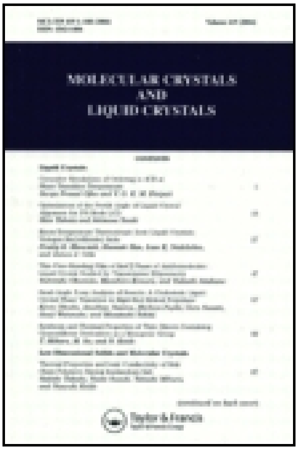

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Even-odd Effect of Chain Length on Glass-forming Property of Oligosilylenes

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Even-odd Effect of Chain Length on Glass-forming Property of Oligosilylenes

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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 had even-odd effect of chain length. Glassy samples were found mainly amorphous with low degree of two-dimensional order of hexagonal packing.

Keywords: σ-conjugated system; even-odd effect; glass-forming property; oligosilylenes; well-defined structures

INTRODUCTION

Since the photo- and electroactivity of the organic conjugated polymeric materials was 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 still ill-established, because of their molecular weight distribution and structural defect.

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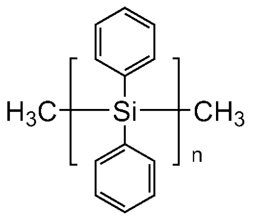


S1 : n = 1
S2 : n = 2
S3 : n = 3
S4 : n = 4
S5 : n = 5
S6 : n = 6
S7 : n = 7

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

Contrary, low-molecular weight organic materials are good candidates for the photo- and electroactive materials to show superior property to those of polymeric materials due to their well-defined structures, although they tend to crystallize. 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 materials are widely used as the thermally stable insulator in photoconductor and photoresist systems, 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 [3]. Very recently, Yatabe and 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 are higher than those of polysilylenes by one order. However, there are no reports on the glass-forming properties of oligosilylenes. Creation of glassy oligosilylenes 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. Here, we report the synthesis and glass-forming properties of novel α,ω-dimethyloligo(diphenylsilylene)s (Fig. 1).

EXPERIMENTAL

General

NMR (^{1}H, 500 MHz; ^{13}C, 125.5 MHz; ^{29}Si, 99.5 MHz) spectra were obtained in $CDCl_3$ on a Varian Unity *INOVA*. Chemical shifts are reported in ppm relative to internal $CHCl_3$ (7.26, ^{1}H), $CDCl_3$ (77.00, ^{13}C), and internal tetramethylsilane (0.00, ^{29}Si). Thermal properties were investigated by differential scanning calorimetry (Seiko Instruments Inc., EXSTAR6000, DSC6200, heating and cooling rate: 10 degree min^{-1}). Powder X-ray diffraction (XRD) was performed with graphite-monochromatized Cu Kα radiation by Rigaku X-ray Diffractomer *RINT*.

Materials

Solvents were dried by standard procedures and distilled before use. 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.

Synthesis of 1,3-Dimethyl-1,1,2,2,3,3-hexaphenyltrisilane (S3)

S2 (3.95 g, 10 mmol) and lithium (0.25 g, 30 mmol) were mixed in THF (50 mL) under Argon, and stirred at room temperature for 12 hr. The solution was filtrated to remove the excess amount of lithium, and poured into THF (25 mL) solution of diphenyldichlorosilane (2.60 g, 10 mmol). The mixture solution was stirred at room temperature for 12 hr. Then, solvent was removed and the residue was washed by water. The crude product was purified by repetitive recrystallization from ethanol to give white needle crystal (2.3 g, 4 mmol, yield 40%). ^{1}H NMR: δ 0.45 (s, C$\boldsymbol{H}_3$, 6H), 7.18 (t, *m*-***H*** in Ph, 4H, $J = 7.32$ Hz), 7.19 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 7.21 (dd, *o*-***H*** in Ph, 8H, $J = 7.32$, 1.37 Hz), 7.29 (tt, *p*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz), 7.30 (dd, *o*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz), 7.31 (tt, *p*-***H*** in Ph, 2H, $J = 7.32$, 1.37 Hz). ^{13}C NMR: δ –3.0 ($\boldsymbol{C}$H$_3$), 127.7 (*m*-***C*** in Ph), 127.8 (*m*-***C*** in Ph), 128.6 (*p*-***C*** in Ph), 128.9 (*p*-***C*** in Ph), 134.6 (*ipso*-***C*** in Ph), 135.4 (*o*-***C*** in Ph), 136.8 (*ipso*-***C*** in Ph), 136.8 (*o*-***C*** in Ph). ^{29}Si NMR: δ -42.2, -21.0. ESI-MS (m/e): 599.20284 (M + Na).

