Graft Polymerization of Dimethylacrylamide onto Polysilsesquioxane Containing Mercapto Groups

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ABSTRACT: Polysilsesquioxane having phenyl and mercapto groups (**PMPSQ**) was prepared from (3-mercaptopropyl)trimethoxysilane (**MTMS**) and phenyltrimethoxysilane (**PTMS**) by co-condensation under basic conditions. The polymerization utilizing mercapto groups on **PMPSQ** with dimethylacrylamide (**DMAA**) under UV irradiation was shown to be a simple and convenient procedure for the formation of the graft polymer (**PMPSQ**-*g*-**PDMAA**). In the photo-initiated radical polymerization, no gelation was observed. The introduction of hydrophilic graft chain was effective to transform the hydrophobic polysilsesquioxane **PTMS** into the amphiphilic **PMPSQ**-*g*-**PDMAA**, which was evaluated by the measurements of contact angle. [DOI 10.1295/polymj.36.761]
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In a previous work of our laboratory, the preparation of grafted derivative of ladder-like polysilsesquioxane by the use of photoiniferter was investigated from the interests in a new kind of hybrid material.[1] The grafted polysilsesquioxanes, soluble in usual organic solvents, are expected to show some specific properties based on the inorganic and organic polymeric components with the structural peculiarity. These should expand the utilities of polysilsesquioxane, which are demonstrated in various investigations concerning electrical, optical, mechanical, and chemical applications of polysilsesquioxanes.[2,3] Furthermore, the expectation is supported by the recent studies on the introduction of polymeric components onto the related polysiloxane compounds such as silica, zeolite, and clay to modify or improve the properties.[4–8] For the effective grafting, the living polymerization techniques *via* radical species such as atom transfer radical polymerization process[9–12] and the use of photoiniferter[13] are appropriately utilized in the recent investigations. These living polymerization techniques contribute to minimize the formation of free chains, control the chain length, and the easy formation of block copolymer chains. However, the use of a metal/ligand complex or the introduction of dithiocarbamate group requires somewhat complicated treatments. On the other hand, thiol compound has been well known as a representative chain transfer reagent in radical polymerizations.[14–16] Therefore, the radical process utilizing mercapto group has been reported as another efficient procedure to introduce

polymeric chains on silica surface.[17,18] Furthermore, very recently, such classical role of thiols is applied to the polymerization of methyl methacrylate without an initiator.[19] In the graft polymerization onto polysilsesquioxane, mercapto group is expected to be the effective initiating site. In addition, the polysilsesquioxane containing mercapto group is easily obtained by the use of commercially available (3-mercaptopropyl)trimethoxysilane (**MTMS**). These will be the essential factors of a simple and practical procedure for the grafting onto polysilsesquioxane. However, such free radical process may result in the formation of gels *via* a radical coupling termination.

In line with the considerations mentioned above, we have started the investigations to examine and know the limitation of the procedure utilizing mercapto group for the graft polymerization onto the ladder-like polysilsesquioxane. Further, the introduction of hydrophilic components leading to an amphiphilic hybrid material is intended as another target. The resulting grafted product, containing both the hydrophobic and hydrophilic polymeric components, promises to show the interesting properties such as self-organizing and self-assembling, which should be utilized as a high performance copolymer.[20,21] In this work, as shown in Scheme 1, the graft polymerization from the polysilsesquioxane having both phenyl and mercaptopropyl groups (**PMPSQ**) with dimethylacrylamide (**DMAA**), being known to afford a hydrophilic polymer, was conducted under UV irradiation to prepare the hybrid graft product **PMPSQ**-*g*-**PDMMA**. In

