Preparation of Stimuli-responsive Polysilsesquioxane Grafted Block Copolymer of Acrylamide Monomers

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The polysilsesquioxanes (**PSQ**s) having the graft block copolymer of *N*-isopropylacrylamide (**NIPAM**) and *N,N*-dimethylacrylamide (**DMAA**), which showed the different sequence and number of the monomer units, were obtained by RAFT process. In addition, the **PSQ** derivatives containing other organic functional groups besides the grafted polymers were prepared by the use of chloromethylphenyl groups on the starting **PSQ**. Through the formation of ester bond and quarternary ammonium salt, phenol, triethylamine, and *N,N*-dimethylaniline groups were introduced into the grafted **PSQ**, respectively. In the behaviors of reversible thermoresponsive aggregation caused by poly(**NIPAM**) component, the almost same Lowest Critical Solution Temperature such as 34 °C was observed for the grafted **PSQ**s, although the poly(**DMAA**), phenol groups, and/or the quarternary ammonium salts were existed on the same **PSQ** backbone. As an additional function, the presence of phenol groups led to pH responsive solubility in water. The solubility of the **PSQ**s in water was also affected by hydrophilic property of the amines to form the quarternary ammonium salts. In addition, a kind of chromism, which related with pH value, was observed in the case containing *N,N*-dimethylaniline moieties.
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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] The graft polymerization from polysilsesquioxane backbone is shown as an effective procedure for the modifications. The methodology enables to provide the additional functions based on the polymeric components without loosing the essential properties of inorganic siloxane structure such as durability for heat and weatherability.[10–16] In the previous works, we also have investigated concerning the graft polymerizations from polysilsesquioxane backbone, which intended to develop the new multi-functional hybrid materials.[17–21] As an example of such graftings, the introduction of block copolymer of *N,N*-dimethylacrylamide (**DMAA**) and *N*-isopropylacrylamide (**NIPAM**) by the living polymerization technique, reversible addition-fragmentation chain transfer (RAFT) process, was reported.[21] In the graft polymerization, the **PSQ** having chloromethylphenyl groups (**CPPSQ**) was prepared from the corresponding trimethoxysilane and, then, *N,N*-dimethyldithiocarbamate (**DTC**) group was introduced as a chain transfer specie for RAFT process.

The previous results demonstrated that the block copolymer grafted **PSQ**s showed an expected amphiphilic property, where the solubility in water was influenced by the sequence and number of the monomer units in the grafted chain.[21] Namely, when the more hydrophilic poly(**DMAA**) was grafted from the polysilsesquioxane backbone at first and poly(**NIPAM**) was grafted after poly(**DMAA**) component [poly(**DMAA**)-*block*-poly(**NIPAM**)], hydrophilic property of the corresponding **PSQ** was effectively improved. When poly(**NIPAM**) was

placed between **PSQ** backbone and poly(**DMAA**) [poly-(**NIPAM**)-*block*-poly(**DMAA**)], the solubility in water was insufficient. Namely, the solubility of the grafted **PSQ**s having poly(**DMAA**)-*block*-poly(**NIPAM**) in water was remarkably improved. Furthermore, the contact angles of the films, obtained from the grafted **PSQ**s, suggested that the other expected property such as thermoresponsive phase separation was given by the grafted poly(**NIPAM**).[22–27] However, the thermoresponsive behavior of the grafted **PSQ**s, which was affected by the environment of poly(**NIPAM**), has not been examined in the report.[21] The component of poly(**DMAA**), which presents more hydrophilic environment compared to the poly(**NIPAM**), in the block copolymer may raise Lowest Critical Phase Separation Temperature (LCST) as shown in the random copolymer prepared from the same monomers.[28,29] While, no influence on the thermoresponsive behavior is observed on the gel containing the block copolymer of **NIPAM**.[30] The examination concerning the behavior of the block copolymer grafted **PSQ**s, in which the hydrophilic environment should be changed by sequence and molecular weight of the polymeric components, was expected to give the information concerning the phenomenon of thermoresponsive phase separation caused by poly(**NIPAM**).

The formation of a multi-functionalized **PSQ**, which expands the utility as the hybrid material, is another interesting theme. Fortunately, **CPPSQ**, chosen as the intermediary derivative for the graftation, contained reactive chloromethylphenyl groups. The utilization of the group for the formation of quarternary ammonium salt is a simple and practical method to provide various functions through the incorporation of organic moieties. In facts, several simple moieties were introduced by

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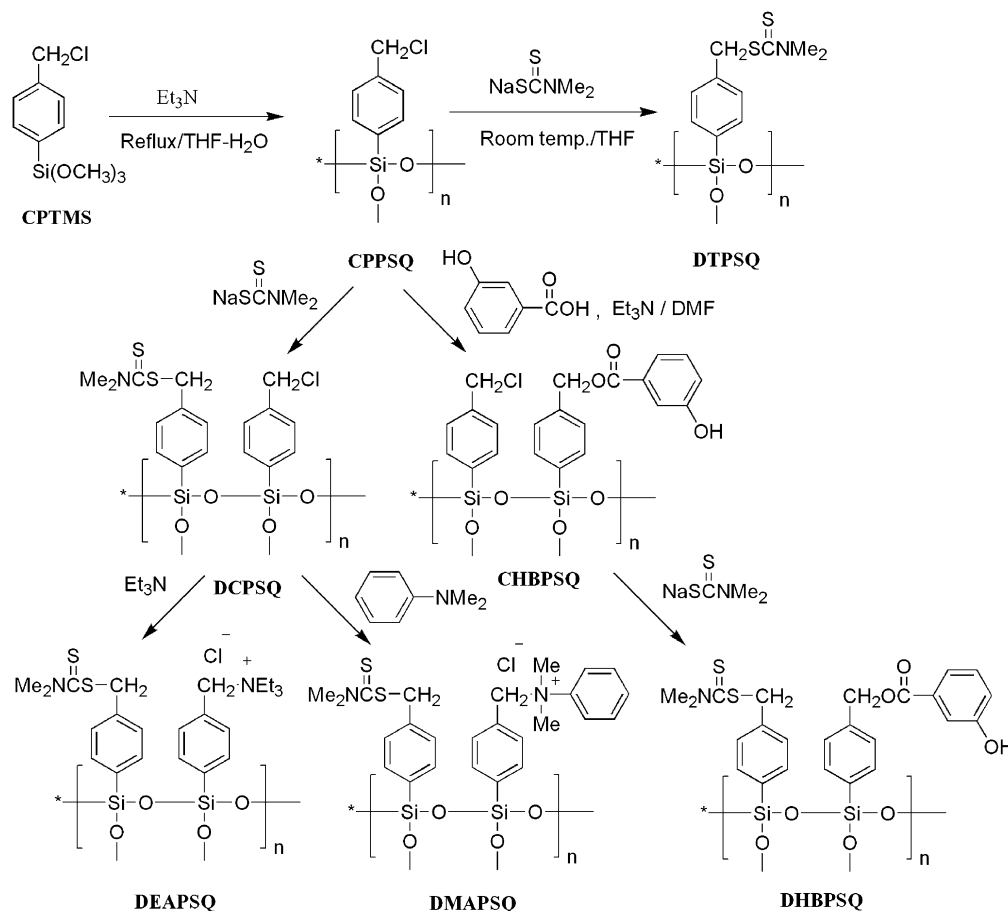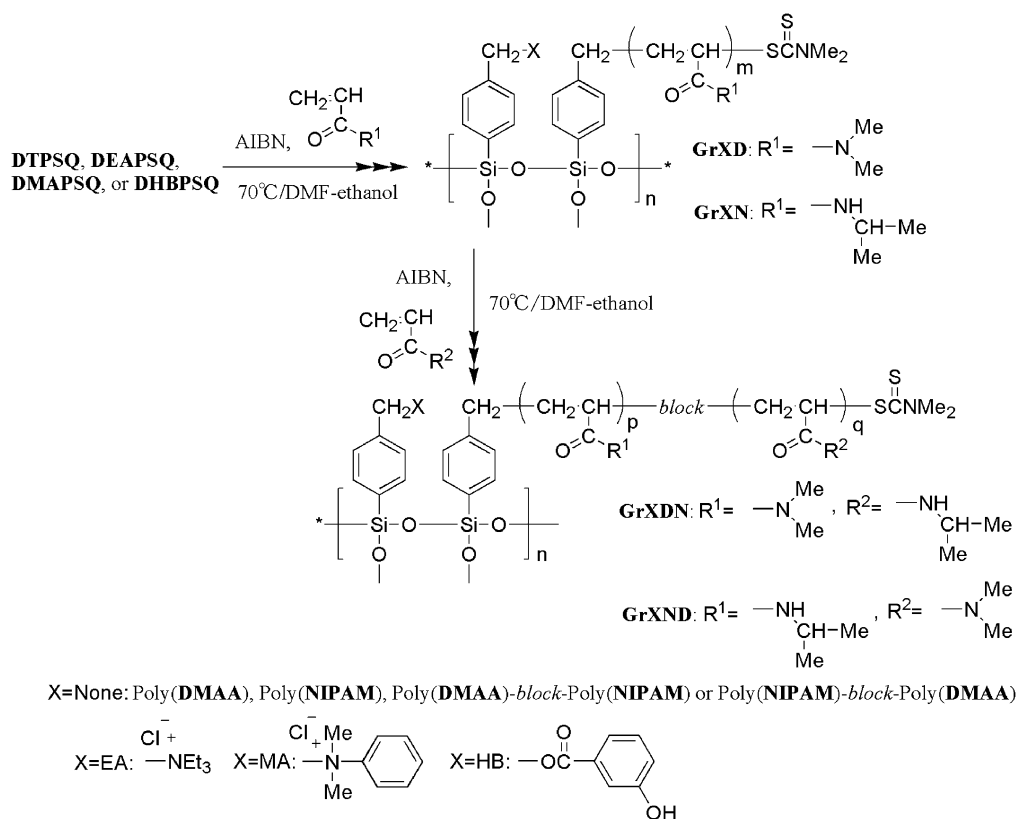
Scheme 1.

