Preparation of Amphiphilic Polysilsesquioxane by Grafting of Block Copolymer of Acrylamide Monomers

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ABSTRACT: The polysilsesquioxane having dithiocarbamate groups was utilized for the graftation of *N*-isopropylacrylamide (**NIPAM**) and *N,N*-dimethylacrylamide (**DMAA**) under thermal polymerization conditions. The controlled graft polymerization through RAFT process proceeded effectively to give several kinds of block copolymer of **NIPAM** and **DMAA** without formation of gel product, in which the sequence and the number of the monomer units were changed. The introduction of the block copolymers provided an amphiphilic property to the polysilsesquioxane. The hydrophilic property, which was shown as solubility in water and contact angle, was affected by the sequence and the number of the monomer units in the graft chain. Furthermore, as the expected property due to a hydrophobic aggregation of **NIPAM** units, the contact angles of the grafted polysilsesquioxanes measured at 60 °C were larger than those at 23 °C. [doi:10.1295/polymj.PJ2006126]

KEY WORDS Amphiphilic Polysilsesquioxane / *N*-Isopropylacrylamide / RAFT Process / Graft Polymerization /

Recently, various investigations on oligomeric and polymeric silsesquioxanes, which stress on the modifications by various organic functional groups, have been presented from the interests in a useful hybrid material.^{1–9} As an effective procedure for the modifications of the silsesquioxanes, the graft polymerization from polysiloxane backbone is nominated.^{10–16} This procedure enables to provide the additional functions based on the polymeric components without losing the essential properties of inorganic polysiloxane backbone such as durability for heat and weatherability. We also have investigated on the graft polymerizations from polysilsesquioxanes, which intended to develop the new multi-functional hybrid materials.^{17–19} As an example of such graftings, the introduction of copolymer of *N,N*-dimethylacrylamide (**DMAA**) and *N*-isopropylacrylamide (**NIPAM**) was reported in the previous work.²⁰ The obtained polysilsesquioxane derivative successfully showed amphiphilicity and thermoresponsive phase separation. The investigations concerning the later property caused by polymerized **NIPAM** (poly**NIPAM**) have been widely developed and various applications are proposed such as microencapsulation, biosensor, and drug delivery.^{21–25} Such facts support the expectation that the polysilsesquioxane, combined the inorganic polysiloxane backbone with the thermoresponsive and amphiphilic graft chains, will be a candidate for high performance hybrid materials.^{26–28}

Our previous grafting was conducted through free

radical polymerization by the use of mercapto groups on the polysilsesquioxane backbone.²⁰ In the use of the procedure, the graft chain was essentially consisted of the random copolymer of **NIPAM** with **DMAA** (poly**NIPAM**-*ran*-poly**DMAA**) and the number of introduced monomer units was limited because of inactivation of radical species during the polymerization. On the other hand, the investigations on such functional polymer are progressed into a new stage with the development of living polymerization techniques. The use of reversible addition-fragmentation chain transfer (RAFT) process is a representative example and contributes to prepare the designed copolymers involving poly**NIPAM** for practical usages.^{29–32} The living polymerization technique also promises the altered formation of our previous polysilsesquioxane derivative having the thermoresponsive grafted copolymer, the sequence and molecular weight of which are controlled. Especially, the hydrophobic polysilsesquioxane backbone generally needed more hydrophilic components such as poly**DMAA** besides poly**NIPAM** to show an amphiphilic property.²⁰ Such requirement led us to the consideration that the sequence and the number of the monomer units in the block copolymers were the important factors to extend the investigation to the designed polysilsesquioxanes. Therefore, we have continuously studied on the preparation of the polysilsesquioxane having the controlled polymeric components as the graft chains.

The polysilsesquioxane having *N,N*-dimethyldithio-

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Scheme 1.

carbamate (**DTC**) groups (**DTSPQ**) was synthesized and employed for RAFT process to prepare several kinds of polysilsesquioxane containing the copolymer of **NIPAM** and **DMAA** (poly**NIPAM**-*block*-poly**DMAA** or poly**DMAA**-*block*-poly**NIPAM**), which showed the different sequence and the number of the monomer units. Then, in this primary report, we focus on the amphiphilic property presented by the graft chains. The promising property of thermoresponsive phase separation has been left as a next theme to be examined and the results will be presented near future. The synthetic routes to the block copolymer grafted polysilsesquioxanes were shown in Scheme 1.

