Preparation of Thermoresponsive Grafted Polysilsesquioxane from Polyacrylamides Having Methoxysilyl End Group

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(3-Mercaptopropyl)trimethoxysilane was employed as a chain transfer for the polymerization of *N*-isopropylacrylamide (**NIPAM**) and *N*,*N*-dimethylacrylamide (**DMAA**) under UV irradiation to obtain the corresponding polymers having methoxysilyl end group. By the condensation reaction of such macrosilane coupling reagents under basic or acidic conditions, the grafted polysilsesquioxanes, which were soluble in usual organic solvents, were formed without gelation. The co-condensation of the macrosilane coupling reagents enabled the preparation of the grafted polysilsesquioxane, in which poly(**NIPAM**) and poly(**DMAA**) were introduced respectively into the polysilsesquioxane main chain. Such macrosilane coupling reagents and the grafted polysilsesquioxanes showed an amphiphilic property. Furthermore, those containing poly(**NIPAM**) showed reversible thermoresponsive aggregation in an aqueous solution. In the thermoresponsive phase separation measured by turbidity, no change of aggregation temperature caused by the presence of poly(**DMAA**) was observed.

KEY WORDS: Polysilsesquioxane / Thermoresponsive Phase Separation / Poly(*N*,*N*-isopropylacrylamide) / Macrosilane Coupling Reagent /

Silsesquioxane, which consisted of T-type siloxane bond, is a kind of useful inorganic-organic hybrid materials. From the interests in a new hybrid material, various investigations concerning the usages of oligo- and poly-silsesquioxane (**PSQ**) have been reported recently.[1–5] In fact, the applications of such silsesquioxanes have been extended to electrical, optical, mechanical, and chemical fields.[6–9] Most of those are performed by the modification of organic functional group, which is contained in the starting trialkoxy- or trichloro-silanes. The graft polymerization onto and from the silsesquioxane main chain has been also recognized as an effective method for the modification, in which the polymeric component provides an additional property besides durability for heat and weatherability based on the inorganic polysiloxane backbone.[10–14] We also presented several reports concerning the grafted **PSQ** which intended to prepare a new multi-functional hybrid material.[15–17] The synthesis of thermoresponsive **PSQ**s, grafted the copolymer of *N*,*N*-dimethylacrylamide (**DMAA**) and *N*-isopropylacrylamide (**NIPAM**), was an example utilizing the modification method.[18–20] The **PSQ**, showing the stimuli-responsive property, has potential to be used in the practical material scenes of microencapsulation, biosensor, and drug delivery as postulated in the investigations concerning poly-(**NIPAM**).[21–27]

For the grafting of the acrylamide polymers from **PSQ** back bone, the mercapto group was usable as a chain transfer specie in photo-polymerization.[28–31] However, the condensation of sole (3-mercaptopropyl)trimethoxysilane (**MTMS**) to prepare the **PSQ** usually resulted in the formation of gel product insoluble in any solvent. Consequently, the co-condensation of **MTMS** with phenyltrimethoxysilane is required to obtain the

PSQ derivative, which was soluble in usual organic solvents. The corresponding functionalized gel is also useful and should be a convenient hybrid compound. Whereas, the **PSQ** soluble in a solvent is usable as a versatile material. Since, a homogeneous solution system is considered to perform the treatment and the reaction effectively in a molecular size mixture, when **PSQ** is utilized as a surfactant, an additive, and a component for the formation of interpenetrating material.

On the other hand, we reported the preparation of grafted **PSQ** by the use of living polymerization technique such as Reversible Addition-Fragmentation Chain Transfer process, in which the block copolymers of **NIPAM** and **DMAA** were introduced into **PSQ** main chain.[20] Such previous results demonstrated that the sequence and the molecular weight of the polymer units in the graft chain showed no influence on the thermoresponsive aggregation temperature. The Lowest Critical Solution Temperatures (LCST) of the **PSQ**s in an aqueous solution were recorded to be an almost same value irrespective of the presence of poly(**DMAA**) unit, which was relatively more hydrophilic and usually increase LCST of random copolymer with **NIPAM**. Therefore, the behavior is thought to be a characteristic of block copolymer of poly(**NIPAM**).[32] The fact led us to examine the thermoresponsive behavior of another type of grafted **PSQ**, which had each poly(**NIPAM**) and poly(**DMAA**) on the same **PSQ** main chain. Such kind of grafted **PSQ** was assumed to be prepared readily by the use of the corresponding polymeric silane coupling reagents. If the polymeric coupling reagent prepared from **MTMS** is used as a building block, the resulting **PSQ** should be same to that obtained from sole **MTMS**. In other words, the synthetic route can avoid the gelation observed at the condensation using sole