the formation of the salts in our previous work.[20] Therefore, the **PSQ** having chloromethylphenyl groups is a convenient material for the preparation of multi-functional hybrid. As another example by the use of the group, the incorporation of functional group through the formation of ester bond was nominated in this work, since chloromethylphenyl group enabled an efficient reaction with carboxylic acid. As mentioned above, several grafted **PSQ**s obtained in the previous work, which contained the different sequence and the molecular weight of polymeric components, were employed for the evaluation of thermoresponsivity.[21] In addition, several **PSQ** derivatives, which had organic functional groups besides the graft copolymers, were newly prepared from the expectation to provide a multi-functionality. For the formations of quarternary ammonium salt, triethylamine or *N,N*-dimethylaniline was treated with chloromethylphenyl group on the **PSQ** backbone, respectively. As another trial to introduce a functional group, *m*-hydroxybenzoic acid was employed to incorporate phenol groups on the **PSQ** backbone. In this case, the **PSQ** having the graft chains and phenol groups was expected to show both pH responsive and thermoresponsive aggregation in an aqueous solution. Such evaluations on the properties of the multifunctional derivatives are thought to afford the information on a multiple characteristic, which is helpful to design a new and a

useful hybrid material based on **PSQ**. The synthetic routes of the **PSQ**s mentioned here were shown in Schemes 1 and 2.

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 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. Tetrahydrofurane (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-

Scheme 2.

chloromethyl)phenyltrimethoxysilane (TCI, 98%), and *N,N*-dimethyldithiocarbamic acid sodium salt dihydrate (TCI, 98%) were used as supplied from commercial sources.

The preparations of the **PSQ**s having chloromethylphenyl groups (**CPPSQ**), **DTC** groups (**DTPSQ**), and the grafted **PSQ**s containing block and random copolymers of **NIPAM** and **DMAA** were reported in the previous work.[21] The **PSQ**s newly prepared in this work were depicted as follows.

Preparation of *PSQ* Having *DTC* Group and Quarternary Ammonium Salt

A solution of **CPPSQ** (2.00 g, chloromethyl group: 9.6 mmol equiv.) and sodium *N,N*-dimethyldithiocarbamate dihydrate (0.96 g, 6.74 mmol) in THF (20 mL) was stirred at 30 °C for 8 h. The resulting solution was evaporated under reduced pressure to concentrate and the residue was poured into methanol. The insoluble solid was collected and washed with water and methanol. After drying at room temperature for 24 h under reduced pressure (<5 mmHg), the **PSQ** having chloromethyl and **DTC** groups (**DCPSQ**) was obtained (2.40 g, 96% yield based on substituted methylphenyl group).

Next, to a solution of **DCPSQ** (1.00 g, Chloromethyl group: 1.4 mmol equiv., **DTC** group: 2.7 mmol equiv.) in DMF (3.2 mL), triethylamine (0.17 g, 1.72 mmol) was added under argon atmosphere and stirred at 50 °C for 18 h. The resulting solution was poured into diethyl ether to precipitate the product. The

insoluble solid was collected and dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the **PSQ** having **DTC** groups and the quarternary ammonium salts of triethylamine (**DEAPSQ**, 1.07 g, 95% yield based on the substituted methylphenyl group). The contents of chloromethyl and **DTC** groups in **DCPSQ** and **DEAPS** were calculated from the peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard: **DCPSQ**; IR (KBr) 3427, 2928, 2925, 1495, 1376, 1256, 1127 (Si-O), 982, 700 cm^{-1}; ^{1}H NMR (DMF-d$_7$, 300 MHz) δ 6.89–7.35 (br m, -C$_6$H$_4$-); 4.70 (br, ClCH$_2$-C$_6$H$_4$-), 4.50 (br, -S-CH$_2$-C$_6$H$_4$-), 3.43 (br, N-CH$_3$), 3.33 (br, N-CH$_3$); ^{13}C NMR (CDCl$_3$,125 MHz) δ 196.3 (C=S); 134.1 (-C$_6$H$_4$-), 128.7 (-C$_6$H$_4$-), 45.8 (ClCH$_2$-C$_6$H$_4$-), 45.3 (-S-CH$_2$-C$_6$H$_4$-), 42.5 (N-CH$_3$), 41.5 (N-CH$_3$); M_n = 4000, M_w/M_n = 1.21. **DEAPSQ**; IR (KBr) 3403, 3050, 2926, 1497, 1376, 1256, 1129 (Si-O), 982, 776, 706 cm^{-1}; ^{1}H NMR (DMF-d$_7$, 300 MHz) δ 6.89–7.91 (br m, -C$_6$H$_4$-); 4.67 (br, N$^+$-CH$_2$-C$_6$H$_4$-), 4.50 (br, -S-CH$_2$-C$_6$H$_4$-), 3.43 (br, N-CH$_3$, N$^+$-CH$_2$CH$_3$), 3.33 (br, N-CH$_3$), 1.37 (br, -CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 200.0 (C=S), 138.9 (-C$_6$H$_4$-), 133.6 (-C$_6$H$_4$-), 52.3 (N$^+$-CH$_2$CH$_3$), 45.9 (-S-CH$_2$-C$_6$H$_4$-, N$^+$-CH$_2$-C$_6$H$_4$-), 41.5 (N-CH$_3$), 12.5 (-CH$_3$); M_n = 5000, M_w/M_n = 1.17.