EXPERIMENTAL

General

^1H NMR and ^{13}C NMR spectra were obtained on a JEOL AL-300 and JNM A-500 spectrometer in CDCl_3 or $\text{DMF}-d_7$. 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 an eluent. Calibration was performed using poly(methyl methacrylate) standards. DMF employed for the reactions was refluxed over calcium hydride and distilled. Ethanol was treated with sodium and magnesium metal before use. Tetrahydrofuran (THF) was refluxed over sodium metal before use. **NIPAM** was recrystallized from the mixed solvent of benzene and *n*-hexane. **DMAA** was distilled over calcium hydride before use. *N,N'*-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other reagents including (4-chloromethyl)phenyltrimethoxysilane (**CPTMS**, TCI, 98%), and *N,N*-dimethyldithiocarbamic acid sodium salt dihydrate (TCI, 98%) were used as supplied from commercial sources.

Preparation of Polysilsesquioxane Having Chloromethylphenyl Groups (**CPPSQ**)

CPPSQ was obtained from **CPTMS** by the modi-

fied method reported before, where THF was used instead of toluene.¹⁸ The M_n and M_w/M_n estimated by GPC were almost in accord with the previous results. The content of chloromethylphenyl group and yield were calculated from the corresponding peak areas due to the protons of methylene group bonded to benzene ring observed in ^1H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard. The yield of **CPPSQ** was estimated to be 68%; IR (KBr) 3393 (weak, OH), 3050 (weak, $-\text{C}_6\text{H}_4-$), 1497 (medium), 1398 (medium), 1269 (medium), 1130 (strong, Si-O), 911 (medium), 704 (medium) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 4.59 (br, $\text{Cl}-\text{CH}_2-\text{C}_6\text{H}_4-$), 6.50–7.80 (br m, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (75.45 MHz, CDCl_3) δ 46.5 ($\text{Cl}-\text{CH}_2-\text{C}_6\text{H}_4-$), 128.8 ($-\text{C}_6\text{H}_4-$), 135.2 ($-\text{C}_6\text{H}_4-$); chloromethylphenyl group = 4.81 mmol equiv./g, $M_n = 4000$, $M_w/M_n = 1.15$.

Preparation of Polysilsesquioxane Having DTC Groups (DTPSQ)

A solution of **CPPSQ** (10.00 g, 48.1 mmol equiv./g) and *N,N*-dimethyldithiocarbamic acid sodium salt dihydrate (9.66 g, 53.9 mmol) in THF (50 mL) was stirred at ambient temperature for 20 h. The solution was evaporated under reduced pressure and the residue was diluted with methanol. The precipitated product was collected and washed with water and methanol. The resulting solid was dried at room temperature for 24 h in a vacuum oven under reduced pressure (<5 mmHg) to obtain **DTPSQ** (12.55 g, 99% conversion to **DTC** group). The contents of **DTC** group was calculated from the peak areas observed in ^1H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard; IR (KBr) 3429 (weak, OH), 3050 (weak, C_6H_5), 2924 (weak, CH_3), 1497 (medium), 1376 (medium), 1256 (medium), 1128 (strong, Si-O), 982 (medium), 706 (medium) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.29 (br, $-\text{N}-\text{CH}_3$), 3.48 (br, $-\text{N}-\text{CH}_3$), 4.43 (br, $-\text{CH}_2-\text{C}_6\text{H}_4-$), 6.50–7.80 (br m, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (75.45 MHz, CDCl_3) δ 41.5 ($-\text{N}-\text{CH}_3$), 42.5 ($-\text{N}-\text{CH}_3$), 45.3 ($-\text{CH}_2-\text{C}_6\text{H}_4-$), 128.7 ($-\text{C}_6\text{H}_4-$), 130.4 ($-\text{C}_6\text{H}_4-$), 196.5 ($-\text{C}=\text{S}$); **DTC** group = 3.79 mmol equiv./g; $M_n = 4500$, $M_w/M_n = 1.40$.

Typical Procedure for Grafting of First Monomer onto DTPSQ

A solution of **DTPSQ** (0.08 g, 0.30 mmol equiv. of dithiocarbamate group), **DMAA** (0.59 g, 6.00 mmol), and AIBN (0.008 g, 0.05 mmol) in the mixed solvents of DMF (1.5 mL) and ethanol (0.5 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 heated at 70 °C for 8 h under argon atmosphere. The resulting solution was evaporated under reduced pressure to concentrate and the residue