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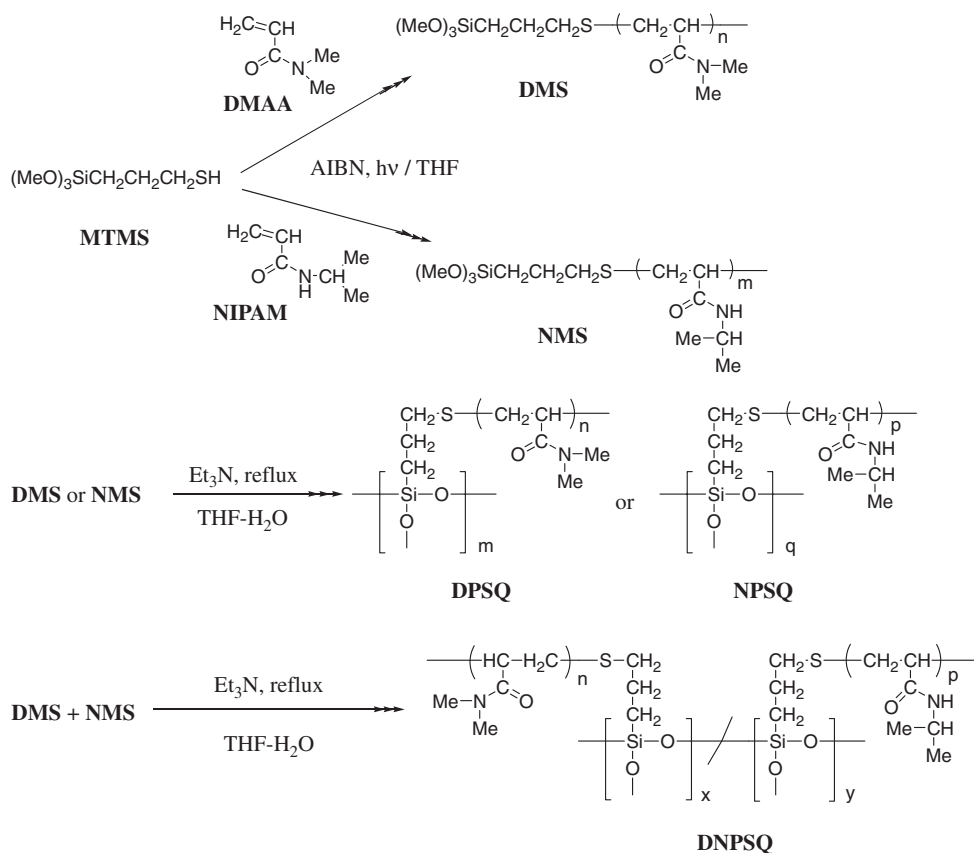
Scheme 1.

MTMS. In addition, the obtained **PSQ** derivative is a new kind of hybrid and expected to be usable in various scenes such as adsorption and adhesion materials. In these applications, both the hydrophilic and hydrophobic properties can be controlled by temperature and such characteristic may enable a fine separation and a changeable adhesive force in the use of column adsorbent and adhesive, respectively.

On the basis of the considerations mentioned above, the preparation and evaluation of the grafted **PSQ** as a new thermoresponsive hybrid are examined in this work. The trimethoxysilyl end-capped polymers have been already reported and utilized as the macrosilane coupling reagents.[33,34] The radical polymerization by the use of **MTMS** is known as an effective procedure to prepare the coupling reagents.[34] Therefore, the photo-polymerization technique was employed as a simple and a practical procedure for the preparation of poly(**NIPAM**) and poly(**DMAA**) from **MTMS**. In the formation of several kinds of grafted **PSQ**, the condensation reaction of the resulting macrosilane coupling reagents was examined under basic and acidic conditions. The syntheses of such materials were shown in Scheme 1.

EXPERIMENTAL

General

^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL AL-300 and JNM A-500 spectrometer in CDCl$_3$ or DMSO-d$_6$. IR spectra were recorded on a JASCO FT/IR 230. 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) employed for the reactions was distilled from sodium benzophenone ketyl before use. The monomer, **NIPAM**, was recrystallized from the mixed solvent of benzene and ^{n}hexane. The other monomer, **DMAA**, was distilled over calcium hydride before use. α,α′-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other reagents including **MTMS** (Chisso, 99% purity) and 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU) were used as supplied from commercial sources.

