Available online at www.sciencedirect.com
ScienceDirect
Polymer 47 (2006) 7693–7701
polymer
www.elsevier.com/locate/polymer

Preparation of polysilsesquioxane having dimethylamino group and grafted thermoresponsive polymer

Shin-ichi Yamamoto [a], Fukutaro Minami [a], Toyoshi Masuda [a], Osamu Moriya [a,*], Mikihiro Kashio [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 19 June 2006; received in revised form 23 August 2006; accepted 24 August 2006
Available online 20 September 2006

Abstract

The polysilsesquioxane having mercapto, dimethylamino, and phenyl groups (**PAMPSQ**) was prepared from the corresponding trimethoxysilanes by co-condensation under basic conditions. The mercapto group on **PAMPSQ** was utilized as an initiator for graft copolymerization of *N*-isopropylacrylamide and *N*,*N*-dimethylacrylamide. The grafting of the copolymer proceeded effectively to give the thermoresponsive polysilsesquioxane derivative (**GrPSQ**) without the formation of gel product. The obtained **GrPSQ** was amphiphilic and provided the property of thermoresponsive reversible aggregation. The aggregation temperatures of **GrPSQ** varied in buffer solutions showing different pH values. Furthermore, the formation of ammonium salts utilizing dimethylaminio groups with carboxylic acids or halogen compounds led to a rise in aggregation temperature.

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

1. Introduction

A variety of investigations on polysilsesquioxane, as a member of polysiloxane compounds and silicon rich organic–inorganic hybrid materials, have been reported recently [1–8]. In the investigations, electrical, optical, mechanical, and chemical applications of polysilsesquioxanes are proposed [9–12]. Such usages of polysilsesquioxanes are linked with a ready modification by various organic functional groups. The existence of functional groups enables further modification of polysilsesquioxane by introducing various organic components. One of the effective methods for such modifications is graft polymerization, in which the introduced polymeric components provide the additional properties besides durability for heat and weatherability based on the inorganic polysiloxane backbone. Indeed, several groups have already reported the modifications of poly- and oligo-silsesquioxane by grafting polymeric components [13–17]. We also have investigated on the graft polymerization from polysilsesquioxanes which intended to prepare a new multi-functional hybrid material [18–20]. Along with such investigations, the introduction of copolymer of *N*,*N*-dimethylacrylamide (**DMAA**) and *N*-isopropylacrylamide (**NIPAM**) was reported in the previous work [21]. In the report, the mercapto group in polysilsesquioxane was demonstrated to be a useful initiator for graft polymerization under UV irradiation. In addition, the obtained polysilsesquioxane derivative successfully showed amphiphilicity and thermoresponsive phase separation. The latter property was provided by the graft chains of the polymerized **NIPAM** (poly**NIPAM**).

The thermoresponsivity provided by the presence of poly**NIPAM** has been well investigated and various applications are proposed such as microencapsulation, biosensor, and drug delivery [22–29]. In such widely expanded investigations, the amphiphilic polysilsesquioxane, consisted of inorganic polysiloxane backbone with thermoresponsive graft chains,

---

[*] 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 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2006.08.061

is regarded as a newcomer of the high performance hybrids [30,31]. Furthermore, the easy introduction of various organic functional groups, which are contained in the starting trichloro- or trialkoxy-silane, is a favorable feature of polysilsesquioxane. This led us to investigate on the multifunctional derivatives of the previous thermoresponsive grafted polysilsesquioxane.

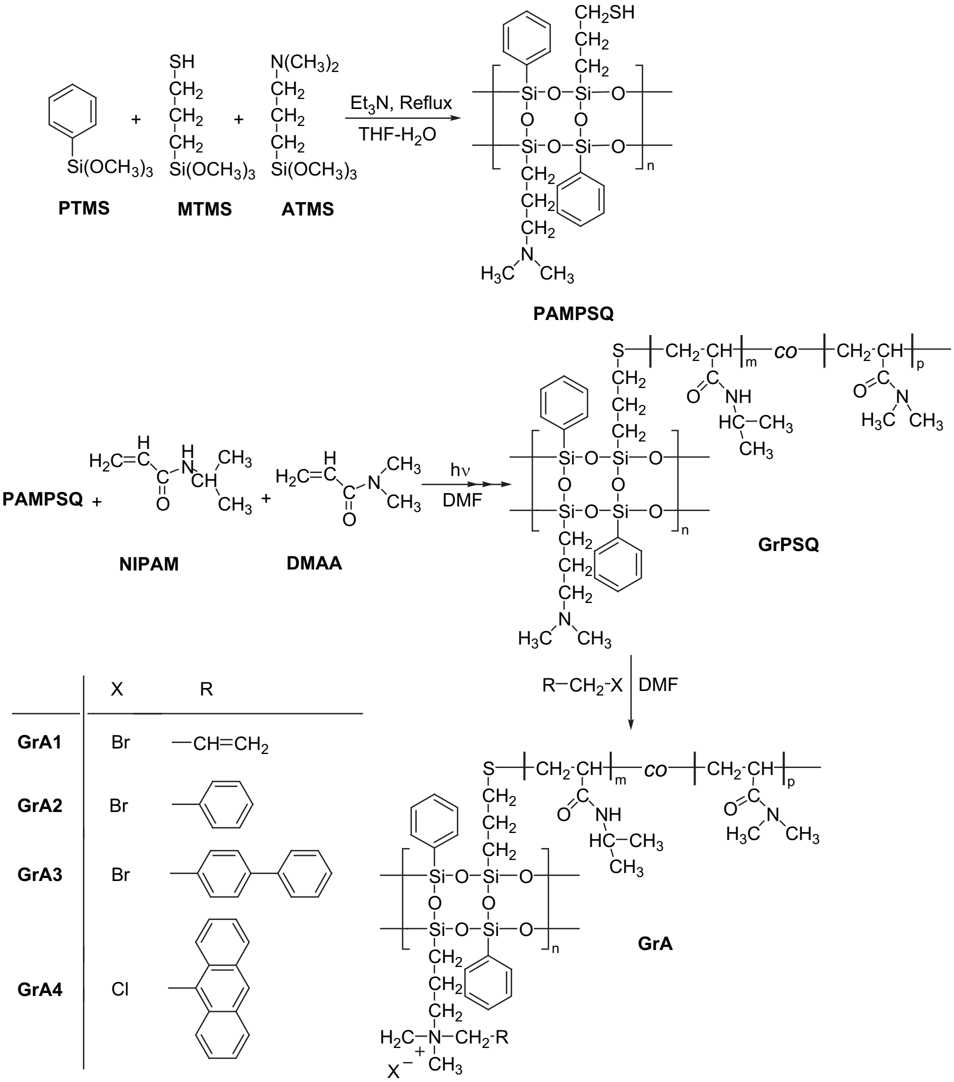
In the investigations concerning poly**NIPAM**, the copolymerization of the monomer having dimethylamino group with **NIPAM** is reported and presents pH sensitivity to the polymer [29,32−34]. From the interests in such reported property, the introduction of the basic group into the thermoresponsive polysiloxane derivative is successively studied. In the use of the polysilsesquioxane, the basic group can be easily introduced into both the graft chains through the copolymerization and the polymer backbone by choosing the starting silanes. In our studies, the latter introducing procedure is adopted to utilize the characteristic of polysilsesquioxanes. When the dimethylamino groups are located around the polysilsesquioxane backbone, they are also expected to affect on lower critical solution temperature (LCST) according to the pH value of aqueous solution. In addition, further modification by the use of the amino group via formation of salts with acids or halogen compounds is possible, which may have an influence on LCST.

