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Necklace-shaped Dimethylsiloxane Polymers Bearing a Polyhedral Oligomeric Silsesquioxane Cage Prepared by Polycondensation and Ring-opening Polymerization

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A series of necklace-shaped dimethylsiloxane (DMS) polymers bearing a polyhedral oligomeric silsesquioxane (POSS) cage were synthesized from bifunctional POSS by two different synthetic routes. One-step or two-step polycondensation between POSS and dimethyloligosiloxane dichloride led to necklace polymers with constant chain lengths ($n = 2$–8). The ring-opening polymerization of octamethylcyclotetrasiloxane (D4) with POSS was also found to provide similar necklace-shaped polymers with dispersed chain lengths of DMS. The thermal properties, decomposition temperature ($T_{\mathrm{d5\%}}$), and glass-transition temperatures (T_{g}) of the polymers were strongly dependent on DMS chain length. The polymers with dispersed chain lengths gave higher T_{g}'s than the polymers with corresponding constant chain lengths. The highest $T_{\mathrm{d5\%}}$ reached 478 °C.

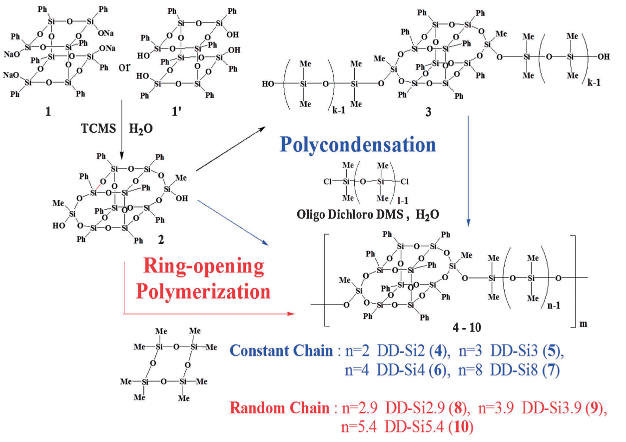

Figure 1. Reaction scheme of ring-opening polymerization of D4 and polycondensation with a bifunctional POSS to produce necklace-type POSS–DMS siloxane polymers.

The great structural possibilities of siloxane molecules lead to a unique variety of chemical structures but also makes rational synthetic control difficult. Among the unlimited structural varieties, polyhedral oligomeric silsesquioxane (POSS)[1] molecules, which possess a nanocage structure, have been studied as a novel class of nanomaterials both from fundamental and industrial aspects. The organic–inorganic composite materials and polymers, which bear or incorporate POSS units, were extensively investigated, because of their expected unique and useful characteristics, such as high heat resistance, low dielectric properties, optical properties, and so on.[2] Among such polymers, POSS units have frequently been applied as pendant units in vinyl polymers and as terminating groups[3] and multifunctional crosslinkers,[4] but incorporation of the polymer bearing POSS cage in the main chain has been very limited[5–7] because of the difficulty of controlling the number of functional units on a POSS. The key for designing siloxane polymers bearing a POSS cage in a main chain is the presence of two reactive units on a silsesquioxane cage.[5–7] As a pioneering work, Lichtenhan and co-workers have reported the synthesis of discrete silsesquioxane–siloxane copolymers bearing a defective octahedral cube of which a part is open.[5] In addition, a fully closed bifunctional POSS molecule has been synthesized from a double-decker-type silsesquioxane.[8] The alternating siloxane copolymers, which consisted of a bifunctional POSS cage and a flexible linear dimethyloligosiloxane (DMS) chain segment, were independently researched by two groups including us. Kawakami[7] has reported polysiloxanes with periodically distributed isomeric double-decker silsesquioxane in the main chain. Here, we report two novel synthetic methodologies to produce necklace-shaped POSS–siloxane polymers by stepwise polycondensation and equilibrium polymerization of octamethylcyclotetrasiloxane (D4).

