Novel Family of Molecular Glasses Based on Silicon-containing Compounds

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Novel family of molecular glasses based on silicon-containing compounds, α,ω-dimethyloligo(diphenylsilylene)s are synthesized and characterized. Glass-forming properties of these materials tended to have even-odd effect of chain length. The morphology of glassy samples was found to be mainly amorphous with only two-dimensional order of hexagonal packing.

Since the photo- and electroactivity of the organic conjugated polymeric materials were found, many types of polymers, such as poly(acetylene)s, poly(thienylene)s, poly(*p*-phenylene vinylene)s, and poly(dialkylsilylene)s, were synthesized and their optical, electrical, photoelectric, and magnetic properties in the solid state were investigated for the application to the photo- and electroactive materials. However, relationship between the structure and properties of these conjugated polymers is ill-established, because of their molecular weight distribution and structural defect.

Contrary, low-molecular weight organic materials are good candidates for the photo- and electroactive materials to show the superior property to those of polymeric materials because of their well-defined structures, although they tend to have crystallinity. To eliminate the problem of crystallinity of low-molecular weight materials, Shirota et al. firstly developed the amorphous glassy materials based on low-molecular weight compounds and introduced the novel concept of "molecular amorphous glasses" into the materials science.[1] After their reports, numerous molecular glasses based on π-electron systems have been synthesized and applied as photo- and electroactive materials, like electroluminescent, photovoltaic, photochromic, and resist materials.

Silicon-containing polymers are widely used as the thermally stable insulator to photoconductors and photoresist, depending on the type of chemical bond.[2] In particular, Si–Si catenated polymers, polysilylenes, are interesting materials from the viewpoint of photo- and electroactive materials, because of σ-conjugation effect, such as electroluminescent and photoresist materials.[2,3] Very recently, Yatabe, Minami and their group reported the liquid crystallinity[4] and the hole-transport property of several oligosilylene derivatives,[5] and showed that their hole drift mobilities in bulk film are higher than those of polysilylenes by one order. However, there are no reports on the glass-forming properties of oligosilylenes. From the above-mentioned points, creation of glassy oligosilylenes will give a novel category of molecular glasses having similar photo- and electroactivities to those of polysilylenes, and so that it is interesting from both the viewpoints of expansion of the range of family of molecular glasses and the development of the new field of application of oligosilylenes, such as hole-transport, electroluminescent, and photoresist materials. Here, we report the synthesis and glass-forming properties of novel α,ω-dimethyloligo(diphenylsilylene)s (Figure 1).

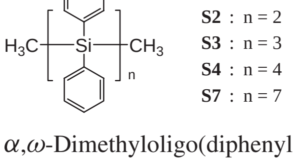
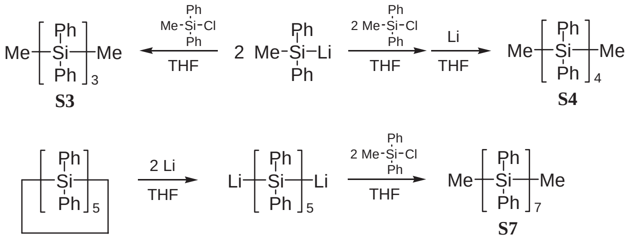


Figure 1. α,ω-Dimethyloligo(diphenylsilylene)s.

Diphenyldichlorosilane and diphenyldimethylsilane (**S1**) were purchased from Shin-Etsu Chemical Co., Ltd. 1,2-Dimethyl-1,1,2,2-tetraphenyldisilane (**S2**)[6] and decaphenylcyclopentasilane[7] were synthesized according to the literatures. 1,3-Dimethyl-1,1,2,2,3,3-hexaphenyltrisilane (**S3**), 1,4-dimethyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane (**S4**), and 1,7-dimethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7-tetradecaphenylheptasilane (**S7**) were synthesized by the coupling reaction of the corresponding chlorosilanes and silyllithiums (Scheme 1). The materials were purified by repetitive recrystallization, and characterized by ^{1}H, ^{13}C, ^{29}Si NMR, IR, and ESIMS spectroscopies and elemental analysis.



Scheme 1. Synthesis of **S3**, **S4**, and **S7**.