In this work, the polysilsesquioxane having phenyl, mercapto, and dimethylaminopropyl groups (**PAMPSQ**) was newly prepared and employed for the grafting of the copolymer of **NIPAM** and **DMAA** (poly**NIPAM**-*co*-poly**DMAA**). Then, to obtain the information concerning the effects of the presence of dimethylaminopropyl group, the thermoresponsive behavior of the grafted polysilsesquioxane (**GrPSQ**) was examined under various conditions. The syntheses of these were shown in Scheme 1.

2. Experimental

2.1. General

^1H 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.



Scheme 1.

IR spectra were recorded on a Jasco FT/IR 230. Gel permeation chromatographic (GPC) analysis was carried out to estimate number-average molecular weight (M_n) and polydispersity (M_w/M_n) on a Shimadzu LC-10VP chromatograph equipped with an evaporative light scattering detector. Three columns such as Shim-pack GPC-80MD, -804D, and -802D were connected in series and *N*,*N*-dimethylformamide (DMF) was used as the eluent. Calibration was performed using poly(methyl methacrylate) standards. 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 comonomer **DMAA** was distilled over calcium hydride before use. Other reagents including phenyltrimethoxysilane (**PTMS**, TCI, 98% purity), (3-mercaptopropyl)-trimethoxysilane (**MTMS**, Chisso, 99% purity), and (3-dimethylaminopropyl)trimethoxysilane (**ATMS**, Gelest, 99% purity) were used as supplied from commercial sources.

2.2. Preparation of polysilsesquioxane (PAMPSQ)

PAMPSQ was prepared by the analogous method reported before [21]. A mixture of **PTMS** (8.00 g, 40.32 mmol), **MTMS** (3.90 g, 20.16 mmol), and **ATMS** (4.18 g, 20.16 mmol) with triethylamine (0.40 g, 4.00 mmol) in the mixed solvent of THF (80 ml) and water (20 ml) was refluxed for 48 h. The resulting solution was concentrated by a rotary evaporator under reduced pressure and, then, an excess amount of methanol was added to the residual oil. The solid that is insoluble in methanol was collected and dried at room temperature for 24 h in a vacuum oven under reduced pressure (<5 mmHg) to obtain **PAMPSQ** (6.70 g, 78% yield from **PTMS**, 70% yield from **MTMS**, and 78% from **ATMS**). The contents of phenyl, mercapto, and dimethylaminopropyl 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−C*H*$_2$−), 1.30 (br, −S*H*), 1.00−1.85 (br, −C*H*$_2$−), 2.25−3.00 (br, −S−C*H*$_2$−, −C*H*$_2$−N−C*H*$_3$), 6.50−7.80 (br m, −C$_6$*H*$_5$); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 12.1 (Si−CH$_2$−), 27.8 (−*C*H$_2$−SH, C−*C*H$_2$−C), 45.2 (−N−*C*H$_3$), 62.2 (−*C*H$_2$−N−), 127.8 (*p*-*C*$_6$H$_5$×3), 130.4 (*o*-*C*$_6$H$_5$×2), 133.9 (Si−*C*$_6$H$_5$); $M_n = 2000$; $M_w/M_n = 1.18$; phenyl unit = 4.65 mmol equiv/g; mercaptopropyl group = 2.11 mmol equiv/g; dimethylaminopropyl group = 2.33 mmol equiv/g.

2.3. Procedure for grafting onto PAMPSQ

A solution of **PAMPSQ** (2.00 g, 4.22 mmol equiv of mercapto group), **DMAA** (1.68 g, 16.9 mmol), and **NIPAM** (3.85 g, 34.0 mmol) in DMF (25 ml) was poured 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 8 h under argon atmosphere. The resulting solution was distilled under reduced pressure to concentrate and the residue was poured into an excess amount of diethyl ether. The insoluble part was dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the poly**NIPAM**-*co*-poly**DMAA** grafted polysilsesquioxane (**GrPSQ**) as a solid (5.55 g, 74% yield based on weight and 73% yield based on Si). The contents of phenyl, mercapto, dimethylaminopropyl groups and the monomer units in **GrPSQ** were calculated from the peak areas observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard; IR (KBr): 3304, 2972, 2933, 1645 (C=O), 1563, 1466, 1132, 798, 729 cm^{-1}; ^{1}H NMR (500 MHz, DMF-*d*$_7$): δ 0.70 (br, −CH$_2$−Si−), 1.00 (br m, −C*H*$_3$), 1.30−1.80 (br m, −C*H*$_2$−), 1.80−2.25 (br, (C=O)−C*H*−), 2.70−3.05 (br m, −S−C*H*$_2$−, −C*H*$_2$−N−C*H*$_3$, (C=O)−N−C*H*$_3$), 3.86 (br, −NH−C*H*−) 7.10−7.80 (br, −C$_6$*H*$_5$, −N*H*−); ^{13}C NMR (125 MHz, DMF−*d*$_7$): δ 22.6 (−*C*H$_3$), 35.7 (−*C*H$_2$−), 37.2 (−*C*H−), 41.2 (−N−*C*H$_3$), 42.3 (−N−*C*H$_3$), 45.1 (−N−*C*H−), 127.8 (−*C*$_6$H$_5$), 131.5 (−*C*$_6$H$_5$), 133.9 (−*C*$_6$H$_5$), 174.4 (−*C*=O); $M_n = 15{,}400$; $M_w/M_n = 1.44$; phenyl group = 1.23 mmol equiv/g; dimethylaminopropyl group = 0.62 mmol equiv/g; **DMAA** unit = 2.25 mmol equiv/g; **NIPAM** unit = 4.43 mmol equiv/g.