was poured into diethyl ether. The insoluble solid was collected and dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the poly-**DMAA** grafted polysilsesquioxane (**GrD2**) (0.58 g, 87% yield based on weight). The contents of **DTC** group and the monomer units in **GrD2** were calculated from the peak areas observed in ^1H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard; IR (KBr) 3304, 2972, 2933, 1645 ($\text{C}=\text{O}$), 1563, 1466, 1132, 798, 729 cm^{-1} ; ^1H NMR ($\text{DMF}-d_7$, 500 MHz) δ 1.30–1.80 (br m, $-\text{CH}_2-$), 2.25–2.70 (br, $-(\text{C}=\text{O})-\text{CH}_2-$, $-\text{CH}_2-\text{C}_6\text{H}_4-$), 2.70–3.05 (br m, $-\text{N}-\text{CH}_3$), 3.31 (br, $-(\text{C}=\text{S})-\text{N}-\text{CH}_3$), 3.48 (br, $-(\text{C}=\text{S})-\text{N}-\text{CH}_3$), 7.10–7.80 (br, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (125 MHz, $\text{DMF}-d_7$) δ 35.7 ($-\text{CH}_2-$), 36.1 ($-\text{CH}_2-$), 37.3 ($-\text{N}-\text{CH}_3$), 127.8 ($-\text{C}_6\text{H}_4-$), 131.5 ($-\text{C}_6\text{H}_4-$), 133.9 ($-\text{C}_6\text{H}_4-$), 174.4 ($-\text{C}=\text{O}$); $M_n = 42000$, $M_w/M_n = 2.80$; **DTC** group = 0.35 mmol equiv./g; **DMAA** unit = 9.1 mmol equiv./g.

Typical Procedure for Grafting of Second Monomer

A solution of **GrD2** (0.41 g, 0.18 mmol equiv. of **DTC** group), **NIPAM** (0.20 g, 1.77 mmol), and AIBN (0.005 g, 0.03 mmol) in the mixed solvents of DMF (0.6 mL) and ethanol (0.2 mL) was treated in a similar manner as mentioned in the preparation of **GrD2**. The insoluble solid in diethyl ether was collected as the polysilsesquioxane grafted by poly**DMAA**-*block*-poly**NIPAM** (**GrD2N**, 0.56 g, 92% yield based on weight); IR (KBr) 3447 (N-H), 2972, 2933, 1636 ($\text{C}=\text{O}$), 1508, 1458, 1139 (Si-O-Si) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.08 (br m, $-\text{CH}_3$), 1.30–1.80 (br m, $-\text{CH}_2-$), 2.25–2.70 (br, $-(\text{C}=\text{O})-\text{CH}_2-$), 2.70–3.05 (br m, $-\text{N}-\text{CH}_3$), 3.31 (br, $-(\text{C}=\text{S})-\text{N}-\text{CH}_3$), 3.48 (br, $-(\text{C}=\text{S})-\text{N}-\text{CH}_3$), 3.86 (br, $-\text{NH}-\text{CH}_2-$), 6.00–7.10 (br, $-\text{C}_6\text{H}_4-$, $-\text{NH}-$); ^{13}C NMR (125 MHz, $\text{DMF}-d_7$) δ 22.5 ($-\text{CH}_3$), 35.6 ($-\text{CH}_2-$), 36.7 ($-\text{CH}_2-$), 37.2 ($-\text{N}-\text{CH}_3$), 42.3 ($-\text{NH}-\text{CH}_2-$), 128.5 ($-\text{C}_6\text{H}_4-$), 134.1 ($-\text{C}_6\text{H}_4-$), 174.6 ($-\text{C}=\text{O}$); $M_n = 53000$, $M_w/M_n = 2.05$; **DTC** group = 0.26 mmol equiv./g; **DMAA** unit = 5.9 mmol equiv./g; **NIPAM** unit = 3.0 mmol equiv./g.

Analogously, several grafted polysilsesquioxanes having poly**NIPAM**-*block*-poly**DMAA** and poly-**DMAA**-*block*-poly**NIPAM** were prepared by changing the feed mole ratio and sequence of the monomers. Furthermore, the polysilsesquioxane having poly**NIPAM**-*ran*-poly**DMAA** (**GrRD2N**) was prepared under the similar conditions by adding the monomers at once.

Graft Polymerization of NIPAM for Verification of RAFT Process

For the time-conversion, $\text{time}-\ln\{[M]/[M_0]\}$, and the conversion- M_n curves, the graft polymerization of **NIPAM** to **DTPSQ** ($M_n = 5400$, **DTC** group =

3.48 mmol equiv./g) was carried out under the similar conditions as mentioned above. In the polymerization, 0.07 g of **DTPSQ** (DTC group = 0.24 mmol equiv.), 40 equiv. of **NIPAM** (1.09 g, 9.63 mmol) to DTC group, and AIBN (0.01 g, 0.06 mmol) in DMF (3.0 mL) and ethanol (1.0 mL) were used and the samples were taken by syringe at appropriate intervals for GPC and ^1H NMR analysis. The results were shown in Figures 3–5.

