Preparation of POSS derivatives by the dehydrogenative condensation of T$_8^H$ with alcohols

Satoru TSUKADA, Yusuke SEKIGUCHI, Shoto TAKAI, Yoshimoto ABE and Takahiro GUNJI

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278–8510, Japan

POSS derivatives were synthesized by the dehydrogenative reaction of octahydrosilsesquioxane with alcohols. The reaction with 2-methacryloyloxyethanol, 1-methacryloyloxy-2-propanol, and diphenyl methanol provided corresponding octaalkoxylated POSS derivatives. The reaction with ethylene glycol provided silica gel, while the reaction with 2,3-butanediol or pinacol provided polymers and oligomers, respectively. The product by the reaction of POSS with 2,2-butanediol was spin-coated on a silicon wafer and heated to provide a silica coating film with a pencil-hardness of 2H.

Key-words : Poly octahedral oligosilsesquioxane, Alcohol, Diol, Dehydrogenative condensation, Polymer

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are cage silsesquioxane compounds with the formula (RSiO$_3$)$_n$ (R: functional group) in which a three-dimensional closed-ring system forms an internal space at the center of the compound.$^{11}$ Cage silsesquioxanes are expected to be next generation materials which is supported by the fact that many review articles and books have been published on the preparation of compounds$^{2–7}$ and polymer composites.$^{8–11}$ These properties can be controlled easily by the chemical and physical properties of the side-chains.$^{12,13}$

Cage silsesquioxanes are synthesized by the hydrolytic polycondensation of tri- or tetra-functional silanes. Octakishydrido-octasilsequioxane with the formula (HSiO$_3$)$_8$ is the most fundamental cage silsesquioxane,$^{14}$ and is abbreviated T$_8^H$.

Cage silsesquioxanes are a new type of organosilicon material because they have a specific size and form, as well as higher Si–O–Si linkage content compared to typical silicones. In addition, they are easily introduced into an organic–inorganic hybrids by applying a technique in traditional polymer composite techniques. Cage-silsesquioxane-containing polymer hybrids are classified into the following three types: (i) pendant; (ii) copolymer; and (iii) additive. Haddad et al. synthesized copolymers by the radical polymerization of styrene and cage silsesquioxane bearing the styrly group. The temperature of 10% weight-loss was observed to be 445°C, higher than that of poly(4-methylstyrene) (388°C)$^{15}$ Laine et al. synthesized siloxy derivatives of cage silsesquioxane and obtained microporous material with pore sizes of 1–2 nm by connecting this cage derivative with hydrosilyl groups. The reaction with ethylene glycol provided silica gel, while the reaction with 2,3-butanediol or pinacol provided polymers and oligomers, respectively. The product by the reaction of POSS with 2,2-butanediol was spin-coated on a silicon wafer and heated to provide a silica coating film with a pencil-hardness of 2H.

2. Experimental procedure

2.1 Reagents and substrate

T$_8^H$ was synthesized by the procedure described in a previous study.$^{14}$ Chloro(trimethyl)silane (Shin-Etsu Chemical Co., Ltd., Tokyo) was distilled before use.

Tetrahydrofuran (THF) and benzene (Wako Pure Chemical Co., Ltd.) were dried by reflux on sodium and the following distillation. Acetone, 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl methacrylate (HPMA), glycidiol, phenol, 2-propanethiol, diphenylmethanol, triphenylmethanol, ethylene glycol (EG), 2,3-butanediol (BD), pinacol (PC), and triethylamine (Wako Pure Chemical Co., Ltd., Tokyo) were dried by molecular sieves overnight. HPMA was found to contain 30% 3-hydroxypropyl methacrylate; however, HMPA was used as received because it was difficult to separate 3-hydroxypropyl methacrylate from 2-hydroxypropyl methacrylate.
Diethylhydroxylamine (Aldrich, Tokyo) was used after drying over molecular sieves 4A overnight. Tricyclohexylmethanol (Aldrich, Tokyo) was used as received. Silicon wafer (E&M Corporation, Ashiya, Hyogo, Japan, P-doped N-type Si wafer 5N100-EFJ1024, thickness 625 ± 25 μm, single mirror treatment) was cut to an appropriate size and cleaned before use with acetone and concentrated nitric acid for 30 min under microwave irradiation.