2.4. Typical procedure for preparation of quarternary ammonium salt

The solution of **GrPSQ** (0.50 g, 0.31 mmol equiv of dimethylaminopropyl group) and benzyl bromide (0.07 g, 0.41 mmol) in DMF (2 ml) was heated at 60 °C for 7 h under Ar atmosphere. The resulting solution was poured into a large amount of diethyl ether. The insoluble part was dried at room temperature for 24 h under reduced pressure (<5 mmHg) to obtain the derivative of **GrPSQ** having benzyl ammonium groups (**GrA2**) as a solid (0.52 g, >99% yield based on weight). The content of benzyl groups in **GrA2** was calculated from the peak area of the signal for the protons of methylene group bonded to benzene ring observed in ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard. In the calculation, the content of dimethylaminopropyl group was estimated from the proton ratio to **NIPAM** units, which was determined in the analysis of **GrPSQ**. Namely, the peak area due to the methine proton of **NIPAM** unit appeared at 3.86 ppm was employed as a standard; IR (KBr): 3299, 2971, 2933, 1644 (C=O), 1563, 1458, 1133, 729, 700 cm^{-1}; ^{1}H NMR (300 MHz, DMF-*d*$_7$): δ 0.70 (br, −CH$_2$−Si−), 1.00 (br m, −C*H*$_3$), 1.30−1.80 (br m, −C*H*$_2$−), 1.80−2.25 (br, (C=O)−C*H*−), 2.70−3.05 (br m, −S−C*H*$_2$−, −C*H*$_2$−N−C*H*$_3$, (C=O)−N−C*H*$_3$), 3.86 (br, −NH−C*H*−), 4.67 (br, −N−C*H*$_2$−Ph), 7.10−7.80 (br, −C$_6$*H*$_5$, −N*H*−); ^{13}C NMR (125 MHz, DMF-*d*$_7$): δ 22.5 (−*C*H$_3$), 35.4 (−*C*H$_2$−), 37.2 (−*C*H−), 41.2 (−N−*C*H$_3$), 42.3 (−N−*C*H$_3$), 45.1 (N*C*H−), 61.0 (−*C*H$_2$−N−Ph), 127.8 (−*C*$_6$H$_5$), 130.7 (−*C*$_6$H$_5$), 133.1 (−*C*$_6$H$_5$), 133.8 (−*C*$_6$H$_5$), 174.2 (−*C*=O); $M_n = 15{,}300$; $M_w/M_n = 1.25$; phenyl group = 1.24 mmol equiv/g (initial dimethylaminopropyl group = 0.62 mmol equiv/g); benzyl group = 0.61 mmol equiv/g; **NIPAM** unit = 4.43 mmol equiv/g.

Analogously, allyl bromide, 4-bromomethylbiphenyl, and 9-chloromethylanthracene were employed to give the corresponding allyl (**GrA1**), methylbiphenyl (**GrA3**), and methylanthracene ammonium derivative (**GrA4**). In the ^{1}H NMR spectrum of **GrA1**, the signals for the protons attached to carbon–carbon double bond were observed at 5.54 and 6.04 ppm. The peak area of these was utilized for the calculation of content of allyl groups. In the cases of **GrA3** and **GrA4**, the signals appeared at 4.83 and 5.85 ppm assigned to the protons of methylene group bonded to benzene ring were adopted for the calculations of the content, respectively. The results are listed in Table 1.

2.5. Measurement of transmittance (%T)

Solution of **GrPSQ** (1.0 wt%) 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 in %*T* were observed from a visible source at 600 nm through a 1 cm quartz sample cell at the rate of 1 °C/30 s during heating and cooling scans. The measurements were repeated three times on each sample, where the observed curves were in good agreement except for the cases of **GrPSQ** with none additive and **GrA4**.

Analogously, the measurements were conducted in the buffer solutions of pH = 4 containing phthalate salt and 7 containing phosphate salt. In addition, the aqueous solution of pH = 9.7 and 10.4 of **GrPSQ** was also employed for the measurement. In the former case, **GrPSQ** was dissolved in 1 M solution of sodium chloride (NaCl) as an additive and, in the latter case, pH value was adjusted by adding an appropriate amount of sodium hydroxide (NaOH). For the measurements containing ammonium salts, 2 equiv of the carboxylic acid such as formic acid (**GrS1**), acetic acid (**GrS2**), or benzoic acid (**GrS3**) to dimethylaminopropyl group were added to 1 wt% solution of **GrPSQ**, respectively. Furthermore, the measurements using **GrA**s containing quaternary ammonium salts were conducted for 1 wt% aqueous solution.

3. Results and discussion

3.1. Preparation of PAMPSQ from PTMS, MTMS, and ATMS

In our preliminary experiments, the condensation using only **MTMS** or **ATMS** under basic conditions gave the corresponding gel product. The co-condensation of **PTMS** with **MTMS** or **ATMS** afforded the polysilsesquioxane soluble in the organic solvents such as chloroform, dimethyl sulfoxide, and DMF. In the co-condensation, at least an equimolar amount of **PTMS** to **MTMS** or **ATMS** was required to avoid the formation of gel product. Therefore, in this work, the mole ratio of **PTMS/MTMS/ATMS** was adjusted to be 2/1/1. The co-condensation in the presence of 5 mol% of triethylamine to the total amount of the trimethoxysilanes proceeded effectively and afforded **PAMPSQ** as a solid insoluble in methanol in 78% yield based on the content of Si, which was estimated by the ^{1}H NMR analysis mentioned below.