Synthesis of 1,4-Dimethyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane (S4)

S2 (1 g, 2.5 mmol) and lithium (70 mg, 10 mmol) were mixed in THF (30 mL) under Argon, and stirred at room temperature for 4 hr. The solution was filtrated to remove the excess amount of lithium, and poured into THF (20 mL) solution of diphenyldichlorosilane (3 g, 10 mmol). The mixture solution was stirred at room temperature for

12 hr. Then, solvent and excess amount of diphenyldichlorosilane was removed in vacuo, and the residue was dissolved in THF (30 mL). Lithium (35 mg, 5 mmol) was added into this solution, and the mixture was stirred at room temperature for 12 hr. Solvent was removed, and the residue was washed by water. The crude product was purified by repetitive recrystallization from hexane to give white powder (0.2 g, 0.5 mmol, yield 20%). ^{1}H NMR: δ 0.34 (s, C***H***$_3$, 6H), 7.04 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 7.06 (dd, *o*-***H*** in Ph, 8H, $J = 7.32$, 1.37 Hz), 7.05 (t, *m*-***H*** in Ph, 8 H, $J = 7.32$ Hz), 7.14 (dd, *o*-***H*** in Ph, 8H, $J = 7.32$, 1.37 Hz), 7.22 (tt, *p*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz), 7.25 (tt, *p*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz). ^{13}C NMR: δ –2.6 (***C***H$_3$), 127.5 (*m*-***C*** in Ph), 127.6 (*m*-***C*** in Ph), 128.5 (*p*-***C*** in Ph), 128.7 (*p*-***C*** in Ph), 134.4 (*ipso*-***C*** in Ph), 135.4 (*o*-***C*** in Ph), 136.8 (*ipso*-***C*** in Ph), 137.2 (*o*-***C*** in Ph). ^{29}Si NMR: δ –38.0, –20.1. ESI-MS (m/e): 781.24314 (M + Na).

Synthesis of 1,5-Dimethyl-1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane (S5)

Decaphenylcyclopentasilane (0.96 g, 1.1 mmol) and lithium (24 mg, 3.4 mmol) were mixed in THF (10 mL) under Argon, and stirred at room temperature for 6 hr. The solution was filtrated to remove the excess amount of lithium, and poured into THF (10 mL) solution of methyliodide (0.52 g, 3.6 mmol). The mixture solution was stirred at room temperature for 12 hr. Then, solvent and excess amount of methyliodide were removed *in vacuo*. The residue was dissolved in toluene:hexane = 1:1, and insoluble inorganic salt was removed by column chromatography. The crude product was purified by preparative GPC and reprecipitation from toluene to hexane to give white powder (73 mg, 0.07 mmol, yield 7%). ^{1}H NMR: δ 0.255 (s, C***H***$_3$, 6H), 6.85 (t, *m*-***H*** in Ph, 4H, $J = 7.32$ Hz), 6.90 (dd, *o*-***H*** in Ph, 8H, $J = 7.32$, 1.37 Hz), 6.92 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 6.76 – 7.01 (m, *o*-***H*** and *m*-***H*** in Ph, 20H), 7.15–7.22 (m, *p*-***H*** in Ph, 10H). ^{13}C NMR: δ –2.3 (***C***H$_3$), 127.4 (*m*-***C*** in Ph), 127.4 (*m*-***C*** in Ph), 127.5 (*m*-***C*** in Ph), 128.3 (*p*-***C*** in Ph), 128.5 (*p*-***C*** in Ph, two signals are overlapped), 133.9 (*ipso*-***C*** in Ph), 134.4 (*ipso*-***C*** in Ph), 135.4 (*o*-***C*** in Ph), 137.0 (*ipso*-***C*** in Ph), 137.3 (*o*-***C*** in Ph), 137.5 (*o*-***C*** in Ph). ^{29}Si NMR: δ –35.4, –34.5, –20.2. ESI-MS (m/e): 963.34040 (M + Na).