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Scheme 1.
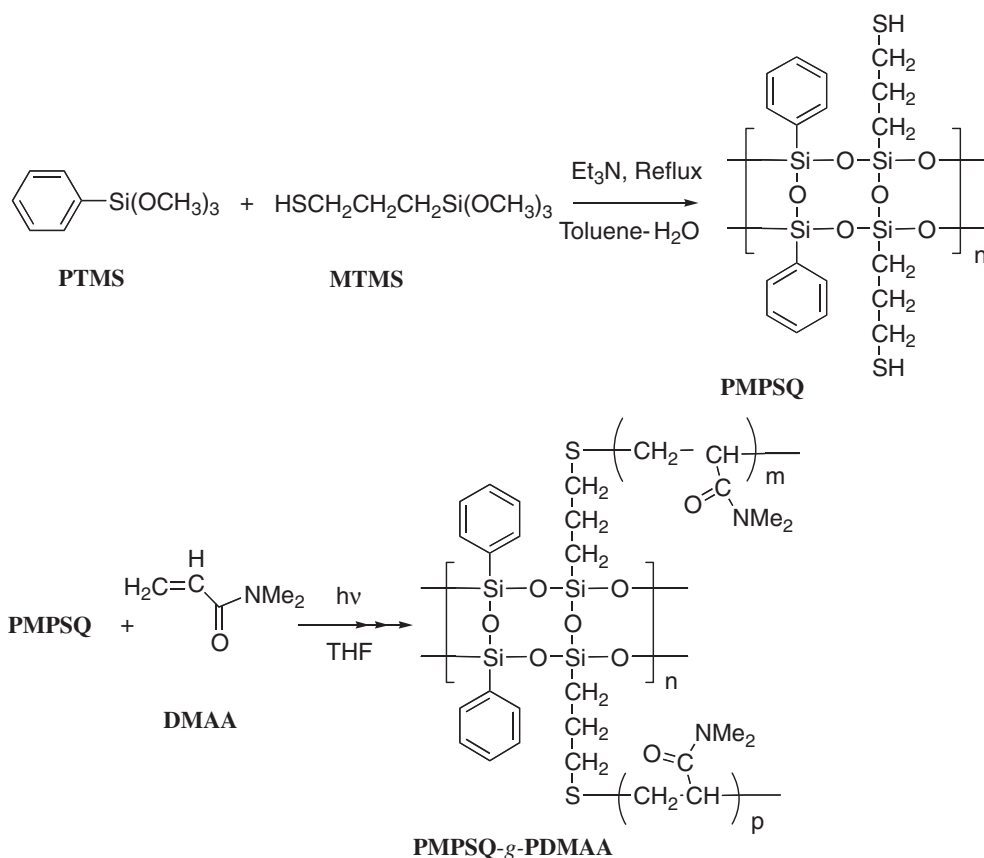
addition, the thermal behavior and the contact angle of **PMPSQ**-*g*-**PDMMA** were examined to obtain the fundamental information on the effects of the grafting.

EXPERIMENTAL

General

^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL FX-270 and JNM A-500 spectrometer in CDCl$_3$. Solid-state CP/MAS NMR measurements were carried out with samples in double air bearing 6 mm rotor of zirconia on a JEOL JNM ECA500 spectrometer, operating at 53.5 MHz for [29]Si. Magic angle spinning was performed at 5.6 kHz spinning rate. The proton 90° pulse was 4 μs for ^{29}Si NMR measurements. Polydimethylsilane was the reference for ^{29}Si NMR spectra. IR spectra were recorded on a JASCO FT/IR 230. Gel permeation chromatographic (GPC) analysis was carried out 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 dimethylformamide (DMF) was used as the eluent. Calibration was performed using poly-methylmethacrylate standards. THF employed for the reactions were refluxed over sodium metal

and distilled. The monomers, dimethylacrylamide (DMAA) was dried with calcium hydride and distilled under reduced pressure before use. Other reagents including benzophenone were used as supplied from commercial sources.

Preparation of PMPSQ

A mixture of phenyltrimethoxysilane (**PTMS**, 4.00 g, 20.16 mmol) and **MTMS** (4.00 g, 20.36 mmol) with triethylamine (0.20 g, 2.00 mmol) in toluene (40 mL) and water (10 mL) was refluxed for 24 h. Organic phase was separated and washed with brine. The organic phase was concentrated by a rotary evaporator under reduced pressure and, then, methanol was added to the residual oil. The resulting wax-like oil insoluble in methanol was dried at room temperature for 24 h in a vacuum oven under reduced pressure (<5 mmHg). **PMPSQ** (3.36 g, 74% yield from **PTMS** and 64% yield from **MTMS**) was obtained as a solid. The contents of phenyl and mercapto groups were calculated from the peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard; IR (KBr) 3450 (weak, OH), 3050 (weak, –C$_6$H$_5$), 2930 (medium, –CH$_2$–), 2560 (weak, SH), 1440 (medium), 1268 (medium), 1134 (strong, Si–O), 1028 (strong, Si–O), 742 (medium), 700 (medium)

cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.45–0.95 (br, –Si–C$\underline{H}_2$–), 1.30 (br, –S$\underline{H}$), 1.45–1.85 (br, –C$\underline{H}_2$–), 2.25–3.00 (br, –S–C$\underline{H}_2$–), 6.50–7.70 (br m, –C$_6$$\underline{H}_5$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.40 (Si–$\underline{C}$H$_2$–), 27.81 (–$\underline{C}$H$_2$–SH, C–$\underline{C}$H$_2$–C), 128.39 (m,p-C$_6$H$_5$ × 3), 131.26 (o-C$_6$H$_5$ × 2), 134.43 (Si–$\underline{C}_6$H$_5$); ^{29}Si CP/MAS NMR (53.5 MHz) δ −85.00 to −73.00, −73.00 to −61.00, −61.00 to −53.00; $M_n = 5700$, $M_w/M_n = 2.07$; phenylsilyl unit = 4.46 mmol equiv./ g, mercapto unit = 3.85 mmol equiv./g.