Figure 1 shows three synthetic routes to necklace-shaped DMS polymers, consisting of a bifunctional POSS unit **2** and DMS chains, by polycondensation and ring-opening polymerization. A key molecule, bifunctional POSS **2** with two silanol groups, was synthesized by the reaction between a double-decker type silsesquioxane intermediate **1** or **1′** (supplied by JNC Co., Ltd.) and trichloromethylsilane (TCMS), followed by hydrolysis of the Cl units remaining on the closed DD intermediate. A series of the necklace-type POSS–DMS polymers (4–7), bearing constant repeating units of DMS chains ($n = 2$, 3, 4, and 8) were synthesized by means of a one-step or two-step reaction with dichlorodimethylsiloxane (DCMS, $l = 2$–4).[18]

On the other hand, it was found that similar polymers were also produced by the simple acid-catalyzed thermal reaction of POSS **2** with octamethylcyclotetrasiloxane (D4).[18] This reaction is known as the ring-opening equilibrium reaction[9–15] of D4 and is used to produce polydimethylsiloxane (PDMS) industrially. As a typical procedure, the ring-opening polymerization of D4 was initiated in toluene solution at 100–130 °C with POSS **2** and water remover $MgSO_4$ by adding of *p*-toluenesulfonic acid. The solution was stirred at the reaction temperature typically for 12 h. After the solution was cooled to room temperature $MgSO_4$ and intact POSS were recovered by filtration. The polymer

Table 1. Average molecular weights, average DMS chain lengths, and thermal properties of POSS–DMS copolymers

Sample No.		Monomer ratio in preparation D4:POSS	Yield (%) (recover% of D4)	M_w/ 10^4	M_w/ M_n	Average DMS length n	T_{d5} /°C	T_g /°C
4	DD-Si2	—	—	9.1	3.7	2	443	237
5	DD-Si3	—	—	17	3.0	3	441	42.9
6	DD-Si4	—	—	26	3.7	4	421	26.7
7	DD-Si8	—	—	8.0	1.8	8	410	9.22
8	DD-Si2.9	1:1	53 (22)	12	2.6	2.9	478	47.7
9	DD-Si3.9	1:2	42 (27)	7.8	1.9	3.9	415	28.4
10	DD-Si5.4	1:4	10 (46)	7.9	1.5	5.4	447	21.6

solution was washed with water until the pH was neutral. No undesired crosslinking by POSS units was observed.[16,17] All polymers **4**–**10** prepared by both methods were dissolved in common organic solvents such as THF, $CHCl_3$, acetone, and toluene and were purified by reprecipitation using toluene and hexane as good and poor solvents, respectively. By the reprecipitation, oligomeric products were removed. Exceptionally, water/methanol mixed solvent was used as a poor solvent for the purification of polymer **7**.

The formation of the polymers bearing POSS cages was confirmed by size exclusion chromatography (SEC) and ^{1}H NMR. Both synthetic methodologies gave necklace-shaped POSS–DMS polymers with high molecular weight (more than seventy thousand) and wide dispersion according to SEC results with polystyrene (PS) standard (Figure S2[18]). The estimated value of $M_n = 1173$ for POSS **2** obtained by SEC using PS standards was very close to the actual molecular weight ($M_n = 1186$), indicating that PS standard M_w is fiducial for POSS–DMS polymers.

Table 1 summarizes M_w's, the dispersions (M_w/M_n), average DMS lengths, decomposition temperatures ($T_{d5\%}$), and glass-transition temperatures (T_g) estimated by thermal gravimetric analysis and thermal mechanical analysis of the polymers. M_w's were strongly dependent on the polymerization conditions for both methods. In the case of polycondensation, the dehydration conditions were crucial to get high-molecular-weight products for polymers (4–7). Slight water contamination led to obvious lowering of M_w. In carefully conducted conditions, an extremely high M_w fraction of greater than a million was frequently formed. Additionally, SEC elution curves showed no dependence on concentration, indicating no aggregation. The agreement of profiles on SEC between refractive index detection and UV adsorption detection at 256 nm to monitor phenyl groups on POSS units proved that there was no formation of intact DMS polymers even in the case of ring-opening polymerization (Figure S2[18]).