Typical Procedure for Preparation of Polymer Having Methoxysilyl End Group as Macrosilane Coupling Reagent

A solution of **MTMS** (0.54 g, 2.70 mmol), **DMAA** (4.00 g, 40.35 mmol), and AIBN (0.15 g, 0.91 mmol) in THF (20 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 18 °C by using a RIKO RH400 UV lamp

Table I. Preparation of macrosilane coupling reagent from **MTMS**

	Reaction conditions[a]	Macrosilane coupling reagent			
Run	Monomer (Concentration [M])	Product (Yield[b], %)	Silyl unit[c] mmol eq./g	Monomer unit[c] mmol eq./g (Molar unit ratio of monomer/Si)	M_n[d] (M_w/M_n)
1	**DMAA** (2)	**DMS** (72)	0.6	9.27 (16.0)	1900 (2.36)
2	**NIPAM** (2)	**NMS** (72)	0.42	5.88 (14.0)	3600 (2.92)
3	**NIPAM** (5)	**NMS** (95)	0.53	7.93 (15.0)	6100 (4.45)

[a]The polymerization was conducted in THF at 18 °C under UV irradiation by 400 W high pressure Hg lamp, in which 15 equiv. of the monomer to mercapto group were employed. The product was isolated as an insoluble part of diethyl ether. [b]Based on the contents of silyl unit, which were estimated from ^{1}H NMR spectral data. [c]Based on proton areas in ^{1}H NMR spectrum measured with hexamethyldisiloxane as an internal standard. [d]Estimated by GPC [Poly-(methyl methacrylate) standard].

equipped with water jacket from a distance of 10 cm for 8 h under argon atmosphere. The resulting solution was distilled under reduced pressure to concentrate and the residue was poured into an excess amount of diethyl ether. The insoluble part was dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the product (**DMS**), as a solid (3.24 g, 71% yield based on weight, 72% yield based on silyl group, and 74% based on **DMAA**). The contents of mercapto-propyl group and **DMAA** unit in **DMS** were calculated from the corresponding peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard (Table I, Run 1); IR (KBr) 2933, 1645 (C=O), 1501, 1356, 1258, 1140, 1083 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.66 (br, -C$\underline{H}_2$-Si-), 1.25–1.68 (br m, -C$\underline{H}_2$-), 2.30–2.61 (br, (C=O)-C$\underline{H}$-, -C$\underline{H}_2$-S-), 2.70–3.05 (br m, (C=O)-N-C$\underline{H}_3$), 3.45 (br m, -OC$\underline{H}_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 35.7 (-$\underline{C}$H$_2$-), 35.8 (-$\underline{C}$H-), 37.1 (-N-$\underline{C}$H$_3$), 50.6 (-O$\underline{C}$H$_3$), 174.7 (-$\underline{C}$=O); M_n = 1900, M_w/M_n = 2.36; silyl group = 0.60 mmol equiv./g, methoxy group = 1.68 mmol equiv./g, **DMAA** unit = 9.27 mmol equiv./g.

Analogously, the polymerizations of **NIPAM** were carried out under the different monomer concentrations such as 2 [M] and 5 [M] in THF solution. The spectral data of the obtained polymer (**NMS**) in the polymerization of the former monomer concentration was as follows; IR (KBr) 3400 (-NH-), 2970, 1648 (C=O), 1546, 1460, 1368, 1174, 1067 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.73 (br, -C$\underline{H}_2$-Si-), 1.09 (br, -C$\underline{H}_3$), 1.45–1.80 (br m, -C$\underline{H}_2$-), 2.00–2.61 (br, (C=O)-C$\underline{H}$-, -C$\underline{H}_2$-S-), 3.50 (br, -OC$\underline{H}_3$), 3.95 (br, -NH-C$\underline{H}$-); ^{13}C NMR (125 MHz, CDCl$_3$) δ 22.6 (-$\underline{C}$H$_3$), 34.2 (-$\underline{C}$H$_2$-), 34.8 (-$\underline{C}$H-), 41.4 (-N-$\underline{C}$H-), 50.6 (-O$\underline{C}$H$_3$), 174.7 (-$\underline{C}$=O); M_n = 3600, M_w/M_n = 2.76; silyl group = 0.42 mmol equiv./g, methoxy group = 1.13 mmol equiv./g, **NIPAM** unit = 5.88 mmol equiv./g.

The results of syntheses of the macrosilane coupling reagents were listed in Table I.

Typical Procedure for Condensation of Macrosilane Coupling Reagent

DMS (0.13 g, silyl group: 0.08 mmol equiv.), **NMS** (0.38 g, Si group: 0.16 mmol eqiv.), M_n of which was 4000 (Table I, Run 2), and triethylamine (Et$_3$N, 0.002 g, 0.02 mmol) in THF

