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Ring-opening polymerization of ε-caprolactone by base catalyst for synthesis of grafted polysilsesquioxane

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ABSTRACT

The polysilsesquioxane having amino and phenyl groups (**APSQ**) was prepared from the corresponding trimethoxysilanes by co-condensation under basic conditions. The amino group on **APSQ** was utilized as an initiator for graft polymerization of ε-caprolactone (**CL**). The ring-opening polymerization of **CL**, in the presence of a catalytic amount of the base prepared from triazabicyclodecene, proceeded effectively to afford the polysilsesquioxane having poly(**CL**) as the graft chains (**GrPSQ**). In the grafting, no formation of cross-linked product was observed. The grafted poly(**CL**) component in **GrPSQ** showed improved durability for heat as an advantage of the hybrid polymer containing polysiloxane structure.

1. Introduction

Among the members of silicone compounds, oligo- and polysilsesquioxane (**PSQ**), prepared from the silane coupling reagents such as trichlorosilanes or trialkoxysilanes, have been expected to be the versatile and useful hybrid materials [1–7]. The presence of functional group in the silane coupling reagent is favorable for ready incorporation of various functional groups or polymeric component into **PSQ**, which enables the various applications in electrical, optical, mechanical, and chemical scenes [8–11]. The introduction of polymeric component is one of the effective methods for the modifications of **PSQ** to utilize it as a practical hybrid material. In such modification, the introduced polymers provide the additional properties besides durability for heat and weatherability based on the inorganic polysiloxane backbone. The graft polymerization onto or from silsesquioxane main chain has been investigated to create such useful hybrid materials [12–16]. In the previous reports, we also reported the graft polymerization from **PSQ** to prepare the new functional hybrids [17–19]. These graftings essentially utilize the techniques based on radical polymerization. On the other hand, ionic polymerization process is also applied to the graftation from silsesquioxane compounds. The ring-opening polymerization of ε-caprolactone (**CL**) from polyhedral oligomeric silsesquioxanes by tin(II) 2-ethylhexanoate is a typical example, in which the polymeric component is formed through an anion specie [20–22].

The combination of the silsesquioxane with polymerized **CL** leads to the new hybrid materials and is expected to be environmentally friendly and applicable to biomedical usages such as drug delivery and tissue engineering. Furthermore, the miscibility is compatible with the versatile polymers such as SAN, ABS, PVC, and nitrocellulose, which presents the abilities of dispersing pigments and low-temperature adhesiveness to the hybrid [20]. The presence of siloxane component may link with a low crystallinity and improvement of mechanistic strength and thermal stability. The use of the tin(II) catalyst enables the living polymerization of **CL** and efficient grafting for the preparation of the hybrid consisted of silsesquioxane structure. However, the complete removal of the catalyst from the final product, which is preferable for using the hybrid in various material scenes, seems to be difficult [23]. Very recently, the procedure to avoid the use of tin(II) catalyst has been reported, in which a living-like polymerization of **CL** proceeds by the use of amidine base catalyst with the initiator compounds such as alcohols or amines [24]. In the strong bases, 1,5,7-triazabicyclo[4.4.0]dec-7-ene (**TBD**) is nominated as one of the most effective catalysts. From the mechanistic analysis of the polymerization, the formation of intermediary amide compound is pointed out to explain the effective catalytic ability of **TBD** [25]. The findings promise to add the technique, utilizing the guanidine base, in the methodology for grafting polymeric component from **PSQ** main chain.

The grafted **PSQ** containing poly(**CL**) is an interesting hybrid material, which should be environmentally gentle and possess the

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improved properties based on polysiloxane structure as mentioned above. Consequently, the graft polymerization of **CL** from **PSQ** main chain by the use of the strong base was examined in this work. For the ring-opening polymerization of **CL**, amino group on **PSQ** main chain was chosen as the initiator, in which poly(**CL**) component was supposed to be connected through amide bond. For the preparation of **PSQ** derivative having amino group, the co-condensation of (3-aminopropyl)trimethoxysilane (**ATMS**) with phenyltrimethoxysilane (**PTMS**) was required. Since, the condensation of sole **ATMS** under basic conditions gave the gel product, which was insoluble in organic solvent. Thus, **PSQ** having both amino and phenyl groups (**APSQ**), which were soluble in organic solvent, was employed for the grafting of poly(**CL**). In addition, the base catalysts were newly prepared from the reaction of **TBD** with allyl- or phenyl-isocyanate to avoid the possibility to form poly(**CL**) from the catalyst itself. These catalysts containing amide bond are thought to be also effective for the polymerization by considering the intermediary structure mentioned above [25]. While, from the interests in the aspects of physical property, the measurement of thermal properties through DSC and TGA on the obtained **PSQ** hybrid was conducted.