Typical Procedure for Grafting onto **PMPSQ**

A solution of **PMPSQ** (0.10 g, 0.45 mmol equiv. of phenyl group and 0.39 mmol equiv. of mercapto group), **DMAA** (0.38 g, 3.83 mmol) in THF (3.2 mL) was introduced into a glass tube. The mixture was purged of air *via* three vacuum–argon cycles. Then, the mixture in the glass tube was irradiated at 20 °C by using a RIKO RH400 UV lamp equipped with water jacket from a distance of 10 cm for 20 h. The resulting solution was evaporated under reduced pressure and the residue was poured into diethyl ether to isolate insoluble wax-like oil. The oil was dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the graft polymer (**PMPSQ**-*g*-**PDMAA**) as a solid (0.37 g, 77% yield based on weight) (Table I, Run 5); IR (KBr) 3470, 2934, 1625 (C=O), 1495, 1400, 1260, 1140, 1095, 1045 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.20 (br, m, –C$\underline{H}_2$–), 1.63–1.73 (br, m, –C$\underline{H}_2$–), 2.15–2.48 (br, –C$\underline{H}_2$–), 3.10 (br, –CH–N–C$\underline{H}_3$), 7.13–7.40 (br, –C$_6$$\underline{H}_5$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.5 (–$\underline{C}$H$_2$–), 35.8 (N$\underline{C}$H$_3$), 36.3 (N$\underline{C}$H$_3$), 37.1 (–$\underline{C}$H–), 125.2 (–$\underline{C}_6$H$_5$), 127.8 (–$\underline{C}_6$H$_5$), 133.7 (–$\underline{C}_6$H$_5$), 174.6 (–$\underline{C}$=O); phenylsilyl unit = 1.18 mmol equiv./g (97% yield based on phenyl group), DMAA unit = 8.10 mmol equiv./g (78% yield based on the monomer).

Analogously, from the reaction of **PMPSQ** (0.10 g, 0.45 mmol equiv. of phenyl group and 0.39 mmol equiv. of mercapto group), **DMAA** (0.76 g, 7.67 mmol) in THF (6.4 mL), **PMPSQ**-*g*-**PDMAA** (0.51 g, 59% yield based on weight) was obtained (Table I, Run 6); phenylsilyl unit = 0.88 mmol equiv./g (100% yield based on phenyl group), **DMAA** unit = 8.60 mmol equiv./g (57% yield based on the monomer).

Analogously, the polymerizations of **PMPSQ** with 6 equiv. of **DMAA** to mercapto group were carried out under various conditions (Figures 4 and 6; Table I, Runs 1–4).

Thermal Analysis

Preparation of Poly(dimethylacrylamide). A solution of **DMAA** (10.00 g, 99.9 mmol), α,α'-azobisiso-butylonitrile (AIBN) (0.20 g, 1.22 mmol) in toluene (30 mL) was introduced into a glass tube. The mixture was purged of air *via* three vacuum–argon cycles. The polymerization was carried out at 80 °C for 8 h under UV irradiation. The resulting solution was evaporated under reduced pressure and the residue was poured into diethyl ether. The precipitated solid was dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the polymer (**PDMAA**) (8.50 g, $M_n = 13000$, $M_w/M_n = 2.20$).

PMPSQ, **PMPSQ**-*g*-**PDMAA** (Table I, Run 5) and **PDMAA** were employed for thermal degradation test by a thermogravimetric analyzer (DTG-60 by Shimadzu Corp.). The measurements were conducted with 10 mg of the sample from room temperature to 800 °C, in which a heating rate was 10 °C min^{-1} under nitrogen.

Contact Angle. A solution of **PMPSQ** or **PMPSQ**-*g*-**PDMAA** (Table I, Run 5 or 6) in toluene was cast on poly(ethylene terephtalate) sheet and, then, removed toluene at 120 °C for 1 min. in an oven. Static contact angle was measured with deionized water

Table I. Preparation of **PMPSQ**-*g*-**PDMAA** from **PMPSQ**

| Run | Reaction conditions[a] | | PMPSQ-*g*-PDMAA | | | |
	Monomer concentration [M]	Ratio of **DMAA**/SH mol/mol	Yield %	Unit ratio of **DMAA**/SH[b] mol eq./mol eq.	M_n[c]	M_w/M_n[c]
1	0.3	6	73	4.2	12800	2.02
2	0.6	6	75	4.3	12500	1.95
3	1.2	6	80	4.7	13000	2.05
4	2.3	6	86	4.9	13600	2.13
5	1.2	10	77	7.8	21800	2.01
6	1.2	20	59	11.3	28600	2.03