(2 mL) and water (0.5 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 precipitated solid was collected and dried at room temperature for 24 h in a vacuum oven under reduced pressure (<5 mmHg) to obtain **DNPSQ1** (0.43 g, 83% yield based on silyl group). The contents of the monomer units and silyl group were calculated from the corresponding peak areas observed in ^{1}H NMR spectrum, in which hexamethyldi-siloxane was used as an internal standard (Table III, Run 4); IR (KBr) 3440 (-NH-), 2973, 1643 (C=O), 1546, 1460, 1387, 1258, 1130, 1097 (Si-O), 628 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.63 (br, -Si-C$\underline{H}_2$-), 1.09 (br, -C$\underline{H}_3$), 1.50–1.85 (br, -C$\underline{H}_2$-), 2.25–2.80 (br, (C=O)-C$\underline{H}$-, -S-C$\underline{H}_2$-), 2.85 (br, C=O)-N-C$\underline{H}_3$), 3.95 (br, -NH-C$\underline{H}$-); ^{13}C NMR (75.45 MHz, CDCl$_3$) δ 22.6 (-$\underline{C}$H$_3$), 35.3 (-$\underline{C}$H$_2$-), 35.8 (-$\underline{C}$H-), 37.2 (-N-$\underline{C}$H$_3$), 41.3 (-N-$\underline{C}$H-), 174.5 (-$\underline{C}$=O); M_n = 13600, M_w/M_n = 1.32; silyl group = 0.20 mmol equiv./g, **DMAA** unit = 7.65 mmol equiv./g, **NIPAM** unit = 3.21 mmol equiv./g.

Analogously, the condensation and co-condensation of the macrosilane coupling reagents were carried out under various conditions. The results were listed in Table II and Table III.

Measurement of Transmittance (%T)

1.0 wt % solution of the product containing poly(**NIPAM**) in deionized water was used for the measurement of transmittance (%T) on a Shimadzu UV-1650 spectrophotometer equipped with a Peltier-type S-1700 thermostatic cell holder. In the measurements, the changes of %T were observed from a visible source at 600 nm through a 1 cm quartz sample cell at the rate of 1 °C/30 s during heating and cooling scans. The measurements were repeated at least three times on each sample until when the observed curves were in good agreement.

RESULTS AND DISCUSSION

Preparation of Macrosilane Coupling Reagent from MTMS

When we tried to prepare the **PSQ** having mercapto groups by condensation reaction using only **MTMS** under basic conditions, the product insoluble in usual organic solvents was obtained. By considering the previous works concerning the syntheses of **PSQ**s, the use of trimethoxysilane having a substituent, which is bulky or shows a mutual interaction such as π-π stacking, seems to be free from the gelation.[1–5] Therefore, the silane coupling reagent, which possess a bulky polymeric component, is supposed to be a candidate for preparing **PSQ** derivative without gelation.

The polymerization of **DMAA** or **NIPAM** with **MTMS** in THF solution was conducted under UV irradiation in the presence of a catalytic amount of AIBN. In the polymerizations, 15 equiv. of the monomer to **MTMS** were used. The results were shown in Table I. From the polymerization conducted in 2 [M] solution of **DMAA**, the product, **DMS**, was obtained in 72% yield and showed the slightly larger M_n such as 1900 compared to the calculated value of 1700 (Table I, Run 1). Analogously, the polymerizations of **NIPAM**

were carried out, in which the monomer concentrations were adjusted to be 2 [M] and 5 [M] (Table I, Run 2 and Run 3). In these cases, the corresponding polymers, **NMS**s were obtained in over 72% yield. However, the M_ns showed the larger values such as 3600 and 6100 in comparison with the calculated M_n such as 1900. In the analyses of ^{1}H NMR spectra of **DMS** and **NMS**s, the decrease of the proton ratio assigned to methoxy group, which should indicate the progress of condensation, was not so obvious. Consequently, the results suggest that the association of the polymeric molecules occurs. Another possible reason to explain the unexpected values of M_n is the coupling reaction during the polymerization. The radical coupling results in the introduction of two methoxysilyl end groups at the both ends of polymer and should lead to the gel product in the condensation of methoxysilyl groups. However, no obvious gelation was observed in the successive condensation reaction using **NMS** (Table I, Run 2) under the conditions mentioned here. Consequently, the former speculation seems to explain the unexpected lager M_ns of **NMS**s.