2. Experimental

2.1. General

^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL AL-300 and Bruker AVANCE-500 spectrometer at 500.13 MHz (^{1}H) and 125.77 MHz (^{13}C, ^{1}H decoupled at 500 MHz) in $CDCl_3$ or DMSO-d_6. IR spectra were recorded on a JASCO FT/IR 230 (KBr disc). Gel permeation chromatographic (GPC) analysis was carried out to estimate number-average molecular weight (M_n) and polydispersity (M_w/M_n) on a Shimadzu LC-10VP chromatograph equipped with an evaporative light scattering detector. Three columns such as Shim-pack GPC-80MD, -804D, and -802D were connected in series and *N*,*N*-dimethylformamide (DMF) was used as the eluent. Calibration was performed using poly(methyl methacrylate) standards. Tetrahydrofuran (THF) and toluene were refluxed over sodium metal and distilled. The monomer **CL** was distilled over calcium hydride before use. Other reagents including **PTMS**, **ATMS**, **TBD**, 1,8-diazabicyclo[5.4.0]undec-7-ene (**DBU**), allylisocyanate, and phenylisocyanate were used as supplied from commercial sources.

2.2. Preparation of polysilsesquioxane (*APSQ*)

APSQ was prepared by the analogous method reported before [19]. A mixture of **PTMS** (5.00 g, 25.22 mmol) and **ATMS** (2.26 g, 12.61 mmol) with triethylamine (0.20 g, 1.98 mmol) in the mixed solvents of THF (40 ml) and water (10 ml) was refluxed for 24 h. The resulting solution was concentrated by a rotary evaporator under reduced pressure and, then, an excess amount of diethyl ether was added to the residual oil. The solid insoluble in diethyl ether was collected and dried at room temperature for 24 h in a vacuum oven under reduced pressure (<2 mmHg) to obtain **APSQ** (4.86 g, 99% yield from **PTMS**, and 88% from **ATMS**). The contents of phenyl and aminopropyl groups were calculated from the peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard; IR (KBr) 3436 (weak, NH_2), 3074 (weak, C_6H_5), 2934 (medium, CH_2), 1631 (weak), 1594 (weak), 1431 (medium), 1134 (strong, Si–O), 1047 (strong, Si–O), 731 (medium), 699 (medium), 496 (medium) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.63 (br, Si–CH_2–), 1.28 (br, C–CH_2–C), 2.44 (br, N–CH_2–), 7.38 (br m, –C_6H_5); ^{13}C NMR (75.45 MHz, DMSO-d_6) δ 9.44 (Si–CH_2–), 26.45 (C–CH_2–C), 43.98 (N–CH_2–), 127.68 (C_6H_5), 130.66 (C_6H_5), 133.67 (Si–C_6H_5); $M_n = 2300$ g/mol, $M_w/M_n = 1.52$; phenyl unit = 5.16 mmol equiv/g, aminopropyl group = 2.29 mmol equiv/g.

2.3. Typical procedure for preparation of catalyst from *TBD*

To a solution of **TBD** (2.00 g, 14.37 mmol) in THF (10 ml), allylisocyanate (1.30 g, 15.64 mmol) was added at 25 °C under argon atmosphere. The solution was stirred at the same temperature for 8 h and, then, evaporated under reduced pressure. The urea product (**1**) was obtained as a colorless oil by distillation of the residual oil under reduced pressure at 165–170 °C/3 mmHg (1.59 g, 50%); IR (neat) 3214 (weak, NH), 2938 (medium), 2874 (medium), 1668 (strong, C=O, C=N), 1551 (medium), 1499 (medium), 1434 (medium), 1381 (medium), 1322 (medium), 1262 (medium), 1204 (medium), 695 (weak) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.82 (m, 2H), 1.92 (m, 2H), 3.15 (m, 2H), 3.18 (m, 2H), 3.32 (m, 2H), 3.83 (m, 2H), 5.01–5.16 (dd, $J = 5.0$ Hz and 7.5 Hz, 2H), 5.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.38 (–CH_2–), 22.84 (–CH_2–), 39.85 (N–CH_2–), 42.53 (N–CH_2–), 46.87 (N–CH_2–), 48.69 (=N–CH_2–), 49.16 (NH–CH_2–), 114.67 (CH_2=CH–), 135.58 (CH_2=CH–), 151.43 (C=O), 156.45 (C=N); Calcd for $C_{11}H_{18}N_4O$: C, 59.44; H, 8.16; N, 25.20; found: C, 59.50; H, 8.50; N, 25.69.

