Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 1837–1844

polymer

www.elsevier.com/locate/polymer

Preparation of polysilsesquioxane grafted thermoresponsive polymer by use of mercapto group

Osamu Moriya [a,*], Masaki Kuga [a], Shin-ichi Yamamoto [a], Mikio Kashio [b], Atsuko Kamejima [b], Toshio Sugizaki [b]

[a] *Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan*
[b] *Research Laboratory, Lintec Co., Nishiki-cho, Warabi 335-0005, Japan*

Received 31 October 2005; received in revised form 16 January 2006; accepted 17 January 2006
Available online 7 February 2006

Abstract

The polysilsesquioxane having mercapto and phenyl groups (PMPSQ) was prepared from the corresponding trimethoxysilanes by co-condensation under basic conditions. The mercapto groups on PMPSQ were utilized as the initiators for the graft polymerization of *N*-isopropylacrylamide (NIPAM) with the comonomer such as *N*,*N*-dimethylacrylamide (DMAA) or hydroxyethyl acrylate under UV irradiation. The grafting of the copolymers proceeded effectively to give the functionalized polysilsesquioxane derivatives, in which the monomer unit ratios almost reflected the feed molar ratios of the monomers and no formation of gel product was observed. These grafted polysilsesquioxanes could be dissolved in water and showed the property of thermoresponsive gel formation.

Keywords: Polysilsesquioxane; Graft polymerization; *N*-isopropylacrylamide

1. Introduction

Recently, a variety of investigations concerning the modification of polysilsesquioxanes has been reported from the interests in new organic–inorganic hybrid materials [1–10]. Through the modification of the hybrid having polysiloxane structure by functional groups, the electrical, optical, mechanical, and chemical applications are proposed [11–14]. The grafting of polymeric components is regarded as one of the effective method for the modification of poly- and oligo-silsesquioxanes [15–19]. We also presented the preparation of the grafted derivatives of polysilsesquioxane, which were soluble in usual organic solvents [20–22]. These intended to utilize the graft polymerization as a method for providing the additional properties, which were based on polymeric components. During the investigations on the graft polymerization onto polysilsesquioxane, mercapto group was found to be a useful functional group and an initiator under UV irradiation [22]. As an example, the hydrophobic polysilsesquioxane containing mercapto groups could be transformed into the amphiphilic derivative by the incorporation of poly(dimethylacrylamide). The result suggests that the simple utilization of mercapto group can be exploited as a practical procedure for the modification of polysilsesquioxane by grafting an appropriate polymeric components [23–26].

On the other hand, the phase separation stimulated by temperature has been recognized as an attractive property. The polymer obtained from *N*-isopropylacrylamide (NIPAM) is well known to show such thermoresponsibility [27–36]. In a large number of the works concerning the thermoresponsive polymer, the grafting of polymerized NIPAM [poly(NIPAM)] onto the polysiloxane gels has been already proposed to be an effective method for affording the hybrid materials applicable to microencapsulation, biosensor, and drug delivery [37–41]. However, the temperature-sensitive polysiloxane derivatives, soluble in both organic solvents and water, have not been investigated so far. Consequently, NIPAM was thought to be an appropriate candidate to investigate the possibility of grafting onto polysilsesquioxane. Furthermore, fortunately, mercapto group has been shown to initiate the graft copolymerization of NIPAM with *N*,*N*-dimethylacrylamide (DMAA) from dextran [36]. These facts promise that the resulting grafted polysilsesquioxane, consisted of both the hydrophobic backbone and the hydrophilic polymeric graft chains, shows the property of temperature sensitive phase separation as a high performance hybrid [42,43].

---

* Corresponding author. Tel.: +81 46 841 3810x2404; fax: +81 46 844 5901.
E-mail address: moriyaos@nda.ac.jp (O. Moriya).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.01.060

In our preliminary experiments for grafting of poly(NIPAM) onto the polysilsesquioxane containing phenyl and 3-mercaptopropyl groups (PMPSQ), the product was slightly soluble in water by the effects of hydrophobic polysilsesquioxane backbone. This led us to consider the incorporation of more hydrophilic units in the graft chains. Therefore, in this work, DMAA and hydroxyethyl acrylate (HEA) were chosen as the comonomers to form the hydrophilic graft chains. The introduction of such comonomer units into the polymer of NIPAM has been known to affect on the temperature for phase separation [36,44–47]. Namely, the grafting of the copolymer of NIPAM with DMAA [poly(NIPAM-*co*-DMAA)] or HEA [poly(NIPAM-*co*-HEA)] was expected to add the function of controllable lower critical solution temperature (LCST) in thermoresponsibility. By considering the information mentioned above, we examined the grafting of poly(NIPAM-*co*-DMAA) or poly(NIPAM-*co*-HEA) onto the PMPSQ in this work. The synthetic image of these was shown in Scheme 1.

