction mixture by fractional crystallization. The structure of 3a was determined unambiguously by single-crystal X-ray diffraction analysis. Compound 3a has cis-trans configuration as shown in Figure 1. The reaction of the di-Grignard reagent of 1,2-diethynyl-1,2-diethyldimethylsilane with 1,2-dichloro-1,2-diethyldimethyldisilane gave 1,2,5,6-tetraethyltetramethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne in 47% yield (ref. 7). Similar reaction of 1,2-diethynyltetraethyldisilane with isopropylmagnesium chloride, followed by 1,2-dichlorotetraethyldisilane produced 1,1,2,2,5,5,6,6-octaethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (3d) in 50% yield. The anionic ring opening polymerization was carried out with the use of n-butyllithium as a catalyst in THF at room temperature. Thus, a mixture of 3a with a catalytic amount of n-butyllithium in THF was stirred at room temperature in a sealed glass tube for 64 h. The mixture was poured into ethanol, and the resulting solid was reprecipitated twice from benzene-ethanol to give poly[(1,2-dimethyldiphenyldisilanyl)ethynylene] (4a) in 35% yield. Molecular weight of the polymer 4a was determined to be $M_w = 8.08 \times 10^4$ ($M_w/M_n = 4.08$), relative to polystyrene standards. The polymer 4a melts at 60-85°C

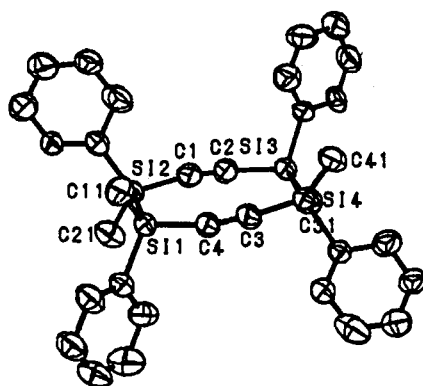


Fig. 1. Molecular structure of 3a

without decomposition and is soluble in common organic solvents, such as benzene, ethers and halocarbons. The structure of 4a was verified by IR and ^1H and ^{13}C NMR spectroscopic analysis. The ring opening polymerization catalyzed by butyllithium is remarkably general for tetrasilacycloocta-3,7-diyne. In fact, similar treatment of 1,2,5,6-tetraethyl(tetramethyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne (3b) with a catalytic amount of *n*-butyllithium in THF at room temperature for 40 h produced poly[(1,2-diethyldimethyldisilanyl)ethynylene] (4b) in 92% yield. The molecular weight of 4b determined by GPC was calculated to be $M_w = 1.05 \times 10^5$ ($M_w/M_n = 3.25$). Similarly, the reaction of 1,1,2,2,5,5,6,6-octaethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (3c) with *n*-butyllithium under the same conditions gave poly[(tetraethyl)ethynylene] (4c) whose molecular weight was determined to be 62,800 in 65% yield. The polymers 4b and 4c melt without decomposition and are soluble in common organic solvents.

The polymers 4a, 4b, and 4c are photoactive and irradiation of their films with a low-pressure mercury lamp resulted in the homolytic scission of silicon-silicon bonds in the polymer chain. When the films of 4a, 4b, and 4c were treated with antimony pentafluoride vapor, the highly conducting films were obtained. The conductivity was determined to be $0.41 \text{ S}\cdot\text{cm}^{-1}$ for 4a, $1.96 \text{ S}\cdot\text{cm}^{-1}$ for 4b, and $0.82 \text{ S}\cdot\text{cm}^{-1}$ for 4c, respectively.

REFERENCES

1. M. Ishikawa and K. Nate, *Inorganic and Organometallic Polymers*, ACS Symposium Series 360 (1988), Chapter 16.
2. K. Nate, M. Ishikawa, H. Ni, H. Watanabe and Y. Saheki, *Organometallics*, 6, 1673 (1987).
3. J. Ohshita, D. Kanaya, M. Ishikawa and T. Yamanaka, *J. Organomet. Chem.*, 369, C18 (1989).
4. J. Ohshita, K. Furumori, A. Matsuguchi and M. Ishikawa, *J. Org. Chem.*, 55, 3277 (1990).
5. J. Ohshita, K. Furumori, M. Ishikawa and T. Yamanaka, *Organometallics*, 8, 2084 (1989).
6. T. Iwahara and R. West, *J. Chem. Soc., Chem. Commun.*, 1989, 954.
7. M. Ishikawa, T. Hasegawa, T. Hatano, A. Kunai and T. Yamanaka, *Organometallics*, 8, 2741 (1989).