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ORIGINAL ARTICLE

Graft polymerization of acrylamide monomers from polysilsesquioxane containing xanthate groups

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Polysilsesquioxanes (PSQs) containing 4-chloromethylphenyl groups were prepared and used for introducing ethylxanthate groups. The obtained PSQs that contained benzyl xanthate structures (XAPSQs) were employed as macroinitiators for grafting acrylamide monomers. The use of XAPSQs for the radical polymerization with acryloylmorpholine (ACMO), *N,N*-dimethylacrylamide (DMAA) or *N*-isopropylacrylamide enabled the preparation of the respective grafted PSQ, in which no cross-linked product was formed. The results of the graft polymerizations from XAPSQs supported the interpretation that the reversible addition-fragmentation chain transfer polymerization progressed effectively using the technique known as macromolecular design via the interchange of xanthate. The introduction of polymerized ACMO and DMAA units provided an amphiphilic property to the grafted PSQ. In addition, the PSQs containing poly(ACMO) components showed reversible hydrophobic aggregation behavior at approximately 80°C in aqueous solution.
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Keywords: acryloylmorpholine; MADIX; polysilsesquioxane; thermoresponsive hybrid; xanthate

INTRODUCTION

Recently, various investigations examining the modifications of oligomeric and polymeric silsesquioxanes with organic functional groups have been presented as a result of interest in their use as a hybrid material.[1–12] The graft polymerization from the silsesquioxane backbone is an effective method for transforming the silsesquioxanes into practical and useful materials.[13–20] Grafted silsesquioxanes are expected to show functions based on the incorporated polymeric components without losing the essential properties of the inorganic polysiloxane structure, such as durability against heat and weatherability. With the regard to this expectation, we also tried to develop new multifunctional hybrid materials using acrylamide monomers by the graft polymerizations from polysilsesquioxane (PSQ).[21–26] In fact, the graftings of polymeric *N,N*-dimethylacrylamide (DMAA) and *N*-isopropylacrylamide (NIPAM) successfully produced amphiphilic and thermoresponsive PSQs.[23,24] For the graft polymerizations, the reversible addition-fragmentation chain transfer (RAFT) process was utilized, in which the *N,N*-dimethyldithiocarbamate (DTC) group was chosen as the chain transfer species.[24] The use of the DTC group was appropriate for designing the sequence and number of monomer units of the graft chains that were the important factors for extending grafted PSQ to a high performance hybrid material. However, in a few examples, the formation of a small amount of by-product that showed unexpectedly high number average molecular weights (M_ns) was observed. This observation has led us to continue trials to find appropriate chain transfer species that enable finely designed grafting from the PSQ backbone.

Additionally, polymeric compounds containing acryloylmorpholine (ACMO) units have been thoroughly investigated as useful amphiphilic materials in the fields of medical devices, absorbents, pigments and others.[27–30] From the previous findings, the combination of the polymeric component with the inorganic PSQ backbone is believed to form a useful hybrid material. For the efficient polymerization of acrylamide monomers, the use of the xanthate group has been attracting recent attention in the RAFT process as the so-called macromolecular design via the interchange of xanthate (MADIX).[31-35] The reported examples have indicated that the RAFT/MADIX process is possibly a versatile and useful technique for enabling the controlled graft polymerization from the PSQ backbone. On the basis of this information and the continuous interests in the efficient incorporation of polymeric acrylamide components into the PSQ backbone, the graft polymerization of ACMO with DMAA, and NIPAM from the PSQ backbone is examined in this work. For the graft polymerization, the ethylxanthate group was utilized rather than the DTC group as the chain transfer species. Furthermore, during the incorporation of the monomer units into the PSQ backbone, which provided amphiphilic properties as a result, the PSQ grafted ACMO units showed thermoresponsive aggregation behavior in an aqueous solution. Therefore, as the second objective of this study, the