The yield and the contents of phenyl, mercaptopropyl, and dimethylaminopropyl groups were estimated by the proton ratios observed in the ^{1}H NMR spectrum (Fig. 1). In the measurement, hexamethyldisiloxane was used as an internal standard, the signal of which appeared at 0 ppm. The signal assigned to the protons of methylene groups bonded to Si was appeared in the region from 0.55 to 0.80 ppm as a broad peak. Other protons showing the presences of $-CH_2-SH$ and $-CH_2-N(CH_3)_2$ were detected at around 2.5 ppm. The signals due to benzene ring were observed at around 7.6 ppm. The signals for estimating the content of mercapto and dimethylaminopropyl groups

Table 1
Preparation of **PAMPSQ**, **GrPSQ**, and **GrA**

Polysilsesquioxane	Feed mole ratio of trimethoxysilane **PTMS**:**APTS**:**MPTS**	Yield based on Si,[a] %	Functional group[a], Ph:N(CH_3)$_2$:SH, mmol equiv/g	M_n[b] (M_w/M_n)
PAMPSQ	1.0:0.5:0.5	78	4.65:2.33:2.11	2000 (1.18)
Polysilsesquioxane	Initial mole ratio of SH:**NIPAM**:**DMAA**	Yield based on Si,[a] %	Functional group[a], Ph:N(CH_3)$_2$:**NIPAM**:**DMAA**, mmol equiv/g	M_n[b] (M_w/M_n)
GrPSQ	1.0:8.0:4.0	73	1.23:0.62:4.43:2.15	15,400 (1.44)
Polysilsesquioxane	Introduced halogen compound	Conversion,[a] %	Content of ammonium salt[a], mmol equiv/g (pH[c])	M_n[b] (M_w/M_n)
GrA1	Allyl bromide	78	0.46 (8.0)	15,500 (1.34)
GrA2	Benzyl bromide	98	0.61 (8.0)	15,300 (1.25)
GrA3	4-Bromomethylbiphenyl	97	0.55 (7.7)	15,600 (1.25)
GrA4	9-Choromethylanthracene	83	0.53 (6.4)	15,700 (1.25)

[a] The Estimation was based on ^{1}H NMR spectral data (see Section 2).

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

[c] Aqueous solution of 1 wt% was used for the measurement at room temperature.

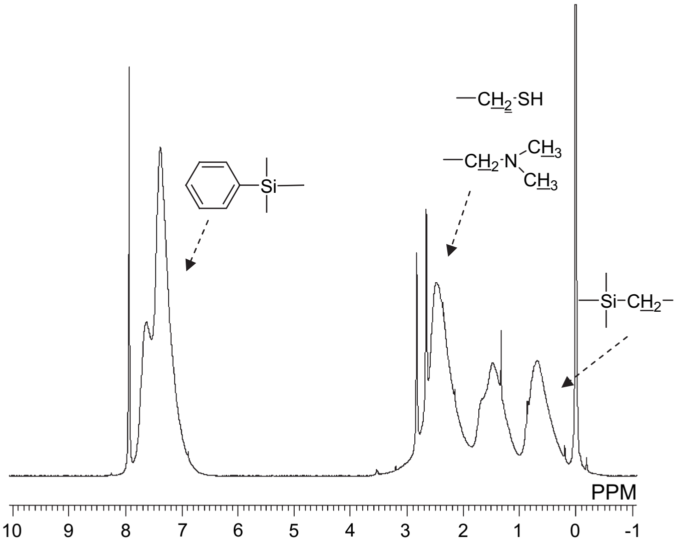


Fig. 1. ^{1}H NMR spectrum (DMF-d_7, 300 MHz) of **PAMPSQ** with hexamethyldisiloxane as an internal standard.

were appeared in the same region. Therefore, the contents of the groups were calculated from the both peak areas at around 0.7 and 2.5 ppm. The peak area based on the signal at 0.7 ppm should include two methylene protons of each mercaptopropyl and dimethylaminopropyl group bonded to Si. The signals at around 2.5 ppm were thought to include eight protons due to dimethylaminopropyl group and two protons of methylene attached to mercapto group. By taking the ratio of these protons into consideration, simultaneous equations on the peak area were solved. From the calculation, the contents of 2.33 mmol equiv/g of dimethylaminopropyl group and 2.11 mmol equiv/g of mercaptopropyl group were determined. The ratio of the groups containing in **PAMPSQ** was almost in accordance with that of the starting trimethoxysilanes. The estimated M_n and M_w/M_n of **PAMPSQ** by GPC were ca. 2000 and 1.18, respectively. The obtained **PAMPSQ** was soluble in chloroform, toluene, acetone, THF, and DMF, but insoluble in ^{n}hexane, methanol, and water. The structure of **PAMPSQ** was supposed to contain a ladder- and an incomplete cage-like polysiloxane, although these have been still unidentified.

3.2. Grafting by photopolymerization

In the previous report, the polysilsesquioxanes having poly**NIPAM**-*co*-poly**DMAA** as the graft chains were prepared under UV irradiation, in which the feed mole ratios of **NIPAM/DMAA** were changed to be 7/3, 5/5 and 3/7 [21]. These grafted polysilsesquioxanes showed good solubility and thermoresponsive phase separation in water. Among the grafted polysilsesquioxanes, the first example, containing almost double monomer units of **NIPAM** to **DMAA**, showed ca. 40 °C of LCST. The hydrophobic aggregation of the others in water occurred over 60 °C. Consequently, in this work, the monomer mole ratio of mercapto group/**NIPAM/DMAA** was adjusted to be 1/8/4 by considering the phase separation temperature, which was assumed to be close to the known LCST of poly**NIPAM** such as ca. 32 °C.