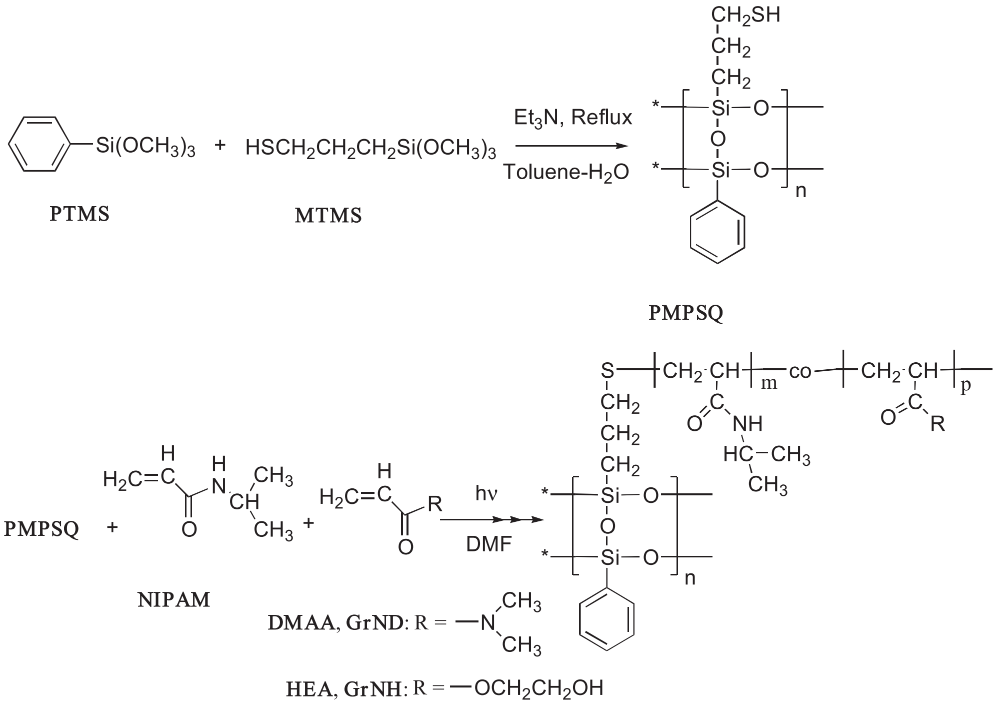
2. Experimental

2.1. 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 dimethylformamide (DMF) was used as the eluent. Calibration was performed using poly(methyl methacrylate) standards. DMF employed for the reactions was refluxed over calcium hydride and distilled. NIPAM was recrystallized from the mixed solvent of benzene and ^{n}hexane. The comonomers DMAA and HEA were distilled over calcium hydride before use. Other reagents including (3-mercaptopropyl)trimethoxysilane (MTMS) and phenyltrimethoxysilane (PTMS) were used as supplied from commercial sources.

2.2. Preparation of polysilsesquioxane (PMPSQ)

PMPSQ was prepared by the method reported before [22]. A mixture of PTMS (8.00 g, 40.32 mmol) and MTMS (8.00 g, 40.72 mmol) with triethylamine (0.40 g, 4.00 mmol) in toluene (80 ml) and water (20 ml) was refluxed for 48 h. Organic phase was separated and washed with brine. The organic phase was concentrated by a rotary evaporator under reduced pressure and, then, methanol was added to the residual oil. The resulting viscous oil insoluble in methanol was dried at room temperature for 24 h in a vacuum oven under reduced pressure (<5 mmHg). PMPSQ (8.00 g, 84% yield from PTMS and 95% yield from MTMS) was obtained as a solid after drying. The contents of phenyl and mercapto groups were calculated from the peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard; IR (KBr) 3450 (weak, OH), 3050 (weak, C_6H_5), 2930 (medium, CH_2), 2560 (weak, SH), 1440 (medium), 1268 (medium), 1134 (strong, Si–O), 1028 (strong, Si–O), 742 (medium), 700 (medium) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$), δ 0.55–0.75 (br, –Si–CH_2–), 1.30 (br, –SH), 1.45–1.85 (br, –CH_2–), 2.25–



Scheme 1.

3.00 (br, –S–CH_2–), 6.50–7.70 (br m, –C_6H_5); ^{13}C NMR (75.45 MHz, $CDCl_3$), δ 12.40 (Si–CH_2–), 27.81 (–CH_2–SH, C–CH_2–C), 128.39 (m, p-$C_6H_5\times 3$), 131.26 (o-$C_6H_5\times 2$), 134.43 (Si–C_6H_5); $M_n=5400$, $M_w/M_n=2.11$; phenyl unit = 4.22 mmol equiv. g^{-1}, mercaptopropyl unit = 4.88 mmol equiv. g^{-1}.

2.3. Typical procedure for grafting onto PMPSQ

A solution of PMPSQ (0.28 g, 1.18 mmol equiv. of phenyl group and 1.37 mmol equiv. of mercapto group), DMAA (0.68 g, 6.86 mmol), and NIPAM (0.78 g, 6.89 mmol) in DMF (6 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 equipped with water jacket from a distance of 10 cm for 20 h under argon atmosphere. The resulting solution was distilled under reduced pressure to concentrate and the residue was poured into diethyl ether. The insoluble part was dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the poly(NIPAM-*co*-DMAA) grafted polysilsesquioxane (GrND2) as a solid (155 g, 89% yield based on weight) (Table 1, Run 3); IR (KBr) 3470, 3280, 2975, 2934, 1640 (C=O), 1560, 1465, 1140 cm^{-1}; ^{1}H NMR (DMF-d_7, 500 MHz), δ 1.06 (br, m, –CH_3), 1.63–1.73 (br, m, –CH_2–), 2.15–2.48 (br, (C=O)–CH–), 2.75–2.97 (br, –N–CH_3), 3.85 (br, –NH–CH–) 7.13–7.40 (br, –C_6H_5, –NH–); ^{13}C NMR (125 MHz, DMF-d_7), δ 22.2 (–CH_3), 24.4 (–CH_2–), 37.9 (–CH–), 39.3 (NCH_3), 39.8 (NCH_3), 40.1 (NCH–), 130.0 (–C_6H_5), 132.5 (–C_6H_5), 135.4 (–C_6H_5), 175.2 (–C=O); $M_n=4400$, $M_w/M_n=1.93$.