Analogously, from **DCPSQ** (1.00 g, chloromethyl group: 1.4 mmol equiv., **DTC** group: 2.7 mmol equiv.) and *N,N*-dimethylaniline (0.21 g, 1.72 mmol), the **PSQ** having **DTC**

groups and the corresponding quarternary ammonium salts (**DMAPSQ**, 0.99 g, 86% yield based on the substituted methylphenyl group) was obtained: IR (KBr) 3425, 3023, 2927, 1503, 1375, 1256, 1129 (Si-O), 984, 691, 522 cm^{-1}; ^{1}H NMR (DMF-d_7, 300 MHz) δ 6.45–7.83 (br m, -C$_6$H$_4$-), 4.65 (br, N$^+$-CH$_2$-C$_6$H$_4$-), 4.50 (br, -S-CH$_2$-C$_6$H$_4$-), 3.43 (br, -N-CH$_3$, N$^+$-CH$_3$), 3.33 (br, -N-CH$_3$, N$^+$-CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 196.4 (C=S), 138.7 (-C$_6$H$_4$-, N$^+$-C$_6$H$_5$), 134.1 (-C$_6$H$_4$-, N$^+$-C$_6$H$_5$), 128.6 (-C$_6$H$_4$-, N$^+$-C$_6$H$_5$), 45.8 (-S-CH$_2$-C$_6$H$_4$-), 42.9 (-N-CH$_3$, N$^+$-CH$_3$), 41.4 (-N-CH$_3$, N$^+$-CH$_3$); $M_n = 5000$, $M_w/M_n = 1.21$.

Preparation of *PSQ* Having Phenol Group

To a solution of **CPPSQ** (1.00 g, chloromethyl group: 4.8 mmol equiv.) and *m*-hydroxybenzoic acid (0.27 g, 1.92 mmol) in DMF (4 mL), triethylamine (0.17 g, 1.70 mmol) was added. The solution was stirred at 50 °C for 8 h. The resulting mixture was poured into diethyl ether. The insoluble solid was collected and washed with water and diethyl ether. The solid was dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the **PSQ** having chloromethylphenyl and phenol groups (**CHBPSQ**) (0.61 g, 52% yield based on substituted methylphenyl group); IR (KBr) 3399 (OH), 3221, 1714 (C=O), 1601, 1452, 1396, 1286, 1130 (Si-O), 758, 690 cm^{-1}; ^{1}H NMR (DMF-d_7, 300 MHz) δ 7.38–6.62 (br m, -C$_6$H$_4$-, -C$_6$H$_4$-OH), 5.27 (br, -CH$_2$-O-C=O-), 4.66 (br, ClCH$_2$-C$_6$H$_4$-); ^{13}C-NMR (CDCl$_3$, 125 MHz) δ 165.2 (-O-C=O-), 157.5 (-C$_6$H$_4$-OH), 133.5 (-C$_6$H$_4$-, -C$_6$H$_4$-OH), 127.6 (-C$_6$H$_4$-, -C$_6$H$_4$-OH), 126.6 (-C$_6$H$_4$-, -C$_6$H$_4$-OH), 119.9 (-C$_6$H$_4$-OH-), 65.2 (-CH$_2$-O-C=O-), 45.0 (Cl-CH$_2$-C$_6$H$_4$-); $M_n = 5000$, $M_w/M_n = 1.15$.

Analogpusly, **CHBPSQ** (0.46 g, chloromethyl group: 1.3 mmol equiv.) was treated with sodium *N,N*-dimethyldithio-carbamate dihydrate (0.24 g, 1.70 mmol) in THF (10 mL) to obtain the **PSQ** having phenol and **DTC** groups (**DHBPSQ**, 0.53 g, 94% yield based on substituted methylphenyl group); IR (KBr) 3427 (OH), 2929 (C$_6$H$_5$), 1714 (-O-C=O-), 1602, 1500, 1454, 1376, 1289 (-O-C=O-C$_6$H$_4$-), 1130 (Si-O), 981, 873, 809, 758, 688 cm^{-1}; ^{1}H NMR (DMF-d_7, 300 MHz) δ 7.61–6.81 (br m, -C$_6$H$_4$-, -C$_6$H$_4$-OH), 5.27 (br, -CH$_2$-O-C=O-), 4.47 (br, -S-CH$_2$-C$_6$H$_4$-), 3.44 (br, -N-CH$_3$), 3.31 (br, -N-CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 194.5 (-C=S), 165.2 (-O-C=O-), 161.7 (-C$_6$H$_4$-OH), 133.4 (-C$_6$H$_4$-, -C$_6$H$_4$-OH), 130.4 (-C$_6$H$_4$-, -C$_6$H$_4$-OH), 130.0 (-C$_6$H$_4$-, -C$_6$H$_4$-OH), 126.6 (-C$_6$H$_4$-, -C$_6$H$_4$-OH-), 120.0 (-C$_6$H$_4$-OH), 66.2 (-CH$_2$-O-C=O-), 44.1 (-S-CH$_2$-C$_6$H$_4$-), 42.3 (-N-CH$_3$), 41.3 (-N-CH$_3$); $M_n = 5000$, $M_w/M_n = 1.15$.

Typical Procedure for Grafting of Block Copolymer

A solution of **DEAPSQ** (0.12 g, **DTC** group: 0.3 mmol equiv.), **DMAA** (0.59 g, 6.00 mmol), and AIBN (0.008 g, 0.05 mmol) in the mixed solvents of DMF (2.0 mL) and ethanol (1.0 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 **PSQ** (**GrEAD2**) (0.65 g, 92% yield based on weight).

The grafting of the second monomer, **NIPAM**, to **GrEAD2** was carried out under the similar conditions mentioned above. For the graft polymerization, the amount of **NIPAM** was adjusted to be 10 equiv. to **DTC** group in **GrEAD2**. The **PSQ** having poly(**DMAA**)-*block*-poly(**NIPAM**) as the graft chains with the ammonium salts (**GrEAD2N**) was isolated as an insoluble solid from diethyl ether in 93% yield based on weights of the substrates. The contents of **DTC** group, ammonium salt, and the monomer units in the products were calculated from the peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard: **GrEAD2N**; IR (KBr) 3443, 2966, 2933, 1631 (C=O), 1547, 1460, 1400, 1139 (Si-O), 1093, 671 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.09–7.89 (br m, -C$_6$H$_4$-), 4.70 (br, N$^+$-CH$_2$-C$_6$H$_4$-), 3.86 (br, -NH-CH-), 3.49 (br, -(C=S)-N-CH$_3$), 3.31 (br, -(C=S)-N-CH$_3$, N$^+$-CH$_2$CH$_3$), 2.70–3.05 (br m, N-CH$_3$), 2.20–2.70 (br, -(C=O)-CH-, -CH$_2$-C$_6$H$_4$-), 1.45–1.80 (br m, -CH$_2$-), 1.05–1.30 (br m, -CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 174.4 (–C=O), 133.9 (-C$_6$H$_4$-), 128.5 (-C$_6$H$_4$-), 42.3 (-N-CH-), 37.3 (N-CH$_3$), 36.1 (-CH-), 35.7 (-CH$_2$-), 22.4 (-CH$_3$), 11.2 (-CH$_3$).