2.2 Synthesis of alkoxylated cage silsesquioxane

Q₈HEMA: 1H NMR (300 MHz, in acetone-d₆) δ 1.92 (24H), 4.12 (16H), 4.25 (16H), 5.65 (8H), 6.12 (8H). ¹³C NMR (300 MHz, in acetone-d₆) δ 18.47, 63.23, 65.87, 126.18, 137.17, 167.45. ²⁹Si NMR (60 MHz, in acetone-d₆) δ -103.07. IR (CCl₄) / cm⁻¹ 3446, 2956, 1723, 1637, 1454, 1320, 1296, 1169, 1109, 592, 473. FAB-MS 1450 [M+H]⁺, 1337 [M-C₆H₉O₂]⁺, 1251 [M-2C₃H₇O₂]⁺.

Q₈HPMA: 1H NMR (300 MHz, in benzene-d₆) δ 1.13 (16.8H), 1.17 (7.2H), 1.94 (24H), 3.85 (4.8H), 4.10 (11.2H), 4.35 (5.6H), 5.13 (2.4H), 5.41 (8H), 6.26 (8H). ¹³C NMR/ppm (75 MHz, in benzene-d₆) δ 15.96, 18.34, 18.38, 19.60, 66.74, 68.76, 69.00, 70.80, 125.46, 125.73, 136.55, 136.91, 166.45, 166.68. ²⁹Si NMR/ppm (60 MHz, in benzene-d₆) δ -102.52, -103.65. IR/cm⁻¹ (CCl₄) 2982, 1722, 1638, 1509, 1453, 1325, 1294, 1171, 1101, 942, 593. FAB-MS 1561 [M+H]⁺, 1434 [M-C₆H₉O₂]⁺, 1266 [M-2C₃H₇O₂]⁺, 1120 [M-C₆H₉O₂-C₃H₇O₂]⁺.

Q₈DPM: 1H NMR (300 MHz, in acetone-d₆) δ 5.83 (1H), 7.25 (10H). ¹³C NMR (75 MHz, in acetone-d₆) δ 78.26, 127.46, 128.28, 129.15, 144.06, 206.29. ²⁹Si NMR (60 MHz, in acetone-d₆) δ -103.91. IR (CCl₄) / cm⁻¹ 3706, 3613, 3065, 3031, 2887, 1168, 1087. ESI-MS 1903 [M+Na]⁺.

2.3 Synthesis of EG-POSS

T₈H 0.3 g (0.71 mmol), THF 30 mL, benzene 40 mL, and the stated amount of ethylene glycol were charged into a 200-mL two-necked flask fitted with a reflux condenser. Diethylhydroxylamine 1.0 μL (10 μmol) was added to this mixture and stirred for 0.5 h at 0°C. Chlorotrimethylsilane 1.4 g (12.6 mmol) was then added and stirred for 0.5 h. Triethylamine 1.3 g (12.6 mmol) and THF 10 mL were added to the mixture and subjected to reflux for 1 h. Triethylenyl-hydrogen chloride salt was separated by filtration. The filtrate was concentrated under reduced pressure to produce a white powder.

2.4 Synthesis of BD-POSS

T₈H 0.3 g (0.71 mmol), THF 30 mL, benzene 40 mL, and the stated amount of 2,3-butanediol were charged into a 200-mL two-necked flask fitted with a reflux condenser. Diethylhydroxylamine 1.0 μL (10 μmol) was added to this mixture and stirred for 0.5 h at 0°C. Chlorotrimethylsilane 1.4 g (12.6 mmol) was then added and stirred for 0.5 h. Triethylenylamine 1.3 g (12.6 mmol) and THF 10 mL were added to the mixture and subjected to reflux for 1 h. Triethylenyl-hydrogen chloride salt was separated by filtration. The filtrate was concentrated under reduced pressure and then methanol was added with vigorous stirring. After filtration, the
residue was dried under reduced pressure to produce a white powder.

2.5 Synthesis of PC-POSS

$T_8^{2H}$ 0.3 g (0.71 mmol), THF 30 mL, benzene 40 mL, and the stated amount of pinacol were charged into a 200-mL two-necked flask fitted with a reflux condenser. Diethylhydroxylamine 1.0 μL (10 μmol) was added to this mixture and stirred for 0.5 h at 0°C. Chlorotrimethylsilane 1.4 g (12.6 mmol) was then added and stirred for 0.5 h. Triethylamine 1.2 g (12.6 mmol) and THF 10 mL were added to the mixture and subject to reflux for 1 h. Triethylamine-hydrogen chloride salt was separated by filtration. The filtrate was concentrated under reduced pressure and then methanol was added with vigorous stirring. After filtration, the residue was dried under reduced pressure to create a white powder.