Analogously, the grafted polysilsesquioxanes GRNDs were prepared by changing the feed molar ratios of NIPAM and DMAA. The polysilsesquioxanes having the graft chains of poly(NIPAM-*co*-HEA) (GrNHs) were also prepared in a similar manner. In addition, the grafted polysilsesquioxane having the homopolymer of NIPAM (GrN) as the graft chains were prepared by the same procedure above, in which 10 equiv. of NIPAM to mercapto group was employed (Table 1, Run 1).

GrNH2 (Table 1, Run 6): IR (KBr) 3400, 3300, 2975, 2954, 1720 (C=O), 1640 (C=O), 1565, 1465, 1384, 1260, 1160, 1138, 1080 cm^{-1}; ^{1}H NMR (DMF-d_7, 500 MHz), δ 0.88 (br, m, –CH_3), 1.21–1.75 (br, m, –CH_2–), 1.85–2.30 (br, (C=O)–CH–), 3.59 (br, –CH_2–OH), 3.84 (br, –NH–CH–), 4.03 (br, –CH_2–O–) 7.13–7.40 (br, –C_6H_5, –NH–); ^{13}C NMR (125 MHz, $CDCl_3$), δ 22.2 (–CH_3), 30.7 (–CH_2–), 34.2 (–CH–), 35.8 (–CH–), 38.9 (N–CH–), 58.9 (HO–CH_2–), 65.6 (–O–CH_2–), 125.0 (–C_6H_5), 128.2 (–C_6H_5), 133.7 (–C_6H_5), 174.6 (–C=O).

The results of the grafting were shown in Table 1.

2.4. Thermal analysis

The grafted polysilsesquioxanes were employed for thermal degradation test by a thermogravimetric analyzer (Shimadzu, DTG-60). The measurements were conducted with 10 mg of the sample from room temperature to 600 °C, in which a heating rate was 10 °C min^{-1} under nitrogen.

2.5. Measurement of contact angle

A solution of the grafted polysilsesquioxane in toluene was cast on poly(ethylene terephtalate) sheet and, then, removed toluene at 120 °C for 1 min in an oven. Static contact angle was measured with deionized water drops on the surface of the resulting sheet within 10 s at room temperature by a face contact angle meter (Kyowa Interface Science, CA-D Type).

2.6. Measurement of transmittance (%T)

A solution of the grafted polysilsesquioxane (0.5 or 1.0 wt%) in deionized water was used for the measurement

Table 1
Graftation onto polysilsesquioxane having mercapto groups (PMPSQ)

Run	Reaction conditions[a]		Grafted polysilsesquioxane			
	Comonomer	Feed molar ratio of NIPAM/ comonomer	Product	Yield (%)[b]	Unit of ratio of NIPAM/comonomer (mol equiv. mol^{-1} equiv. $^{-1}$)[c]	M_n (M_w/M_n)[d]
1	–	10/0	GrN	81	10/0	30,400 (1.93)
2	DMAA	7/3	GrND1	86[e]	8/2	31,400 (2.42)
3	DMAA	5/5	GrND2	89[e]	5/5	29,800 (2.25)
4	DMAA	3/7	GrND3	92[e]	2/8	40,800 (1.94)
5	HEA	7/3	GrNH1	92[f]	7/3	42,700 (1.45)
6	HEA	5/5	GrNH2	95[f]	5/5	49,000 (1.40)
7	HEA	3/7	GrNH3	91[f]	2/8	47,200 (1.93)

[a] The polymerization was conducted at 18 °C under UV irradiation (400 W high-pressure mercury lamp) for 20 h in DMF, in which the total monomer concentration was ca. 2.3 [M].

[b] The yields were based on the weights of the substrates.

[c] The estimation was based on ^{1}H NMR spectral data.

[d] DMF was used as an eluent and the calibration was performed with poly(methyl methacrylate) standards.

[e] Insoluble part of diethyl ether.

[f] Insoluble part of ^{n}hexane.

of %T on a Shimadzu UV-1650 spectrophotometer equipped with a Peltier-type S-1700 thermostatic cell older, where the changes in %T were observed from a visible source at 500 nm through a 1 cm quartz sample cell at the rate of 1 °C/30 s during heating and cooling scans.

3. Results and discussion

3.1. Preparation of PMPSQ from PTMS and MTMS

In our previous work, the condensation using only MTMS under basic conditions was reported to give a gel product. The introduction of phenyl groups besides mercaptopropyl groups is found to be effective for the preparation of the polysilsesquioxane soluble in several usual organic solvents. Consequently, the polysilsesquioxane having phenyl and mercaptopropyl groups, the ratio of which was adjusted to be almost equal, was prepared in this work. The obtained PMPSQ was supposed to contain a ladder- and an incomplete cage-like polysiloxane structures, although it has been still unidentified and left as a problem to be solved.