Analogously, the reaction of **TBD** (1.00 g, 7.18 mmol) and phenylisocyanate (0.94 g, 7.89 mmol) was conducted. After the evaporation, the solid insoluble in diethyl ether was collected by filtration and recrystallized from the mixed solvents of benzene and *n*-hexane to obtain the urea product (2, 1.60 g, 87%): mp = 81–82 °C; IR (KBr) 3428 (weak, NH), 2949 (weak), 2860 (weak), 1680 (strong, C=O), 1609 (strong, C=N), 1590 (strong), 1562 (strong), 1441 (medium), 1381 (medium), 1314 (medium), 1271 (medium), 1209 (medium), 755 (medium), 694 (medium) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.86 (m, 2H), 1.94 (m, 2H), 3.15 (m, 2H), 3.20 (m, 2H), 3.44 (m, 2H), 3.87 (m, 2H) 6.97 (m, 1H), 7.23 (m, 2H), 7.47 (m, 2H); ^{13}C NMR (125 MHz, DMF-d_7) δ 21.85 (–CH_2–), 22.77 (–CH_2–), 39.70 (N–CH_2–), 42.80 (N–CH_2–), 48.66 (N–CH_2–), 49.21 (=N–CH_2–), 120.32 (–C_6H_5), 124.56 (–C_6H_5), 126.47 (–C_6H_5), 149.81 (C=O), 153.86 (C=N); Calcd for $C_{14}H_{18}N_4O$: C, 65.09; H, 7.02; N, 21.69; found: C, 65.15; H, 7.07; N, 21.43.

2.4. Typical procedure for graft polymerization of *CL* from *APSQ*

APSQ (0.07 g, 0.16 mmol equiv of amino group) and **1** (0.03 g, 0.14 mmol) were charged in a flask equipped with rubber septum under argon atmosphere. **CL** (0.30 g, 2.63 mmol) was added into the flask by a syringe and, then, the mixture was heated at 60 °C. After the polymerization was continued for 4 h, an excess amount of *n*-hexane was added into the mixture. The precipitated product was collected by filtration. The solid was dissolved into a small amount of THF and re-precipitated from an excess amount of diethyl ether. The resulting solid was dried at room temperature for 24 h under reduced pressure (<2 mmHg) to obtain the poly(**CL**) grafted **PSQ** (**GrPSQ**) (0.30 g, 81% yield based on weight and 88% yield based on phenyl group). The contents of phenyl group and the monomer unit in **GrPSQ** were calculated from the peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard. The content of amino group was estimated from that of phenyl group as shown in the starting **APSQ** (Table 1, Run 1); IR (KBr) 3441 (weak), 2946 (weak), 2867 (weak), 1726 (strong, C=O), 1644 (weak, C=O), 1368 (weak), 1295 (weak), 1244 (medium), 1192 (medium, C–O), 1109 (medium, Si–O), 1047 (weak), 733 (weak) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.34 (m, –CH_2–), 1.60 (m, –CH_2–), 2.25 (m, –CH_2–(C=O)), 4.92 (m, O–CH_2–), 7.10–7.60 (br, –C_6H_5,); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.60 (–CH_2–), 24.72 (–CH_2–), 28.37 (–CH_2–), 34.15 (–CH_2–(C=O)), 64.13 (O–CH_2–), 127.75 (–C_6H_5), 133.98 (–C_6H_5), 173.63 (–C=O); $M_n = 10\,000$ g/mol,

Table 1
Graft polymerization of ε-caprolactone (**CL**) from polysilsesquioxane having amino group (**APSQ**)

