REGULAR ARTICLE

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Synthesis of Grafted Polysilsesquioxane by Ring-Opening Polymerization of Lactide

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The polysilsesquioxane having amino and phenyl groups (**APSQ**) was utilized as a macroinitiator for the ring-opening polymerization of L-(−)-lactide (**LA**). The combination of amino group on **APSQ** and a catalytic amount of the base, prepared from triazabicyclodecene and allyl isocyanate, enabled the efficient ring-opening polymerizations to afford the polysilsesquioxanes having the graft chains of poly(**LA**). The procedure was further applied to the introduction of the block copolymer of **LA** and ε-caprolactone (**CL**) into **APSQ**, in which the polysilsesquioxane having the graft chains of poly(**CL**) was used as the macroinitiator. These grafted polysilsesquioxane derivatives showed the characteristic thermal properties in the measurements of thermogravimetric analysis and differential scanning calorimetry.

KEY WORDS: Polysilsesquioxane / Graft Polymerization / Lactide / Ring-Opening Polymerization / Triazabicyclodecene /

Oligomeric and polymeric silsesquioxanes prepared from the silane coupling reagents such as trichlorosilanes or trialkoxysilanes are developed to be the practical and useful hybrid materials. From such interests, various investigations have been continuously reported.[1–9] The grafting of polymeric organic component is an effective method for transforming the silsesquioxane into a variety of practical hybrid materials. By such modifications, the polymeric component should provide the additional properties besides durability for heat and weatherability based on the inorganic polysiloxane backbone. Indeed, a variety of graft polymerizations onto or from oligo- or poly-silsesquioxane main chain has been investigated to create the useful hybrid materials including our works.[10–16]

One of the interesting modifications is the ring-opening polymerization of ε-caprolactone (**CL**) from the oligomeric silsesquioxane containing hydroxyl groups by tin(II) 2-ethylhexanoate.[17–19] The silsesquioxane grafted polymerized **CL** should be an environmentally friendly material and favorable for the applications to biomedical usages such as drug delivery and tissue engineering. Furthermore, the miscibility compatible with the versatile polymers such as SAN, ABS, PVC, and nitrocellulose due to poly(**CL**) is expected to provide the abilities of dispersing pigments and low-temperature adhesiveness to the silsesquioxane.[17] By considering such findings, we have started the studies on the grafting of poly(**CL**) from polysilsesquioxane (**PSQ**), in which the ring-opening polymerization by the catalytic use of amidine base is adopted. Since, from the mechanistic analysis, the use of 1,5,7-triazabicyclo[4.4.0]dec-7-ene (**TBD**) catalyst with alcohol or amine as an initiator is reported to enable the living-like polymerization of **CL**.[20,21] In addition, the procedure is free from the use of metal catalyst, which is sometimes difficult to remove from the product completely. The results of our previous examination demonstrated that the procedure was applicable to the graft ring-opening polymerization of **CL** from the polysilsesquioxane having phenyl and amino groups (**APSQ**).[22]

Along with the investigations concerning the utilization of the ring-opening polymerization, the graftings of L-(−)-lactide (**LA**) and the block copolymer of **LA** and **CL** from **APSQ** were mentioned in this report. The introduction of polymeric **LA** component besides **CL** units is expected to change the properties of the graft chains such as grass transition temperature (T_g) and melting point (T_m) of the resulting **PSQ** derivative. These are thought to lead to a usable adhesive material which we intend to develop by considering the expectation mentioned above.[17] The synthetic routes were shown in Scheme 1. In the ring-opening polymerization, the catalyst (**1**) derived from **TBD** and allylisocyanate was used. Since, as shown in the previous reports, the intermediary amide compound is pointed out to be a functional group for the effective catalytic ability of **TBD**.[21] Namely, the formation of hydrogen bond between amide group and carbonyl group in the lactone is thought to enhance the ring-opening reaction. In addition, the graft chains in **PSQ**s are speculated to show the characteristic thermal properties due to the presence of polysiloxane structure. Consequently, thermogravimetric (DTTGA) and differential scanning calorimetry (DSC) analyses were conducted on the grafted **PSQ** derivatives.