The graft polymerization onto **PAMPSQ** was carried out in DMF solution under UV irradiation using a 400 W high pressure mercury lamp at 18 °C for 8 h, in which the monomer concentration was adjusted to be 2 M. The polymerization proceeded effectively without the formation of gel product to give the grafted polysilsesquioxane **GrPSQ** in 74% yield which was based on the weight of the substrates. The estimated yield from the content of phenyl group was 73%, which was based on ^{1}H NMR spectral data and represented the content of polysilsesquioxane backbone in the product. The grafted product was soluble in water, methanol, acetone, and DMF, but insoluble in diethyl ether. In GPC measurement of **GrPSQ** using DMF as an eluent, the product showed a unimodal peak in the elution profiles. This indicated that the polymerization progressed primarily to form the grafted derivative of **PAMPSQ**. The M_n of **GrPSQ** was estimated to be 15,400. The estimated value was larger than the calculated one such as ca. 6600. Our speculation to explain the large value of M_n was that the grafted **GrPSQ** might form spherical structure and flow smoothly in a GPC column. However, we have no supporting data for the speculation and the reason has not been clarified.

The presence of the monomer units in **GrPSQ** was demonstrated in the spectral data. The IR spectrum of **GrPSQ** showed a strong absorbance at 1640 cm^{-1} due to carbonyl group of the grafted amide units. The absorbance at around 1100 cm^{-1} was assigned to silicon–oxygen bond of the polysiloxane backbone. In the ^{1}H NMR spectrum of **GrPSQ**, the signals due to the protons of methylene and methine groups were detected in the range from 1.2 to 1.8 ppm. The broad signal due to methylene protons attached to Si was slightly recognized at 0.6 ppm. Other signals due to methyl protons of dimethylamino group of **DMAA** unit and protons of benzene ring were appeared at around 3.0 and 7.2 ppm, respectively. The signal appeared at 3.86 ppm was assigned to the methine proton bonded to nitrogen of **NIPAM** unit. The each peak area of the signals at 3.0, 3.86, and 7.2 ppm was utilized for the calculation of the monomer unit content in the graft chains of **GrPSQ**. The spectral data of ^{1}H NMR demonstrated that the contents of the monomer units in **GrPSQ** reflected the feed mole ratios of **NIPAM** and **DMAA**. However, it was difficult to determine the accurate contents of dimethylaminopropyl group and **DMAA** unit from the corresponding signal area, since the broad signal involved the protons of methyl and methylene due to these and thioether groups. Consequently, the contents of dimethylaminopropyl and thioether groups were estimated on the basis of the peak area for phenyl group by taking the assumption that the mole ratios of these groups to phenyl group were same to those observed in the starting **PAMPSQ**. The calculations indicated that the mole ratios of **NIPAM** unit and **DMAA** unit to dimethylaminopropyl group were 7.2/1 and 3.6/1, respectively. However, these were rough estimations based on the overlapped signals in the ^{1}H NMR spectrum and accompanied with an error. The ^{1}H NMR spectrum of **GrPSQ** is shown in Fig. 2.

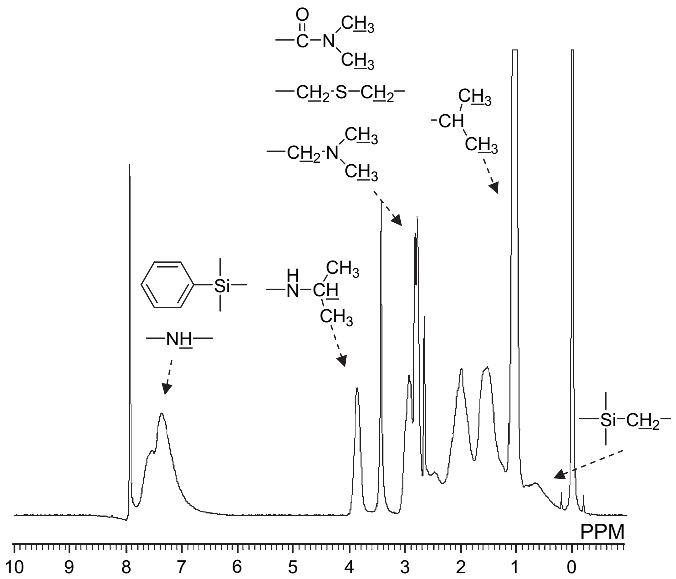


Fig. 2. ^{1}H NMR spectrum (DMF-d_7, 300 MHz) of **GrPSQ** with hexamethyldisiloxane as an internal standard.

^{13}C NMR spectrum of **GrPSQ** also supported the incorporations of the corresponding graft chains. The signals observed at 41.2, 42.3, and 45.1 ppm were assigned to the carbons of methyl and methine groups bonded to nitrogen of **DMAA** and **NIPAM** units. A slightly detected signal at 61.0 ppm was assigned to the methylene carbon bonded to nitrogen of dimethylaminopropyl group. In the spectral data, the grafting of poly**NIPAM**-*co*-poly**DMAA** was demonstrated, although no clear observation to confirm the presence of the dimethylaminopropyl and the thioether groups on polysilsesquioxane backbone could be presented. The existence of dimethylaminopropyl groups in **GrPSQ** was supported by the formation of quaternary ammonium salts and the behavior of thermoresponsive aggregation under various conditions as mentioned later.

3.3. Formation of quaternary ammonium salt

The formation of ammonium salt by the use of dimethylaminopropyl group seems to be a convenient procedure for introduction of various functional groups into **GrPSQ**. To demonstrate this, several simple halogen compounds, which gave the characteristic signals in the ^{1}H NMR spectra of the resulting products, were chosen and employed for the reaction with **GrPSQ**. The reaction of halogen compound with **GrPSQ** was carried out at 60 °C in DMF. The **GrA** containing quaternary ammonium salt moieties was isolated as an insoluble solid of diethyl ether.