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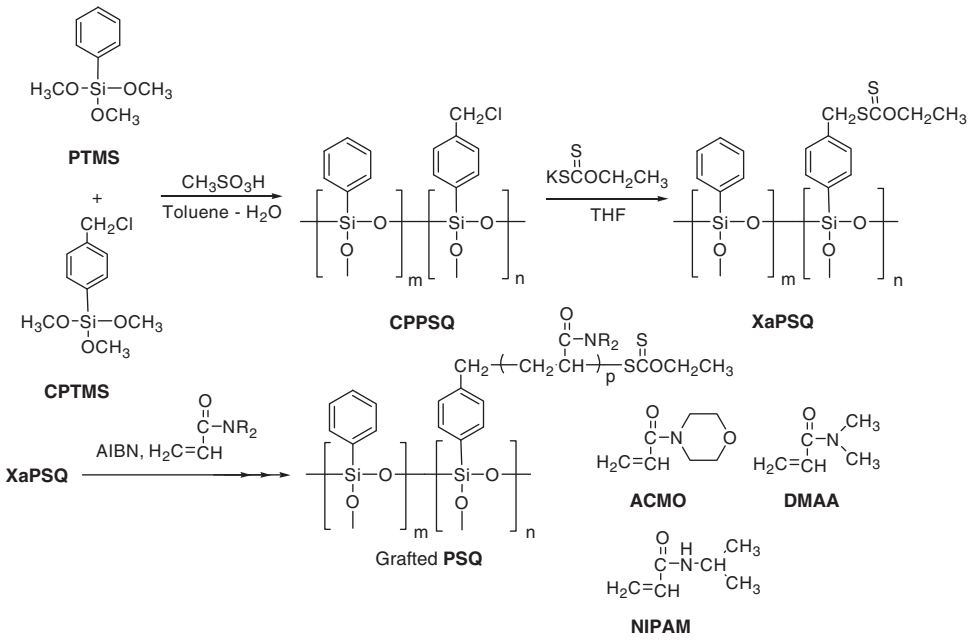

Figure 1 Synthesis of grafted PSQ.

thermoresponsive properties of the resulting PSQs were also evaluated. The synthetic route from the PSQ containing ethylxanthate groups (XAPSQs) to the grafted PSQs is shown in Figure 1.

EXPERIMENTAL PROCEDURE

General

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance500 spectrometer (Bruker Biospin, Rheinstetten, Germany), in $CDCl_3$ or DMF-d_7. IR spectra were recorded on a Perkin Elmer FT-IR 1600 (Perkin Elmer, Waltham, MA, USA). Gel permeation chromatographic (GPC) analysis was performed to estimate the M_n and polydispersity (M_w/M_n) on a TOSOH HLC-8320 chromatograph equipped with UV and RI detectors. Three columns, including TSK gel SuperHM-H and SuperH2000, were connected in series and *N,N*-dimethylformamide (DMF) was used as an eluent. Calibration was performed using poly(styrene) standards.

Toluene (Kanto Chemical, Tokyo, Japan, 99.5%), anisole (Kanto Chemical, 99.0%) and tetrahydrofurane (THF; Kanto Chemical, 99.5%) were refluxed over sodium metal before use. NIPAM (Tokyo Chemical Industry, Tokyo, Japan, 98.0%) was recrystallized from a mixed solvent of benzene and *n*hexane. DMF (Kanto Chemical, 99.7%), ACMO (Kohjin, Tokyo, Japan, 98.0%) and DMAA (Tokyo Chemical Industry, 97.0%) were distilled over calcium hydride before use. *N,N′*-Azobisisobutyronitrile (AIBN, Wako Pure Chemicals, Tokyo, Japan, 98.0%) was recrystallized from methanol. Methanol (Kanto Chemical, 99.8%), *n*hexane (Kanto Chemical, 96.0%), methanesulfonic acid (Tokyo Chemical Industry, 99.0%), 4-(chloromethyl)phenyltrimethoxysilane (CPTMS, Azmax, Chiba, Japan, 98%), phenyltrimethoxysilane (PTMS, Azmax, 98%) and potassium ethylxanthate (Tokyo Chemical Industry, 90.0%) were used as supplied from commercial sources.

Preparation of CPPSQ

CPPSQ was produced from the corresponding silane-coupling reagents using the previously reported modified method.[22] CPTMS (12.30 g, 49.84 mmol), PTMS (9.91 g, 49.98 mmol) and methanesulfonic acid (0.48 g, 5.00 mmol) were added to the mixed solvent of toluene (100 ml) and water (50 ml). The solution was stirred at ambient temperature for 16 h and then distilled under reduced pressure to remove the solvents. An excess amount of *n*hexane was added to the residual viscous oil. The resulting solid was filtered and washed several times with *n*hexane. The solid was dried under reduced pressure (<5 mm Hg) for 24 h to obtain CPPSQ1 (12.50 g). The chloromethylphenyl group content and yield were calculated from the corresponding peak areas from the protons of the methylene group of the benzyl structure and benzene ring observed in the ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard. The CPPSQ1 yield was estimated to be 90%, which was based on the content of the chloromethylphenyl group; IR (KBr) 3393 (weak, OH), 3050 (weak, –C_6H_4–), 1497 (medium), 1398 (medium), 1269 (medium), 1130 (strong, Si-O), 911 (medium), 704 (medium) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.59 (br, Cl–$\underline{C}H_2$–C_6H_4–), 6.50–7.80 (br m, –$C_6\underline{H}_4$–, –$C_6\underline{H}_5$); ^{13}C NMR ($CDCl_3$) δ 46.5 (Cl–$\underline{C}H_2$–C_6H_4–),128.8 (–$\underline{C}_6H_4$–, –$\underline{C}_6H_5$), 135.2 (–$\underline{C}_6H_4$–, –$\underline{C}_6H_5$); chloromethylphenyl group = 3.57 mmol equiv. per g, phenyl group = 3.80 mmol equiv. per g, M_n = 3500, M_w/M_n = 1.76.