Reaction conditions[a]						Grafted **PSQ**			
Run	Catalyst	Temp. (°C)	Solvent	Time (h)	Feed mole ratio of **CL**/amino group	Yield based on weight (%)	Molar ratio of **CL** unit/amino group[b]	Calcd. M_n (DP[c])	M_n (M_w/M_n) based on GPC[d]
1	**1**	60	None	4	16	81	13	9400 (15)	10 000 (1.57)
2	**1**	60	None	4	30	90	26	19 300 (29)	18 000 (1.71)
3	**1**	60	Toluene	8	16	89	14	10 300 (16)	10 000 (1.55)
4	**1**	60	THF	8	16	84	14	9600 (15)	10 000 (1.38)
5	**1**	80	Toluene	4	30	83	25	15 000 (28)	14 000 (1.68)
6	**1**[e]	80	Toluene	8	16	86	14	10 500 (16)	11 000 (1.82)
7	**2**	60	None	4	16	92	14	11 700 (16)	13 000 (1.54)
8	**2**	60	Toluene	8	30	92	26	18 900 (28)	18 000 (2.08)
9	**DBU**[f]	80	Toluene	4	16	0	–	–	–

[a] The feed mole ratio of amino group/catalyst was 0.8 and the concentration of **CL** in the solution was 2.6 [M].
[b] The content of the unit was estimated from ^{1}H NMR spectral data.
[c] Degree of polymerization. DP was calculated from the contents of amino group and **CL** unit.
[d] The values were based on poly(methyl methacrylate) standards.
[e] The feed mole ratio of **1**/amino group was 0.5.
[f] 1,8-Diazabicyclo[5,4,0]undec-7-ene.

$M_w/M_n = 1.57$; phenyl group = 1.01 mmol equiv/g, aminopropyl group = 0.45 mmol equiv/g, **CL** unit = 7.08 mmol equiv/g.

Analogously, the graft polymerizations were carried out under various conditions as shown in Table 1.

For the measurement of time *vs* conversion and conversion *vs* number-average molecular weight (M_n) or dispersity (M_w/M_n) as shown in Figs. 1 and 2, the samples were taken by a syringe at the appropriate times during the polymerization and treated with a small amount of acetic acid. The samples were employed for the measurements of ^{1}H NMR and GPC without removal of the solvent.

2.5. Thermal analysis

TGA analysis was performed on Shimadzu DTG-60. The measurement was performed under nitrogen atmosphere with 10 mg of sample from 30 °C to 600 °C, in which a heating rate was 10 °C/min.

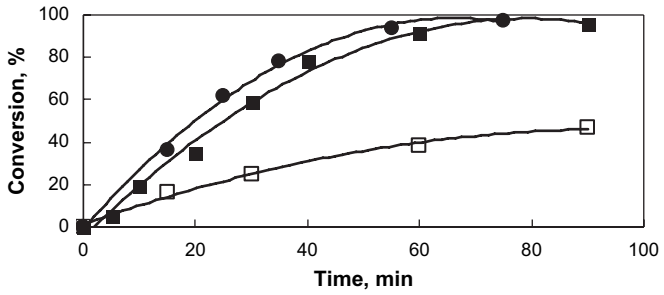


Fig. 1. Relationships between time and conversion of **CL** in the graft polymerization from **APSQ** with 0.8 equiv of **1** (■), 0.8 equiv of **2** (●), and 0.5 equiv of **1** (□) to amino group.

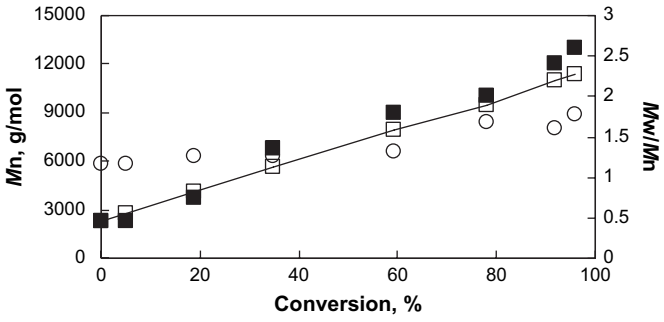


Fig. 2. Relationships between conversion of **CL** and M_n (■), calculated M_n (□), or M_w/M_n (○) in the graft polymerization from **APSQ** with 0.8 equiv of **1** to amino group.