2.6 Preparation of coating films

Coating solution was prepared by dissolving BD-POSS in THF and then filtering with a membrane filter (pore size 0.5 μm). The coating film was prepared by spin-coating the solution on a silicon wafer (2000 rpm for 30 s) using a spin-coating machine (Kyowariken K-359 S-1), followed by heating in an electrical furnace at 100–800°C for 1 h under an air atmosphere.

2.7 Measurements

The $^1$H, $^{13}$C, and $^{29}$Si NMR spectra were recorded using a JEOL ECP-500 ($^1$H at 500.00 MHz, $^{13}$C at 125.00 MHz, and $^{29}$Si at 99.00 MHz) spectrometer. Chemical shifts were reported as $\delta$ units (ppm) relative to tetramethylsilane, and the residual solvent peaks were used as the standard.

The Fourier transform infrared (FTIR) spectra were measured with a JASCO FT/IR-6100 IR spectrophotometer. A sample was dissolved in carbon tetrachloride and measured so called as CCl$_4$ solution method.

Gel permeation chromatography (GPC) was performed with high-performance liquid chromatography (Shimadzu Co., Ltd.), with a Polymer Laboratories Mixed D column (PL gel 5 μm), an LC-6AD pump, and a RID-10A detector (Shimadzu Co., Ltd.); THF was used as an eluent at a flow rate of 1.0 mL/min. Poly-styrene was used as a standard.

Recycle-type GPC was performed with high-performance liquid chromatography (Shimadzu Co., Ltd.), with a Polymer Laboratories Mixed D column, an LC-6AD pump, and a RID-10A detector (Shimadzu Co., Ltd.) using THF as an eluent at a flow rate of 8.0 mL/min.

Thermogravimetric/differential thermal analysis (TG/DTA) was performed using Mac Science TG/DTA 2020s under a nitrogen and air atmosphere. The heating rate was 10°C/min.

The pencil-hardness was tested using the Yasuda Seiki Seisakusho electric system pencil hardness tester No. 533-M1, and the heating rate was 10°C/min. The heating rate was 8.0 mL/min.

The reaction of $T_8^{2H}$ with HPMA was therefore examined in the same manner described above. $Q_8^{HPMA}$ was isolated by a recycle type gel permeation chromatography as a transparent and viscous liquid in 44% yield. The high yield of $Q_8^{HPMA}$ compared with $Q_8^{HEMA}$ was due to the limited production of polymeric compounds. The $^1$H NMR spectrum of $Q_8^{HPMA}$ revealed that the allyloxy group in $Q_8^{HPMA}$ was a mixture of 2-methacryloyloxy-1-methylethyl group (2-HPMA) and 3-methacryloyloxypropy group (1-HPMA) in the molar ratio of 7:3, because the HPMA solution was a mixture of 2-hydroxypropyl methacrylate and 2-hydroxypropyl methacrylate was difficult to separate. The $^{29}$Si NMR spectrum of $Q_8^{HPMA}$ also showed two signals due to 2-HPMA and 1-HPMA at $-103.65$ and $-102.25$ ppm, respectively, in the molar ratio of 7:3. The increased stability against hydrolysis would be due to the reaction with secondary alcohol and the substitution of methacryloxy group to create a bulky group.

$T_8^{2H}$ was reacted with DPM to provide $Q_8^{DPM}$. On the other hand, triphenylmethanol provided tetra-substituted $T_8^{2H}$, but the substituted position could not be determined by NMR spectra. The substitution of the second triphenylimethoxyl group would be disturbed by the steric hindrance of the first triphenylimethoxyl group. In addition, no reaction was observed for tricyclohexylmethoxyl group because of the bulky tricyclohexylmethoxyl group.

The reaction of $T_8^{2H}$ with other compounds with active hydrogens was examined utilizing glycidol, phenol, and 2-propanediol. The progress of the substitution reaction with glycidol or phenol was monitored by the evolution of hydrogen gas, but gel was recovered because of the instability of the silicon-oxygen-carbon linkage toward hydrolysis.