Analogously, CPPSQ2 was prepared using only CPTMS. The yield of CPPSQ2 was 90%, which was based on the content of the chloromethylphenyl group: chloromethylphenyl group = 6.01 mmol equiv. per g, M_n = 4400, M_w/M_n = 1.80.

Preparation of the polysilsesquioxane containing ethylxanthate groups (XAPSQ)

A solution of CPPSQ1 (5.64 g, chloromethylphenyl group: 20.13 mmol equiv.) and potassium ethylxanthate (3.23 g, 20.15 mmol) in THF (50 ml) was stirred at ambient temperature for 20 h. After filtration of precipitated solid, the filtrate was evaporated under reduced pressure and then the residue was diluted with methanol. The precipitated product was collected and washed with water and methanol. The resulting solid was dried at room temperature for 24 h in a vacuum oven under reduced pressure (<5 mm Hg) to obtain XAPSQ1 (5.24 g, 73% based on xanthate group). The xanthate group content was calculated from the peak areas observed in the ^{1}H NMR spectrum, in which hexamethyldisiloxane was used as an internal standard: IR (KBr) 3630 (weak, OH), 3050 (weak, C_6H_5), 2981 (weak, CH_3), 1604 (medium), 1430 (medium), 1397 (medium), 1221 (medium, S–C), 1130 (strong, Si–O), 1049 (strong), 699 (medium) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (br, –$\underline{C}H_3$), 4.30 (br,

Table 1 Preparation of grafted polysilsesquioxane[a]

XaPSQ	Monomer (molar ratio of monomer/xanthate group	Solvent	Temperature °C	Product (Yield[b], %)	M_n (M_w/M_n) × 10^4 GPC[c]	M_n (M_w/M_n) × 10^4 Calcd.[d]
XAPSQ1	ACMO (20)	Anisole	60	GrMP1 (95)	3.4 (1.61)	3.0
XAPSQ1	ACMO (20)	THF	60	GrMP2 (95)	1.3 (2.01)	2.2
XAPSQ1	ACMO (20)	DMF	60	GrMP3 (99)	2.0 (1.84)	2.2
XAPSQ1	ACMO (10)	Anisole	60	GrMP4 (91)	1.3 (1.59)	1.2
XAPSQ1	ACMO (40)	Anisole	60	GrMP5 (98)	3.6 (1.89)	4.0
XAPSQ1	ACMO (20)	Anisole	80	GrMP6 (98)	3.0 (1.62)	3.0
XAPSQ1	ACMO (20)	Anisole	110	GrMP7 (98)	3.0 (1.65)	3.0
XAPSQ2	ACMO (20)	Anisole	60	GrMP8 (98)	5.1 (1.94)	5.0
XAPSQ1	DMAA (20)	Anisole	60	GrDA (92)	1.9 (1.37)	1.6
XAPSQ1	NIPAM (20)	Anisole	60	GrNI (98)	2.6 (1.70)	1.8
——[e]	ACMO (20)	Anisole	60	FPMP (98)	22.5 (2.55)	——

[a]The polymerization was carried out with 11 mol% of AIBN to xanthate group for 8 h, in which the concentration of the monomer was adjusted to be 3.3[M].
[b]The yield was based on the weights of the substrates.
[c]Estimated by GPC with poly(styrene) standards, in which THF was used as an eluent.
[d]Calculation was based on the content of the XAPSQ and the monomer unit, which were estimated from the ^{1}H NMR spectral data.
[e]The polymerization was carried out without XAPSQ.