EXPERIMENTAL

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-

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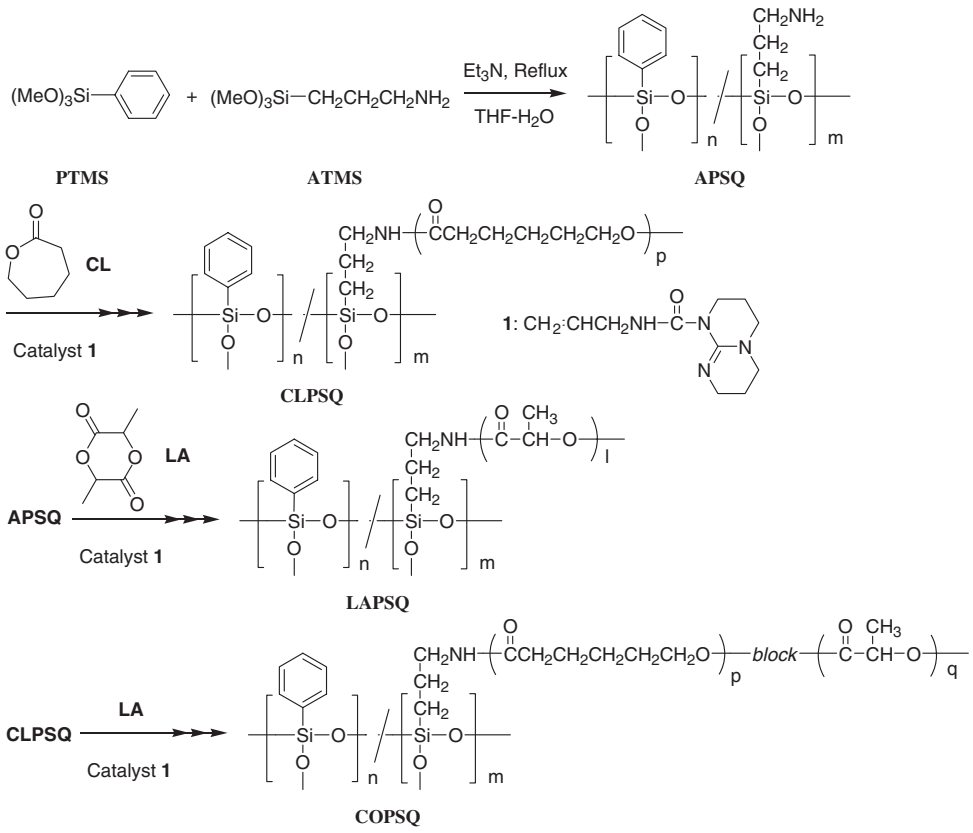

Scheme 1.

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) was refluxed over sodium metal and distilled. The monomer **CL** was distilled over calcium hydride before use. **LA** was recrystallized from toluene and n-hexane before use. Other reagents including phenyltrimethoxysilane (**PTMS**), (3-aminopropyl)trimethoxysilane (**ATMS**), **TBD**, and allyl isocyanate were used as supplied from commercial sources. The **PSQ** grafted poly(**CL**) (**CLPSQ**), **APSQ** and the base catalyst (**1**), obtained from **TBD** and allyl isocyanate, were prepared in the previous work.[22] The analytical data of **APSQ** and **CLPSQ**s were as follows.

APSQ: aminopropyl group = 2.29 mmol eq./g, phenyl group = 5.16 mmol eq./g, M_n = 2300 g/mol, M_w/M_n = 1.52; **CLPSQ1**: M_n = 12900 g/mol, M_w/M_n = 1.54, phenyl group = 1.03 mmol eq./g, aminopropyl group = 0.46 mmol equiv./g, **CL** unit = 6.44 mmol equiv./g; **CLPSQ2**: M_n = 18200 g/mol, M_w/M_n = 1.71, phenyl group = 0.62 mmol eq./g, aminopropyl group = 0.28 mmol equiv./g, **CL** unit = 8.08 mmol equiv./g.