The formation of the polymers having methoxysilyl end group was confirmed by the IR and NMR spectra. In the IR spectra of **DMS** and **NMS**s, the strong absorbance at *ca.* 1640 cm^{-1} due to carbonyl group was observed. The absorption around 1100 cm^{-1} was assigned to silicon-oxygen bond of methoxysilyl group. In the ^{1}H NMR spectra of **DMS** and **NMS**s, the small signal due to methylene protons bonded to Si was recognized at *ca.* 0.6 ppm. The signals assigned to methyl protons of methoxy group were appeared at 3.4 ppm. The contents of silyl group and methoxy group in the polymers were based on the peak areas of these signals. The signal due to methyl protons of dimethylamino group of **DMAA** unit was observed around 3.0 ppm. The signal appeared at 3.86 ppm was assigned to the methine proton bonded to nitrogen of **NIPAM** unit. The respective peak areas of the signals at 3.0 and 3.86 ppm were utilized for the calculation of content of the monomer units. The ^{1}H NMR spectrum of **DMS** (Table I, Run 1) was shown in Figure 1 and that of **NMS** (Table I, Run 2) was in Figure 2, respectively. ^{13}C NMR spectra of **DMS** and **NMS**s also supported the formation of the desired polymers. The signals observed in the range of 37 ppm to 42 ppm were assigned to the carbons of methyl and methine groups bonded to nitrogen of **DMAA** and **NIPAM** units. The signal detected at 175 ppm was assigned to the carbon of carbonyl group. The signals assigned to methylene carbons of **MTMS** group were difficult to detect, but that observed at 50 ppm indicated the presence of methoxy group. The spectral information demonstrated that the polymerization proceeded effectively to give the polymers having methoxysilyl end group. The obtained polymers, **DMS** and **NMS**s, were soluble in water, methanol, THF, chloroform, and DMF, but insoluble in diethyl ether and ^{n}hexane.

Condensation of Macrosilane Coupling Reagent

The condensation of **DMS** to give the corresponding **PSQ** derivative was carried out under various conditions. The results were listed in Table II. In the condensations, the mole ratio of
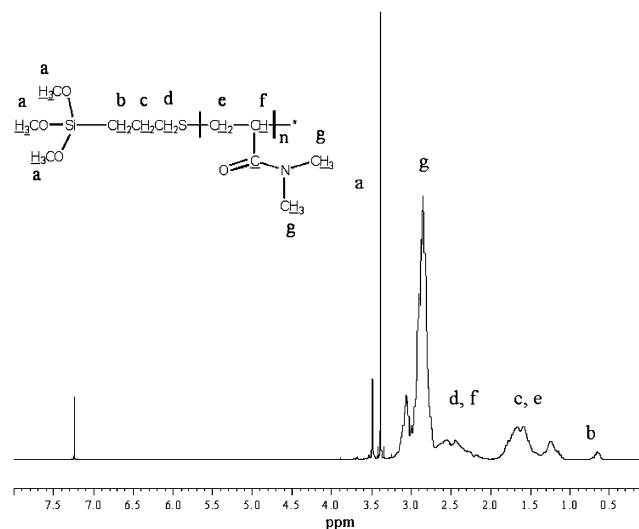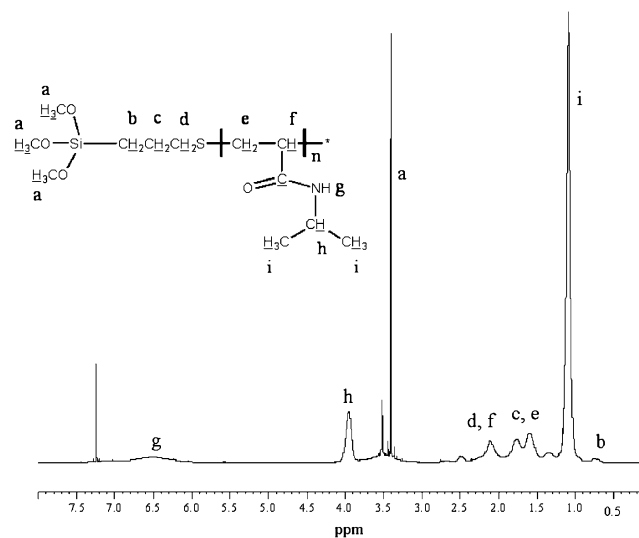

Figure 1. ^{1}H NMR spectrum of **DMS**.

Figure 2. ^{1}H NMR spectrum of **NMS** (Table I, Run 2).

base or acid to silyl group was adjusted to be 5 mol %. When the condensation of **DMS** in the mixed solvents of THF and water with a catalytic amount of triethylamine was carried out under reflux for 24 h, the corresponding **PSQ** (**DPSQ**) was isolated from diethyl ether as an insoluble solid in 67% yield (Table II, Run 1). The M_n of **DPSQ** estimated by GPC was 17700. In the condensation conducted for 72 h, the yield and M_n were increased to be 81% and 29200, respectively (Table II, Run 5). However, in the reactions continued for more than 72 h, no obvious increase of yield and M_n was observed. Sodium hydroxide and DBU were also effective basic catalysts for the condensation (Table II, Run 2 and 3). The condensation analogously proceeded under acidic conditions where a catalytic amount of methanesulfonic acid was used. In this case, the yield was 94% and M_n was estimated to be 13400 (Table II, Run 4). In those condensations, the yields