Analogously, from **DMAPSQ** and 20 equiv. of **DMAA** to **DTC** group, the grafted **PSQ** having *N,N*-dimethylaniline moieties (**GrMAD2**) was obtained in 94% yield. The grafting of 10 equiv. of **NIPAM** to **GrMAD2** also conducted to afford the corresponding **PSQ** (**GrMAD2N**) in 91% yield: **GrMAD2N**; IR (KBr) 3442, 2980, 1631 (C=O), 1542, 1458, 1141 (Si-O), 1098, 624 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.50–7.72 (br m, -C$_6$H$_4$-), 4.70 (br, N$^+$-CH$_2$-C$_6$H$_4$-), 3.86 (br, -NH-CH-), 3.50 (br, -(C=S)-N-CH$_3$), 3.31 (br, -(C=S)-N-CH$_3$, N$^+$-CH$_3$), 2.70–3.07 (br m, N-CH$_3$), 2.20–2.70 (br, -(C=O)-CH-, -CH$_2$-C$_6$H$_4$-), 1.38–1.89 (br m, -CH$_2$-), 1.05–1.30 (br m, -CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 174.7 (–C=O), 134.1 (-C$_6$H$_4$-), 128.6 (-C$_6$H$_4$-), 42.3 (-NH-CH-), 37.3 (N-CH$_3$), 36.1 (-CH-), 35.7 (-CH$_2$-), 22.4 (-CH$_3$).

Analogously, the graftings of 10 equiv. of **NIPAM**, used as the first monomer, onto **DEAPSQ** or **DMAPSQ** were conducted to obtain the corresponding products (**GrEAN** or **GrMAN**), respectively. Then, 20 equiv. of **DMAA** to **DTC** group were grafted onto each **GrEAN** and **GrMAN** as the second step to obtain the corresponding **PSQ**s having poly-(**NIPAM**)-*block*-poly(**DMAA**) graft chains (**GrEAND2** and **GrMAND2**).

DHBPSQ was also treated with 20 equiv. of **DMAA** and 10 equiv. of **NIPAM** to **DTC** group under the same conditions mentioned above. The **PSQ**s having poly(**DMAA**)-*block*-poly(**NIPAM**) graft chains (**GrHBD2N**) and poly(**NIPAM**)-*block*-poly(**DMAA**) graft chains (**GrHBND2**) were obtained as desired; **GrHBD2N**; IR (KBr) 3447 (N-H), 2970, 2933, 1632 (C=O), 1546, 1460, 1400, 1368, 1257, 1141, 1093, 629 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.61–6.81 (br m, -C$_6$H$_4$-, -C$_6$H$_4$-OH), 5.27 (br, -CH$_2$-O-C=O-), 3.86 (br, -NH-CH-),

Table I. Preparation of functional **PSQ**

Product	Yield[a] %	Content of chloromethyl group[b] mmol equiv./g	Content of DTC group[b] mmol equiv./g	Content of functional group[b] mmol equiv./g
DCPSQ	96	1.4	2.7	—
DEAPSQ	95	—	2.6	1.2
DMAPSQ	86	—	2.5	1.1
CHBPSQ	52	2.7	—	1.6
DHBPSQ	94	—	2.2	1.5

[a]Based on the content of phenyl group. [b]Estimated by ^{1}H NMR spectral data.

3.42 (br, -N-C$\underline{H}_3$), 3.24 (br, -N-C$\underline{H}_3$), 3.05–2.70 (br m, -N-C$\underline{H}_3$), 2.70–2.20 (br, -(C=O)-C$\underline{H}$-, -C$\underline{H}_2$-C$_6$H$_4$-), 1.80–1.45 (br m, -C$\underline{H}_2$-), 1.30–1.05 (br m, -C$\underline{H}_3$); ^{13}C-NMR (CDCl$_3$, 125 MHz) δ 174.6 (–$\underline{C}$=O), 134.2 (-$\underline{C}_6$H$_4$-, -$\underline{C}_6$H$_4$-OH), 128.6 (-$\underline{C}_6$H$_4$-, -$\underline{C}_6$H$_4$-OH), 41.2 (-NH-$\underline{C}$H-), 37.3 (-N-$\underline{C}$H$_3$), 36.4 (-$\underline{C}$H-), 35.6 (-$\underline{C}$H$_2$-), 22.4 (-$\underline{C}$H$_3$).

The results of those syntheses were listed in Tables I and II.

Measurement of Transmittance (%T) for Solubility in Water, Thermoresponsive Behavior, and Chromism

1 wt % solution of the grafted **PSQ** 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 °C/30 s. 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 °C. In the measurements for the **PSQ**s containing the ammonium salts obtained from *N,N*-dimethylaniline, ethanol was added as a co-

solvent. The volume ratio of ethanol/water was adjusted to be 1/9 in the mixed solvents. The UV absorption of **GrMAND2** in the mixed solvent of water and ethanol was measured at 20 °C by adjusting the pH values to 3, 7, and 11. In the adjustments of pH value of the aqueous solutions, 1N HCl was used for pH = 3 and NaOH for pH = 11 and 12.

RESULTS AND DISCUSSION

Preparation of Grafted *PSQ* Having Functional Group

In the previous report, the **PSQ** having **DTC** groups was shown to be effective for the grafting of block copolymer of **NIPAM** and **DMAA** through RAFT process.[21] For the introduction of **DTC** group, chloromethylphenyl group on **PSQ** backbone was usable. The presence of such reactive benzylchloride group enables a ready introduction of various organic moieties, which leads to the preparation of multi-functional **PSQ** derivatives. One of simple and convenient procedures was the formation of quaternary ammonium salt by the treatment with amines.[31] As the examples for proving the functionalities, triethylamine and *N,N*-dimethylaniline were employed to form the qurternary ammonium salt moieties on **PSQ** backbone.

At first, the reaction of **CPPSQ** and sodium *N,N*-dimethyl-dithiocarbamate was conducted to transform a part of chloromethyl groups into **DTC** groups. The reaction proceeded almost quantitatively and *ca.* 65% of chloromethyl groups were converted to **DTC** groups in the resulting **DCPSQ**. Next, **DCPSQ** was treated with 1.2 equiv. of triethylamine to the remaining chloromethyl groups at 50 °C in DMF. The contents of the functional groups were estimated from the ^{1}H NMR spectral data as mentioned later. The estimations showed that the formation of the ammonium salt also proceeded effectively to give the product **DEAPSQ**, which had 2.6 mmol equiv./g of **DTC** group and 1.2 mmol equiv./g of the ammonium salt. In a

Table II. Preparation of multi-functional grafted **PSQ**

Conditions[a]		Multi-functional **PSQ** grafted the block copolymer					
Functional **PSQ**	1st Monomer (2nd Monomer)	Product[b] (Total yield, %)	M_n[c] (M_w/M_n)	Content of 1st monomer unit[d] mmol equiv./g	Content of 2nd monomer unit[d] mmol equiv./g	Content of DTC group[d] mmol equiv./g	Content of functional group[d] mmol equiv./g
DEAPSQ	**DMAA** (**NIPAM**)	**GrEAD2N** (86)	51000 (2.17)	5.9	3.0	0.3	0.1
	NIPAM (**DMAA**)	**GrEAND2** (88)	52000 (2.08)	2.9	5.7	0.3	0.1
DMAPSQ	**DMAA** (**NIPAM**)	**GrMAD2N** (85)	48000 (1.88)	5.7	2.9	0.3	0.1
	NIPAM (**DMAA**)	**GrMAND2** (82)	49000 (1.56)	2.9	5.5	0.3	0.1
DHBPSQ	**DMAA** (**NIPAM**)	**GrHBD2N** (81)	49000 (1.63)	5.8	2.9	0.3	0.2
	NIPAM (**DMAA**)	**GrHBND2** (77)	52000 (1.47)	2.9	5.9	0.3	0.2