Typical Procedure for Graft Polymerization of LA from APSQ

APSQ (0.07 g, 0.16 mmol eq. of amino group) and the catalyst **1** (0.03 g, 0.13 mmol) were charged in a flask equipped with rubber septum under argon atmosphere. THF (1 mL) and **LA** (0.38 g, 2.64 mmol) were added into the flask by a syringe and, then, the mixture was heated at 60 °C. After the polymerization was continued for 8 h, an excess amount of diethyl ether was added into the mixture. The resulting insoluble wax was washed with diethyl ether several times by decantation. The wax was dissolved into a small amount of acetone and re-precipitated from an excess amount of *n*-hexane. The resulting solid was collected by filtration and dried at room temperature for 24 h under reduced pressure (<2 mmHg) to obtain the poly(**LA**) grafted **PSQ** (**LAPSQ**) (0.37 g, 82% yield based on weight). The contents of phenyl group and monomer unit of lactic acid (**LAM**) in **LAPSQ** 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. The result was shown in Table I (Run 1); IR (KBr) 3428 (weak), 2996 (weak), 2945 (weak), 1759 (strong, C=O), 1455 (weak), 1383 (weak), 1269 (weak), 1186 (strong), 1133 (strong, C-O), 1093 (strong, Si-O), 1047 (weak), 701 (weak) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.56 (br m, -C$\underline{H}_3$), 5.14 (br m, O-C$\underline{H}$(CH_3)-), 7.20–7.60 (br, -$C_6\underline{H}_5$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.82 (-$\underline{C}H_3$), 69.08 (-$\underline{C}$H-), 169.69 (–$\underline{C}$=O); phenyl group = 0.96 mmol equiv./g, aminopropyl group = 0.43 mmol equiv./g, **LAM** unit = 11.95 mmol equiv./g; M_n = 13400 g/mol (Calcd M_n = 12800), M_w/M_n = 1.24.

Table I. Graft polymerization of **LA**[a]

Reaction conditions[a]			**LA** Grafted **PSQ**						
Run	Macroinitiator	Feed mole ratio of **LA**/**CL**/amino group[b]	Product	Content of amino group[b] mmol eq./g (Yield, %)	Content of **CL** unit[b] mmol eq./g (Yield, %)	Content of **LAM** unit,[b] mmol eq./g (Yield, %)	Molar unit ratio of **LAM**/**CL**	Calcd M_n[c]	M_n (M_w/M_n) estimated by GPC[d]
1	**APSQ**	16/0/1	**LAPSQ**	0.43 (99)	—	11.95 (84)	—	12800	13400 (1.24)
2	**CLPSQ1**	15/14/1	**COPSQ1**	—	3.88 (90)	5.50 (70)	1.29	21500	22700 (1.88)
3	**CLPSQ2**	8/29/1	**COPSQ2**	—	6.89 (64)	1.41 (49)	0.20	21100	20700 (1.36)
4	**CLPSQ3**	15/29/1	**COPSQ3**	—	5.45 (79)	3.19 (43)	0.59	22400	23900 (1.48)

[a]The feed mole ratio of the catalyst **1** to amino group was adjusted to be 0.8 and the concentration of **LA** in the solution was 2.3 [M]. [b]The contents of the group and the monomer units were estimated from ^{1}H NMR spectral data, in which hexamethyldisiloxane was used as an internal standard. The content of amino group was based on that of **CL** unit. [c]Calculated from the contents of the monomer units. [d]Estimated relative to poly(methyl methacrylate) standards.

In the grafting of block copolymer of **CL** and **LA**, two grafted **PSQ**s were used. The one of the **PSQ**s, **CLPSQ1**, had 14 eq. of **CL** unit and the other, **CLPSQ2**, had 29 eq. of **CL** unit to amino group, respectively. The results of the graft polymerizations to give the **PSQ**s having the block copolymers (**COPSQ**), conducted under the analogous conditions as above, were listed in Table I (Run 2–4).

Thermal Analysis

Thermogravimetric analysis (DT-TGA) was run using 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.

The differential scanning calorimetry (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 analyses, poly(**LA**) was prepared without the use of **APSQ** by the analogous treatments mentioned above. The ring-opening polymerization of **LA** (1.32 g, 9.16 mmol) with *n*-butylamine (0.02 g, 0.41 mmol) and **TBD** (0.04 g, 0.29 mmol) at 60 °C in THF for 8 h gave the product (0.54 g, 41%). The M_n and M_w/M_n of poly(**LA**) was 5500 g/mol and 1.05, respectively.