In the case of ring-opening polymerization, water contamination does not seem to be severe because of the high reaction temperature. However, the M_w was strongly dependent on the temperature and the time of reaction. Very high polymers, such as $M_w = 250000$ for DD-Si3.9, could also be obtained.

Figure 2 shows typical ^{1}H NMR spectra of the polymer prepared by both polymerizations. The necklace-shaped alternate structures of the siloxanes **4**–**7** with constant lengths of DMS chains were characterized by ^{1}H NMR (Figure S3[18]).

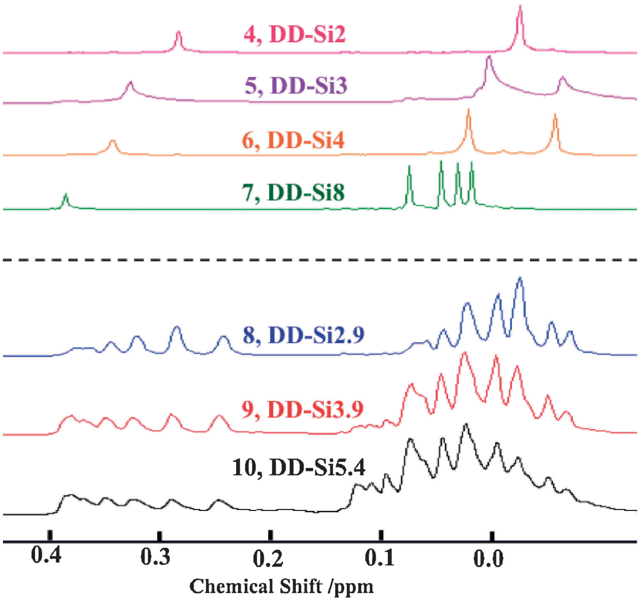

Figure 2. ^{1}H NMR spectra of POSS–DMS polymers bearing constant length DMS chains **4**–**7** and random length **8**–**10** DMS chains prepared by polycondensation and ring-opening polymerization, respectively.

^{1}H NMR signals of the series of polymers were assigned to phenyl units and methyl units on a POSS and methyl units on a DMS chain based on resonances observed at between 7.62 and 7.18, 0.247 and 0.381, and −0.0682 and 0.122 ppm, respectively. In addition, the terminal silanol unit on POSS and methyl units on D4 are observed at 6.31 and 0.108 ppm respectively. Average repeating unit length (n) of DMS was obtained from the ratio between phenyl and methyl moieties. As expected, the repeating unit length (n) of DMS moieties obtained from ^{1}H NMR was consistent for the polymers.[4–7] The results proved the formation of "one by one" alternate siloxane copolymer by the polycondensation. No unexpected DMS fragments, for instance, a double length unit, were observed.

In contrast, the polymers,[8–10] prepared by ring-opening polymerization, had a diversity of DMS chain lengths. No direct connection of POSS to POSS without DMS and no formation of PDMS without POSS were observed, indicating that the polymers possessed a POSS–DMS alternate structure even for the polymers prepared by the ring-opening method. Interestingly, not only multiples of four, Si4 and Si8, expected as a simple ring-opening polymerization of D4, but also other lengths including shorter DMS chains, such as Si1, Si2, and Si3, were always formed during the polymerization. This revealed that cleavage and recombination of DMS chains simultaneously proceeds catalytically during an equilibrium polymerization. It should be emphasized that the cage structure of POSS units was stable during the reaction, although DMS chains were attacked continuously. In a similar control reaction of the POSS cage in the presence of p-toluenesulfonic acid and $MgSO_4$ and in absence of D4, no reaction occurred and only unreacted POSS cage was recovered. As we mentioned, insoluble crosslinked polymers, which were expected to be formed from an opened structure of POSS, were not obtained at