Measurement of Contact Angle

A solution of the grafted polysilsesquioxane (0.05 g) in THF (5 mL) was cast on poly(ethylene terephthalate) sheet (150 mm $\times$ 200 mm) and, then, THF was removed by heating at 80 $^{\circ}\text{C}$ for 1 min in an oven. The resulting film of the grafted polysilsesquioxane showed *ca.* 200 nm thickness. The static contact angle was measured on the coated film with deionized water drops at 23 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$ by a Krüss DSA100 Automatic Contact Angle Meter, in which relative humidity was kept to be 50% and the observation was conducted within 10 s. The measurement was performed three times for a sample. The average angles of the observed values were listed in Table III.

Measurement of Transmittance (%T) for Solubility in Water

1 wt % solution of the grafted polysilsesquioxane 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, where the changes of %T were observed from a visible source at 600 nm through a 1 cm quartz sample cell during heating and cooling scans. The rate of heating and cooling was adjusted to be 1 $^{\circ}\text{C}/1$ min. The cycle of heating and cooling was repeated three times for a sample, in which almost same curves indicating the thermoresponsive behavior were observed. The value indicating solubility in water was the %T observed at 20 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Preparation of **CPPSQ** and **DTPSQ**

By the method reported before, the condensation of **CPTMS** in the presence of 5 mol % of triethylamine was carried out under reflux conditions in the mixed solvents of THF and water.¹⁸ **CPPSQ** was obtained from methanol as an insoluble solid in 63% yield, which was based on the content of chloromethyl group estimated by the ^1H NMR spectral data mentioned below. Next, the reaction of **CPPSQ** with *N,N*-dimethyldithiocarbamic acid sodium salt dihydrate was carried out at ambient temperature in THF solution. The substitution reaction proceeded readily

Figure 1. ^1H NMR spectrum (DMF- d_7 , 300 MHz) of **DTPSQ** with hexamethyldisiloxane as an internal standard.

to afford the polysilsesquioxane having *N,N*-dimethyldithiocarbamate groups as an insoluble solid in methanol. The ^1H NMR spectral data showed the quantitative introduction of DTC group.

The contents of chloromethylphenyl and DTC group were estimated by the proton ratios observed in the ^1H NMR spectrum. In the measurements, hexamethyldisiloxane was used as an internal standard, the signal of which appeared at 0 ppm. The spectrum of **DTPSQ** was shown in Figure 1. The signal assigned to the protons of methylene group bonded to benzene ring was observed at 4.59 ppm in the spectrum of **CPPSQ**. In the spectrum of **DTPSQ**, the corresponding signal was shifted to 4.43 ppm by changing chlorine to DTC group. The contents of chloromethyl and DTC group were calculated from the peak areas of these easily distinguishable signals. From the estimation, **CPPSQ** was shown to contain 4.81 mmol equiv./g of chloromethyl group. After the reaction, the signal at 4.59 ppm was disappeared completely and the presence of 3.28 mmol equiv./g of DTC group in **DTPSQ** was calculated. The calculation indicated that chlorine in **CPPSQ** was converted almost quantitatively to DTC group in **DTPSQ**. Furthermore, the signals at 3.29 and 3.48 ppm were newly observed, which were assigned to methyl protons of DTC group.

Other spectral data such as ^{13}C NMR and IR also supported the formation of **CPPSQ** and **DTPSQ**. In the IR spectra of **CPPSQ** and **DTPSQ**, the presence of silicon-oxygen bond was shown by the strong absorbance at 1100 cm^{-1} . In the ^{13}C NMR spectrum of **DTPSQ**, the carbon of introduced methyl groups bonded to nitrogen was detected at 41.5 and 42.5 ppm. The carbon of methylene attached to benzene ring was observed at 46.5 ppm in the case of **CPPSQ**.

Table I. Preparation of grafted polysilsesquioxane^a

1st Monomer (Feed mole ratio to DTC group)	2nd Monomer (Feed mole ratio to DTC group)	Product (Yield ^b , %)	M_n (M_w/M_n) estimated by GPC ^c	DP ^d of 1st monomer block		DP ^d of 2nd monomer block	
				GPC ^c	NMR ^e	GPC ^c	NMR ^e
DMAA (10)	—	GrD1 (94)	22000 (2.74)	10.4	11.0	—	—
—	NIPAM (10)	GrD1N (91)	43000 (2.55)	10.4	11.0	10.9	10.3
DMAA (20)	—	GrD2 (87)	42000 (2.80)	22.2	26.0	—	—
—	NIPAM (10)	GrD2N (92)	53000 (2.05)	22.2	22.7	7.1	11.5
DMAA (30)	—	GrD3 (92)	55000 (2.13)	29.9	33.3	—	—
—	NIPAM (10)	GrD3N (92)	66000 (1.83)	29.9	31.9	7.0	10.0
NIPAM (10)	—	GrN (86)	23000 (2.39)	10.2	10.3	—	—
—	DMAA (10)	GrND1 (87)	47000 (2.51)	10.2	10.0	13.3	12.4
—	DMAA (20)	GrND2 (92)	58000 (2.20)	10.2	10.7	21.0	21.7
—	DMAA (30)	GrND3 (99)	64000 (2.07)	10.2	10.0	30.8	33.3
DMAA (20)	—	GrRD2N (91)	55000 (2.03)	—	20.7	—	—
NIPAM (10)	—	—	—	—	—	—	10.3