[a]The polymerization of **PMPSQ** containing 3.85 mmol eq./g of mercapto groups was conducted at 20 °C in THF under UV irradiation for 10 h. [b]The molar ratio of **DMAA** unit and SH unit was calculated on the basis of integrals in the ^{1}H NMR spectra measured with hexamethyldisiloxane as an internal standard. The content of SH unit was estimated from the amount of phenyl group, the ratio of which and SH unit was assumed to be same to that in the starting **PMPSQ**. [c]Determined by GPC with polymethylmethacrylate standards.

drops on the surface of the resulting sheet within 10 s. at room temperature by a Face Contact Angle Meter (CA-D Type by Kyowa Interface Science Co., Ltd.).

RESULTS AND DISCUSSION

Preparation of PMPSQ from PTMS and MTMS

The polysilsesquioxane, **PMPSQ**, having phenyl and mercaptopropyl groups was prepared as the starting material in this work. Usually, the ladder-like poly(phenylsilsesquioxane), soluble in various organic solvents, could be obtained effectively as an easy handling solid under basic conditions from **PTMS**.[22,23] On the other hand, the condensation using sole **MTMS** proceeded with gelation in the presence of a basic catalyst. Consequently, the introduction of phenyl groups was required to isolate the polysilsesquioxane containing mercaptopropyl groups as a solid soluble in usual organic solvents. Furthermore, the presence of phenyl groups was thought to be preferable in the ^{1}H NMR analyses of **PMPSQ** and the products, since the signal assigned to phenyl group was available as a standard for the calculation of the composition of several groups containing in the derivatives of **PMPSQ**. The co-condensation of **PTMS** and **MTMS** with a catalytic amount of triethylamine was carried out to prepare **PMPSQ**. The starting material, **PMPSQ**, contained the almost same molar ratio of phenyl and mercaptopropyl groups, was obtained in the good yield such as 74% as a wax-like oil insoluble in methanol. After drying under vacuum at room temperature, the wax-like oil changed to the easy handling solid. The composition of the groups in **PMPSQ** reflected the feed molar ratio of **PTMS** and **MTMS**. Such estimations of the yield and the contents of phenyl and mercapto groups were based on the proton ratios observed in the ^{1}H NMR spectral data.

In the ^{1}H NMR measurements of **PMPSQ**, hexamethyldisiloxane was used as an internal standard, the signal of which appeared at 0 ppm. As shown in Figure 1, the signals assigned to the protons for $-CH_2CH_2SH$ were observed in the range from 1.30 to 1.85 ppm. Other protons showing the presences of $SiCH_2-$ and benzene ring were detected around 0.9 ppm and 7.6 ppm, respectively. From the proton ratios of these signals, the contents of 3.85 mmol equiv./g of mercapto group and 4.46 mmol equiv./g of phenyl group were estimated. In the spectrum of ^{13}C NMR, shown in Figure 2, the signals due to the groups mentioned above were also detected. The carbons assigned to $SiCH_2-$ and $-CH_2SH$ were appeared at 12.40 ppm and 27.81 ppm, respectively. The later signal also showed the presence of another methylene carbon as previously reported in the solid-state ^{13}C NMR measurements.[24–26] The spectral data of [29]Si
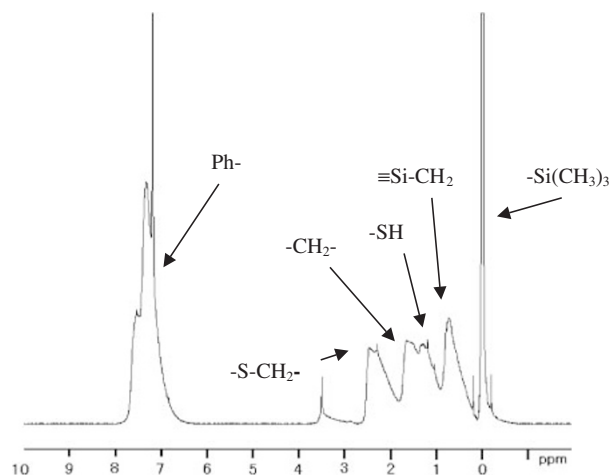
Figure 1. ^{1}H NMR spectrum (CDCl$_3$, 270 MHz) of **PMPSQ**.
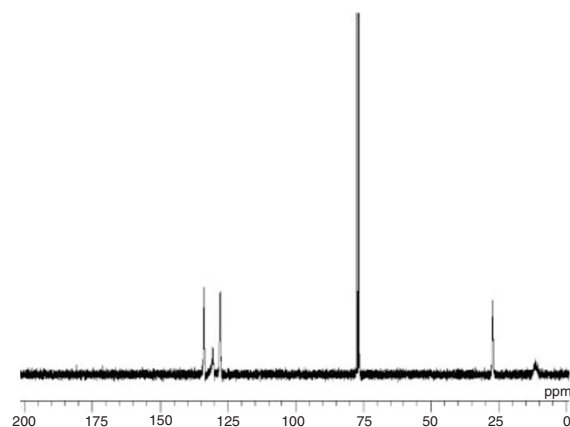
Figure 2. ^{13}C NMR spectrum (CDCl$_3$, 67.5 MHz) of **PMPSQ**.
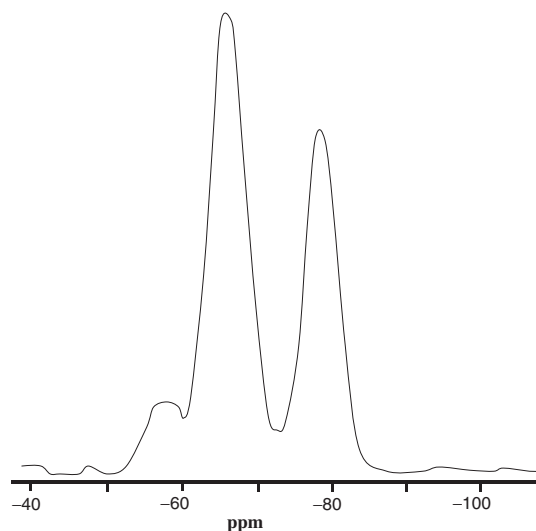
**Figure 3.** Solid-state ^{29}Si NMR spectrum of **PMPSQ**.