RESULTS AND DISCUSSION

Preparation of Grafted PSQ

In our previous work, **APSQ**, which was soluble in DMF, was prepared by the co-condensation using **ATMS** and **PTMS**. The contents of phenyl and aminopropyl groups were estimated by the proton ratios observed in the ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard. 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 estimated M_n of **APSQ** by GPC was 2300 g/mol. The structure of **APSQ** was supposed to be consisted of a ladder- and an incomplete cage-like polysiloxane, although these have been still unidentified. The obtained **APSQ** having amino and phenyl groups was employed as a macroinitiator for the following graft polymerization.

The ring-opening polymerization of **LA** from **APSQ** in the presence of the base catalyst **1** was carried out under the previously reported conditions.[22] The results were shown in Table I. When the graftation of **LA**, using 16.5 eq. to amino group in **APSQ**, was conducted at 60 °C in THF solution, **LAPSQ** was obtained in 84% yield based on weight of the substrates (Run 1). The presence of **LA** and **PSQ** units in **LAPSQ** was confirmed by spectral data. The IR spectrum showed a strong absorption at 1759 cm^{-1} due to carbonyl group of **LAM** units. The absorption at 1133 cm^{-1} was assigned to carbon-oxygen bond of **LAM** units and that at 1093 cm^{-1} was to silicon-oxygen bond of the polysiloxane main chain. In the ^{1}H NMR spectrum of **LAPSQ**, the signal due to the methyl proton was detected at 1.56 ppm. The signal observed at 5.14 ppm was assigned to methine proton attached to oxygen. The signal assigned to methylene protons 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. These peak areas of the signals were utilized for the calculations of content of amino group and **LAM** unit in **LAPSQ**. ^{13}C NMR spectrum of **LAPSQ** also supported the incorporation of poly(**LA**) as the graft chain. The observed signals at 16.82, 69.08, and 169.69 ppm exhibited the presences of methyl, methine, and carbonyl group of **LAM** unit, respectively. The presence of **PSQ** unit was thought to be shown by the small signals around 130 ppm, which were assigned to benzene carbons.

The estimated value of M_n by GPC, 13400 g/mol, was thought to be reasonable in comparison with that of 12800 calculated from the ^{1}H NMR spectral data. Thus, the use of the base catalyst **1** was shown to be effective for grafting of **LA** from **APSQ** through ring-opening polymerization. In addition, no obvious formation of gel product, which seemed to be produced by intermolecular transesterification, was observed. This demonstrated that the living-like polymerization progressed similarly to the case of the grafting of **CL** as mentioned in the previous work.[22]

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As a possible application of the ring-opening polymerization using the catalyst **1**, the grafting of block copolymer of **CL** and **LA** from **APSQ** was examined. At first, the grafting of **CL** from **LAPSQ** was tried in a solution or bulk at 80 °C. However, in the trials, no desired graftation of the block copolymer was observed. In the trials, the change of the catalyst from **1** to **TBD** were also tried. In addition, the random copolymerization of the cyclic esters from **APSQ** was conducted under various conditions, in which **APSQ**, **CL** and **LA** was charged at once with the catalyst **1**. In such polymerizations, the grafted **PSQ**s were obtained, but the graft chains were mainly consisted of poly(**LA**) and contained a small amount of poly(**CL**) chain. The reason why such selective ring-opening polymerization is observed has not been clarified. At this stage, we speculated that the secondary alcohol formed as an end group of poly(**LA**) was a less active initiator to progress the further polymerization of **CL**.