The co-condensation of PTMS and MTMS with a catalytic amount of triethylamine proceeded efficiently to give PMPSQ in the good yield such as 84% as a viscous oil insoluble in methanol. After drying under vacuum at room temperature, the viscous oil transformed into an easy handling solid. The yield and the contents of phenyl and mercaptopropyl groups were estimated by the proton ratios observed in the ^{1}H NMR spectrum. In the ^{1}H NMR measurements of PMPSQ, hexamethyldisiloxane was used as an internal standard, the signal of which appeared at 0 ppm. The signals assigned to the protons for the methylene groups of $–CH_2CH_2SH$ were observed in the region from 1.30 to 1.85 ppm. Other protons showing the presences of $SiCH_2–$ and benzene ring were detected around 0.6 and 7.6 ppm, respectively. From the calculation based on the proton ratios of these signals, the contents of 4.88 mmol equiv. g^{-1} of mercaptopropyl group and 4.22 mmol equiv. g^{-1} of phenyl group were determined. The estimated M_n and M_w/M_n of PMPSQ by GPC were ca. 4400 and 1.93, respectively. The obtained PMPSQ was soluble in diethyl ether, chloroform, benzene, acetone, THF, and DMF, but insoluble in methanol, ^{n}hexane and water. Such PMPSQ was used as the macroinitiator for the graft polymerization of NIPAM and the comonomers.

3.2. Grafting by photopolymerization

As a preliminary experiment, the polymerization of NIPAM onto PMPSQ under UV irradiation using a 400 W high pressure mercury lamp at 18 °C was carried out, in which 10 equiv. of NIPAM to mercapto group was employed. In the polymerizations mentioned here, the initial concentration of the monomers was fixed to be ca. 2 M in DMF. The polymerization proceeded effectively to give the polysilsesquioxane GrN having only poly(NIPAM) in 86% yield (Table 1, Run 1). However, this grafted derivative GrN was insoluble in water. Such a low solubility in water despite to the introduction of the hydrophilic graft chains was thought to be caused by the presence of the hydrophobic polysiloxane backbone which contains phenyl and propyl groups. Consequently, the graftings of the copolymers, which contained the more hydrophilic monomer units such as DMAA or HEA, were examined.

The polysilsesquioxanes having poly(NIPAM-*co*-DMAA) or poly(NIPAM-*co*-HEA) as the graft chains were prepared under UV irradiation, in which the feed molar ratios of NIPAM/comonomer were changed to be 7/3, 5/5 and 3/7. The graftings of NIPAM and the comonomer onto PMPSQ proceeded effectively to give the products in high yields over 86%. The obtained grafted products were soluble in methanol, acetone, and DMF, but insoluble in diethyl ether. In GPC measurements of the grafted polysilsesquioxanes using DMF as an eluent, M_ns were estimated to be in the region from 29,800 to 49,000 and all the products showed unimodal peak in the elution profiles. This indicated that the polymerizations progressed primarily to form the grafted derivative of PMPSQ.

The presence of the monomer units in the grafted derivatives of PMPSQ was supported by the spectral data. The IR spectra of GrNDs, having NIPAM and DMAA units in the graft chains, showed a strong absorbance at 1640 cm^{-1}. In the spectra of the grafted polysilsesquioxanes GrNHs, containing NIPAM and HEA units, two peaks around 1720 and 1640 cm^{-1} due to carbonyl group were shown. The former spectral data demonstrated that the presence of the analogous amide groups. The later spectral information indicated that GrNHs contained amide and ester groups. In the IR spectra of GrNHs, several additional peaks due to HEA unit were

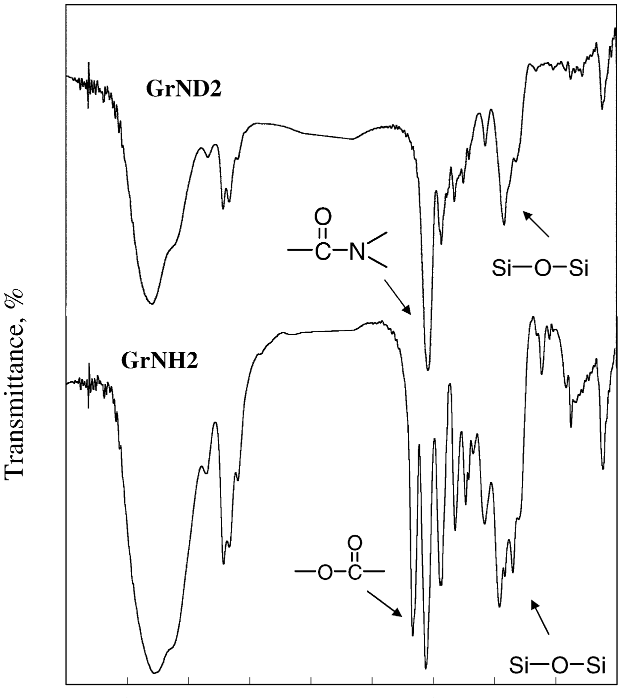


Fig. 1. IR spectra (KBr) of GrND2 (Table 1, Run 3) and GrNH2 (Table 1, Run 6).