NMR of **PMPSQ** presented the information about the structure of polysiloxane backbone as shown in Figure 3. The signal observed at −78 ppm demonstrated that the polymerized structure contained phenyl

substituted silicon–oxygen T^3 units. The signal at *ca.* -66 ppm seemed to contain the signals assigned to T^2 units of phenyl substituted silicon and mercaptopropyl substituted T^3 units. The presence of T^2 units of mercaptopropyl silicon–oxygen was exhibited by the signal appeared at -58 ppm. The reported spectral data of silica immobilized mercaptopropyl groups support those interpretations.[7] Generally, the chemical shifts of T^2 and T^3 were reported to vary with the difference of structures and molecular weights.[27,28] In the ^{29}Si NMR spectra of oligo- and poly(phenylsilsesquioxane), T^3 silicone signal of oligocyclic one is observed at -64.1 ppm and that of polymerized one is at -83.7 ppm.[28] The later chemical shifts of the polysilsesquioxane, M_n of which is 53800, is explained by the environmental homogeneity of each repeating unit. The chemical shift of **PMPSQ**, *ca.* -78 ppm, was in the middle of those reported values. This may indicate that siloxane backbone of **PMPSQ** involve the regular ladder-like repeating units, cyclic units, and irregular silsesquioxane units. However, the assignments on the overlapped signals made it difficult to estimate the contents of two kinds of silicon having phenyl and mercaptopropyl group, respectively.

The IR spectrum of **PMPSQ** also supported the presences of phenyl and mercapto groups as shown in Figure 4. The absorption observed at 3025 cm^{-1} and weak absorptions around 1650 cm^{-1} in the spectrum were assigned to phenyl groups on the ladder-like siloxane backbone. The presence of mercapto groups was shown in the weak absorption observed at 2560 cm^{-1}. The strong and broad absorption appeared around 1130 cm^{-1} was assigned to T^2 and T^3 units consisted of Si–O bonds. These were reported to be observed at 1132 cm^{-1} and 1078 cm^{-1} in the IR spectra of poly(methylsilsesquioxane).[29] The number-average molecular weights (M_n) and polydispercity
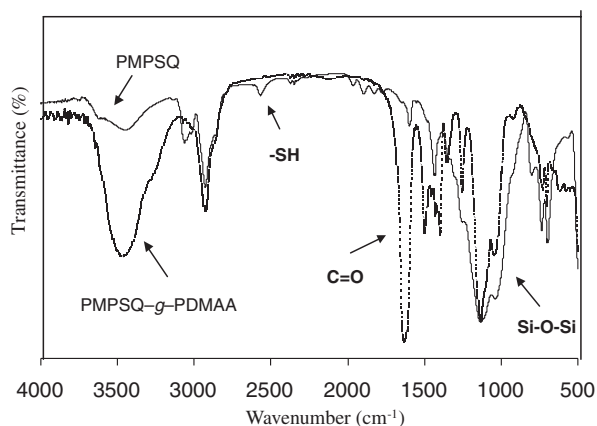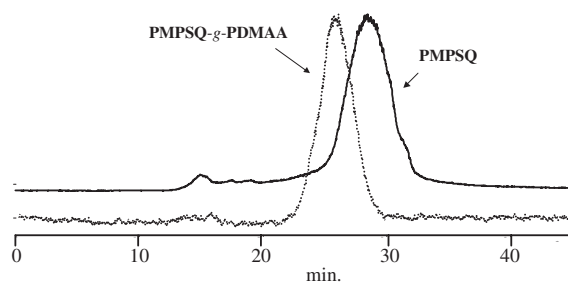

Figure 5. GPC traces for **PMPSQ** (—) and **PMPSQ**-*g*-**PDMAA** ($\cdots$) (Table I, Run 5).