Next, **CLPSQ1**, the M_n of which was estimated to be 12900 by GPC,[22] was employed as the macroinitiator for the incorporation of poly(**LA**). In the grafting, the content of the end hydroxyl group in **CLPSQ1** was thought to be 0.46 mmol eq./g. The content was based on that of amino group, which was the initiator specie in **APSQ** for the first grafting of poly(**CL**), and the number of the end hydroxyl group of **CL** unit was assumed to be same to that of the initiator specie. The ring-opening polymerization using 15 equiv. of **LA** to one of the end hydroxyl groups progressed and gave **COPSQ1** containing the block copolymer of **CL** and **LA** as recorded in Table I (Run 2). The yields of starting **PSQ** unit and incorporated **LAM** unit were 90% and 70%, respectively, which were calculated from ^{1}H NMR spectral data. From the GPC measurement of **COPSQ1**, M_n was estimated to be 22700 and the calculated value on the basis of the content of incorporated **LAM** unit was 21500. The use of **CLPSQ2** having the longer graft chains of poly(**CL**), which contained 29 eq. of **CL** unit to amino group, also gave the **PSQ**s having the block copolymer. From the graft polymerizations using 8 eq. and 15 eq. of **LA** to one of the end groups of **CLPSQ2**, the respective products such as **COPSQ2** and **COPSQ3** were obtained (Run 3 and 4). The yields of **PSQ** unit and **LAM** unit were lower than those recorded in the case using **CLPSQ1**. In these graftings, the yields based on the content of **LAM** unit were in the range from 43% to 49%. The M_ns of **COPSQ2** and **COPSQ3** estimated by GPC were 20700 and 23900 and the calculated values from the contents of the monomer unit, which were based on the ^{1}H NMR spectral data, were 21000 and 22400, respectively. The peaks for **COPSQ**s observed in the GPC chromatograms were all unimodal. For the examples, the chromatograms of **CLPSQ1** and **COPSQ1** were shown in Figure 1. This suggested that the graftings occurred primarily from **CLPSQ**s.

The introduction of **LAM** unit was confirmed by ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra of **COPSQ**s, the signals due to both **CL** and **LAM** units were appeared. The signal observed at 4.02 ppm was assigned to methylene protons bonded to oxygen in **CL** unit. The corresponding methine proton of **LAM** unit was detected at 5.14 ppm. Furthermore, a small signals around 7.4 ppm due to benzene protons showed the presence of **PSQ** main chain. The peak areas were utilized for the calculation of contents of the corresponding units in **COPSQ**s. In the ^{13}C NMR spectra of **COPSQ**s, the signals assigned to the carbon of carbonyl group were appeared at 169.69 and 173.53 ppm. The presence of former signal demonstrated the incorporation of **LAM** unit and the signal was detected as single peak. According to the reports presented before, this indicated that the graft chain was consisted of the block copolymer of **CL** and **LA**.[23,24] For the examples, the spectra of ^{1}H and ^{13}C NMR of **COPSQ1** were shown in Figure 2 and Figure 3, respectively. Thus, the results of GPC measurements and the spectral data demonstrated that the ring-opening polymerization of **LA** was possible by the use of the end group of poly(**CL**) graft chain.

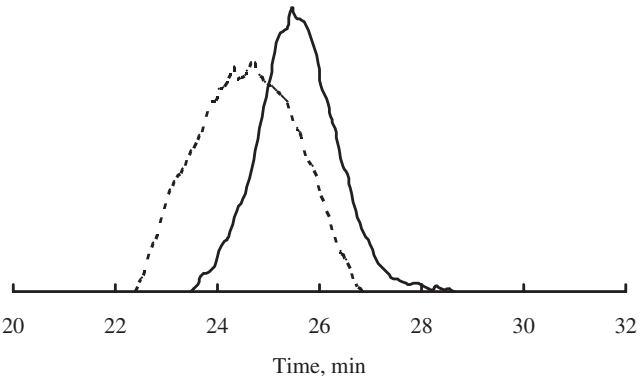

Figure 1. GPC chromatogram of **CLPSQ1** and **COPSQ1**.