observed. The characteristic strong peaks at 3000 and 1180 cm^{-1} indicated the presence of hydroxy and carbon–oxygen bond, respectively. In addition, the peak around 1100 cm^{-1} due to silicon–oxygen bond was observed in the IR spectra of GrNDs and GrNHs. As the examples of IR spectra, these of GrND2 and GrNH2 were shown in Fig. 1. In the ^{1}H NMR spectra of the grafting polysilsesquioxanes, the signals due to the protons of methylene and methine groups were detected in the range from 1.2 to 1.8 ppm. However, the broad signal due to methylene protons attached to Si was hardly observed at ca. 0.6 ppm in the both spectra of GrNDs and GrNHs. Other signals due to methyl protons of dimethylamino group and protons of benzene ring were appeared around 3.0 and 7.2 ppm, respectively. The signal appeared at 3.85 ppm was assigned to the methine proton bonded to nitrogen of NIPAM. These signals could be utilized for the calculation of the monomer unit ratios of the graft chains of GrNDs. In the cases of GrNHs, the signals appeared at 3.59 and 4.03 ppm were assigned to the methylene protons bonded to oxygen. The composition of graft chains of GrNHs was estimated by the proton areas of these signals with that at 3.84 ppm for methine proton of NIPAM unit. The spectral data of ^{1}H NMR, utilized for the estimation of compositions of the graft chains, demonstrated that NIPAM, DMAA, and HEA could be polymerized effectively according to the feed molar ratios of the monomers. The ^{1}H NMR spectra of GrND2 and GrNH2 were shown in Fig. 2. The signals due to the characteristic carbons of the monomer units detected in ^{13}C NMR spectra of GrNDs and GrNHs also supported the incorporations of the corresponding graft chains. The signals observed at 39.3, 39.8, and 40.1 ppm in the spectra of GrNDs were assigned to the carbons of methyl and methine groups bonded to nitrogen of polymerized DMAA unit. The carbons of methylene groups attached to oxygen of polymerized HEA unit were appeared at 58.9 and 65.6 ppm.

3.3. Thermal and hydrophilic properties

The thermal stability of the graft polymers GrN, GrND2 and GrNH2 was examined by TGA analysis. The TGA curves were shown in Fig. 3. In the measurements, the weight of GrN decreased more readily than those of GrND2 and GrNH2. In the curves of GrND2 and GrNH2, the degradation seemed to progress through three stages. In the case of GrNH2, the curve at the first stage until ca. 340 °C almost overlapped with that of GrN and, then, the slope became gentle at the second stage. In the case of GrND2, the slope of the curves was almost same until ca. 390 °C to that of GrN. The different inclinations of the

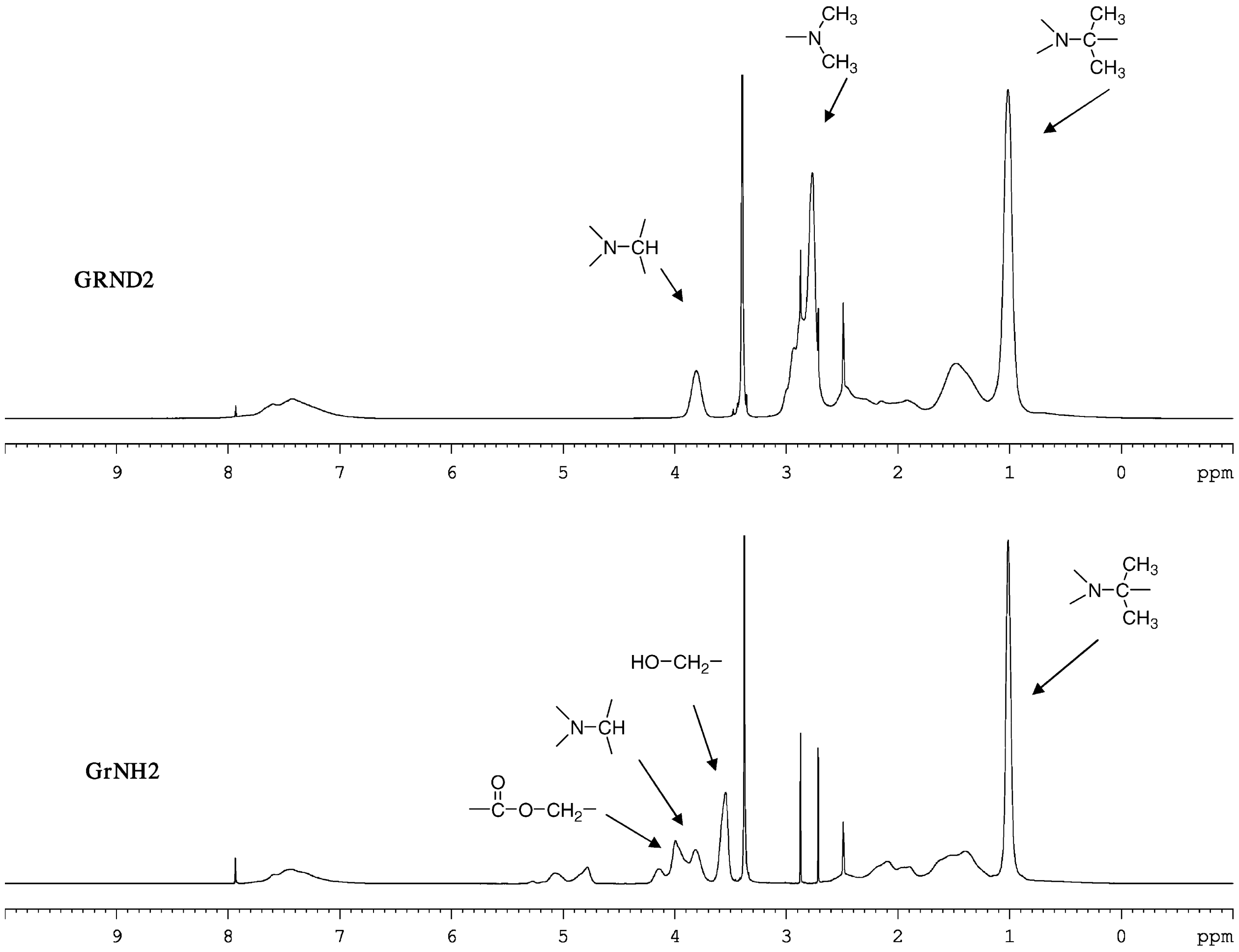


Fig. 2. ^{1}H NMR spectra (DMF-d_7, 300 MHz) of GrND2 (Table 1, Run 3) and GrNH2 (Table 1, Run 6).