–O–C$\underline{H}_2$–), 4.63 (br, –C$\underline{H}_2$–C_6H_4–), 6.40–7.70 (br m, –$C_6\underline{H}_4$–, –$C_6\underline{H}_5$); ^{13}C NMR (DMSO-d_6) δ 13.9 (–$\underline{C}H_3$), 40.4 (–$\underline{C}H_2$–C_6H_4–), 70.2 (–O–$\underline{C}H_2$–), 127.8, 128.4, 130.3, 134.2 (–$\underline{C}_6H_4$–, –$\underline{C}_6H_5$), 213.9 (-$\underline{C}$=S); xanthate group = 2.79 mmol equiv. per g; M_n = 3600, M_w/M_n = 1.56.

Analogously, the reaction of CPPSQ2 with potassium ethylxanthate produced XAPSQ2 (81% based on xanthate group): xanthate group = 3.74 mmol equiv. per g, M_n = 4700, M_w/M_n = 1.90.

Typical procedure for grafting from XAPSQ

A solution of XAPSQ1 (0.39 g, 1.09 mmol equiv. of xanthate group), ACMO (2.82 g, 19.98 mmol) and AIBN (0.02 g, 0.12 mmol) in anisole (6.0 ml) was introduced into a glass tube. The mixture was purged of air using three vacuum-argon cycles. Then, the mixture in the glass tube was heated at 60 °C for 8 h under an argon atmosphere. The resulting solution was poured into diethyl ether. The insoluble solid was collected and dried at room temperature for 24 h under reduced pressure (<5 mm Hg) to obtain the poly(ACMO) grafted PSQ (2.57 g, 95% yield based on weight, GrMP1): IR (KBr) 3511, 2964, 2921, 2857, 1640 (C=O), 1444, 1115, 1031, 700 cm^{-1}; ^{1}H NMR (DMF-d_7) δ1.30–1.80 (br m, –C$\underline{H}_2$–), 2.50–2.70 (br, –(C=O)–C$\underline{H}$–), 3.20-3.80 (br m, –N–C$\underline{H}_2$–C$\underline{H}_2$–O–), 4.65 (br, –C$\underline{H}_2$–$C_6\underline{H}_4$–), 6.80–7.70 (br, –$C_6\underline{H}_4$–); ^{13}C NMR (DMF-d_7) δ 17.5 (–$\underline{C}H_3$), 35.4 (–C$\underline{H}_2$–), 36.1 (–C$\underline{H}$–), 42.6, 46.3 (–N–C$\underline{H}_2$–), 67.0 (–O–C$\underline{H}_2$–), 72.5 (–C(=S)O–C$\underline{H}_2$–), 128.7, 134.4 (–$\underline{C}_6H_4$–), 173.4 (–$\underline{C}$=O); 214.0 (–$\underline{C}$=S). M_n = 34 000, M_w/M_n = 1.61.

Analogously, the graft polymerizations of DMAA or NIPAM from XAPSQs were performed. The spectral data of the PSQs containing poly(DMAA) or poly(NIPAM) were in agreement with our previous data.[23] The results and the conditions of the graft polymerizations are listed in Table 1.

Measurement of transmittance in water for thermoresponsive property

A 1.0-wt% solution of the poly(ACMO) grafted PSQ in distilled water, obtained from EYELA SA-2100 A (Tokyo Rikakikai, Tokyo, Japan), was used for the measurement of transmittance (%T) on a Shimadzu UV-1650 spectrophotometer equipped with a Peltier-type S-1700 thermostatic cell holder. The changes in %T were observed by a visible source at 800 nm through a 1-cm quartz sample cell during heating and cooling scans. The heating and cooling rate was adjusted to 1 °C per 1 min. The heating and cooling cycle was repeated three times per sample, in which similar curves indicating the thermoresponsive behavior were observed.

RESULTS AND DISCUSSION

Preparation of XAPSQ

Two types of CPPSQ that were used as the precursors of the macroinitiators, XAPSQs, were prepared from the condensation of the corresponding trimethoxysilanes with 5 mol% of metanesulfonic acid in the mixed solvents of toluene and water at ambient temperature. CPPSQ1 that contained phenyl and chloromethylphenyl groups was prepared from PTMS and CPTMS by co-condensation, where an equivalent amount of the silane-coupling reagents were employed. The molar ratio of the phenyl group to the chloromethylphenyl group in the resulting CPPSQ1 was almost the same as the feed mole ratio of the silane-coupling reagents. Analogously, CPPSQ2, which contained a sole chloromethylphenyl group as the organic substituent, was prepared by condensation using CPTMS. Next, the reaction of CPPSQs with potassium ethylxanthate was performed to produce XAPSQs at ambient temperature in a solution of THF. The substitution reaction proceeded effectively to produce the PSQs containing ethylxanthate groups as insoluble solids in methanol.