[a]The graft polymerization was carried out by using 20 equiv. of **DMAA** or 10 equiv. of **NIPAM** in the presence of 17 mol % of AIBN to **DTC** group at 70 °C for 18 h. The monomer concentration in the mixed solvent of DMF and ethanol was adjusted to be 2[M]. [b]The yield was calculated thorough the graft polymerizations of two steps and based on the weights of the substrates. [c]Estimated by GPC [Eluent: DMF, Standard: poly(methylmethacrylates)]. [d]The content was based on ^{1}H NMR spectral data.

same manner, **DCPSQ** was treated with *N,N*-dimethylaniline to give **DMAPSQ** containing 2.5 mmol equiv./g of **DTC** group and 1.1 mmol equiv./g of the salt. The M_ns of **DEAPSQ** and **DMAPSQ** estimated by GPC became somewhat larger values such as 5000 compared to that of the starting **DCPSQ** such as 4000. The results were shown in Table I.

The graft polymerizations of **DMAA** and **NIPAM** from **DEAPSQ** and **DMAPSQ** were performed under the same thermal polymerization conditions to that reported in the previous work.[21] The polymerizations progressed at 70 °C in the presence of the catalytic amount of AIBN such as 17 mol % to **DTC** group. In this work, the feed mole ratios of **DMAA** and **NIPAM** to **DTC** group were adjusted to be 20 and 10 equivalents, respectively. 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 first grafting of poly-(**DMAA**) afforded the intermediary grafted **PSQ**s. The degrees of polymerization estimated by the data of GPC and ^{1}H NMR spectra showed almost same values around 20, which was in good agreement with the theoretical value. In the cases using 10 equiv. of **NIPAM** to **DTC** group as the first monomer also proceeded successfully to give the **PSQ**s in the high yields over 88%. In addition, in the application of RAFT process, almost quantitative amount of **DTC** groups was recovered after the first grafting of **DMAA** or **NIPAM**. The obtained **PSQ**s grafting the first polymer components were isolated as the insoluble parts in diethyl ether and, then, employed for the further grafting.

The graft polymerizations of the second monomers to introduce the block copolymer could be achieved as desired. The introductions of poly(**NIPAM**) to the **PSQ**s having poly(**DMAA**) chains proceeded to graft the block copolymer, poly(**DMAA**)-*block*-poly(**NIPAM**), in over 91% yield. The M_ns of the resulting **PSQ**s, **GrEAD2N** and **GrMAD2N** were 51000 and 48000, respectively. Similarly, the graft polymerizations to obtain the **PSQ**s having poly(**NIPAM**)-*bock*-poly(**DMAA**) such as **GrEAND2** and **GrMAND2** were carried out under the same conditions. The GPC analyses showed the analogous M_ns such as 52000 for **GrEAND2** and 49000 for **GrMAND2** to those of **GrEAD2N** and **GrMAD2N**. In such graft polymerizations of the second monomers, the data of GPC and ^{1}H NMMR spectra demonstrated the reasonable contents of the monomer units around 20 for the grafting of **DMAA** and 10 for **NIPAM**. Furthermore, in the chromatograms of GPC for the grafted **PSQ**s, a unimodal peak was observed.

In the preparation of the **PSQ** having phenol groups, the esterification of **CPSQ** using *m*-hydroxybenzoic acid was carried out at first and, then, **DTC** groups were introduced. The esterified product, **CHBPSQ**, was obtained, but the isolated yield such as 52% was lower compared to other **PSQ** derivatives. Such low yield may be attributed to a solubility of **CHBPSQ** in diethyl ether, which increased by the presence of phenol groups. The reaction of **CHBPSQ** with sodium *N,N*-dimethyldithiocarbamate proceeded almost quantitatively to give **DHBPSQ**, which had both phenol and **DTC** groups. The graft polymerizations of **NIPAM** and **DMAA** onto **DHBPSQ**

were achieved under the same conditions mentioned above. By the graftings, the **PSQ**s having phenol groups with poly(**DMAA**)-*block*-poly(**NIPAM**), **GrHBD2N**, and poly-(**NIPAM**)-*block*-poly(**DMAA**), **GrHBND2**, were prepared. The degree of polymerizations at the first graftings and the second ones calculated by GPC and ^{1}H NMR spectral data were reasonable. The M_n of the **PSQ** grafted 20 equiv. of **DMAA** such as 28000 increased to 49000 for **GrHBD2N** after the grafting of **NIPAM**. In the preparation of **GrHBND2**, the M_n was recorded to be 52000. The results indicated the graft polymerizations progressed effectively even when phenol groups were existed on the same **PSQ** backbone.

The contents of **DTC** group, the ammonium salts, phenol group, and the monomer units were estimated by ^{1}H NMR spectral data. In the ^{1}H NMR spectrum of **DCPSQ**, the signal due to the protons of methylene bonded to **DTC** group was detected at 4.50 ppm. The signal appeared at 4.70 ppm was assigned to the protons of the remaining chloromethylphenyl group. After the introduction of triethylamine, the signal assigned to methyl protons was newly detected at 1.37 ppm due to methyl protons in the spectrum of **DEASPQ**, although the signal at 4.70 ppm was not shifted. The content of triethylamine moiety was calculated from the both peak areas of the signal at 4.70 ppm and 1.37 ppm. The calculations gave almost same values. This demonstrated that the formation of the ammonium salt proceeded almost quantitatively. The peak area of the signal at 4.70 ppm was also employed for the estimation in the case of **DMAPSQ**. In addition, the content of **DTC** group was based on the areas of two signals due to methyl protons appeared at 3.33 ppm and 3.43 ppm. In the case of **DHBPSQ**, a characteristic signal was observed at 5.27 ppm, which was assigned to the methylene group bonded to ester. The proton area of the signal was used for the calculation of content of phenol group. In the grafted **PSQ**s, the additional signals due to the monomer units were observed. In the spectra of the **PSQ**s containing **DMAA** units, the peak area due to methylene protons detected at *ca.* 1.6 ppm was usable for the calculation. The content of **NIPAM** unit was easily calculated by the use of the peak area of the signal at 3.86 ppm which appeared as an easily distinguishable peak. In the grafted **PSQ**s containing the both monomer units, the two areas mentioned above were utilized for the estimation of the contents. However, after the grafings of the monomers, the signals assigned to the functional groups became so small. This might result in inaccurate estimations to determine the contents of the functional groups. For the examples, the ^{1}H NMR spectra of **DEAPSQ** and **GrEAD2N** were shown in Figures 1 and 2, respectively.