The reaction of $T_8^{2H}$ with other compounds with active hydrogens was performed in the same manner described above. The reaction of $T_8^{2H}$ with alcohol was studied, and alkoxylated cage silsesquioxanes were obtained as shown above. The reactivity increased in order of tertiary, secondary, and primary alcohols. Among these alcohols, secondary alcohols provided alkoxylated cage silsesquioxanes due to the limited production of polymeric compounds of $Q_8^{HEMA}$, polymeric compounds, and unreacted compounds. $Q_8^{HEMA}$ could be isolated by recycle type gel permeation chromatography as a transparent and viscous liquid in 28% yield. The relatively low yield of $Q_8^{HEMA}$ was probably due to the instability of silyl ether against water, because HEMA is a primary alcohol of relatively small steric hindrance.

The reaction of $T_8^{2H}$ with HPMA was therefore examined in the same manner described above. $Q_8^{HPMA}$ was isolated by a recycle type gel permeation chromatography as a transparent and viscous liquid in 44% yield. The high yield of $Q_8^{HPMA}$ compared with $Q_8^{HEMA}$ was due to the limited production of polymeric compounds. The $^1$H NMR spectrum of $Q_8^{HPMA}$ revealed that the allyloxy group in $Q_8^{HPMA}$ was a mixture of 2-methacryloyloxy-1-methylethyl group (2-HPMA) and 3-methacryloyloxypropoxy group (1-HPMA) in the molar ratio of 7:3. The increased stability against hydrolysis would be due to the reaction with secondary alcohol and the substitution of methacryloxy group to create a bulky group.

3.2 Results of the cage silsesquioxane hybrid polymers

The reaction of $T_8^{2H}$ with alcohol was studied, and alkoxylated cage silsesquioxanes were obtained as shown above. The reactivity increased in order of tertiary, secondary, and primary alcohols. Among these alcohols, secondary alcohols provided alkoxylated cage silsesquioxanes due to the lower hydrolyzability of the allyloxy group based on the steric hindrance around the silicon atom. Cage silsesquioxane polymer could be prepared by reaction of polyol with $T_8^{2H}$. 1,2-diols are the simplest polyols that can be used to synthesize cage silsesquioxane polymers. Therefore, ethylene glycol (EG), 2,3-butanediol (BD), and pinacol (PC) were subjected to the reaction with $T_8^{2H}$ to provide cage silsesquioxane polymers such as EG-POSS, BD-POSS, and PC-POSS, respectively.

Table 1 summarizes the results of EG-POSS, BD-POSS, and PC-POSS polymer syntheses. The reaction of $T_8^{2H}$ with EG was carried out by changing the molar ratio of EG/$T_8^{2H}$ as 2, 4, and 6 (runs 1–4). The progress of the reaction was monitored by the evolution of hydrogen gas during the stirring in the ice-bath. The gel permeation chromatography of the crude product in run 3 showed a weight-average molecular weight of 33,000 supporting formation of EG-POSS. Isolation of EG-POSS was attempted
by condensation and reprecipitation to provide gel during the removal of solvent under reduced pressure.

BD was subjected to the reaction with T8H by changing the molar ratio of BD/T8H as 1, 2, 4, and 6 (runs 5–8). Gel forms during the condensation process in runs 5 and 8 because of the hydrolysis and condensation of the residual hydrosilyl group. BD-POSS was recovered as white powder in runs 6 and 7. The weight-average molecular weight was 41,000 (run 6) and 35,000 (run 7). The lower molecular weight of BD-POSS in run 7 compared to that in run 6 suggests that substitution with BD is less favored by the utilization of secondary alcohol. BD-POSS was soluble in THF, chloroform, carbon tetrachloride, acetone, and ethanol, while it was insoluble in hexane and methanol.

The reaction of T8H with PC was carried out by changing the molar ratio of PC/T8H as 2, 4, and 6 (runs 9–11). PC-POSS was isolated as a viscous liquid with the weight-average molecular weight of 2,000. The reaction of T8H with tertiary alcohol is less favored to provide 2-(1,3-dimethyl-3-hydroxybutyl)oxy group substituted cage silsesquioxane.

IR spectra of BD-POSS, T8H, and BD are shown in Fig. 1. The absorption band at 2290 cm⁻¹ due to Si-H was decreased, and the band at 3400 cm⁻¹ due to OH disappeared, which supported the formation of silyl ester by dehydrogenative condensation in the reaction of T8H with BD. The absorption band at 1250 cm⁻¹ is ascribed to the Si-CH₃ bond. The relatively broad band at 1080 cm⁻¹ is ascribed to the siloxane bond in cage structure, which supported the formation of BD-POSS from T8H and BD.