(M_w/M_n) of **PMPSQ** estimated by GPC data were *ca.* 5700 and 2.07, respectively as shown in Figure 5. **PMPSQ** was soluble in diethyl ether, chloroform, benzene, acetone, THF, and DMF, but insoluble in methanol, *n*-hexane and water. Such **PMPSQ** was used as the starting material for the graft polymerization.
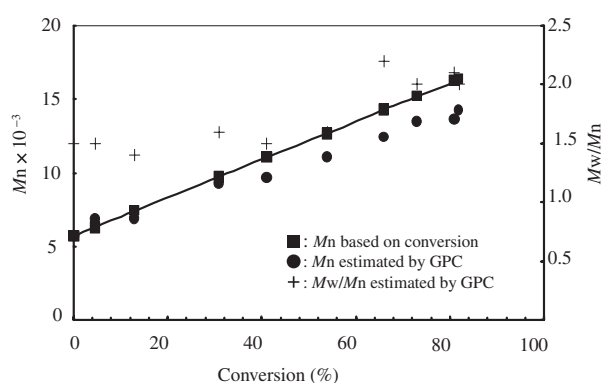
Graft Polymerization

The photopolymerization of **DMAA** with **PMPSQ** under UV irradiation using a high pressure merculy lamp at 25 °C was carried out in THF with or without a catalytic amount of benzophenone or α,α'-azobisisobutyronitrile (AIBN). The yields and M_ns of the products were almost same under these conditions. The results suggested that this radical polymerization proceeded similarly to the reported one of methyl methacrylate, in which no initiator was employed.[19] According to the report, the polymerization was speculated to begin from the step of polar hydrogen transfer from mercapto group to methyl methacrylate and, then, radical species were generated. The similar mechanism may be applicable to explain the efficient graft polymerization of **DMAA** in our polymerization system. From those results, the graft polymerizations in this work were examined without a photo-sensitizer or radical-initiator.

At first, the graft polymerization using six equiv. of **DMAA** to mercapto group in 1.2 [M] solution of THF was conducted, in which the conversions of **DMAA** were monitored by ^{1}H NMR spectra and the M_ns of the corresponding graft polymer were by GPC. As shown in Figure 6, the plot of relative conversion of the monomer *vs.* time indicated that the conversion reached to *ca.* 80% after 6 h. The linear line of the calculated M_ns from the conversions, where the converted monomers were assumed to be grafted completely, was shown in Figure 7. The M_ns of the graft polymer estimated by GPC also increased along with the calculated line, although the values became somewhat smaller in the region of higher conversions. The increase of polydispersities (M_w/M_n) from *ca.* 1.5 to *ca.* 2.0 according to the increase of the conversions

Figure 4. IR spectra of **PMPSQ** (—) and **PMPSQ**-*g*-**PDMAA** ($\cdots$) (Table I, Run 5).
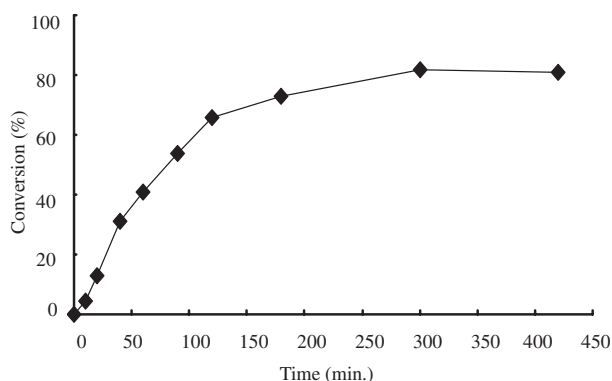
Figure 6. Time–conversion relation in graft polymerization of **PMPSQ** (0.10 g) using six equiv. of **DMAA** (2.34 mmol) to mercapto group in THF (2.0 mL) at 20 °C (Table I, Run 3).


Figure 7. Conversion-M_n and M_w/M_n relations in graft polymerization of **PMPSQ** (0.10 g) using six equiv. of **DMAA** (2.34 mmol) to mercapto group in THF (2.0 mL) at 20 °C (Table I, Run 3).

was observed. These results seemed to show that the monomer essentially grafted on **PMPSQ**. However, a slight deviation of M_ns from the line of the calculated M_ns may suggest the formation of the homopolymer of **DMAA**.