^aThe polysilsesquioxane **DTPSQ**, M_n of which was estimated to be 4500, contained 3.79 mmol eq./g of **DTC** group. The polymerization was conducted in the presence of 17 mol % of AIBN to **DTC** group at 70 °C for 18 h in the mixed solvents of DMF and ethanol, in which the concentration of the monomer was adjusted to be 2.3 [M]. ^bThe yield was based on the weights of the substrates.

^cEstimated by GPC with poly(methyl methacrylate) standards, in which DMF was used as an eluent. ^dDegree of polymerization. ^eThe content was based on ¹H NMR spectral data.

This was shifted to 45.3 ppm in the spectrum of **DTPSQ**. The estimated M_n and M_w/M_n of **CPPSQ** by GPC were *ca.* 4000 and 1.15, respectively. After the reaction, the M_n of **DTPSQ** was estimated to be the somewhat larger value such as 4500. The obtained **CPPSQ** and **DTPSQ** were soluble in chloroform, acetone, THF, and DMF, but insoluble in *n*-hexane and methanol. By taking into the consideration of the spectral data and solubility in the usual organic solvents, the obtained polysilsesquioxanes **CPPSQ** and **DTPSQ** were supposed to contain a ladder- and an incomplete cage-like polysiloxane structures, although these have been still unidentified.

Grafting of Copolymer of **NIPAM** and **DMAA** onto **DTPSQ**

In the preliminary experiments, the grafting of homopolymer of **NIPAM** from **DTPSQ** was conducted under UV irradiation, in which **DTC** group was regarded as a photoiniferter. Although the grafting progressed efficiently without formation of gel product, the content of **DTC** group in the obtained polysilsesquioxane derivative was estimated to be about 75% of the initial one. This was inadequate to prepare the well controlled block copolymers as the graft chains. Therefore, the grafting of the copolymer was examined under thermal-polymerization conditions, where the polymerization was expected to proceed through RAFT process. In various reports concerning the RAFT process, the use of thioester, dithioester, and trithiocarbonate compounds is shown to be effective for chain transfer reaction. These reagents are usually

obtained as the phenyl and alkyl derivatives.^{33–36} In the application of such chain transfer groups to our polysilsesquioxane derivative, we presumed the difficulty to estimate the content of the groups from the peak areas observed in the corresponding ¹H NMR spectrum. Since, the signals, which indicate the presence of the group and the grafted polymers, usually show the analogous chemical shifts. On the other hand, *N,N*-dimethyldithiocarbamate group was thought to be an appropriate group. The characteristic signals due to methyl protons of **DTC** group were detected in the distinguishable region from those due to polymeric **DMAA** and **NIPAM**. In addition, as mentioned above, the introduction of the group could be readily achieved by the simple substitution reaction. From such reasons, **DTC** group was employed for the controlled graft polymerizations by RAFT process.

The polymerization was carried out at 70 °C in the presence of AIBN, the amount of which was adjusted to be 17 mol % to **DTC** groups. In the polymerizations, the concentration of the monomer was fixed to be *ca.* 2.5 [M] in the mixed solvents of DMF and ethanol. The results were listed in Table I. In the both cases using **DMAA** and **NIPAM** as the first monomer, the grafted polysilsesquioxanes **GrDs** and **GrN** were obtained in the high yields over 86% and no cross-linked product was detected in the products. The M_n s estimated by GPC analyses were 22000 for **GrD1**, 42000 for **GrD2**, and 55000 for **GrD3**, in which the numbers of the monomer unit were estimated to be 10, 22, and 30 for one **DTC** group, respectively. The M_n s increased with the content of the

Figure 2. GPC chromatogram of (—) DTPSQ, (---) GrD2, and (···) GrD2N.

monomer units as expected. The polydispersities of GrDs were in the range from 2.13 to 2.80. The M_n of GrN, intended to introduce 10 equiv. of NIPAM units to DTC group, showed the similar value such as 23000 to that estimated for GrD1 which contained *ca.* 10 equiv. of DMAA unit. In the application of RAFT process under thermal polymerization conditions, almost quantitative amount of DTC groups was recovered after the first grafting of DMAA or NIPAM. The degree of polymerization (DP) based on GPC essentially reflected the feed mole ratio of the monomers, although somewhat larger values of DP were estimated in the ^1H NMR analyses for GrD2 and GrD3. The polysilsesquioxanes introducing the first monomer units were isolated as the insoluble parts in diethyl ether and, then, employed for the further grafting.