A ²⁹Si NMR spectrum of BD-POSS is shown in Fig. 2. The signals at 12.4, -84.8, -103, and -109.4 ppm were ascribed to M, T₃, Q₃, and Q₄ structures, respectively. The appearance of signals due to Q₃ and Q₄ suggests the formation of BD-POSS by the linkage of T8H by BD.

The peak area ratio of M:T₃:Q₃:Q₄ was calculated as 1:0.6:1.7:2.4. The silicon atoms in BD-POSS were arranged as 1-2 for terminated Q₄, 2.5-3.5 for the Q₄-Q₃ connection, 2.4 for the Q₃-BD connection, and 1 for unreacted T₃. The average unit structure was estimated as shown in Fig. 3. The Q₄-Q₃ connection would be formed by the condensation of the silanol group, which was formed by the reaction of T₈H with water or the hydrolysis of silyl ester.

TG-DTA curves for BD-POSS are shown in Fig. 3. The temperature of 5% degradation was 309.3°C, and the ceramic yield at 1000°C was 79.6%. Exothermic peaks were observed at 279.5

---

**Table 1. Results of the synthesis of EG-POSS, BD-POSS, and PC-POSS**

| Run | Product | Spacer | Molar ratio | Yield (%) | State       | GPCb) |
|-----|---------|--------|-------------|-----------|-------------|-------|
| 1   | EG-POSS | EG     | 2           | —         | Gel         | —     |
| 2   | EG-POSS | EG     | 4           | 0.41      | Viscous liquid | 3.3   |
| 3   | EG-POSS | EG     | 4           | —         | Gel         | —     |
| 4   | EG-POSS | EG     | 6           | —         | Gel         | —     |
| 5   | BD-POSS | BD     | 1           | —         | Gel         | —     |
| 6   | BD-POSS | BD     | 2           | 68        | White powder | 4.1   |
| 7   | BD-POSS | BD     | 4           | 33        | White powder | 3.5   |
| 8   | BD-POSS | BD     | 6           | —         | Gel         | —     |
| 9   | PC-POSS | PC     | 2           | —         | Viscous liquid | 0.2   |
| 10  | PC-POSS | PC     | 4           | —         | Viscous liquid | 0.2   |
| 11  | PC-POSS | PC     | 6           | —         | Viscous liquid | 0.2   |

a) Scale in operation: T₈H 0.03 g (0.71 mmol), Me₃SiCl 0.46 g (1.42 mmol), Et₃N 0.43 g (1.42 mmol). b) Calculated based on standard polystyrene. c) Crude product. d) Yield (g).
Q8DPM, respectively. On the other hand, the reaction with phenol, polymer by control of the molar ratio of T8H with BD. PC-POSS was recovered as a gel. BD-POSS provided a stable propanethiol. The reaction of T8H with HEMA, HPMA, and DPM proceeded successfully to provide Q8HEMA, Q8HPMA, and Q8DPM, respectively. A coating prepared from BD-POSS on silicon wafer afforded a polymer with low molecular weight due to low reactivity. A coating of Q8DPM was heated to form silica coating film with a pencil hardness 2H.

and 312.3°C; these were ascribed to the condensation of the silanol group and combustion of the methyl group, respectively, to provide silica.

BD-POSS was spin-coated onto a silicon wafer. Table 2 shows the pencil-hardness of BD-POSS coatings on heating. At 100 and 200°C, coating films did not form. When heated at 300°C, the pencil hardness was HB, because siloxane bonding formed by condensation of silanol groups. The coating was 2H over 400°C due to the formation of siloxane bonding by the combustion of the trimethylsilyl group or organic group to keep the pencil hardness at 2H. As a result, silica coating film was prepared by spin-coating and following pyrolysis over 400°C.

4. Conclusions

POSS derivatives with functional organic groups as side chains were synthesized by the reaction of T8H with alcohols and 2-propanethiol. The reaction of T8H with HEMA, HPMA, and DPM proceeded successfully to provide Q8HEMA, Q8HPMA, and Q8DPM, respectively. On the other hand, the reaction with phenol, glycidol, or 2-propanethiol was unsuccessful.

The reaction of T8H with EG, BE, or PC was examined to synthesize EG-POSS, BD-POSS, and PC-POSS, respectively. EG-POSS was recovered as a gel. BD-POSS provided a stable polymer by control of the molar ratio of T8H with BD. PC-POSS afforded a polymer with low molecular weight due to low reactivity. A coating film of BD-POSS was heated to form silica coating film with a pencil hardness 2H.