Thermal Analysis

The improvement of thermal stability caused by the presence of **PSQ** structure was reported in the previous work.[22] In this report, to get the information concerning the thermal properties of each graft chains of poly(**CL**) and poly(**LA**), the measurements of DSC and TGA were conducted on the grafted **PSQ**s. The results obtained from DSC measurements of **CLPSQ1**, **LAPSQ**, **COPSQ**s, and poly(**LA**) containing no **PSQ** structure were exhibited in Figure 4. The melting point, T_m, of poly(**CL**) has been reported to be around 60 °C.[21] On the other hand, poly(**LA**) shows the endotherm due to T_m over 150 °C.[23–26] In the thermogram of **CLPSQ1**, the melting endotherm was observed at 53.8 °C. However, no endotherm peak over 150 °C was found in the case of **LAPSQ**. The point of inflection in the curve of **LAPSQ** around 48 °C seemed to be T_g of poly(**LA**) chain. Analogously, in the measurements of **COSPQ1-3** having the block copolymers of poly(**CL**) and poly(**LA**) as the graft chains, the peaks assigned to T_m of poly(**CL**) were observed at *ca.* 52 °C, but no endotherm was found around 150 °C. In the previous reports dealing with the usual block copolymer of **CL** and **LA**, both the endotherm peaks are found.[23–26] Indeed, poly(**LA**), prepared independently without **APSQ**, showed the endotherm at *ca.* 140 °C, although it was somewhat obscure. Namely, the polymeric **LA**

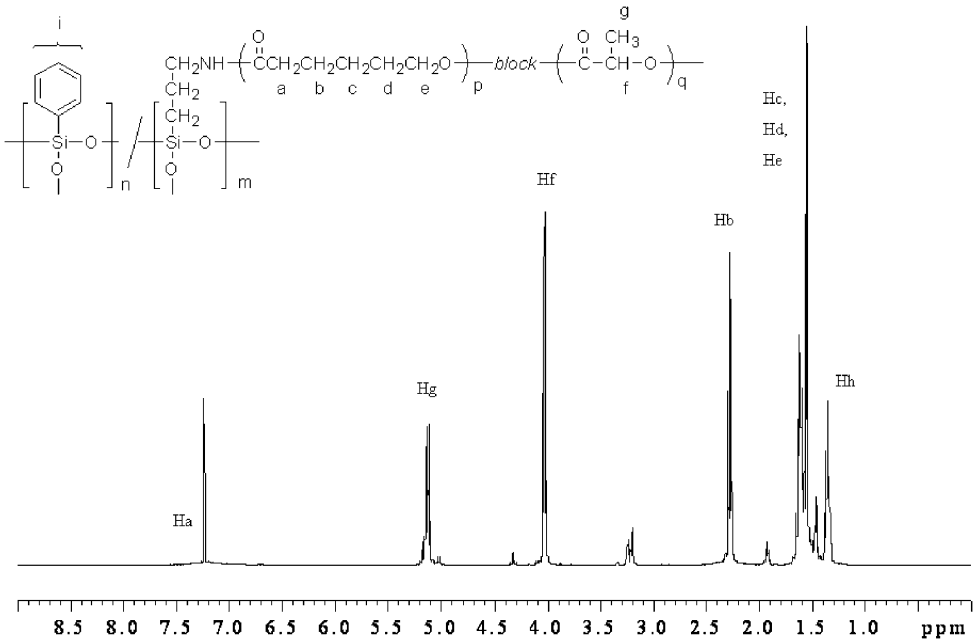

Figure 2. ^{1}H NMR spectrum of **COPSQ1**.