^{13}C NMR spectrum of the grafted **PSQ**s supported the incorporations of the functional groups and the graft chains. In the case of **DHBPSQ**, the presence of ester bond was demonstrated by the signal detected at 165.2 ppm due to carbonyl group. However, unfortunately, no distinguishable signal for *N,N*-dimethylaniline moiety was found in the ^{13}C NMR spectrum of **DMAPSQ**. The signal of carbon for **DTC** group assigned to thiocarbonyl group was found at 196 ppm in all the ^{13}C NMR spectra before grafting. After the
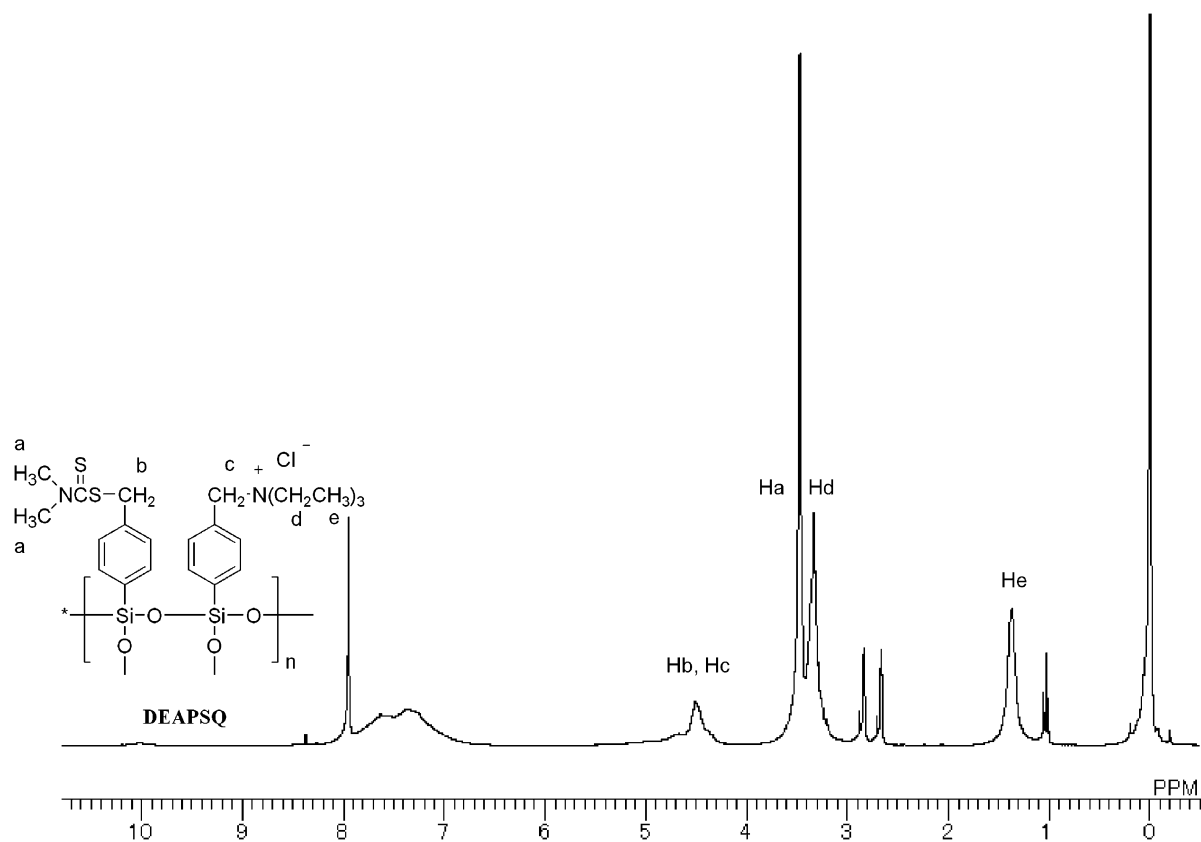
Polymer
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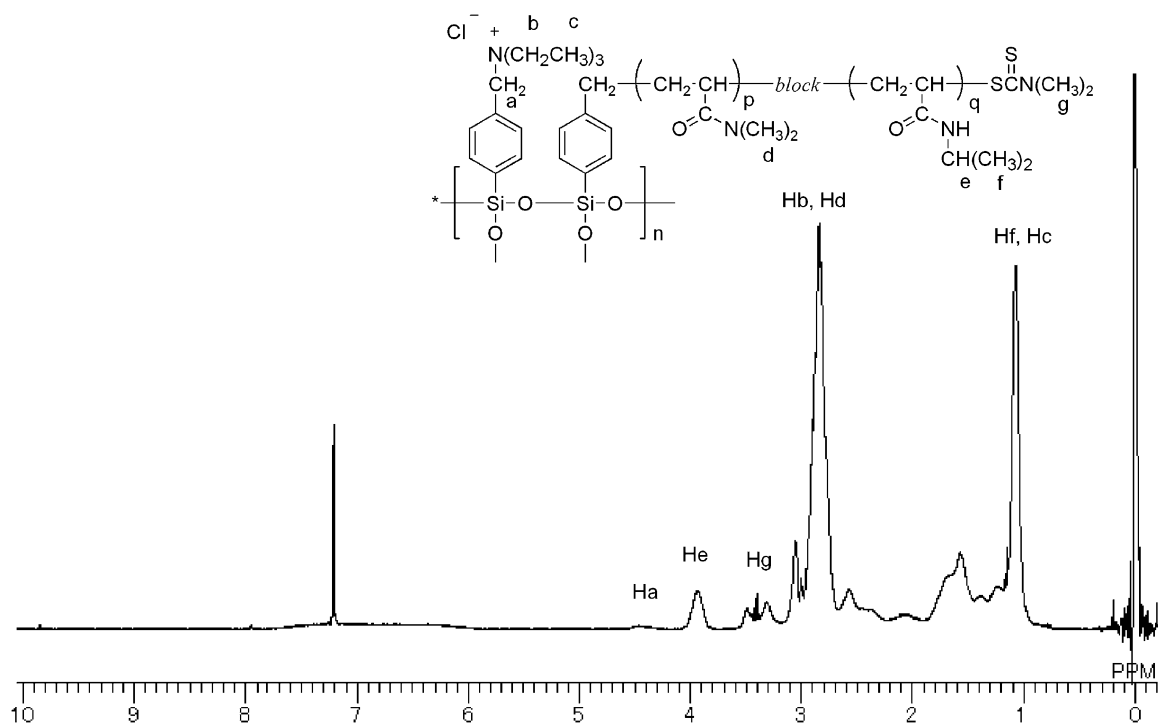**Figure 1.** ^{1}H NMR spectrum (DMF-d$_7$, 300 MHz) of **DEAPSQ**.

**Figure 2.** ^{1}H NMR spectrum (DMF-d$_7$, 300 MHz) of **GrEAD2N**.

graft polymerizations of the block copolymers, the corresponding signals to **DMAA** and **NIPAM** units were observed easily. The carbon of amide group of both **NIAPM** and **DMAA** units was observed as a signal appeared at 174.6 ppm. Furthermore, the presence of the monomer units and polysiloxane structure 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 multi-functional grafted **PSQ**s, which contained the different sequences and numbers of **DMAA** and **NIPAM** units in the graft chains, were prepared in this work, and the analytical data was listed in Table II.

Thermoresponsive Behavior and Additional Property of the Grafted *PSQ*

The previous measurement of contact angle using the coated films of the grafted **PSQ**s on polyethylene terephtalate sheet with water drop demonstrated the clear hydrophilic property in comparison with the starting **PSQ** having chloromethylphenyl groups.[21] In addition, the contact angles observed at 60 °C in comparison with those at 20 °C suggested that a hydrophobic aggregation in the graft chain occurred even in the films of the grafted **PSQ**s. However, the film, obtained from the **PSQ** grafting the random copolymer of **DMAA** and **NIPAM**, **GrRD2N**, showed no change of contact angle at the temperatures. While, the solubility in water, which was indicated as %T observed from a visible source of 600 nm at 20 °C, was affected clearly according to the difference of the graft chains. When poly(**DMAA**) in the block copolymer was placed near the hydrophobic **PSQ** backbone and poly(**NIPAM**) was located as the end component, the solubility of the grafted **PSQ** in water was improved markedly.[21] Whereas, the **PSQ**s having poly(**DMAA**) as the end component in the graft chain, the solubility in water was reduced. Another result obtained in the evaluation of solubility in water was that the values of %T increased reasonably with the increase of content of **DMAA** unit in the graft chain. These demonstrated the changes of hydrophiilic environment around **PSQ** backbone. Analogously, the environments of the multi-functional **PSQ**s seem to be influenced by the presences of phenol or ammonium salt moieties. Especially, the ammonium salt obtained from triethylamine was assumed to make more hydrophilic environment than that from *N,N*-dimethylaniline.