The contents of xanthate group were estimated by the proton ratios observed in the ^{1}H NMR spectrum. During the measurements, hexamethyldisiloxane was used as an internal standard, the signal of which appeared at 0.03 p.p.m. The spectrum of XAPSQ1 is shown in Figure 2. The signal from the protons of the methylene group bonded to the benzene ring was observed at 4.59 and 4.63 p.p.m., respectively, in the spectra of CPPSQ1 and XAPSQ1. In the XAPSQ spectra, the signals from the methyl and methylene protons of the xanthate group were observed at 1.38 and 4.30 p.p.m., respectively. The broad signals appearing between 6.40 and 7.80 p.p.m. were assigned to the protons of the benzene rings that were commonly contained in CPPSQs and XAPSQs. These signal areas were employed for the calculation of the contents of the phenyl and xanthate groups. The ratios of the peak areas assigned to the benzene protons and methyl protons of the xanthate group were almost in agreement with those of the benzene and methylene protons of the starting CPPSQs. The analytical information indicated that almost all of the chloromethyl groups in CPPSQ were converted to introduce xanthate groups.

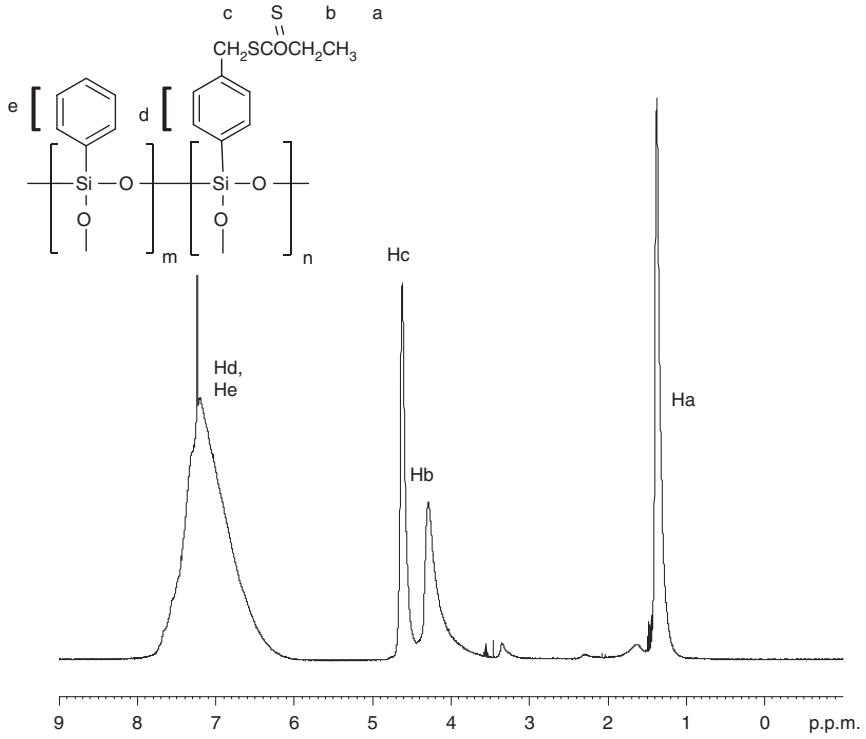

Figure 2 ^{1}H NMR spectrum of XAPSQ1.