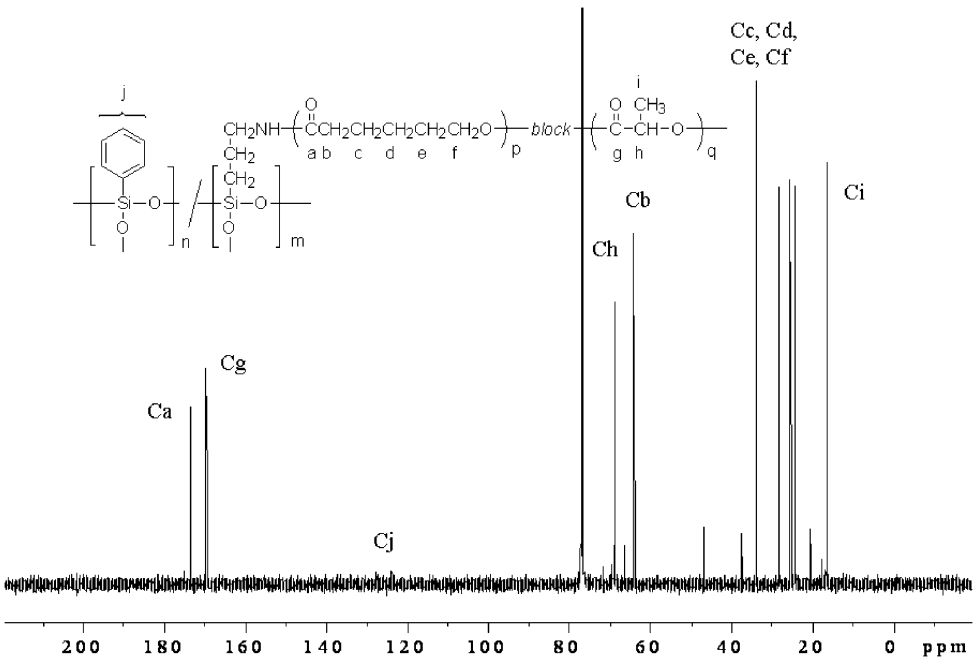

Figure 3. ^{13}C NMR spectrum of **COPSQ1**.

component, prepared under the conditions mentioned here, should show T_m. These results suggested that the presence of **PSQ** main chain was unfavorable to form the crystallized domain of poly(**LA**) segment. However, the difference of M_n of poly(**LA**) component may be another reason to explain the absence of T_m. Since, the M_n of poly(**LA**) such as 5500 was larger than that of the introduced **LAM** units of the grafted **PSQ**s. In the case of **LAPSQ**, the M_n of one graft chain was estimated to be *ca.* 2000. The other interesting observation was that several peaks of T_m were observed in the thermograms of **COPSQ2** and **COPSQ3**, which contained a larger number of **CL** units compared to **COPSQ1**. This may indicate that multi-crystallization occurs in the graft chains. The crystallization was thought to be affected by the polymerization conditions such as reaction temperature and the number of introduced **CL** unit. The result caused by the later factor also varied in such formation of block copolymer. When a smaller amount of second monomer was introduced as shown in the case of **COPSQ2**, the difference of the ratios of **CL** unit and the second monomer units in each graft chains should be obvious.

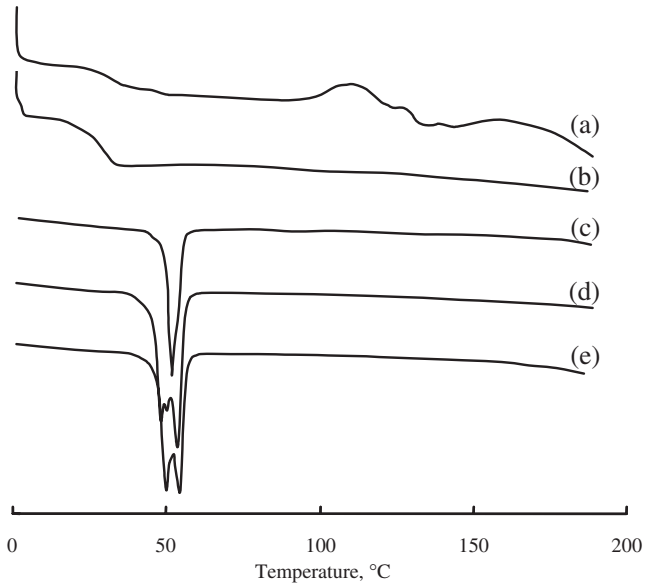

Figure 4. DSC curves of: poly(**LA**) (a), **LAPSQ** (b), **COPSQ1** (c), **COPSQ2** (d), and **COPSQ3** (e).

This might lead to detection of a larger number of peaks showing T_m in the thermogram of **COPSQ2** compared to that of **COPSQ3**. In addition, the disappearance of peak, assigned to T_g around 48 °C in the thermograms of **COPSQ**s, seemed to be explained by such crystallization, which occupied a large part of structure of the graft chains.