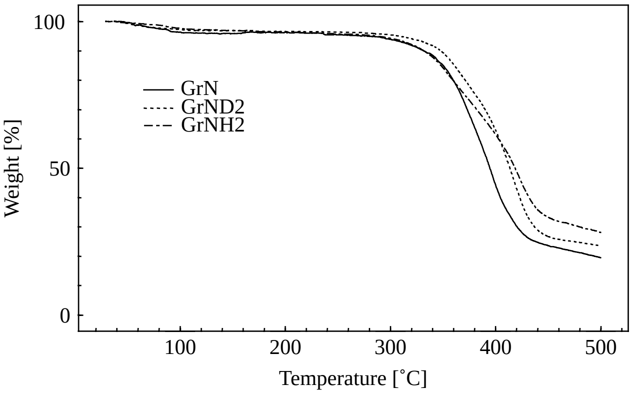


Fig. 3. TGA curves of GrN (—) (Table 1, Run 1), GrND2 (···) (Table 1, Run 3), and GrNH2 (— - —) (Table 1, Run 6).

curves observed at the second stage seemed to show the effects of the polymerized comonomers DMAA and HEA on the degradation. The results was interpreted that the incorporation of DMAA or HEA units into the polymer of NIPAM improved the tolerance of the graft chains to heat. At the third stage, the degradation around polysilsesquioxane backbone seemed to begin. Since, the analogous loss of weight was observed at the similar temperature such as ca. 440 °C in the case of PMPSQ as shown in the previous report [22]. In all the thermal profiles of the grafted products, the total weight loss of each sample at 600 °C was reasonable. When the grafted polymers, phenyl groups, and propyl groups were assumed to be lost completely, the estimated weight loss due to those components should be ca. 90%. The observed total weight loss of those samples was close to the presumed value.

The effect of incorporation of the hydrophilic units into the graft chains was evaluated by the measurement of contact angle on the films obtained from the grafted products. The contact angles of water drop on the surface of the films of GrNDs and GrNHs, measured at room temperature within 10 s, were shown in Table 2. The hydrophobic PMPSQ provided the reasonable angle such as 98° in the previous report [22]. The value decreased to be 54° by grafting of the poly(NIPAM) as shown in the example of GrN. The value was further decreased with the presences of the hydrophilic monomer units. When the molar unit ratio of NIPAM/DMAA in poly(NIPAM-*co*-DMAA) chain was 2/8, the contact angle of GrND3 became 27°. This was predictable by considering the contact angle of the analogous polysilsesquioxane grafted only DMAA units, in which the contact angle of the polysilsesquioxane containing 7.8 monomer units to one mercapto group was 18° [22]. In the incorporations of HEA units, the values were varied in the range from 47 to 38° with the increase of content of HEA units as shown in the series of GrNHs. These indicated that the effect of DMAA unit on hydrophilicity appeared more markedly compared to that of HEA unit. The grafted polysilsesquioxane, GrN, having the homopolymer of NIPAM was difficult to dissolve in water. While, GrNDs showing the lower contact angles were readily soluble in water. In the series of GrNHs, GrNH3, the graft chain of which was mainly consisted of HEA units, was soluble in water. However, GrNH1 and GrNH2, the molar ratios of NIPAM unit/HEA unit of which were 2/8 and 5/5, could not be dissolved in water freely. Such grafted polysilsesquioxanes showing a good and moderate solubility in water were used for the following examination on the thermoresponsive phase separation.

3.4. Thermally reversible phase separation

The change of LCST of poly(NIPAM) caused by the introduction of DMAA and 2-hydroxyethyl methacrylate units has already been presented in various works [36,44–47]. These previous results promised that a thermally reversible phase separation of GrNDs and GrNHs occurred at different temperatures by reflecting the content of the hydrophilic monomer units. To get the information on the thermoresponsive property, the aggregation behavior of the grafted polysilsesquioxanes was evaluated by the turbidity in an aqueous solution, which was indicated as transmittance. The concentrations of the samples were adjusted to be 1 wt% for GrNDs and 0.5 wt% for GrNHs by considering the solubility in water. The relationships between %T versus temperature of GrNDs and GrNHs measured at 500 nm under heating were shown in Figs. 4 and 5, respectively. The LCSTs of those

Table 2
Hydrophilic property of grafted polysilsesquioxane

Material	PMPSQ[a]	GrN	GrND1	GrND2	GrND3	GrNH1	GrNH2	GrNH3
Contact angle (deg.)[b]	98	54	38	30	27	47	45	38
LCST (°C)[c]	–	–	49	73	>100	–	48	55

[a] Ref. [22].

[b] Contact angle of water.

[c] Aqueous solution of 1 wt% for GrNDs and 0.5 wt% for GrNHs were used in the measurements of optical transmittance.

samples were listed in Table 2. No reverse profile was depicted here, but all the samples showed the behavior of reversible phase separation according to the temperature.

