Novel disilane-bridged 1,4-cyclophanes: Synthesis and ring-opening polymerization

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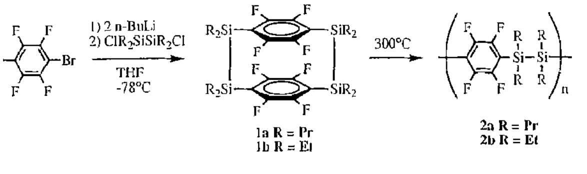
Novel disilane-bridged 1,4-cyclophanes, $(SiR_2SiR_2\text{-}C_6F_4)_2$ (1), were prepared by the reactions of a 1,2-dichlorodisilane with a 1,4-dilithiobenzene. Thermolysis of the 1,4-cyclophanes in an evacuated sealed Pyrex tube at 300°C gave the corresponding poly(disilanylene-1,4-phenylene)s (2), $\text{-}(SiR_2SiR_2\text{-}C_6F_4)_n\text{-}$. The molecular weight of **2a** (R = propyl) obtained by thermal ring-opening polymerization was much higher than that of **2a** derived from the coupling reaction of 1,2-dichlorodisilane with 1,4-dilithiotetrafluorobenzene in THF. The regular repetition of disilanylene-1,4-phenylene units in a polymer chain of **2a** and **2b** was confirmed by analyzing the ^{29}Si, ^{13}C, and ^{19}F NMR spectra.

Introduction

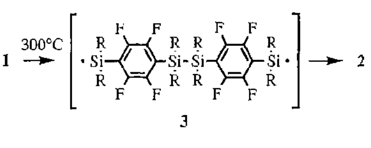
There has been a considerable interest in the chemistry of polymers based on inorganic elements because of their unique physical and chemical properties. Silicon containing polymers represent a novel class of these materials, which exhibit σ- or σ-π conjugation. Such characteristics have led to potential application as photoconductors, photoresists, and nonlinear optical materials.[1)] Recently, Ishikawa and co-workers have reported the synthesis and properties of the polymers that have a regular alternating arrangement of a silicon-silicon unit and a π-conjugated system such as ethynylene, arylene, and oligoarylene in the polymer backbone.[2)] However, there has been no report on the σ-π hybrid polymers having perfluorophenylene π system, where the fluorine atom serves as an electron donor via π conjugation to the π system, while as an electron acceptor through σ bond. In this respect, we reported that novel photoisomerization, which proceeded via simultaneous 1,3-migrations of a β-silyl group and an ortho-fluorine atom, occurred preferably under irradiation of perfluorophenyldisilanes.[3)] Herein is reported a novel synthesis of poly(disilanylene-1,4-phenylene)s having perfluorinated aromatic rings via thermal ring-opening polymerization of the corresponding novel disilane-bridged 1,4-cyclophanes, $(SiR_2SiR_2\text{-}C_6F_4)_2$ (**1**).

Results and Discussion

Novel cyclophanes **1** were synthesized by a coupling reaction of 1,2-dichlorotetrapropyldisilane with 1,4-dilithiotetrafluorobenzene which was prepared from 1,4-dibromotetrafluorobenzene and n-butyllithium in THF at −78°C. The compound of **1a** (R = propyl) was obtained in 23% yield. The structure of these compounds was determined by means of ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR (nuclear magnetic resonance), UV-Vis spectroscopy, and mass spectrometry. When the Cyclophane **1a** was heated for 20 h in an evacuated sealed Pyrex tube at 300°C, poly(disilanylene-1,4-phenylene) **2a** was obtained in 73% yield after isolation by preparative high-performance liquid chromatography (Scheme 1). The molecular weight (Mw) of **2a** was determined to be 54000 vs. polystyrene standards. The polymer **2a** was highly soluble in chloroform, benzene, and THF, suggesting that no appreciable crosslinking took place during the thermolysis. Since the ^{13}C, ^{19}F, and ^{29}Si NMR signals of **2a** in $CDCl_3$ solution were sharp, **2a** should hold regular repetition of disilanylene-1,4-phenylene units. When thermal copolymerization of a mixture of the cyclophane **1a** and **1b** was performed in an evacuated sealed Pyrex tube at 300°C, the polymer **2c** was obtained. The structure of **2c** was determined by comparing the ^{13}C and ^{29}Si NMR spectra with those of the analogous polymers. The ^{29}Si NMR spectrum of **2c** showed four signals (Fig. 1); the resonances at −12.6 ($SiEt_2$) and −16.9 ppm ($SiPr_2$) for 1,1-diethyl-2,2-dipropyldisilanylene segments ($\text{-}SiEt_2SiPr_2\text{-}$), at −12.8 ppm for tetraethyldisilanylene segments ($\text{-}SiEt_2SiEt_2\text{-}$), and at −16.7 ppm for tetrapropyldisilanylene segments ($\text{-}SiPr_2SiPr_2\text{-}$). The results suggest that the thermal ring-opening polymerization proceeds via a biradical (**3**) formed by an Si-Si bond cleavage of the cyclophanes (Scheme 2).



Scheme 1



Scheme 2

The polymers **2a** and **2b** were also prepared by the coupling reaction of the corresponding 1,2-dichlorodisilanes with 1,4-dilithiotetrafluorobenzene in THF at −78°C, under the conditions of high concentrations of substrates. However, the

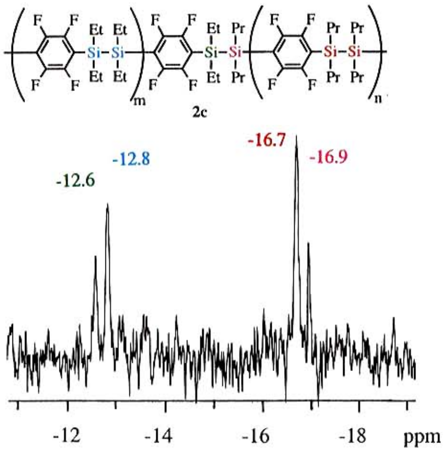


Fig. 1. ^{29}Si NMR spectrum of **2c** in $CDCl_3$.

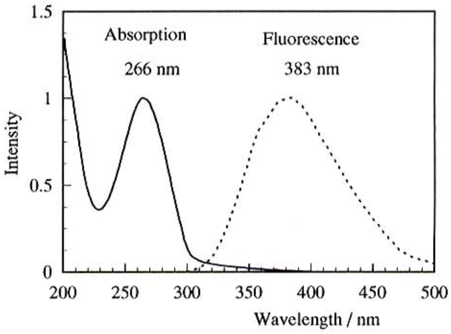


Fig. 2. Absorption and fluorescence spectra of **2c** obtained by the coupling reaction in n-hexane.

molecular weight of **2a** obtained by the coupling reaction (Mw = 13000) was much lower than that of **2a** derived from the ring-opening polymerization of **1a**. The regular repetition of disilanylene-1,4-phenylene units in a polymer chain of **2a** and **2b** by the coupling reaction were also confirmed by NMR spectroscopy. UV spectrum of **2a** obtained by the thermal ring-opening polymerization ($\lambda_{\max}$ 265 nm) was almost the same as that derived by the coupling reaction. A broad and structureless fluorescence spectrum of **2a** with large Stokes shift was observed as shown in Fig. 2. The maximum wavelength and the intensity increased significantly with increasing relative amount of dichloromethane in a mixture of dichloromethane and n-hexane; the fluorescence was quenched by ethanol. These results indicate that the fluorescence is assigned to the emission from the $\sigma\pi^*$ charge-transfer excited state.[4] The optoelectronic properties of these copolymers are now under investigation in detail.

References

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