The content of the introduced halogen compound was estimated from ^{1}H NMR spectral data similarly to those mentioned above (Fig. 3). In the ^{1}H NMR spectrum of **GrA1** obtained from **GrPSQ** and allyl bromide, the signals assigned to the protons at carbon–carbon double bond were observed at 5.54 and 6.04 ppm. The peak areas of these were used for the estimation of content of allyl group. In the calculation, the peak area of the signal appeared at 3.86 ppm due to **NIPAM** unit was utilized as a standard for determining the content of dimethylaminopropyl group before and after the formation of quaternary ammonium salt. The use of benzyl bromide, 4-bromomethylbiphenyl, and 9-chloromethylanthracene also gave the corresponding products having quaternary ammonium salts successfully. For the calculation of the content of these introduced halogen compounds, the signals due to methylene protons attached to benzene ring, which were observed in the region from 4.67 to 5.85 ppm, were available. These results of the preparations of **GrA**s including the M_ns estimated by GPC analyses and pH values of 1 wt% aqueous solution are listed in Table 1.

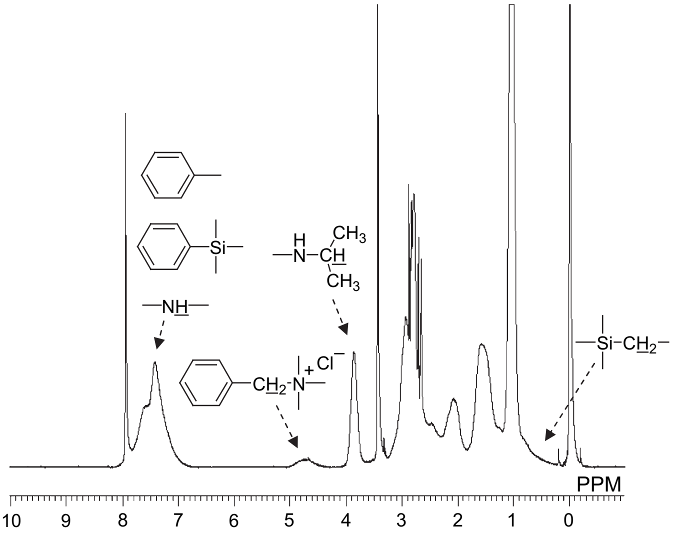


Fig. 3. ^{1}H NMR spectrum (DMF-d_7, 300 MHz) of **GrA2** with hexamethyldisiloxane as an internal standard.

3.4. Thermally reversible aggregation

The effects on LCST of poly**NIPAM** caused by the introduction of basic groups have been already presented in several works [29,32]. In these previous works, the copolymerization of **NIPAM** with the acrylate monomer having dimethylamino group is utilized and intended to afford thermo- and pH-responsive materials. On the other hand, dimethylaminopropyl groups were introduced into polysilsesquioxane backbone in our case. This meant that **GrPSQ** showed less content of the group compared to the reported ones. Furthermore, the groups were located near the polysiloxane main chain and might be covered with the graft chains. Consequently, the phase separation of **GrPSQ** in an aqueous solution was expected to show a different behavior from those observed in the previous works. To obtain the information on the behavior mentioned above, 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 was adjusted to be 1 °C/30 s. Such measurements were made at least three times for each sample mentioned here.

The phase separation of the aqueous solution of **GrPSQ** started at 37 °C and the aggregation was achieved at ca.

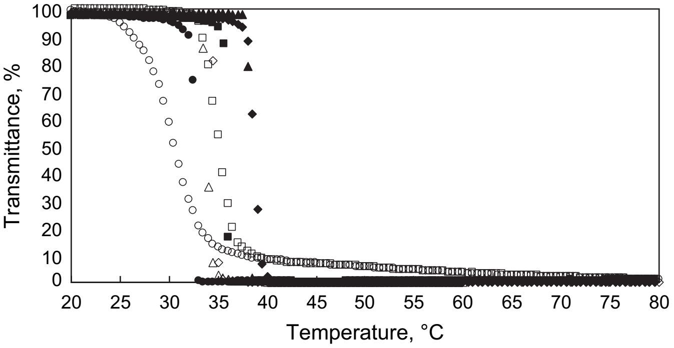


Fig. 4. Temperature dependence of optical transmittance (%*T*) at 600 nm for 1.0 wt% aqueous solution of **GrPSQ** under heating and cooling: at pH = 4, heating (●) and cooling (○); at pH = 7, heating (▲) and cooling (△); at pH = 9.5, heating (◆) and cooling (◇); at pH = 10.4, heating (■) and cooling (□).

40 °C under heating, in which pH value was 9.5, as shown in Fig. 4. In cooling, the transmittance began to increase at 35 °C and colorless solution was recovered at 33 °C. However, a small amount of insoluble solid was left in the aqueous solution. Namely, the incomplete reversible phase separation was observed in the case of **GrPSQ**. The spectral data such as ^{1}H NMR and IR of the recovered solid were similar to those of **GrPSQ**. The formed solid after cooling was soluble in DMF and precipitated from diethyl ether again. In the measurement using the recovered sample, the similar phase separation behavior was observed. Such results suggested that the conformation of **GrPSQ**, formed by the intra- and/or intermolecular hydrophobic aggregation, was unfavorable to be hydrated again. Such behavior was not observed on the grafted polysilsesquioxane reported before, which possessed the analogous graft chains but no dimethylaminopropyl group [21]. Therefore, the presence of dimethylaminopropyl groups on the polysiloxane backbone seemed to provide a relatively hydrophobic circumstance to retard re-hydration.

The phase separation behavior was examined in water containing the salt such as NaCl, phthalate, or phosphate, where **GrPSQ** was placed in more hydrophilic conditions. The 1 M aqueous solution of NaCl showed the pH value of 9.7 in the presence of **GrPSQ**. The pH values of phthalate and phosphate buffer solutions containing **GrPSQ** were 4.0 and 7.0, respectively. Further, 1 wt% aqueous solution of **GrPSQ** with an appropriate amount of NaOH, pH value of which showed 10.4, was also employed for the measurement. As shown in Fig. 4, the curve for the aggregation behavior of **GrPSQ** in phosphate buffer solution, showing 7.0 of pH value, was almost same to that in the simple aqueous solution. However, the phase separation in phosphate buffer solution was reversible and no insoluble solid was appeared. This was interpreted that the presence of the salt contributed to increase an affinity of **GrPSQ** to water. The addition of NaCl or NaOH was also effective for the complete reversible phase separation of **GrPSQ**. In these cases, the LCSTs were recorded in the almost same range from 36 to 38 °C. The reversible phase separation was also observed in the phthalate buffer solution of pH = 4 and the recorded LCST was 31 °C. The reason for the fall of LCST in this case has not been clarified. At least, the direct interaction of phthalate salt with dimethylaminopropyl groups in **GrPSQ** was excluded, because the presence of carboxylic acids and the formation of quarternary ammonium salts mentioned later resulted in a rise of LCST.