The DSC was measured on TA instruments DSC Q2000. The purge gas was nitrogen at a flow rate of 50 ml/min. The sample was kept for 5 min at 0 °C prior to be heated at a rate of 10 °C/min.

For the thermal analysis, poly(**CL**) was prepared to compare the behavior with that of **GrPSQ** by the analogous treatments mentioned above. The ring-opening polymerization of **CL** (0.30 g, 2.62 mmol) in the presence of **TBD** (0.04 g, 0.29 mmol) at room temperature for 8 h gave the product (0.26 g, 79%). The M_n and M_w/M_n of poly(**CL**) were 5500 g/mol and 1.05, respectively.

3. Results and discussion

3.1. Preparation of *APSQ* from *PTMS* and *ATMS*

In our preliminary experiments, the condensation using only **ATMS** under basic conditions gave the gel product. The co-condensation of **PTMS** with **ATMS** afforded the polysilsesquioxane soluble in the organic solvents such as DMSO and DMF. In the co-condensation to avoid the formation of gel product, an equimolar amount of **PTMS** and **ATMS** was at least required. In this work, the feed mole ratio of **PTMS**/**ATMS** was adjusted to be 2/1. The co-condensation in the presence of 5 mol% of triethylamine to the total amount of the trimethoxysilanes proceeded effectively and afforded **APSQ** as a solid insoluble in diethyl ether and methanol. The yield and the contents of phenyl and aminopropyl groups were estimated by the proton ratios observed in the ^{1}H NMR spectrum. In the measurement, hexamethyldisiloxane was used as an internal standard, the signal of which appeared at 0 ppm. The broad signal assigned to the protons of methylene groups bonded to Si was found around 0.6 ppm. Other signals showing the presence of aminopropyl group were detected around 1.3 ppm and 2.4 ppm. The signals due to benzene ring were observed around 7.4 ppm. The contents of the groups were calculated by the use of these peak areas. From the calculation, the contents of 2.29 mmol equiv/g of aminopropyl group and 5.16 mmol equiv/g of phenyl group were determined. The ratio of the groups was almost same to that of the starting trimethoxysilanes. From the values, the yields based on phenyl unit and aminopropyl unit were 99% and 88%, respectively. The estimated M_n and M_w/M_n of **APSQ** by GPC were ca. 2300 g/mol and 1.52, respectively. The structure of **APSQ** was supposed to be consisted of a ladder- and an incomplete cage-like polysiloxane, although these have been still unidentified.

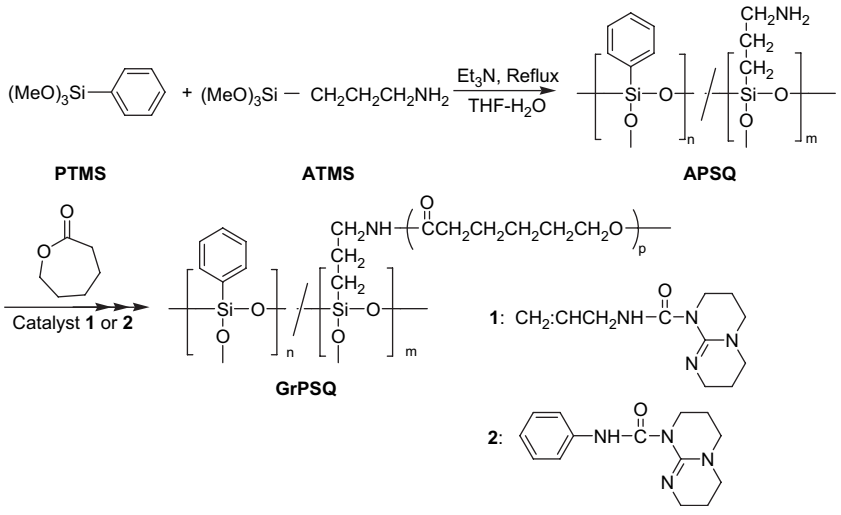
3.2. Graft polymerization of **CL** from **APSQ**