Synthesis of 1,6-Dimethyl-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane (S6)

Methyllihium (1.2 M in diethylether, 0.85 mL, 1 mmol) was added into THF (10 mL) solution of decaphenylcyclopentasilane (0.91 g, 1 mmol), and stirred at room temperature for 20 min. Diphenylmethylchlorosilane (0.28 g, 1.2 mmol) was added into this solution, and the mixture solution was stirred at room temperature for 12 hr. Solvent and excess amount of diphenylmethylchlorosilane were removed *in vacuo*. The residue was dissolved in toluene, and insoluble inorganic salt was removed by column chromatography. The crude product was purified by preparative GPC and reprecipitation from toluene to hexane to give white powder (46 mg, 0.04 mmol, yield 4%). ^{1}H NMR: δ 0.14 (s, C$\boldsymbol{H}_3$, 6H), 6.71 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 6.78–6.83 (m, *o*-***H*** in Ph, 24H), 6.89 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 6.95 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 7.10–7.16 (m, *p*-***H*** in Ph, 8H), 7.18 (tt, *p*-***H*** in Ph, 4H, $J = 1.37$, 7.32 Hz). ^{13}C NMR: δ –2.4 (***C***H$_3$), 127.2 (*m*-***C*** in Ph, two signals are overlapped), 127.3 (*m*-***C*** in Ph), 128.2 (*p*-***C*** in Ph), 128.3 (*p*-***C*** in Ph), 128.3 (*p*-***C*** in Ph), 133.7 (*ipso*-***C*** in Ph), 134.6 (*ipso*-***C*** in Ph), 135.4 (*ipso*-***C*** in Ph), 137.1 (*ipso*-***C*** in Ph), 137.3 (*o*-***C*** in Ph), 137.5 (*o*-***C*** in Ph). ^{29}Si NMR: δ –35.8, –31.4, –21.0. ESI-MS (m/e): 1145.38139 (M + Na).

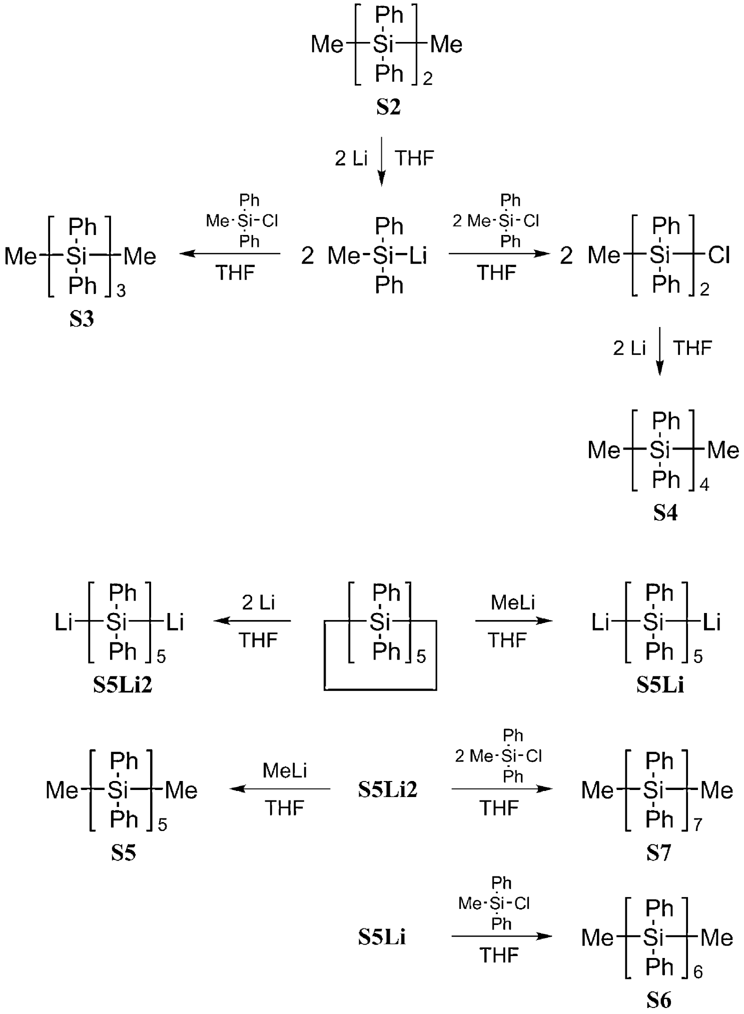
Synthesis of 1,7-Dimethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7-tetradecaphenylheptasilane (S7)