The graft polymerization of the second monomer to obtain the block copolymer as the graft chains also proceeded effectively. In this work, the feed mole ratio of NIPAM was fixed to be 10 equivalents to DTC group. The introductions of polyNIPAM to GrDs and polyDMAA to GrN proceeded to give the polysilsesquioxanes having the block copolymers in over 87% yield. The M_n s of the resulting polysilsesquioxanes increased in comparison with those of the polysilsesquioxanes having the first monomer units. In addition, the polysilsesquioxane having polyNIPAM-*ran*-polyDMAA (GrRD2N) was prepared under the same conditions by single step polymerization. GrRD2N was obtained in 91% yield and showed the analogous M_n such as 55000 to those of GrD2N and GrND2.

In the chromatograms of GPC for the grafted polysilsesquioxanes, a unimodal peak was observed.

Figure 3. Relationship between time and conversion in the polymerization using 40 equiv. of NIPAM to DTC group in DMF and ethanol.

For the examples, the chromatograms of DTPSQ, GrD2, and GrD2N were shown in Figure 2. The increases of M_n s through the grafting of the second monomer seemed to be reasonable except for the cases of GrD2N and GrD3N. In these cases, the DPs based on the ^1H NMR analyses showed the presence of *ca.* 10 equiv. of NIPAM unit to DTC group as expected from the feed mole ratio. However, the DPs calculated from the changes of M_n s were the insufficient values such as *ca.* 7. This may indicate the presence of homopolymer of NIPAM. To obtain the information concerning this possibility, the graft polymerization of NIPAM to DTPSQ was independently examined. The time-conversion, time- $\ln\{[M_0]/[M]\}$, and conversion- M_n curves of the polymerization were shown in Figures 3–5, respectively. In the use of 40 equiv. of NIPAM to DTC group, the values of conversion increased with the reaction time reasonably (Figure 3) and the linear relationship of $\ln[M_0]/[M]$ with time was observed (Figure 4). In addition, the

Figure 4. Relationship between time and $\ln\{[M_0]/[M]\}$ in the polymerization using 40 equiv. of **NIPAM** to **DTC** group in DMF and ethanol. $[M_0]$ is the initial monomer concentration and $[M]$ is the monomer concentration.

Figure 5. Relationships between conversion and ($\square$) M_n , ($\triangle$) theoretical M_n , or ($\blacksquare$) M_w/M_n in the polymerization using 40 equiv. of **NIPAM** to **DTC** group in DMF and ethanol.

M_n of the grafted polysilsesquioxane also increased linearly according to the increase of conversion (Figure 5). Such observations supported the speculation that the polymerization proceeded living fashion under the conditions adopted in this work. However, in the relationship between conversion- M_n , the line gradually deviated from that on the basis of theoretical values. Namely, the experimental values of M_n became smaller compared to the theoretical ones after *ca.* 30% conversion. The result suggested that the DP estimated from GPC analysis appeared smaller than the real one in the grafting of **NIPAM**. Therefore, the observations seemed to support the interpretation that the graft polymerization progressed primarily to form the grafted derivative from **DTPSQ** as the main product.

The contents of **DTC** group and the monomer units in the graft chains, utilized for the estimations of DP, were based on ^1H NMR spectral data. As an example, the ^1H NMR spectrum of **GrD2N** was shown in Figure 6. In the ^1H NMR spectrum of **GrD2**, the signals due to the protons of methylene and methine groups were detected in the range from 1.2–2.5 ppm. The signals due to the protons of benzene ring were

Figure 6. ^1H NMR spectrum (DMF- d_7 , 300 MHz) of **GrD2N** with hexamethyldisiloxane as an internal standard.

appeared at 7.2 ppm. The protons of two methyl groups of **DMAA** unit were appeared as a broad signal at *ca.* 2.84 ppm. The analogous methyl protons of **DTC** group were assigned to two signals observed at 3.31 and 3.48 ppm. The peak areas of those signals were employed for the calculation of the contents of **DMAA** unit and **DTC** group. The further introduction of **NIPAM** units was confirmed by the characteristic signals. The signal newly observed at 1.08 ppm was assigned to the methyl protons of isopropyl group of **NIPAM** units. A distinguishable signal was detected at 3.86 ppm due to the methine proton bonded to nitrogen. This was convenient for the calculation to determine the content of **NIPAM** unit. In addition, a broad peak, overlapped with those due to benzene ring, was appeared at 7 ppm. The peak was assigned to the proton attached to nitrogen of **NIPAM** unit. The mole ratios of **DTC** group, **DMAA** unit, and **NIPAM** unit in the grafted polysilsesquioxanes were estimated by the peak areas mentioned above. The estimated ratios were almost in accord with the prospected ones based on the feed mole ratios of the substrates. However, the content of **DMAA** unit may be inaccurate because of the difficulty to detect the clearly distinguishable signals for the unit. The ratios of the units based on ^1H NMR spectral data were listed in Table II.