In the previous report, the ring-opening polymerization of **CL** progressed effectively by the use of **TBD** as a catalyst [24]. While using *N*-methylated **TBD** or **DBU** instead of **TBD**, thiourea compound was required as an additive for the efficient polymerization. The former polymerization is thought to proceed through *N*-carbonyl intermediate formed by the reaction with **TBD** and **CL** [24]. The later fact suggests that the formation of hydrogen bonding between carbonyl oxygen of **CL** and thiourea contributes to activate the ring-opening step and accelerate the polymerization. The mechanistic speculation seems to promise that the derivative of **TBD** having urea bond is an effective catalyst for the polymerization of **CL**. Furthermore, the use of **TBD** as the catalyst may lead to the formation of poly(**CL**) having **TBD** end group, which is regarded as a competitive polymerization of that from amino group in **APSQ**. Such consideration made us to employ the catalysts, which were newly prepared by the reaction of **TBD** with allyl- and phenylisocyanate, respectively. The simple mixing of **TBD** and allylisocyanate in THF carried out at room temperature gave the oily catalyst **1**. Similarly, from phenylisocyanate and **TBD**, the catalyst **2** was afforded as a solid. The catalysts **1** and **2**, consisted of incomplete urea bond, were employed for the graft polymerization of **CL** from **APSQ** as shown in Scheme 1.

At first, the relationships between time and conversion were examined in toluene solutions of **APSQ** and **CL** at 80 °C, in which the monomer concentration was adjusted to be 2.6 [M]. The conversion of **CL** was calculated by the proton areas of the characteristic signals in ^{1}H NMR spectrum which is mentioned later. **APSQ** was practically insoluble in toluene, but the polymerization could be conducted in a clear solution after the addition of **CL**. The results are shown in Fig. 1. When the feed mole ratios of the catalyst/amino group/**CL** were adjusted to be 0.8/1/16, the monomer was consumed almost quantitatively within 1.5 h in both the polymerization systems using the catalysts **1** and **2**. In these polymerizations, no difference of catalytic activity between **1** and **2** was observed. In the polymerization using 0.5 equiv of **1** to amino group, the rate of consumption of **CL** slowed down to ca. 1/2. Furthermore, the GPC measurements of the above samples, collecting in the polymerization using the catalyst **1**, presented the conversion *vs* M_n and M_w/M_n curves as shown in Fig. 2. The M_ns increased almost linearly along with those calculated from the conversion of **CL** monomer. The M_n of **GrPSQ** was reached to the value of 13 000. This was a little larger than the calculated one such as ca. 11 400. The polydispersities of the samples ranged from 1.17 to 1.78. In such measurement of GPC, the products showed a unimodal peak. These results lead to the conclusion that the ring-opening polymerization of **CL** proceeded essentially from amino groups to afford the grafted **PSQ**.

Next, the ring-opening polymerization of **CL** from **APSQ** was carried out under various conditions. The results are listed in Table 1. When no solvent was used, the efficient graft polymerization was observed at 60 °C. Even in the case using 30 equiv of **CL** to amino group in **APSQ**, **GrPSQ** was obtained in 90% yield (Run 2). The graftation at 60 °C in the solution of toluene or THF was also effective to obtain the product by lengthening the reaction time to 8 h (Runs 3 and 4). The use of half equivalent of the catalyst **1** to amino group gave the **GrPSQ** in a high yield, although the longer reaction time such as 8 h was required as supposed from the relationship of time *vs* conversion (Run 6). The polymerization using the catalyst **2** with 30 equiv of **CL** to amino group, conducted at 60 °C for 8 h in toluene solution, progressed to give **GrPSQ** in 92% yield (Run 8). As mentioned above, this also showed that the urea derivative **2** was an effective catalyst. Whereas, **DBU** showed no catalytic activity in the graftation (Run 9). This was supported by the reported fact, in which thiourea compound was needed as an additive for the polymerization. The values of degree of polymerization (DP) based on ^{1}H NMR spectral data were almost in accord with the feed mole ratios of amino group to the monomer **CL**. Furthermore, the M_ns of the products estimated by GPC showed reasonable values in comparison with those calculated from the ^{1}H NMR spectral data. Thus, the results demonstrated that the use of the urea derivatives obtained from **TBD** enabled the efficient ring-opening polymerization of **CL** from **APSQ**. In those graftations, no obvious formation of gel product, which may be produced by intermolecular transesterification, was observed. However, an insoluble part might be removed by filtration for re-precipitaion of the products. Consequently, it may be said at least in this work that the living-like polymerization proceeded under the conditions as reported previously [24].