Table II. Preparation of **DPSQ** by condensation of **DMS**

	Reaction conditions[a]			DPSQ	
Run	Organic solvent	Catalyst	Time h	Yield[b] %	M_n[c] (M_w/M_n)
1	THF	Et₃N	24	67	17700 (1.32)
2	THF	NaOH	24	67	16900 (1.39)
3	THF	DBU	24	84	17100 (1.44)
4	THF	CH₃SO₃H	24	94	13400 (2.17)
5	THF	Et₃N	72	81	29200 (1.43)

[a]The reaction was conducted under reflux conditions in organic solvent with H₂O, in which the volume ratio of organic solvent/H₂O was adjusted to be 4/1. The product was isolated as an insoluble part of diethyl ether. [b]Based on the content of silyl unit, which was calculated by the proton areas in ¹H NMR spectrum measured with hexamethyldisiloxane as an internal standard. [c]Estimated by GPC [Poly(methyl methacrylate) standard].
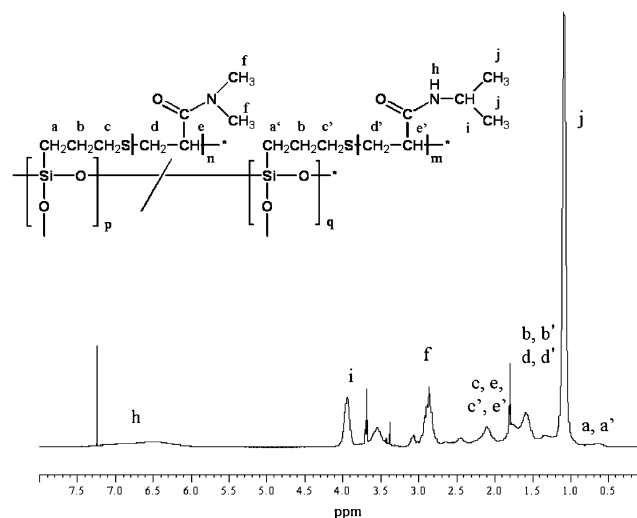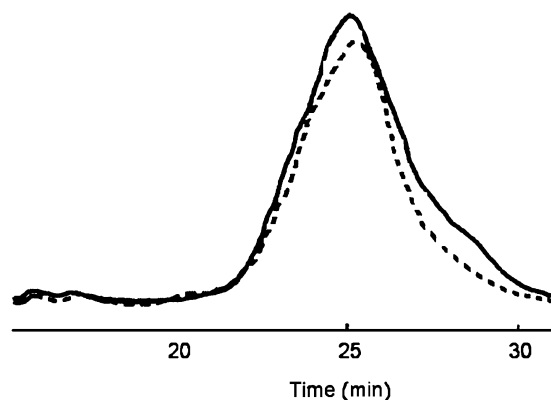
Table III. Preparation of **NPSQ** and **DNPSQ** by condensation of **NMS** and **DMS**

		Reaction conditions[a]		Grafted PSQ		
Run	Polymer	Monomer unit ratio of **DMAA/NIPAM**	Reaction Time h	Product (Yield,[b] %)	Monomer unit ratio of **DMAA/NIPAM**	M_n[c] (M_w/M_n)
1	**NMS**	—	3	**NPSQ1** (79)	—	6100 (2.46)
2	**NMS**	—	24	**NPSQ2** (86)	—	11300 (1.95)
3	**NMS**	—	120	**NPSQ3** (94)	—	23100 (1.35)
4	**DMS**, **NMS**	0.5	24	**DNPSQ1** (83)	0.4	13600 (1.82)
5	**DMS**, **NMS**	2.0	24	**DNPSQ2** (75)	1.7	13200 (1.89)

[a]The reaction was conducted with 5 mol % of triethylamine to silyl group in the mixed solvents of THF and water under reflux, in which **NMS**, showing M_n of 3600 (Table I, Run 2), was used and the product was isolated as an insoluble part of diethyl ether. [b]Based on the content of silyl group, which was calculated from proton ratios in ¹H NMR spectrum measured with hexamethyldisiloxane as an internal standard. [c]Estimated by GPC [Poly(methyl methacrylate) standard].

Figure 3. ¹H NMR spectrum of **DNPSQ1**.

Figure 4. GPC chromatograms of **NPSQ2** (----) and **DNPSQ1** (—).

of **DPSQ** were based on the content of silyl group, which was calculated from the proton area of the signal detected at 0.6 ppm in ¹H NMR spectra.