Decaphenylcyclopentasilane (4.6 g, 5 mmol) and lithium (0.15 g, 20 mmol) were mixed in THF (50 mL) under Argon, and stirred at room temperature for 2 hr. The solution was filtrated to remove the excess amount of lithium, and poured into THF (20 mL) solution of diphenylmethylchlorosilane (3.3 g, 14 mmol). The mixture solution was stirred at room temperature for 12 hr. Then, solvent was removed, and the residue was washed by water. The crude product was purified by repetitive recrystallization from toluene-hexane to give white powder (1.4 g, 1 mmol, yield 20%). ^{1}H NMR: δ 0.025 (s, C$\boldsymbol{H}_3$, 6H), 6.47 (t, *m*-***H*** in Ph, 4H, $J = 7.32$ Hz), 6.54 (dd, *o*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz), 6.65 (dd, *o*-***H*** in Ph, 8H, $J = 7.32$, 1.37 Hz), 6.73 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 6.75 (dd, *o*-***H*** in Ph, 8H, $J = 7.32$, 1.37 Hz), 6.77 (dd, *o*-***H*** in Ph, 8H, $J = 7.32$, 1.37 Hz), 6.83 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 6.92 (t, *m*-***H*** in Ph, 8H, $J = 7.32$ Hz), 7.03 (tt, *p*-***H*** in Ph, 2H, $J = 7.32$, 1.37 Hz), 7.10 (tt, *p*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz), 7.12 (tt, *p*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz), 7.14 (tt, *p*-***H*** in Ph, 4H, $J = 7.32$, 1.37 Hz). ^{13}C NMR: δ –2.6 (***C***H$_3$), 127.1 (*m*-***C*** in Ph, two signals are overlapped), 127.2 (*m*-***C*** in Ph, two signals are overlapped), 128.0 (*p*-***C*** in Ph, two signals are overlapped), 128.2 (*p*-***C*** in Ph), 128.3 (*p*-***C*** in Ph), 133.4 (*ipso*-***C*** in Ph), 133.9 (*ipso*-***C*** in Ph), 134.4 (*ipso*-***C*** in Ph), 135.3 (*o*-***C*** in Ph), 137.0 (*ipso*-***C*** in Ph), 137.2 (*o*-***C*** in Ph), 137.5 (*o*-***C*** in Ph, two signals are overlapped).

^{29}Si NMR: δ –36.9, –31.5, –29.0, –20.8. ESI-MS (m/e): 1327.37325 (M + Na).

RESULTS AND DISCUSSION

Synthetic route of oligosilylenes is shown in Scheme 1. **S3** was synthesized by the coupling reaction of diphenyldichlorosilane with 2eq of



SCHEME 1 Synthesis of oligosilylenes.

diphenylmethylsilyllithium obtained by the cleavage reaction of **S2** with lithium. **S4** was also synthesized by the homocoupling reaction of 1-chloro-1,1,2,2,2-pentamethyldisilane, which was obtained by the coupling reaction of 1eq of diphenyldichlorosilane with 1eq of diphenylmethylsilyllihitum. Oligosilylenes having 5–7 silylene units were synthesized by the ring-opening reaction of decaphenylcyclopentasilane with lithium or methyllihium followed by quenching with methyliodide or diphenylmethylchlorosilane. In each case, starting material is still remained in the crude product. Since the solubility of **S7** is lower than that of decaphenylcyclopentasilane, **S7** can be easily purifed by the repetitive recrystallization. However, because the solubility of **S5** and **S6** is similar to that of diphenylcyclopentasilane, preparative GPC was used for their purification. All samples were characterized by spectroscopic techniques.