The thermoresponsive aggregation was evaluated by the turbidity, which was indicated as a transmittance at 600 nm. The relationships between %T *vs.* temperature were measured under heating and cooling, the rate of which were adjusted to be 1 °C/30 s. In Figure 3, the phase separation behavior of **GrD2N**, which had 20 equiv. of **DMAA** unit and 10 equiv. of **NIPAM** unit to **DTC** group in the graft chains of poly-(**DMAA**)-*block*-poly(**NIPAM**), under heating were shown. The phase separation of the aqueous solution started at 34 °C and the aggregation was completed at *ca.* 37 °C under heating, In cooling, %T began to increase at 35 °C and colorless solution was recovered at 30 °C. Such reversible phase separation was
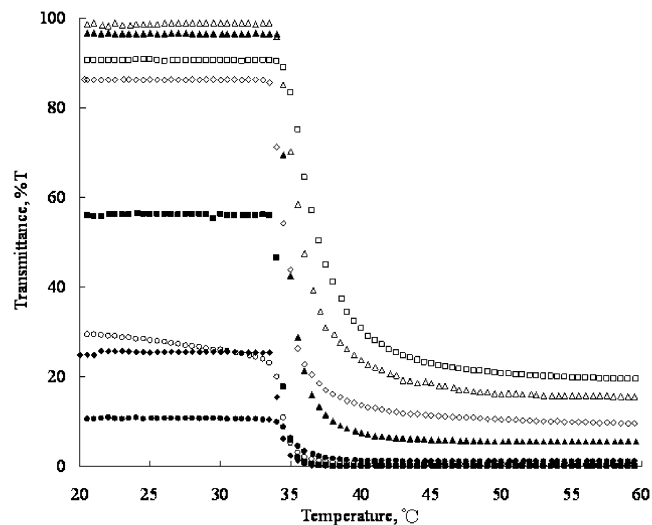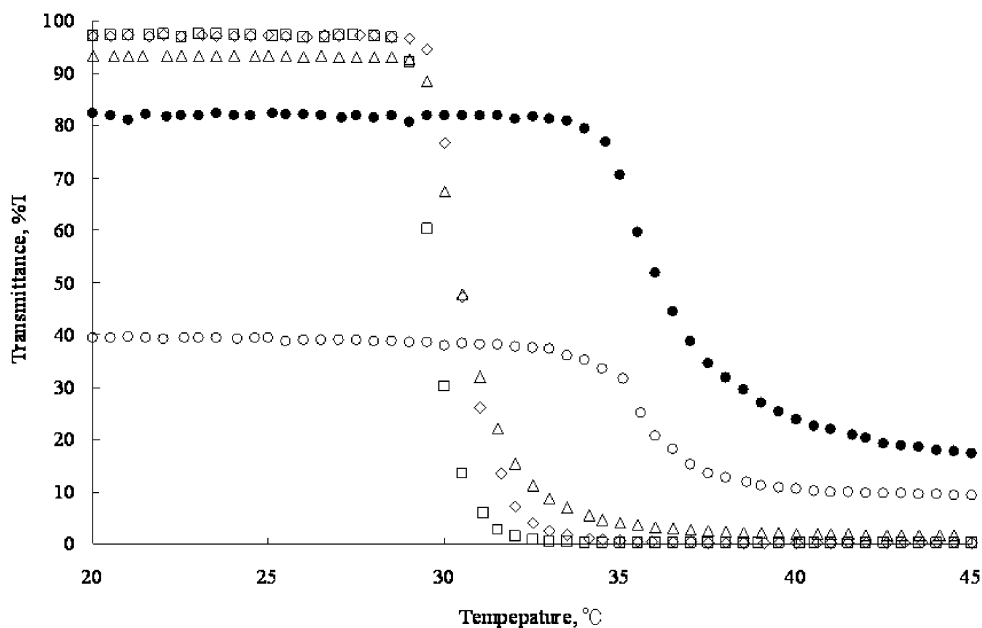

Figure 3. Temperature dependence of optical transmittance (%T) for 1 wt % aqueous solution at 600 nm under heating: (○) **GrDN**, (◇) **GrD2N**, (□) **GrD3N**, (●) **GrND**, (◆) **GrND2**, (■) **GrND3**, (△) **GrEAD2N**, and (▲) **GrEAND2**.

observed in all the aqueous solutions of the grafted **PSQ**s examined in this work. However, to avoid a complicated view, the curves observed under cooling were excluded in the Figures. As mentioned above, the **PSQ**s having poly(**DMAA**)-*block*-poly(**NIPAM**) chains such as **GrDN**, **GrD2N**, and **GrD3N** usually showed a better solubility in water than those having poly(**NIPAM**)-*block*-poly(**DMAA**) chains such as **GrND**, **GrND2**, and **GrND3**. However, the same LCST such as *ca.* 34 °C was recorded in all the samples. Analogously, no relationship between the content of **DMAA** unit, which should increase a hydrophilic property of **PSQ**, with LCST was observed as shown in the cases of **GrDN**, **GrD2N**, and **GrD3N**. On the other hand, the aggregation started at 80 °C in the aqueous solution of **GrRD2N** having the random copolymer of **DMAA** and **NIPAM**, the behavior of which was not depicted here. The LCST of **GrRD2N** was markedly increased as predicted from the previous reports.[28,29] This can explain the previous finding that no change of contact angle was detected in the measurements at 20 °C and 60 °C.[21] Namely, the both temperatures for the measurement were lower than that of hydrophobic aggregation of **GrRD2N**.

The hydrophilic environment around poly(**NIPAM**) chains mentioned above didn't affect on LCST, but it was related with the sensitivity of the aggregation as indicated by the temperature width for the change of the phase from solution to complete gel formation. In the measurements of thermoresponsive behavior of **GrDN**, the change of the phase accomplished within *ca.* 2 °C as shown in Figure 3. The temperature width for complete aggregation of **GrD3N**, which contained 3 times of **DMAA** unit compared to **GrDN**, under heating was 7 °C. When **NIPAM** was grafted as the first monomer, no relationships of content of hydrophilic poly(**DMAA**) chain with the sensitivity was observed. In the measurements of **GrND**, **GrND2**, and **GrND3**, the aggregation accomplished

Figure 4. Temperature dependence of optical transmittance (%T) at 600 nm under heating for 1 wt% aqueous solution of **GrHBND2**: (○) at pH = 6, (●) at pH = 12, and for 1 wt% solution of **GrMAND2** in water and ethanol: (△) at pH = 3, (□) at pH = 7, (◇) at pH = 11.

within 2 °C. Consequently, the hydrophilic property of poly-(**DMAA**) in the block copolymer was reflected in the sensitivity of thermoresponsive phase separation only when the grafted chain was placed between the hydrophobic **PSQ** backbone and poly(**NIPAM**) component. The findings suggested that an enough part of the **PSQ** was required to be free from water molecules to show the completion of aggregation. Namely, it took a longer time to aggregate an enough amount of **NIPAM** units by moving away water molecules, when the hydrophilic **DMAA** units or the functional groups were existed around the **PSQ** backbone. This seemed to be reflected the sensitivity.