The procedure using Et₃N catalyst was applied to the condensation of **NMS**, M_n of which was 3600 (Table I, Run 2), and co-condensation with **DMS** as shown in Table III. The condensation of **NMS** also proceeded effectively and afforded the **PSQ** derivative (**NPSQ**). Three kinds of **NPSQ**, M_ns of which were 6100 (**NPSQ1**), 11300 (**NPSQ2**), and 23100 (**NPSQ3**), were prepared by changing the reaction time, respectively (Table III, Run 1–3). Analogously, the co-condensations of **NMS** with **DMS**, in which the monomer unit ratios of **DMAA/NIPAM** were adjusted to be 0.5 and 2, were tried. These co-condensations afforded the corresponding **PSQ**s in over 75% yield (Table III, Run 4 and 5). The monomer unit ratio of **DMAA/NIPAM** in the grafted **PSQ** (**DNPSQ1**), obtained from the former feed ratio, was estimated to be 0.4. In the case of the later feed mole ratio, the resulting **PSQ** (**DNPSQ2**) showed 1.7 of the monomer unit ratio of **DMAA/NIPAM**. As an example, ¹H NMR spectrum of **DNPSQ1** was shown in Figure 3. The respective M_ns of

DNPSQ1 and **DNPSQ2** were 13600 and 13200. In such GPC chromatograms, the product was detected as a unimodal peak. The observation of unimodal peak suggested that the condensations of **DMS** and **NMS** proceeded at the same time and showed an analogous reactivity. This was thought to be the supporting data for the co-condensation. For the examples, the chromatograms of **NPSQ2** and **DNPSQ1** were shown in Figure 4. Thus, the **PSQ** derivatives, which had the graft chains of poly(**NIPAM**) and poly(**DMAA**), were obtained efficiently through the building up procedure by the use of the macrosilane coupling reagents. The obtained **PSQ**s, containing poly(**NIPAM**) in the graft chains, were employed for the evaluation of thermoresponsive behavior.

Thermally Reversible Phase Separation

The thermoresponsive aggregation was indicated by the turbidity measured as %T at 600 nm under heating and cooling. All the samples mentioned here showed the reversible thermoresponsive phase separation in an aqueous solution. However, except for the case of **NMS**, the plots under cooling were not depicted in the following Figures for easy viewing.
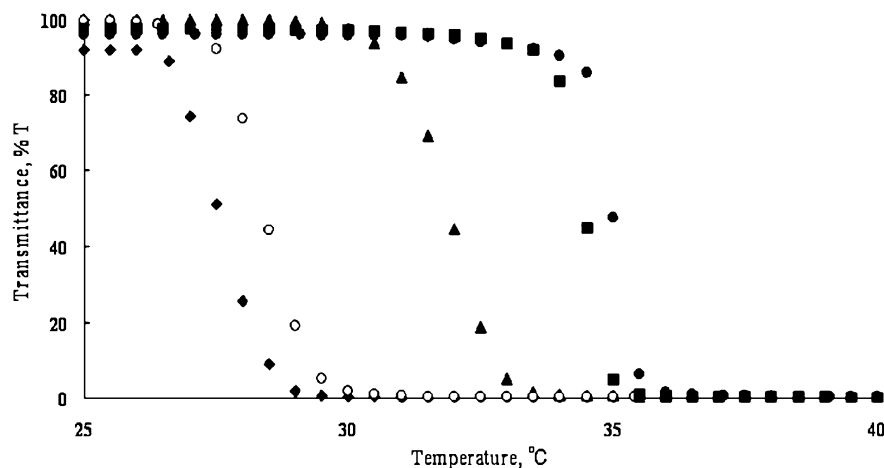
Figure 5. Temperature dependence of optical transmittance (%T) at 600 nm for 1 wt% aqueous solution of **NMS** (Table I, Run 2, ●: Heating, ○: Cooling), **NPSQ1** (■: Heating), **NPSQ2** (▲: Heating), and **NPSQ3** (◆: Heating).
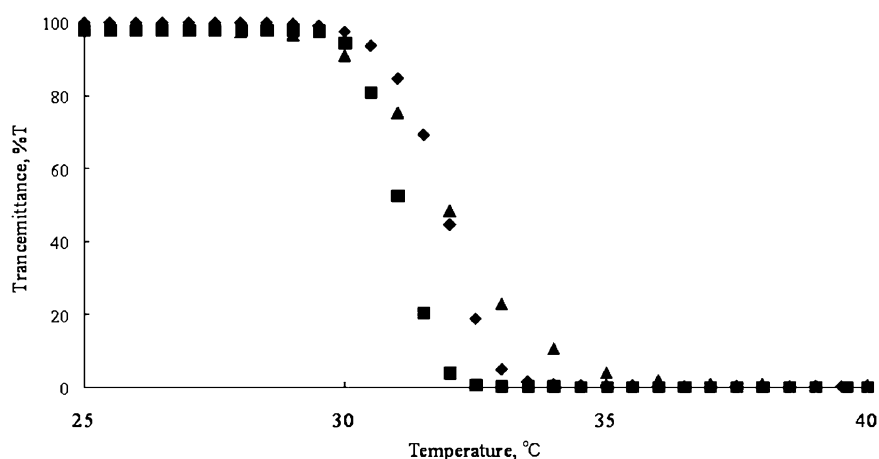
Figure 6. Temperature dependence of optical transmittance (%T) at 600 nm for 1 wt% aqueous solution of **NPSQ2** (■: Heating), **DNPSQ1** (◆: Heating), and **DNPSQ2** (▲: Heating).