The presence of **CL** and **PSQ** units in **GrPSQ** was confirmed by the following spectral data. The IR spectrum of **GrPSQ** showed a strong absorbance at 1726 cm^{-1} due to carbonyl group of **CL** units. The absorbance at 1192 was assigned to carbon–oxygen of **CL** units and that at 1109 cm^{-1} was to silicon–oxygen bond of the polysiloxane main chain. In the ^{1}H NMR spectrum of **GrPSQ**, the signals due to the methylene protons were detected in the range from 1.3 ppm to 1.6 ppm. The signal assigned to methylene protons



Scheme 1.

attached to Si became scarcely recognized at 0.6 ppm after the graftation. However, the broad signal showing the presence of benzene ring in **PSQ** unit was observed around 7.3 ppm. This peak area of the signal was utilized for the calculations of content of amino group and **PSQ** unit in **GrPSQ**. The characteristic signals due to methylene protons of **CL** unit were detected at 2.25 ppm and 4.92 ppm. The former signal was assigned to methylene protons attached to carbonyl group and the later corresponded to those bonded to oxygen, which could be used for the calculation of content of **CL** unit. Such spectral data of ^{1}H NMR demonstrated that the contents of the monomer units in **GrPSQ** reflected the feed mole ratios of **APSQ** and **CL**. For an example, the ^{1}H NMR spectrum of **GrPSQ** (Run 3) is shown in Fig. 3. ^{13}C NMR spectrum of **GrPSQ** also supported the incorporations of the corresponding graft chains. The signals in the region of 24.6–28.4 ppm exhibited the presence of methylene groups in the grafted **CL** units. The signals observed at 34.2 ppm and 64.1 ppm were assigned to the carbons of methylenes bonded to carbonyl group and oxygen, respectively. Further, the signal to indicate the presence of carbon of carbonyl group was detected at 173.6 ppm. The presence of the **PSQ** main chain was demonstrated by the signals around 130 ppm assigned to benzene carbons.

3.3. Thermal analysis

To get the information concerning the effects of **PSQ** main chain on the thermal property of poly(**CL**) graft chain, the measurements of DSC and TGA on **GrPSQ** (Run 3) were conducted. For the measurement of DSC, poly(**CL**), prepared independently from **CL** and a catalytic amount of **TBD** without using the initiator such as alcohol and amine, was also employed. These curves are exhibited in Fig. 4. The melting point (T_m) of poly(**CL**) was reported to be around 60 °C [24]. In the curve of poly(**CL**) prepared in this work, the melting endotherm was observed at 55.6 °C. Such endotherm was similarly detected at somewhat lower temperature such as 53.8 °C in the case of **GrPSQ**. The results indicated that the presence of **PSQ** structure just made the melting temperature of poly(**CL**) lower and the polymeric component essentially kept the characteristic of crystallization.

The TGA measurements were made on **GrPSQ** (Run 3), poly(**CL**) mentioned above, and **APSQ**, in which **PSQ** backbone was expected to make some changes in thermal behavior to the grafted polymer. The TGA curves are shown in Fig. 5. The weight loss began at 340 °C in the case of **APSQ**. This was attributed to the decomposition of

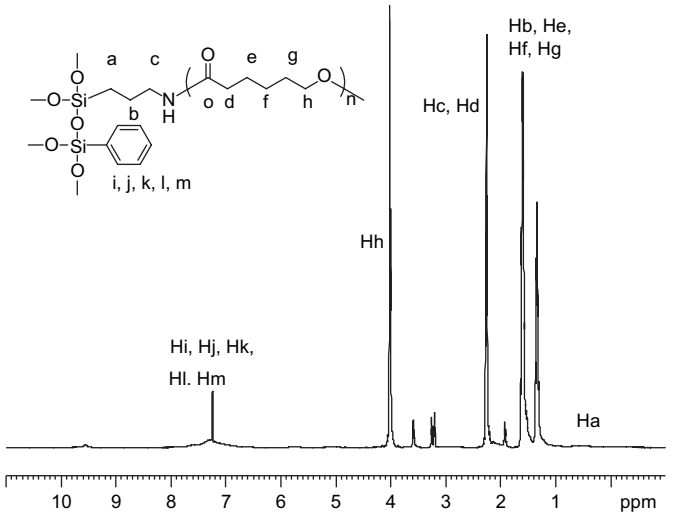


Fig. 3. ^{1}H NMR spectrum of **GrPSQ** (Table 1. Run 3).