Next, the thermoresponsive aggregation was measured in the presence of three kinds of carboxylic acid, which were prospected to form the salts with dimethylaminopropyl groups in **GrPSQ**. The behaviors measured under heating conditions are shown in Fig. 5. No reverse profile was depicted here, but all the samples showed the reversible phase separation. In the aggregation of **GrPSQ** with 2 equiv of the acids to dimethylaminopropyl group, the LCSTs rose over 45 °C, in which pH values of the aqueous solutions were in the region of 3.3–4.8. The LCST of **GrPSQ** in phthalate buffer solution, showing the analogous pH value such as 4.0, was 31 °C. Consequently, such increases of LCSTs seemed to demonstrate the formation of salt, which should lead dimethylaminopropyl group to be more hydrophilic one. The introduction of hydrophilic units into poly**NIPAM** by copolymerization has been reported to bring about a rise in LCST [35–37]. These previous facts support our speculation concerning a hydrophilic effect caused by the formation of the salts. In addition, the change in the LCSTs according to a hydrophobic factor of the acid was expected. In the case of **GrS3** using benzoic acid, the transmittance could not reach 100% below the LCST. This demonstrated that the presence of benzoic acid changed **GrPSQ** somewhat hydrophobic and retarded to make a complete aqueous solution. On the other hand, in the aqueous solutions containing formic and acetic acid, **GrPSQ** could be dissolved completely. However, in the presence of formic, acetic, and benzoic acids, the corresponding LCSTs showed almost same values such as 47, 46, and 45 °C, respectively. The results indicated that the organic moiety of the acids affected on solubility of **GrPSQ** in water, but not on LCST.

The effects of the introduced organic moieties on thermoresponsive aggregation behavior were further examined for the derivatives of **GrPSQ** containing quarternary ammonium salts. All the derivatives, **GrA**s, could be dissolved in water readily. The pH values of 1 wt% aqueous solutions of **GrA**s

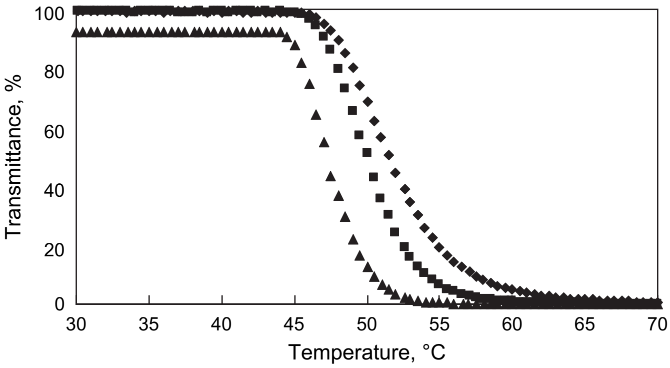


Fig. 5. Temperature dependence of optical transmittance (%*T*) at 600 nm for 1.0 wt% aqueous solution of **GrPSQ** in the presence of carboxylic acid under heating: **GrS1**, formic acid at pH = 3.2 (◆); **GrS2**, acetic acid at pH = 4.4 (■); **GrS3**, benzoic acid at pH = 4.8 (▲).

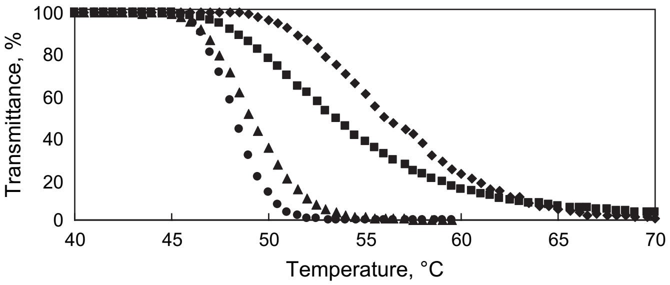


Fig. 6. Temperature dependence of optical transmittance (*%T*) at 600 nm for 1.0 wt% aqueous solution of **GrA** under heating: **GrA1** at pH = 8.0 (▲); **GrA2** at pH = 8.0 (●); **GrA3** at pH = 7.7 (■); **GrA4** at pH = 6.4 (◆).

were in the range from 6.4 to 8.0. The behaviors according to temperature under heating conditions are shown in Fig. 6. In the measurements of **GrA1**, **GrA2**, and **GrA3**, having allyl, benzyl, methylbiphenyl moieties, respectively, showed the reversible aggregation behavior. Whereas, in the case of **GrA4** containing anthracenyl moiety, a small amount of insoluble solid in water was found after a cycle of heating and cooling. The solid was soluble in DMF. This was the same phenomenon to that observed in the aqueous solution of **GrPSQ** with none additive. Namely, the presence of methylanthracene group seemed to induce a hydrophobic circumstance around the polysiloxane backbone and retard the hydration to dissolve **GrA4** again in water. However, such hydrophobic property had no influence on the aggregation temperature as mentioned in the cases using the carboxylic acids. The LCSTs of the aqueous solutions of **GrA1−3** showed the same value such as 47 °C. The LCST of **GrA4**, which was thought to be in more hydrophobic conditions, was 49 °C.

The pH values indicated that the aqueous solutions of **GrA**s were almost neutral and those of **GrS**s, added 2 equiv of the acid to dimethylaminopropyl group, were in acidic conditions. However, the LCSTs of **GrA**s and **GrS**s were in the same temperature range. In other words, the similar LCSTs irrespective of pH values were shown by the formation of the salt moieties from dimethylaminopropyl group with the carboxylic acids and the halogen compounds.