In the aqueous solution of 1 wt% of **NMS**, M_n of which was 3600 (Table I, Run 2), the phase separation started at 34 °C and reached to 0 %T at *ca.* 36 °C under heating as shown in Figure 5. Under cooling, the transmittance began to increase at 30 °C and a transparent solution was recovered at 28 °C. The aggregation of **NPSQ1**, **NPSQ2**, and **NPSQ3** began at 33 °C, 31 °C, and 28 °C, respectively. The results demonstrated that the increase of M_n led to the decrease of LCST. This may be explained by the speculation that the aggregation of a smaller number of polymeric molecules was enough to bring about the obvious decrease of %T in the case of **NPSQ3** showing a larger M_n. In other words, the removal of a smaller number of water molecules around **NIPAM** units, which can be achieved by a smaller energy, seems to lead to the effective hydrophobic aggregation.

Next, the thermoresponsive behavior of the **PSQ**s having two kinds of graft chains, one of which was poly(**DMAA**), was examined. The random copolymer of **NIPAM** and **DMAA** generally shows a higher LCST than the homopolymer of **NIPAM**.[35–37] The introduction of poly(**DMAA**), which was recognized as a more hydrophilic component than poly-(**NIPAM**), provided a hydrophilic environment. However, the recorded values of LCST of **DNPSQ1** and **DNPSQ2** were same to that observed in the case of **NPSQ2** as shown in Figure 6. Such phase separation behavior of **DNPSQ**s was similar to that of the block copolymer of **NIPAM**, in which no influence of presence of poly(**DMAA**) unit was observed.[32] The presence of poly(**DMAA**) was indicated by the change of sensitivity of aggregation to temperature. In the aqueous solution of **NPSQ2**, the aggregation started at 30 °C and was completed at 32 °C. While, the temperature range from 30 °C to 36 °C was recorded in the case of **DNPSQ2**. The results of thermoresponsive behavior of the **PSQ**s demonstrated that the graft chains of poly(**NIPAM**) began to aggregate irrespective of a hydrophilic environment provided by poly(**DMAA**). This may be explained by the situation of poly(**NIPAM**), which is introduced as a block. In the random copolymer, the presence of the hydrophilic monomer unit near **NIPAM** unit was unfavorable to remove water molecules efficiently around them. Contrary to this, when **NIPAM** units are located as a

block, the interpenetration of hydrophilic units is difficult. This should enable to keep a hydrophobic environment around poly(**NIPAM**) chain. In the analogous reason, the block copolymer of **NIPAM** and **DMAA** showed the similar behavior irrespective of the composition of the both polymeric components as shown in the previous works including us.[20,32] Thus, when the graft chains of poly(**NIPAM**) and poly-(**DMAA**) were introduced respectively, the thermoresponsive behavior of the grafted polymer essentially controlled by the sole poly(**NIPAM**) chains. In addition, it may be allowed to say that the presence of the relatively hydrophilic poly-(**DMAA**) chains in **DNPSQ**s only retards the nimble aggregation between the grafted **PSQ** molecules.

CONCLUSION

The use of **MTMS** for the polymerization of **NIPAM** and **DMAA** under UV irradiation enabled the preparation of the corresponding polymers having methoxysilyl end group. The polymers were utilized as the macrosilane coupling reagents and the building blocks for the **PSQ** derivatives. Furthermore, the condensation of the macrosilane coupling reagents was effective for the formation of the grafted **PSQ** containing the different kinds of graft chains in the same main chain. Through those steps, no obvious gelation was observed. Consequently, the procedure presented a usable synthetic route for the multifunctional organic-inorganic hybrid polymers based on **PSQ** structure, which were soluble in usual organic solvents.

In the thermoresponsive behavior of the grafted **PSQ** containing poly(**NIPAM**), the effect of M_n on LCST was observed. Contrary to this, no hydrophilic influence due to the presence of poly(**DMAA**) graft chains on LCST was observed. Even in the case of **DNPSQ2**, which contained the larger number of poly(**DMAA**) chain, LCST was same to that of **NPSQ2** having only poly(**NIPAM**) graft chains. These suggests that the additional functional groups can be introduced without change of thermoresponsive behavior, when poly-(**NIPAM**) component is existed as a block. The information seems to be helpful for designing a multi-functional **PSQ**.

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