Differential scanning calorimetry (DSC) thermograms of **S4** and **S7** are shown in Figure 2, and the data of all materials are summarized in Table 1. While **S1** is liquid at room temperature, **S2**, **S3**, **S4** and **S7** are solid at room temperature and showed an endothermic peak at 142, 103, 215, and 217 °C, respectively, due to the melting behavior in the first heating process. **S2** showed the same melting behavior in the second heating process after the melt sample was cooled, and this behavior did not change by changing the cooling rate from 1 to 50 degree min^{-1}. **S4** showed similar melting behavior, but showed glass-transition temperature at 31 °C in the second heating process, when the melt sample was cooled faster than 10 degree min^{-1}, followed by crystallization at 86 °C and melting at 215 °C. Interestingly enough, oligosilylenes having odd number of silylene units, i.e., **S1**, **S3**, and **S7**, showed only glass-transition temperatures, and did not crystallize in the second heating process (from the first heating process in the case of **S1**). This behavior was observed even when the melt sample was cooled at 1 degree min^{-1}. Especially, the glassy state of **S7** is fully stable at room temperature for several months. It is known that poly- and oligosilylenes adopt trans-zigzag or helical structures depending on the structure of side-chains. If oligosilylenes studied in this report adopts trans-zigzag structure, the direction of the methyl terminal group is parallel for the oligosilylenes having even number of silylene unit, but nonparallel for the oligosilylenes having odd number of silylene unit, and the former is symmetric but the later is not. Thermal properties of pentamer and hexamer are not investigated yet because of the difficulty of the synthesis of them, but this assumption is possibly reasonable to explain the even-odd effect of chain length on the glass-forming properties. Although such even-odd effect is known for the effect of alkyl spacer length of liquid crystalline materials, there is no report of the effect on glass-forming property.

Table 1. Thermal properties of oligosilylenes[a]

	T_g/°C[b]	T$_\mathrm{c}$/°C[c]	T_m/°C[d]
S1	−89		
S2			142
S3	14[e]		103[f]
S4	(31)[g]	(86)[g]	215[f]
S7	77[e]		217[f]

[a] Scan rate: 10 degree min^{-1}. [b] Glass-transition temperature. [c] Crystallization temperature. [d] Melting temperature. [e] Second heating. [f] First heating. [g] Second heating after the melt was cooled faster than 10 degree min^{-1}.

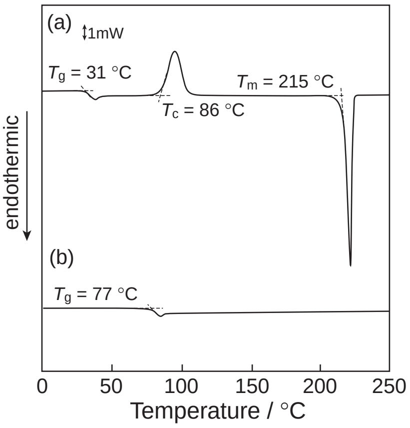


Figure 2. DSC thermograms of second heating process of (a) **S4** and (b) **S7**. Scan rate = 10 degree min^{-1}.

To obtain the information on the morphology of the glassy samples, X-ray diffraction (XRD) was investigated (Figure 3). While XRD of recrystallized **S7** showed typical sharp peaks due to the crystallinity of the sample, XRD of the glassy **S7** showed two broad peaks at $2\theta = 8.5°$ ($d = 10.4$ Å) and 20.6° ($d = 4.31$ Å). It is reported that polysilylenes having two alkyl groups show a strong peak at 7–9° indexed as superposition of d_{110} and d_{020} of an orthorhombic lattice with hexagonally packed chains, and a broad peak centered at around 20° indexed as d_{013}.[8] Thus, peaks observed in glassy **S7** can be assigned similarly to the above-mentioned case of polysilylenes. From these data, the distance between two neighbor oligosilylenes can be estimated as 12.0 Å, which is coincident with the diameter of the oligo(diphenylsilylene) molecules having trans-zigzag structures. In polarized microscopy, the image of glassy samples in cross-nicol state is dark, and suggests to be isotropic. Thus, the arrangement of molecules in glassy **S7** might be mainly amorphous, with only two-dimensional order of hexagonally packed structure.

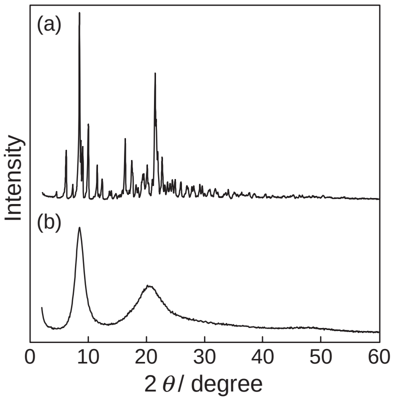


Figure 3. X-ray diffraction patterns of (a) crystalline and (b) glassy **S7**.

To our best knowledge, our result is the first report on the creation of glassy low-molecular weight materials based on silicon-containing compounds.

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