^{13}C NMR spectrum of the grafted polysilsesquioxanes also supported the incorporations of the graft chains. The signals observed at 22.46 ppm due to methyl carbon demonstrated the presence of isopropyl group of **NIPAM** unit. Other signals at 37.2 and 42.3 ppm were assigned to the carbons of methyl and methine groups bonded to nitrogen of polymerized **DMAA** and **NIPAM** unit, respectively. The carbon of amide groups of both **NIPAM** and **DMAA** unit ob-

Table II. ^1H NMR analysis of grafted polysilsesquioxane^a

Product	Content of 1st monomer unit ^c mmol eq./g	Content of 2nd monomer unit ^c mmol eq./g	Content of DTC group ^c mmol eq./g (Remained group, %)
GrD1	7.9	—	0.72 (93)
GrD1N	4.1	3.8	0.37 (>99)
GrD2	9.1	—	0.35 (83)
GrD2N	5.9	3.0	0.26 (85)
GrD3	9.0	—	0.27 (87)
GrD3N	6.7	2.1	0.21 (91)
GrN	7.2	—	0.70 (94)
GrND1	3.4	4.2	0.34 (96)
GrND2	2.9	6.3	0.29 (97)
GrND3	2.1	7.0	0.21 (80)
GrRD2N	6.0	3.0	0.29

^aThe content was based on ^1H NMR spectral data measured with hexamethyldisiloxane as an internal standard.

served as a signal appeared at 174.6 ppm. Furthermore, the presence of the monomer units in the grafted polysilsesquioxanes was demonstrated in the IR spectra. In the spectra, a strong absorbance at 1640 cm^{-1} due to amide group and that at 1100 cm^{-1} assigned to silicon-oxygen bond of the polysiloxane backbone were obviously observed.

Thus, the polysilsesquioxanes listed in Table I, which showed the different sequences and numbers of **DMAA** and **NIPAM** units in the graft chains, were prepared efficiently by the use of RAFT technique, in which no gelation was observed. The facts indicated that the **DTC** group on polysilsesquioxane was usable in RAFT process and enabled the controlled introduction of the acrylamide polymers as the graft chains. Furthermore, the main peak was appeared as a unimodal one in the chromatogram of the GPC measurements for the grafted polysilsesquioxanes except for a few cases, in which a small peak was detected in the region indicating an extraordinary molecular weight.

Hydrophilic Property of the Grafted Polysilsesquioxanes

The introduction of copolymer of **NIPAM** and **DMAA** was an effective procedure to transform the

hydrophobic polysilsesquioxane to the hydrophilic one as reported previously. Especially, the grafting of **DMAA** units contributed to provide an amphiphilic property.¹⁷ The fact suggests that the location of **DMAA** units in the graft chain is an important factor to change the property of the polysilsesquioxane derivative. Namely, when poly**DMAA** chains are placed near the hydrophobic polysilsesquioxane backbone, its solubility in water is expected to be improved more effectively. To obtain the information which supports such speculation, the effect of sequence of the monomer units on the property was evaluated by contact angle and the transmittance of 1 wt % aqueous solution of the grafted polysilsesquioxanes.

For the measurement of contact angle, the coated film of the grafted polysilsesquioxanes on polyethylene terephthalate sheet was used. The results were listed in Table III. At first, the contact angle of water drop on the surface of the film was measured at 23°C within 10 s. The starting polysilsesquioxane **CPPSQ** was enough hydrophobic as shown in the angle such as 98° compared to the polyethylene terephthalate sheet, which showed 74° of contact angle.¹⁷ The angle decreased remarkably to be 20° by grafting of poly**DMAA-block-polyNIPAM** as observed in the case of **GrD2N**. The analogous values of 24° and 22° were recorded in the measurement for **GrRD2N** containing poly**NIPAM-ran-polyDMAA** and **GrND2** containing poly**NIPAM-block-polyDMAA**, respectively. These samples were consisted of the same molar ratios and the number of the monomer units to **GrD2N**. In the cases of **GrD3N** and **GrND3**, the contact angles were also in the range from 21° to 23° . The results demonstrated that the grafting of the hydrophilic polymeric components brought about the obvious decrease of the contact angle. However, no effect of the sequence and the number of the monomer units in the graft chains was observed. This may indicate that the graft chains randomly surround the polysilsesquioxane backbone in the film and/or are too short to show the influence of the end monomer units of the graft chains.