When the ratio of NIPAM unit/DMAA unit was 8/2, the LCST of GrND1 was recorded to be 49 °C. Such phase separation in the aqueous solution of GrND1 started at 37 °C and the gel was almost completely formed at ca. 49 °C mentioned as LCST. The LCST of GrND2, which contained same molar ratio of NIPAM and DMAA units, increased to be 73 °C, in which such gel formation of GrND2 was started at 54 °C. In this case, the %T could not reach to 0% under the conditions mentioned here. In the case of GrND3, which contained the highest molar ratio of DMAA unit among GrNDs, the value was over 100 °C. Thus, LCST of the grafted polysilsesquioxanes increased markedly with the content of DMAA unit.

The solubility of GrNH1 and GrNH2 in water was not enough as predicted by the values of contact angle and the later sample was practically unsuitable to the measurement. Therefore, the measurements of thermoresponsive property of GrNHs were conducted on GrNH2 and GrNH3 where the concentration of the sample was adjusted to be 0.5 wt% solution in water. The results indicated that the effects of HEA unit on LCST were less obvious compared to those of DMAA unit. When the unit ratios of NIPAM/HEA was 5/5, the LCST of GrNH2 was 42 °C. The LCST of GrNH3, which contained double the molar ratio of HEA unit to NIPAM unit, rose to 49 °C. These observations were shown in Fig. 5. In addition, under such conditions, the value of %T for GrNH2 was retained at ca. 50%, even when the gelation was completed.

The copolymer of NIPAM with the hydrophilic comonomer DMAA is known to show a higher value of LCST in comparison with poly(NIPAM) [36,44–46]. The results obtained here were in accord with such previous findings. The graft chains consisted of NIPAM and HEA units combination also brought a rise of LCST. However, the difference of values of LCST according to the contents of HEA units was not obvious. The less hydrophilic HEA unit, as supposed by the values of contact angle, was less effective for the change of the thermoresponsive property. This tendency was predictable from the reported thermoresponsibility of the analogous copolymer of NIPAM with 2-hydroxyethyl methacrylate [47].

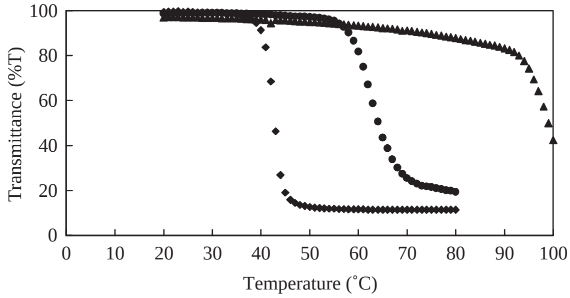


Fig. 4. Temperature dependence of optical transmittance (%T) at 500 nm for 1.0 wt% aqueous solution of GrNDs under heating: GrND1 (◆), GrND2 (●), and GrND3 (▲).

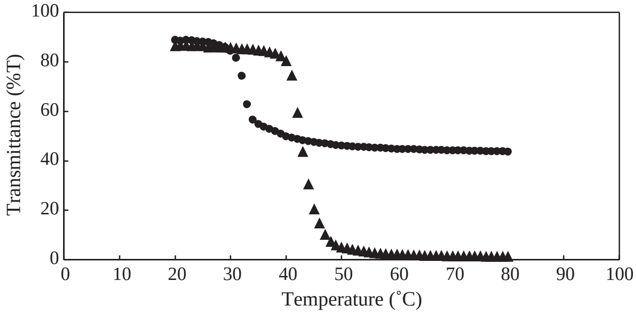


Fig. 5. Temperature dependence of optical transmittance (%T) at 500 nm for 0.5 wt% aqueous solution of GrNHs under heating: GrNH2 (●) and GrNN3 (▲).

The thermosensitivity of GrNDs to the phase transition was deteriorated than that of the reported poly(NIPAM-*co*-DMAA) [36,44–46]. Temperature width of 12 °C was necessary for the complete phase transition of GrNH1 and 19 °C for that of GrNH2. A steric factor of the polysilsesquioxane backbone may be a reason besides the effects of molecular weight to explain the slow phase separation. The polysilsesquioxane backbone is thought to be consisted of a ladder- and/or an incomplete cage-like structure. Consequently, that is more bulky and rigid compared to a usual linear polymer backbone. Such steric factor is unfavorable for the intermolecular aggregation of the grafted polysilsesquioxane. This seems to cause the retardation of intermolecular association of the grafted polysilsesquioxane macromolecules except for intramolecular assembly of NIPAM units.

4. Conclusion

The polysilsesquioxane containing phenyl and mercaptopropyl groups was employed for the grafting of thermoresponsive poly(NIPAM-*co*-DMAA) or poly(NIPAM-*co*-HEA) to afford the new functional organic–inorganic hybrid material. The results demonstrated that mercapto group on the polysilsesquioxane backbone act as an efficient initiator for the grafting under photopolymerization conditions without formation of cross-linked product. Through the grafting, the expected physical property, a thermally reversible gel formation, was given to the polysilsesquioxane, although the introduction of more hydrophilic monomer units such as DMAA or HEA was required besides NIPAM units to increase the solubility in water. In the use of the hydrophilic comonomers, the temperature of phase separation varied according to the contents of the comonomer units. Such results seem to be available for the design of the polysilsesquioxane derivative, which shows a desired aggregation temperature, although a decline in thermosensitivity was observed.