As shown in Figure 5, the TGA measurements were made on the grafted **PSQ**s. The weight loss began at 340 °C in the case of **APSQ**. This was attributed to the decomposition of aminopropyl and/or phenyl groups bonded to Si. Further, a slight weight loss of **APSQ** below 340 °C may indicate the occurrence of a further condensation of polysiloxane structure. The weight loss of **CLPSQ1** began at the lower temperatures such as 280 °C. These demonstrated that the thermal decomposition of polymeric **CL** component occurred prior to that of aminopropyl and phenyl groups. In the measurement of **LAPSQ**, a less durability for heat of poly(**LA**) component, which began to decompose at *ca.* 200 °C, was observed. In the case of the independently prepared poly(**LA**), a weight loss was observed also at 200 °C. From the results, the effect of polysiloxane structure to improve thermal stability of graft chain of poly(**LA**) was scarcely observed. Poly(**LA**) component decomposed mainly in the region from 200 °C to 300 °C and the most part of grafted poly(**CL**) in **COPSQ1** seemed to decompose over 320 °C. When the profiles of **LAPSQ** and **COPSQ1** were compared, the later showed somewhat good durability for heat. In the heating from 220 °C to 240 °C, the weight loss of **COPSQ1** was *ca.* 7%. On the other hand, **LAPSQ** lost *ca.* 10% of the weight in the temperature range. The presence of poly(**CL**) chain seemed to contribute for the improvement of thermal stability of poly(**LA**) chain.

CONCLUSION

The polysilsesquioxane containing phenyl and aminopropyl groups was employed for the grafting of biodegradable poly(**LA**) through ring-opening polymerization by the base catalyst obtained from **TBD**. The results demonstrated that the effective graft polymerization by the use of amino group under anionic polymerization conditions proceeded to give the **PSQ** having poly(**LA**) graft chains. In addition, the use of **CLPSQ**, having poly(**CL**) as the macroinitiator, enabled the introduction of the block copolymer of **CL** and **LA** as the graft chains. However, such living-like ring-opening polymerization from the end group of poly(**LA**) graft chain was ineffective as shown in the use of **LAPSQ** as a macroinitiator.

In the examinations on thermal properties of the grafted **PSQ**s, the analytical data of TGA demonstrated that **LAM** units decomposed at first. In addition, the presence of poly(**CL**) brought an improved durability for heat to the polymeric **LA** chain. In the measurements of DSC, poly(**LA**) on the **PSQ** structure showed no endotherm due to T_m, although the peak

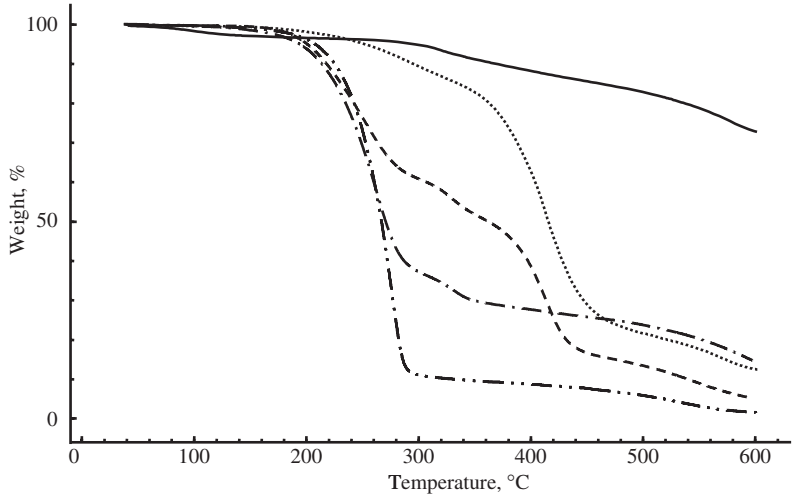

Figure 5. TGA curves of: **APSQ** (—), **CLPSQ1** (···), **COPSQ1** (- - - -), **LAPSQ** (–·–), and poly(**LA**) (–··–).

of T_m for poly(**CL**) was observed. This suggested that the presence of polysiloxane structure was unfavorable for the crystallization of **LAM** units, although the smaller M_n was considered as another reason for the difficulty of crystallization of the units.

Thus, aminopropyl group in **PSQ** main chain could be utilized as the initiator for grafting of the polyester through ring-opening polymerization by the use of the urea type base **1** obtained from **TBD**. The procedure is applicable to the introduction of block copolymer into the graft chain, but the choice of macroinitiator specie was required. The findings in this work are expected to be utilized for the modifications of **PSQ**, which leads to the formation of new functionalized hybrid materials.

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