Next, the measurement for the contact angle was conducted at 60°C , where a change of angle was presumed as reported in the previous study of the hybrid

Table III. Contact angle of grafted polysilsesquioxane^a

Temperature	Grafted polysilsesquioxane						
	GrD1N	GrD2N	GrD3N	GrND1	GrND2	GrND3	GrRD2N
23°C	38°	20°	23°	35°	21°	21°	24°
60°C	68°	66°	54°	70°	66°	59°	28°

^aThe static contact angle was measured for the coated film of the grafted polysilsesquioxane on polyethylene terephthalate sheet with deionized water drop. The relative humidity was kept to be 50% during the measurement and the observation was performed within 10 s.

Figure 7. Optical transmittance (600 nm) of 1 wt % aqueous solution of the grafted polysilsesquioxane at 20 °C.

of silica and polyNIPAM.³⁷ In the case of **GrD2N**, the value of 20° at 23 °C changed to 66° at 60 °C. For other samples, the contact angles of *ca.* 20° at 23 °C increased to over 54° with the raise of temperature to 60 °C. When the measurements were made once again at the lower temperature, the contact angles of the samples showed the values near 20°. The results were interpreted that a hydrophobic aggregation of polyNIPAM occurred even in the films of the grafted polysilsesquioxanes at 60 °C and disaggregation progressed by lowering the temperature to 23 °C. In the case of **GrRD2N**, no change of the contact angle with the rise of temperature was observed as expected. The coil-globule transition of **GrRD2N** having polyNIPAM-*ran*-polyDMAA was observed around 80 °C. Therefore, the aggregation, resulted in the increase of contact angle, could not be observed at 60 °C. Such thermoresponsive behavior of the grafted polysilsesquioxanes will be reported in near future as mentioned above. Thus, the results suggested that the property of thermoresponsive phase separation was maintained even in the coating films of the grafted polysilsesquioxanes.

Contrary to the results of the measurements of contact angle, the solubility of the grafted polysilsesquioxanes in water was affected obviously by the sequence of the monomer units. The transmittances of the grafted polysilsesquioxanes at 20 °C were shown in Figure 7. The %T of **GrD2N** was 75% and that of **GrND2** was 18%. On the other hand, **GrRD2N** showed the moderate %T such as 45%. The analogous tendency was recorded in the combination of **GrD1N** and **GrND1**. The %T of the former sample, containing DMAA units near the polysilsesquioxane backbone, was 30%. However, the lower %T such as 10% was recorded in the case of **GrND2**, which sandwiched NIPAM units between the backbone and DMAA units. The facts indicated that the position of DMAA units was an important factor to provide a hydrophilic property to the hydrophobic polysilsesquioxane. Namely, the hydrophilic DMAA units placed near the polysilsesquioxane backbone im-

proved the solubility in water efficiently. When polyDMAA was located as the end units in the graft chain, the effect of the hydrophilic units on the solubility of the grafted polysilsesquioxane in water was reduced. In addition, the transmittances of **GrD3N** and **GrND3** reasonably showed the higher values of %T than those of **GrD2N** and **GrND2**, respectively.

CONCLUSIONS

The polysilsesquioxane having DTC groups was employed for the grafting of block copolymer of NIPAM and DMAA through RAFT process. The results demonstrated that the effective graft polymerization by the use of DTC group under thermal-polymerization conditions proceeded without formation of cross-linked product. By the grafting procedure, the block copolymers showing several kinds of sequence and number of the monomer units were successfully introduced onto the polysilsesquioxane backbone. Such designed grafted derivatives of polysilsesquioxane were provided an amphiphilic property by the grafted polymeric components.

The sequence and number of the monomer units in the graft chains affected on the solubility of the polysilsesquioxane in water. The hydrophilic polyDMAA located near the polysilsesquioxane backbone, as shown in the cases of **GrDNs**, reduced the hydrophobicity due to the polysilsesquioxane backbone effectively. However, when polyNIPAM was placed between the polysilsesquioxane backbone and polyDMAA as shown in the series of **GrNDs**, such role to improve the solubility in water was insufficient. The solubility of the polysilsesquioxanes **GrRD2N**, containing polyNIPAM-*ran*-polyDMAA, in water was middle of **GrD2N** and **GrND2**.

In the measurements of contact angle, the grafted polysilsesquioxane was shown to keep the property of thermoresponsive phase separation even in the film. Such reversible thermoresponsive behavior of the polysilsesquioxane derivative as a multi-functional hybrid is under investigation now, in which the information mentioned above should be helpful.

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