The temperature sensitivity of the aggregation, which was indicated by the temperature width for the change of the phase from solution to complete gel formation, depended on the situation of dimethylamino group. In the measurements of thermoresponsivity of **GrPSQ**, the change in the phase was accomplished within ca. 4 °C, as shown in Fig. 4. When the salts were formed as shown in the cases of **GrS**s and **GrA**s, a fall of sensitivities was observed. The curves depicted in Fig. 5 indicated that the temperature width for complete aggregation of **GrS1** under heating was 11 °C. In the presence of benzoic acid, the sensitivity of **GrS3** was rather improved and the temperature width was 5.5 °C. The formation of the quarternary ammonium salts also led to an inferior sensitivity as shown in Fig. 6. The phase separation of **GrA2**, the salt of benzyl bromide, required the temperature width of 6 °C. Such results seem to be explained by the hydrophilic effects caused by the formation of ammonium salts, which is unfavorable for the hydrophobic aggregation of **NIPAM** units. While, the better sensitivities within 4 °C were found in the cases using **GrPSQ** with the additives or in buffer solutions. This suggested that the ability of dimethylaminopropyl groups, located around the polysilsesquioxane backbone, for changing a hydrophobic circumstance to a hydrophilic one was limited, but the groups had the potential to change the circumstance through the formation of salt. In addition, it may be said that the presence of the additives such as NaCl, phthalate salt, phosphate salt, or NaOH essentially improves a hydrophilic property of the graft chains, but not that of dimethylaminopropyl group.

4. Conclusion

The polysilsesquioxane containing phenyl, dimethylaminopropyl, and mercaptopropyl groups was employed for the grafting of thermoresponsive poly**NIPAM**-*co*-poly**DMAA** to afford a new functional organic−inorganic hybrid material. The results demonstrated that the effective graft polymerization by the use of mercapto group under photopolymerization conditions proceeded to give the polysilsesquioxane having dimethylaminopropyl groups and thermoresponsive graft chains without formation of cross-linked product. By the grafting, the property of thermally reversible aggregation was provided to the polysilsesquioxane, but not a pH responsive property, which was presumed to be given by the presence of the basic dimethylaminopropyl groups. However, the dimethylaminopropyl group still possessed the ability to form various salts by the combination with carboxylic acids and halogen compounds. In addition, as shown in the changes of LCST, the basic groups bonded to the polysilsesquioxane backbone contributed to bring about a hydrophilic circumstance by transforming into the salt. Thus, the polysilsesquioxane having dimethylaminopropyl groups and thermoresponsive graft chains was demonstrated to be usable as a multi-functional intermediary material for incorporating the additional organic groups, which was accompanied with the change in the hydrophilic property and thermoresponsive behavior.

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] Roy DA, Shea KJ. Chem Rev 1995;95:1409.
[5] Mao L, Kagi D. J Mater Sci 1996;31:3185.
[6] Kondo T, Yoshi K, Horie K, Itoh M. Macromolecules 2000;33:3650.
[7] Lee J-K, Char K, Rhee H-W, Ro HW, Yoo DY, Yoon D. Polymer 2001; 42:9085.
[8] Yamamoto S, Yasuda N, Ueyama A, Adachi H, Ishikawa M. Macromolecules 2004;37:2778.
[9] Gozdz A. Polym Adv Technol 1993;5:70.
[10] Tanaka T, Morita M, Onose K. Jpn J Appl Phys 1985;24:L112.
[11] Chang C-L, Ma C-CM. J Polym Sci Part A Polym Chem 2003;41:1371.
[12] Krishnan PSG, He C. Macromol Chem Phys 2003;204:531.
[13] Pyun J, Matyjaszewski K. Chem Mater 2001;13:3436.
[14] Kim K-M, Keum D-K, Chujo Y. Macromolecules 2003;36:867.
[15] Cardoen G, Coughlin EB. Macromolecules 2004;37:5123.

[16] Fu BX, Lee A, Haddad TS. Macromolecules 2004;37:5211.
[17] Ohno K, Sugiyama S, Koh K, Tsujii Y, Fukuda T, Yamahiro M, et al. Macromolecules 2004;37:8517.
[18] Moriya O, Yamamoto S, Kumon S, Kageyama T, Kimura A, Sugizaki T. Chem Lett 2004;33:224.
[19] Sugizaki T, Kashio M, Kimura A, Yamamoto S, Moriya O. J Polym Sci Part A Polym Chem 2004;42:4212.
[20] Yamamoto S, Shimada T, Kimura A, Sugizaki T, Moriya O. Polym J 2004;36:761.
[21] Moriya O, Kuga M, Yamamoto S, Kashio M, Kamejima A, Sugizaki T. Polymer 2006;47:1837.
[22] Guillet JE. J Macromol Sci Chem 1968;A2:1441.
[23] Fujishige S, Kubota K, Ando I. J Phys Chem 1989;93:3311.
[24] Chen GH, Hoffman AS. Nature 1995;373:49.
[25] Pelton RH. Adv Colloid Interface Sci 2000;85:1.
[26] Ray B, Isobe Y, Matsumoto K, Habaue S, Okamoto Y, Kamigaito M, et al. Macromolecules 2004;37:1702.
[27] Meyer S, Richtering W. Macromolecules 2005;38:1517.
[28] Kim KS, Vincent B. Polymer 2005;37:565.
[29] Huh KM, Hashi J, Ooya T, Yui N. Macromol Chem Phys 2000;201:613.
[30] Anthonietti M, Főrster S, Hartmann J, Oestreich S. Macromolecules 1996;29:3800.
[31] Sciborek M, Gladkova NK, Chojnowski J. Polym Bull 2000;44:377.
[32] Yusa S, Shimada Y, Mitsukami Y, Yamamoto T, Marishima Y. Macromolecules 2004;37:7507.
[33] Mitsukami Y, Donovan MS, Lowe AB, McComick CL. Macromolecules 2001;34:2248.
[34] Liu S, Weaver JVM, Tang Y, Billingham NC, Armes SP, Tribe K. Macromolecules 2002;35:6121.
[35] Yoshida R, Sakai K, Okano T, Sakurai Y. J Biomater Sci Polym Edn 1994;6:585.
[36] Kaneko Y, Nakamura S, Sakai K, Kikuchi A, Aoyagi T, Sakurai Y, et al. J Biomater Sci Polym Edn 1999;10:1079.
[37] Tian J, Seery TAP, Weiss RA. Macromolecules 2004;37:9994.