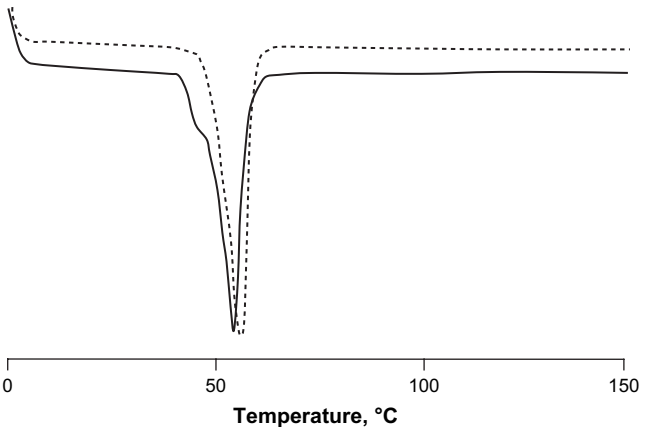


Fig. 4. DSC curves of **GrPSQ** (—) (Table 1, Run 3) and poly(**CL**) (·····).

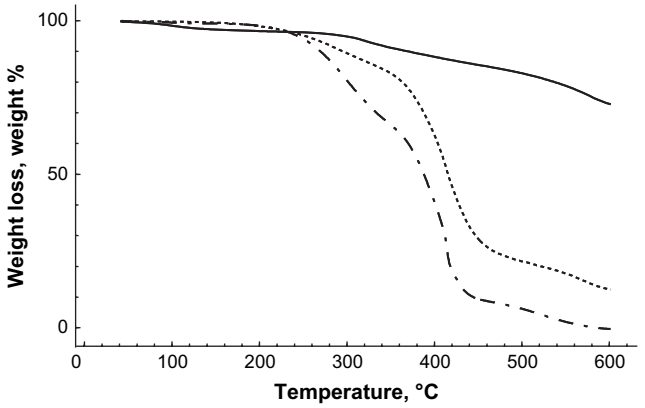


Fig. 5. TGA curves of **APSQ** (—), **GrPSQ** (·····) (Table 1, Run 3), and poly(**CL**) (-·-).

aminopropyl and/or phenyl groups bonded to Si. Poly(**CL**) and **GrPSQ** began to lose their weights at the lower temperatures such as 240 °C and 280 °C, respectively. These demonstrated that the thermal decomposition of polymeric **CL** component occurred prior to that of aminopropyl and phenyl groups. In comparison with the profiles of **GrPSQ** and poly(**CL**), the weight loss of poly(**CL**) in the range from 350 °C to 400 °C was 27%. Whereas, the lower weight loss such as 19% was recorded in the case of **GrPSQ**. The results demonstrated that the expected improvement of thermal stability was presented by combining poly(**CL**) with polysiloxane structure in **GrPSQ**.

4. Conclusion

The polysilsesquioxane containing phenyl and aminopropyl groups was employed for the grafting of biodegradable poly(**CL**) to afford a new functional organic–inorganic hybrid material. The results demonstrated that the effective graft polymerization by the use of amino group under anionic polymerization conditions proceeded to give **PSQ** having poly(**CL**) graft chains. Such effective living-like ring-opening polymerization was achieved by the use of the urea derivatives from **TBD** as the catalysts. In the examination on thermal properties of the hybrid, the presence of polysiloxane structure brought an improved durability for heat to the polymeric **CL** chain. However, no obvious change of T_m of poly(**CL**) was observed as shown in DSC measurement.

Thus, aminopropyl group on **PSQ** main chain could be utilized as the initiator for grafting of the polyester and the urea type

derivatives **1** and **2**, obtained from **TBD**, were exhibited to be the effective catalysts for the ring-opening polymerization. The procedure is expected to enable the modifications of polysiloxane compounds by various cyclic esters and be usable for the formation of functionalized hybrid materials.

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