Next, the thermoresponsive behaviors of the multi-functional grafted **PSQ**s having phenol groups or quarternary ammonium salts were examined. The measurements of %T for the aqueous solution of **GrHBD2N** and **GrHBND2** at 25 °C showed the effects of phenol group as shown in Figure 4. In the solution of **GrHBD2N**, which showed a good solubility in water by the grafting of poly(**DMAA**)-*block*-poly(**NIPAM**) chain, the recorded transmittances were over 80% in spite of the change of pH values. While, in the measurements of the solution of **GrHBND2**, 38% of %T at pH = 6 became 82% at pH = 12. The later results were interpreted that phenol group as a weak acid brought pH responsive property into the **PSQ** by forming sodium salt. Furthermore, such responsibility could not be observed in the former case having the graft chains of poly(**DMAA**)-*block*-poly(**NIPAM**), because the **PSQ**, **GrHBD2N**, essentially showed a good solubility in water. However, such pH responsive solubility in water of **GrHBND2** was unrelated with LCST. The starting temperatures of aggregation at pH = 6 and pH = 12 showed the same value such as 34 °C. The temperature was also in accord with the recorded LCST of the grafted **PSQ**s having no additional

functional group. In these cases, the solubility in water was also reflected in the sensitivity of the phase separation. The temperature width for the aggregation at pH = 12 showed the larger value such as 8 °C in comparison with *ca.* 3 °C at pH = 6.

The **PSQ**s introducing triethylamine, **GrEAD2N** and **GrEAND2**, showed a good solubility in water regardless of sequence of the monomer units. However, these samples also showed the same LCST to the grafted **PSQ**s mentioned above as depicted in Figure 3. On the other hand, the **PSQ**s having aniline moieties showed a poor solubility in water even in the **PSQ** having the graft chains of poly(**DMAA**)-*block*-poly-(**NIPAM**) such as **GrMAD2N**. Consequently, the measurements of thermoresponsive aggregation for **GrMAD2N** and **GrMAND2** were conducted in the mixed solvents of water and ethanol, the volume ratio of which was adjusted to be 9 to 1. Even in these samples, no different behavior was observed in comparison with other grafted **PSQ**s as shown in Figure 4, although LCST was fallen to 30 °C. The fall of LCST was explained by the presence of ethanol, which seemed to made a hydrophobic environment around poly(**NIPAM**) chain. Indeed, LCST of **GrD2N**, which possessed no ammonium salt moiety, became 30 °C in the mixed solution. The results concerning the **PSQ**s having the graft chains and ammonium salts indicated that the sequence of the monomer units and the presence of ammonium salt on **PSQ** backbone brought about no change of the aggregation temperature. Such findings were supported by our previous experimental facts reported on the **PSQ**s introducing ammonium salt moieties and graft chains of poly(**NIPAM**).[20]

During the measurement of %T for the **PSQ**s containing aniline moieties, the color of the solution faded from violet to colorless with the increase of pH value. In usual, such phenomena, including change of colors, have been observed in
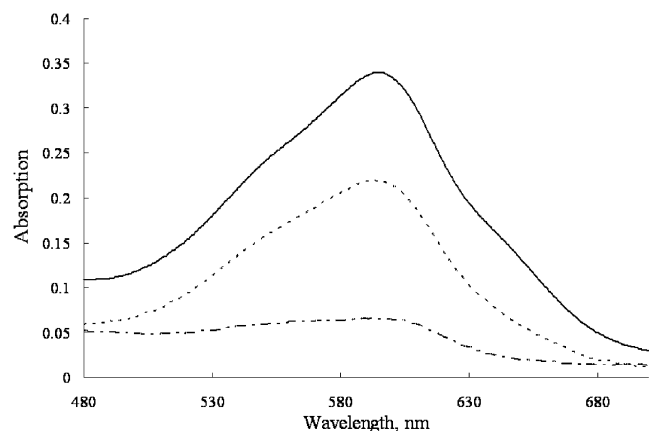
Figure 5. Relationships between pH and absorption of **GrMAND2**: (—) at pH = 3, (···) at pH = 7, and (—·—) at pH = 11.

various chromophore consisted of conjugated ammonium salt.[32] In the case of **GrMAND2**, a kind of chromism was provided by the formation of the simple qurternary ammonium salt as an additional function. The UV spectra, which demonstrated the changes of absorption at 20 °C, were shown in Figure 5. The absorption of 0.35 at pH = 3 was remarkably decreased to be 0.05 at pH = 11. For the adjustment of pH value of 3 and 11 in the mixed solvent of water and ethanol, hydrochloric acid and sodium hydroxide were employed, respectively. Such chromism showed no relation with the thermoresponsive behavior. Since, the aggregation started at 30 °C in all the solutions, of which pH were adjusted to be 3, 7, and 11 as shown in Figure 4. These demonstrated that a kind of halo-chromism was presented without changing the property of thermoresponsive phase separation.

The findings on the properties of the multi-functional **PSQ**s demonstrated that the characteristics due to the organic groups could be observed, although the contents of the groups were so small compared to those of the monomer units. In addition, the properties appeared independently without affecting the thermoresponsive behavior of the graft chains introduced on the same **PSQ** backbone. This may be explained by the presence of poly(**NIPAM**) as a block, which can act independently irrespective of environment. In other words, the presence hydrophilic monomer unit neighboring **NIPAM** unit retards to exclude water molecules around them in the random copolymer, but the block of **NIPAM** unit having no hydrophilic unit around it primarily reach a hydrophobic situation easily. Analogously, such property of a block of **NIPAM** unit should not be affected by the existence of the functional groups, which locate on **PSQ** backbone.

CONCLUSIONS

The **PSQ**s having the block copolymers of **NIPAM** and **DMAA**, which showed several kinds of sequence and number of the monomer units, were prepared through RAFT process by the use of **DTC** group. Furthemore, the introduction of quarternary ammonium salt moieties or phenol groups besides

the graft chains on **PSQ** backbone could be performed as designed to prepare the new multi-functional organic-inorganic hybrid materials. The presence of phenol groups on the **PSQ** backbone contributed to provide the pH responsive solubility in water as an additional function. The introduction of ammonium salt moieties demonstrated that the amphiphilic property of the **PSQ** could be controlled by the choice of amine species. In addition, the use of *N,N*-dimethylaniline for the formation of ammonium salt was a convenient technique to utilize the **PSQ** as a chromophore.

In the measurements of thermoresponsive behavior of the grafted **PSQ**s, the sequence and number of hydrophilic **DMAA** units in the block copolymer showed no effect on the aggregation temperature. In the **PSQ**s, which contained the functional groups on **PSQ** backbone with the graft chains, the unchanged LCST was also observed. The results demonstrated that the poly(**NIPAM**) chains in the copolymer aggregated efficiently even when a hydrophilic environment was formed around the block of NIPAM units. Consequently, the incorporation of other monomer units to form the random copolymer with **NIPAM** was required to change LCST.

The pH responsible solubility caused by phenol group and a kind of halo-chromism by *N,N*-dimethylaniline salt moiety were the typical examples for the preparations of multi-functional **PSQ** hybrid materials, in which the functions could be provided independently with thermoresposive aggregation property. In addition, the use of **PSQ** as a polymeric backbone was demonstrated to be a convenient and a practical method for the formation of multi-functional materials. Such information was thought to be helpful for designing a stimuli-responsive hybrid material consisted of polysiloxane structure.

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