Next, the graft polymerizations were carried out under several different conditions. The results were shown in Table I. In the polymerizations, in which the concentrations of the monomer were adjusted to be in the range from 0.3 mol/L to 2.3 mol/L, the yields increased from 75% to 86% as the increase of the concentrations (Table I, Runs 1–4). The values of M_n estimated by GPC were also increased according to the conversion from 12500 to 13600. In the concentrations of 1.2 and 2.3 mol/L, the increase of the conversion and M_n of the resulting polymer was small. The other factor, which related to the efficiency of grafting or polymerization, was the molar feed ratio of mercapto group to the monomer. This was demonstrated by changing the feed molar ratios of **DMAA** to mercapto group (Table I, Runs 3, 5, and 6). In the cases using 6 and 10 equiv. of **DMAA**, the insoluble solid in diethyl ether was obtained in the analogous yields

such as 77%. However, the decrease of the yield, 59%, was recorded in the use of 20 equiv. of **DMAA**. These yields were thought to relate directly with the incorporated monomer units. Because, the estimation based on the ^{1}H NMR spectral data indicated that **PMPSQ** unit was quantitatively recovered as the main chain of **PMPSQ**-*g*-**PDMAA**. This meant that the yields were essentially depended on the amount of polymerized **DMAA**. Furthermore, in GPC profiles of the starting **PMPSQ** and the products, one main peak was observed, respectively, and no additional peak was appeared after grafting. This supported the assumption mentioned above that **DMAA** was primarily incorporated into **PMPSQ** as the graft chain and the content of the homopolymer should be small even if it was formed. The GPC curves of **PMPSQ**-*g*-**PDMAA** (Table I, Run 5) and **PMPSQ** was shown in Figure 5. In these graft polymerizations, **PMPSQ**-*g*-**PDMAA**s were isolated as the wax-like oil insoluble in diethyl ether, but soluble in water, methanol, acetone, chloroform, benzene, THF, and DMF. Furthermore, it was noteworthy that no cross-linked product was detected in such simple radical polymerization system.

The spectral data of IR and NMR supported the incorporation of the graft chains onto **PMPSQ**. In all the IR spectra of the grafted products, the broad absorptions around 1200 cm^{-1} assigned to C–O bond were observed, where the absorption due to Si–O bond might be included. The absorptions due to carbonyl group of the acrylamide polymer appeared clearly at *ca.* 1630 cm^{-1} in the spectra of the polylsilsesquioxanes after grafting. The weak absorption at 2560 cm^{-1} assigned to SH group was disappeared in the spectra of **PMPSQ**-*g*-**PDMAA**. The spectra of **PMPSQ** and **PMPSQ**-*g*-**PDMAA** were shown in Figure 4. The presence of grafting components was, further, confirmed by the spectral data of NMR. In the ^{1}H NMR spectra of the grafting polysilsesquioxanes, the signals due to the protons of methylene and methine groups were detected in the range from 1.2–1.8 ppm. The methylene protons attached to Si was observed at 0.7 ppm in the spectra of **PMPSQ**-*g*-**PDMAA**, which was prepared from **PMPSQ** with six equiv. of **DMAA**. Other signals due to methyl protons of dimethylamino group and protons of benzene ring were appeared around 3.0 ppm and 7.2 ppm, respectively. In the spectra used for the examination on the relationship of time *vs.* conversion, vinyl protons were detected in the region of 5.5 ppm to 6.8 ppm. The proton ratios of the signals due to vinyl, phenyl, dimethyl, methylene, and methyl, were employed for the calculations of the contents of the monomer, the polymerized monomer, and polysilsesquioxane backbone, which were based on that of hex-
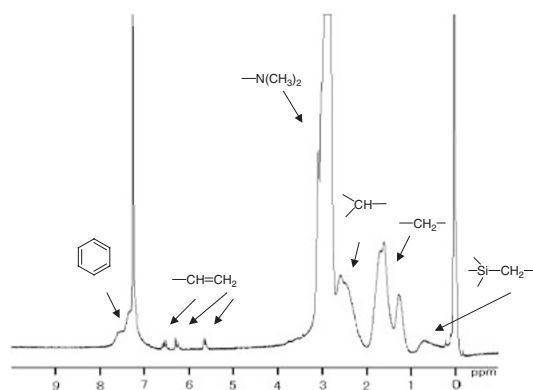
Figure 8. ^{1}H NMR spectrum (CDCl$_3$, 270 MHz) of the mixture in the graft polymerization (Table I, Run 4).

amethyldisiloxane as an internal standard. An example of the spectra was shown in Figure 8. The existences of the monomer unit in the graft polysilsesquioxanes were also confirmed by the ^{13}C NMR spectra. The signals around 130 ppm and 36 ppm observed in all the spectra of the graft polymers were assigned to carbons of phenyl and dimethylamino group, respectively. The signal appeared around 178 ppm exhibited the incorporation of carbonyl groups of the monomer units after grafting process.