**Table 2. Pencil-hardness of coating film prepared from BD-POSS on silicon wafer**

| Heating temp (°C) | Pencil-hardness | Heating temp (°C) | Pencil-hardness |
|-------------------|-----------------|-------------------|-----------------|
| 100               | Less than 6B    | 500               | 2H              |
| 200               | Less than 6B    | 600               | 2H              |
| 300               | HB              | 700               | 2H              |
| 400               | 2H              | 800               | 2H              |

a) Evaluated based on the Japanese Industrial Standard JIS-K5600.

**References**
1) Y. Abe and T. Gunji, *Prog. Polym. Sci.*, 29, 149–182 (2004).
2) K. Tanaka and Y. Chuo, *Polym. J.*, 45, 247–254 (2013).
3) K. Tanaka and Y. Chuo, *J. Netowork Polym. Jpn.*, 32, 233–244 (2011).
4) Y. Kaneko, *Hyomen (Surface)*, 48, 92–104 (2010).
5) Y. Chuo, “Advances in Organic-Inorganic Nano-Hybrid Materials”, CMC, Tokyo (2009).
6) Y. Abe and T. Gunji, *Jpn. Jpn. Soc. Colour Mat.*, 80, 458–461 (2007).
7) G. Li and C. U. Pittman, Jr., Ed. by A. S. Abd-El-Aziz, C. E. Carraher, C. U. Pittman and M. Zeldin, “Macromolecules Containing Metal and Metal-Like Elements Volume 4 (Group IV A Polymers)” (2005) pp. 79–131.
8) E. Ayandele, B. Sarkar and P. Alexandridis, *Nanomat.*, 2, 445–475 (2012).
9) K. Tanaka and Y. Chuo, *J. Mater. Chem.*, 22, 1733–1746 (2012).
10) M. Itoh, “Chemistry of Silsesquioxane Materials and Their Applications”, CMC, Tokyo (2007).
11) G. Li, L. Wang, H. Ni and C. U. Pittman, Jr., *J. Inorg. Organomet. Polym.*, 11, 123–154 (2002).
12) A. J. Barry, W. H. Daudt, J. J. Domicone and J. W. Gilkey, *J. Mater. Chem.*, 20, 244 (2011).
13) F. J. Feher, D. A. Newman and J. F. Walzer, *Inorg. Chem.*, 34, 1743 (1995).
14) P. A. Agaskar, *Inorg. Chem.*, 30, 2707–2708 (1991).
15) T. S. Haddad and J. D. Lichtenhan, *Macromolec.*, 26, 7302–7304 (1996).
16) A. Sellinger, C. Zhang and R. M. Laine, *Polym. Preprints*, 36, 282–283 (1995).
17) K.-M. Kim, T. Inakura and Y. Chuo, *Polym.*, 43, 1171–1175 (2002).
18) M. Yoshimatsu, K. Komori, Y. Ohnagamitsu, N. Sueyoshi, N. Kawashima, S. Chinen, Y. Murakami, J. Izumi, D. Inoki, K. Sakai, T. Matsuo, K. Watanabe and M. Kunitake, *Chem. Lett.*, 41, 622–624 (2012).
19) N. Ueda, T. Gunji and Y. Abe, *Mater. Technol.*, 26, 162–169 (2008).
20) T. Gunji, T. Shioda, K. Tsuchihira, H. Seki, T. Kajiwara and Y. Abe, *Appl. Organomet. Chem.*, 24, 545–550 (2010).
21) T. Shioda, T. Gunji, N. Abe and Y. Abe, *Appl. Organomet. Chem.*, 25, 661–664 (2011).
22) M. Kanezashi, T. Shioda, T. Gunji and T. Tsuji, *AIChE J.*, 58, 1733–1743 (2012).
23) Y. Uchimaru, J. Dong, H. Yamashita and L. Han, *Polym. Preprints Jpn.*, 59, 4249–4250 (2010).
24) The reaction was carried out under argon atmosphere using dried apparatus. The water may come from T8H as additional water molecules which was estimated by IH NMR spectrum of T8H. The signal due to water decreased by a continuous drying but T8H was gelled. The detection of water molecules is now under investigation.

**Acknowledgment** This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas ‘New Polymeric Materials Based on Element-Blocks’ (no. 2401) (24102008A02) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.