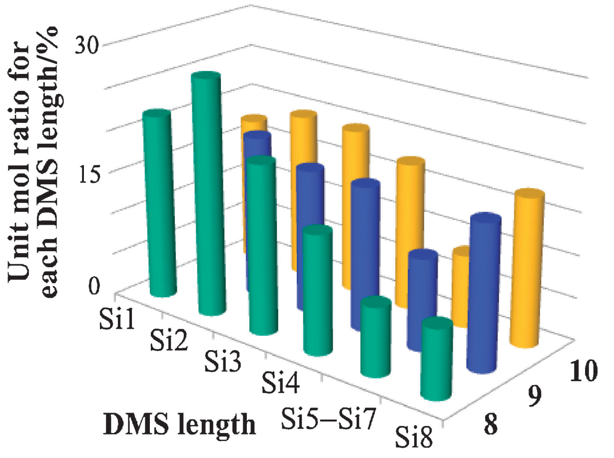

Figure 3. DMS chain length distribution of POSS–DMS polymers, DD-Si2.9 (**8**), DD-Si3.9 (**9**), and DD-Si5.4 (**10**).

all. In addition, the content of Si8, which would be a simple ring-opening product, was remarkably higher than other short chain fragments in the polymer **10**, which was produced in conditions with a relatively higher molar ratio of D4/POSS.

The fraction molar ratios of polymers **8**–**10** were characterized and compared with polymers **4**–**7**, which had constant chain lengths (Figure 3). For characterization, the ^{1}H NMR signals of methyl units on POSS were applied, because the chemical shift of methyl units on POSS, which were formed by the capping reaction of **1**, was more sensitive to the DMS chain length than methyl units on DMS. The assignment of Si1–Si4 and Si8 was achieved by comparison of the polymers **4**–**7**. Those of Si5, Si6, and Si7 were calculated as a mixed fraction, because they could not be assigned separately. The average DMS chain length (n) was roughly controllable by means of the molar ratio of D4 and POSS. The n value increased with the increasing D4/POSS ratio in preparation. In the case of molar ratio D4/POSS = 1 compared with that of 4, the content of short chains from Si1 ($n = 1$) and Si4 ($n = 4$) was higher than the content of longer chains.

By simple solvent casting, polymers **4**–**6** and **8**–**10** (but not **7**) gave transparent thermoplastic sheets, suggesting amorphous polymers. As expected, the flexibility increased with increasing chain lengths. In the case of the polymers bearing short chains ($n < 3$), the polymers with M_w of several tens of thousands and greater than 100000 gave rather brittle and robust plastics, respectively. The polymers with middle chain lengths (**6**, **9**, and **10**) gave transparent, robust and flexible sheets. The polymer with the longest chain, **7**, was a high-viscosity liquid at room temperature.

These polymers showed extremely high $T_{d5\%}$, for example, 478 °C for DD-Si2.9, which is much higher than that obtained for PDMS ($T_{d5\%}$ = ca. 300 °C). The higher $T_{d5\%}$ is due to the high content of homogeneously dispersed POSS units in the polymers, in which all connections are made up of siloxane bonds. The incorporation of silsesquioxane segments into linear siloxane polymers enhances the thermal stabilities.[5,7] The values of both $T_{d5\%}$ and glass-transition temperatures (T_g's) increased with decreasing DMS chain lengths for the polymers prepared by both methods. The extension of the flexible silicone chain units led to a decrease of T_g. In addition, a liquid-crystal phase was not observed for any of the polymers over the whole temperature range. Interestingly, the polymers **8** and **9** with dispersed chain lengths gave higher T_g's compared with the polymers **5** and **6** having constant chain lengths, a finding probably due to the former's higher homogeneity in terms of dispersiveness of POSS units in the polymers.

The POSS–DMS siloxane copolymers having well-defined nanostructures will provide fundamental knowledge about the correlation between nanostructure and physical properties for the development of new silsesquioxane-based materials. The details of the research to elucidate the correlation between physical properties and the design of necklace-shaped POSS–DMS polymers in terms of chain lengths and arrangements will be forthcoming in a future publication.

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