The thermal stability of the graft polymer **PMPSQ**-*g*-**PDMAA** (Table I, Run 5) was examined by TGA analysis and compared with those of poly(dimethylacrylamide) **PDMAA** and **PMPSQ** as shown in Figure 9. **PDMAA** was prepared by free radical polymerization, M_n of which was 13000. In the measurements, conducted a heating rate of 10 °C min^{-1} under nitrogen, the obvious degradation of poly(dimethylacrylamide) chain began at *ca.* 380 °C in all samples.
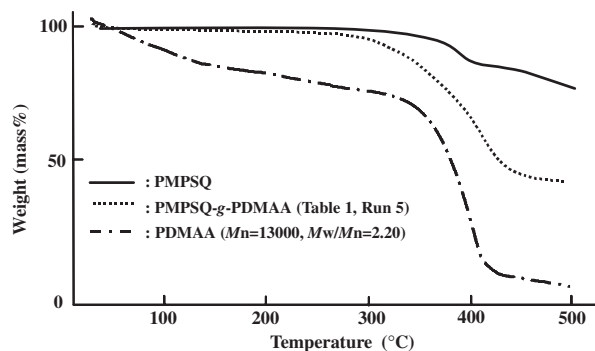
Figure 9. TGA curves of **PMPSQ** (—), **PMPSQ**-*g*-**PDMAA** (···) (Table I, Run 5), and **PDMAA** (–·–).

In comparison with the weight loss until 300 °C, that of **PMPSQ**-*g*-**PDMAA** was *ca.* 5%. In the case of **PDMAA**, the weight loss was *ca.* 25%. Such results seem to demonstrate the improved heat-stability of the graft polysilsesquioxane **PMPSQ**-*g*-**PDMAA**. However, the tolerance of the grafting units to heat, caused by the combination with polysiloxane structure, was not so obvious. Since, the decrease of the weights of **PMPSQ**-*g*-**PDMAA** and **PDMAA** began at almost the same temperature such as *ca.* 170 °C.

The effect of incorporation of the hydrophilic graft chains was evaluated by the measurement of contact angle on the films obtained from **PMPSQ**-*g*-**PDMAA**s. The contact angles of the water drop and the surface, measured at room temperature within 10 s, were shown in Table II. The hydrophobic **PMPSQ** provided the reasonable angle such as 98°. The contact angle of **PMPSQ**-*g*-**PDMAA** containing 7.8 monomer units to one mercapto group (Table I, Run 5) obviously decreased to be 18°. In the case of **PMPSQ**-*g*-**PDMAA** containing 11.3 monomer units (Table I, Run 6), the angle was 12°. Thus, the angle decreased with the increase of contents of the hydrophilic monomer units, although the accuracy of the values of **PMPSQ**-*g*-**PDMAA**s might be governed by an experimental error.

CONCLUSIONS

The ladder-like polysilsesquioxane containing phenyl and mercaptopropyl groups was employed as an effective starting material for the preparation of grafted hybrid polymer. From the results, mercapto groups in the polysilsesquioxane were revealed to be the effective initiation sites for the graft polymerization under UV irradiation. In the graft polymerizations of **PMPSQ** with **DMAA**, no formation of cross-linked product was detected. As an expected physical property, the graft polymers should show a better thermal stability in comparison with the homopolymer. This was not obviously demonstrated, but it might say at least that the weight-loss of **PMPSQ**-*g*-**PDMAA** was smaller below 300 °C compared to that of the homopolymer **PDMAA**. The use of **DMAA** as the monomer to give the hydrophilic graft chains was successfully shown in the decreases of contact angle of **PMPSQ**-*g*-**PDMAA**. Thus, the introduction of the hydrophilic graft chains enabled the preparation of the

Table II. Contact angle of water on the surface of **PMPSQ** and **PMPSQ**-*g*-**PDMAA**

Material	**PMPSQ**	**PMPSQ**-*g*-**PDMAA**	
Molar unit ratio of **DMAA**/SH	0	7.8 (Table I, Run 5)	11.3 (Table I, Run 6)
Contact angle	98°	18°	12°

ladder-like polysilsesquioxane soluble in water. Such graft polymer is expected to be a widely utilized amphiphilic hybrid material showing a higher thermal stability and weather durability for a polymeric surfactant and the additive in paint and adhesive.

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