Thus, the photopolymerization procedure by the simple use of mercapto groups enabled the ready introduction of polymeric components onto the polysilsesquioxane structure. This also promises that the grafting of appropriate polymeric chains enables the facile and versatile preparation of multifunctional polysilsesquioxanes.

References

[1] Baney RH, Cao X. In: Johns RG, Ando W, Chojnowski J, editors. Silicon-containing polymers. Dordrecht: Kluwer; 2000.
[2] Sprung MM, Guenther FO. J Polym Sci 1958;28:17.
[3] Brown Jr JF, Vogt Jr LH, Katchman A, Eustance JW, Kaiser KM, Krantz KW. J Am Chem Soc 1960;82:6194.
[4] Delattre L, Dupuy C, Babonneau F. J Sol–Gel Sci Technol 1994;2:185.
[5] Roy DA, Shea KJ. Chem Rev 1995;95:1409.
[6] Mao L, Kagi D. J Mater Sci 1996;31:3185.
[7] Li Z, Cao X, Xu H, Xie P, Cao M, Zhang R. React Funct Polym 1999;39:1.
[8] Kondo T, Yoshi K, Horie K, Itoh M. Macromolecules 2000;33:3650.
[9] Lee J-K, Char K, Rhee H-W, Ro HW, Yoo DY, Yoon D. Polymer 2001;42:9085.
[10] Yamamoto S, Yasuda N, Ueyama A, Adachi H, Ishikawa M. Macromolecules 2004;37:2778.
[11] Gozdz A. Polym Adv Technol 1993;5:70.
[12] Tanaka T, Morita M, Onose K. Jpn J Appl Phys 1985;24:L112.
[13] Chang C-L, Ma C-CM. J Polym Sci Polym Chem 2003;41:1371.
[14] Krishnan PSG, He C. Macromol Chem Phys 2003;204:531.
[15] Pyun J, Matyjaszewski K. Chem Mater 2001;13:3436.
[16] Kim K-M, Keum D-K, Chujo Y. Macromolecules 2003;36:867.
[17] Cardoen G, Coughlin EB. Macromolecules 2004;37:5123.
[18] Fu BX, Lee A, Haddad TS. Macromolecules 2004;37:5211.
[19] Ohno K, Sugiyama S, Koh K, Tsujii Y, Fukuda T, Yamahiro M, et al. Macromolecules 2004;37:8517.
[20] Moriya O, Yamamoto S, Kumon S, Kageyama T, Kimura A, Sugizaki T. Chem Lett 2004;33:224.
[21] Sugizaki T, Kashio M, Kimura A, Yamamoto S, Moriya O. J Polym Sci Polym Chem 2004;42:4212.
[22] Yamamoto S, Shimada T, Moriya O, Kimura A, Sugizaki T, Moriya O. Polym J 2004;36:761.
[23] Huan M-Y, Wu R, Jiang L-R. Polym Bull 1983;9:5.
[24] Xia C, Cheng H, Yan D. J Appl Polym Sci 1992;45:579.
[25] Mercier L, Pinnavaia T. Adv Mater 1997;9:500.
[26] Lecamp L, Houllier F, Bunel BYC. Polymer 2000;42:2727.
[27] Guillet JE. J Macromol Sci Chem 1968;A2:1441.
[28] Pelton RH, Cibante P. Colloid Surf 1986;20:247.
[29] Fujishige S, Kubota K, Ando I. J Phys Chem 1989;93:3311.
[30] Chen GH, Hoffman AS. Nature 1995;373:49.
[31] Pelton RH. Adv Colloid Interface Sci 2000;85:1.
[32] Hu T, You Y, Pan C, Wu C. J Phys Chem B 2002;106:6659.
[33] Ray B, Isobe Y, Matsumoto K, Habaue S, Okamoto Y, Kamigaito M, Sawamoto M. Macromolecules 2004;37:1702.
[34] Meyer S, Richtering W. Macromolecules 2005;38:1517.
[35] Kim KS, Vincent B. Polymer 2005;37:565.
[36] Huh KM, Hashi J, Ooya T, Yui N. Macromol Chem Phys 2000;201:613.
[37] Yoshioka H, Mikami M, Nakai T, Mon Y. Polym Adv Technol 1995;6:418.
[38] Suzuki K, Yumura T, Tanaka Y, Akashi M. J Control Release 2001;75:183.
[39] Rao GVR, Krug ME, Balamurugan S, Xu H, Xu Q, Lopez GP. Chem Mater 2002;14:5075.
[40] Serizawa T, Wakita K, Akashi M. Macromolecules 2002;35:10.
[41] Okubo T, Hase H, Kimura H, Kokufuta E. Langmuir 2002;18:6783.
[42] Anthonietti M, Főrster S, Hartmann J, Oestreich S. Macromolecules 1996;29:3800.
[43] Sciborek M, Gladkova NK, Chojnowski J. Polym Bull 2000;44:377.
[44] Yoshida R, Sakai K, Okano T, Sakurai Y. J Biomater Sci Polym Ed 1994;6:585.
[45] Kaneko Y, Nakamura S, Sakai K, Kikuchi A, Aoyagi T, et al. Sakurai. J Biomater Sci Polym Ed 1999;10:1079.
[46] Tian J, Seery TAP, Weiss RA. Macromolecules 2004;37:9994.
[47] Çiçek H, Tuncel A. J Polym Sci Part A: Polym Chem 1998;36:527.