Differential scanning calorimetry (DSC) thermograms of **S6** and **S7** are shown in Figure 2, and the data of all samples are summarized in Table 1. While **S1** is liquid at room temperature, the other oligosilylenes are solid at room temperature and showed an endothermic peak at 142 (**S2**), 103 (**S3**), 215 (**S4**), 183 (**S5**), 205 (**S6**), and 217 (**S7**)°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

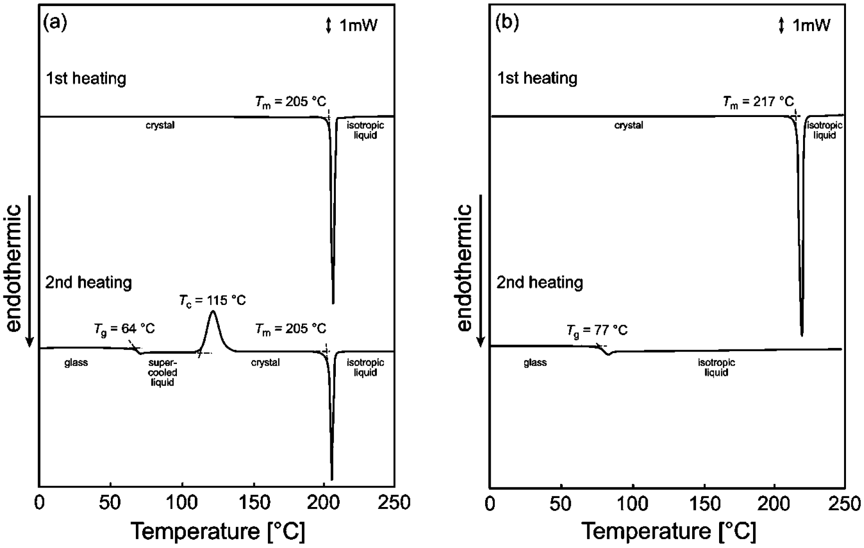


FIGURE 2 DSC thermograms of (a) **S6** and (b) **S7**. Scan rate = 10 degree min^{-1}.

TABLE 1 Thermal Properties of Oligosilylenes[a]

	T_g [°C][b]	T_c [°C][c]	T_m [°C][d]
S1	–89		
S2			142
S3	14[e]		103[f]
S4	(31)[g]	(86)[g]	215
S5	47[e]		183[f]
S6	64[e]	115[e]	205
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}.

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. In the case of **S6**, the first heating process showed only endothermic peak due to the melting behavior, but the second heating process showed glass transition, crystallization, and melting behaviors even though the melt **S6** was cooled at 1 degree min^{-1}. Interestingly enough, oligosilylenes having odd number of silylene units, i.e., **S1**, **S3**, **S5**, 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 **S5** and **S7** is fully stable at room temperature for several months.

To obtain the information on the morphology of the glassy samples, X-ray diffraction (XRD) was investigated (Fig. 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,

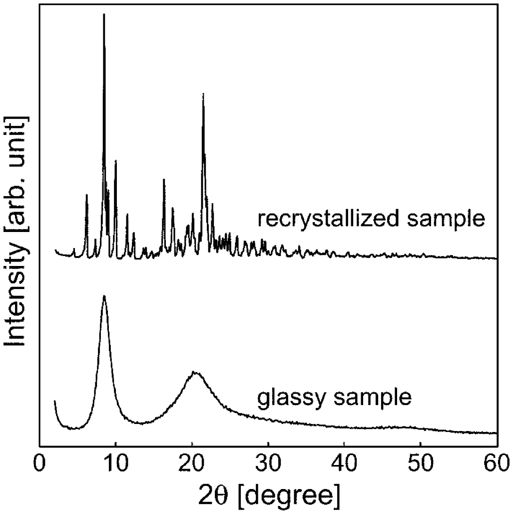


FIGURE 3 X-ray diffraction patterns of recrystallized (top) and glassy (bottom) **S7**.

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.

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

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