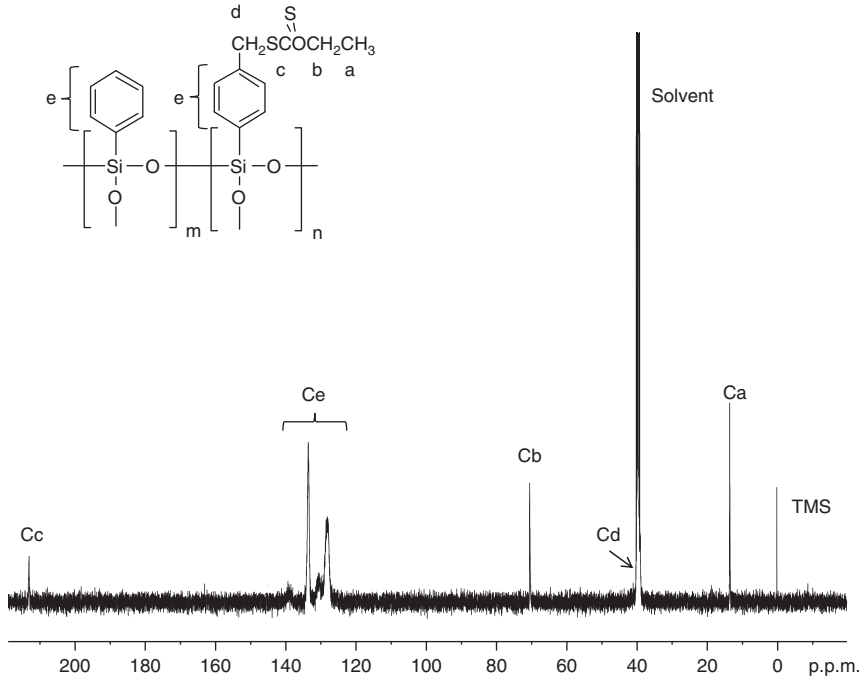

Figure 3 ^{13}C NMR spectrum of XAPSQ1.

Other spectral data, such as ^{13}C NMR and IR, also supported the formation of XAPSQs. In the IR spectra of XAPSQs, the presence of a silicon–oxygen bond was indicated by the strong absorbance at 1120 cm^{-1}. The absorbance at ca. 1050 cm^{-1} seemed to show the presence of a thiocarbonyl group. In the ^{13}C NMR spectrum of XAPSQs, the carbon of the introduced methyl group was detected at 13.9 p.p.m. The methylene carbon attached to the ester bond was observed at 70.2 p.p.m. The signal that appeared at 213.9 p.p.m. was

assigned to the carbon of thiocarbonyl group. As an example, the ^{13}C NMR spectrum of XAPSQ1 is shown in Figure 3. The M_n and M_w/M_n of the CPPSQs and XAPSQs were estimated using GPC, in which DMF was used as an eluent with poly(styrene) standards. During the transformation of CPPSQ1 into XAPSQ1, M_n slightly increased from 3500 to 3600 after the introduction of xanthate groups. Similarly, the M_n of CPPSQ2 changed from 4400 to 4700 in the case of XAPSQ2. The obtained CPPSQs and XAPSQs were soluble in chloroform, acetone, THF and DMF, but insoluble in ^{n}hexane and methanol. The spectral data and solubility in the usual organic solvents seemed to indicate that the obtained CPPSQs and XAPSQs were constructed by incomplete ladder- and cage-like polysiloxane structures, but not, at least, by a randomly cross-linked structure.[22]

The introduction of the xanthate group could be readily achieved using a simple substitution reaction with benzylchloride structures in the CPPSQs. In addition, the signals of the methylene and methyl protons from this group were distinguishable in the ^1H NMR spectrum of the grafted product. This observation means that the xanthate group was a convenient chain transfer species for our intended grafting procedure.

Graft polymerization of acrylamide from XAPSQ

The graft polymerization of ACMO from ethylxanthate groups in XAPSQ1 was performed per several different conditions, where the polymerization was expected to proceed through the RAFT/MADIX process. The concentration of the monomer was fixed to be ca. 3[M] in the solution and the amount of AIBN was adjusted to be approximately 10 mol% to xanthate group for the polymerization. The results from the preliminary experiments conducted at 60 °C showed that approximately 20 equivalents of ACMO to the xanthate group were consumed within 6 h. Consequently, the polymerization time for the grafting from XAPSQs was set to 8 h. The results are listed in Table 1.

From the polymerizations conducted in different solvents such as anisole, THF and DMF, the grafted PSQs were obtained with high yields, over 95%, and no cross-linked product was detected. The M_n and the M_w/M_n of the grafted PSQ (GrMP1) obtained in the anisole solution were 34 000 and 1.61, respectively. The M_n was close to the calculated value of 30 000, which was based on the content of the monomer unit shown in the ^1H NMR spectral data. The expected M_n estimated from the feed molar ratio of ACMO to the xanthate group, such as 20, was 32 000. This similarly demonstrated that the grafting proceeded almost quantitatively. From the polymerizations conducted in THF and DMF, the number of the incorporated monomer units was quite smaller and the values of M_w/M_n were larger (GrMP2 and GrMP3). From the calculated M_n of 20 000, approximately 12 monomer units to one initiator species were speculated to be grafted from the PSQ backbone during those polymerizations. Generally, the M_ns should increase with the feed mole ratio of ACMO in the initiating species. In fact, the M_n of the grafted PSQ (GrMP4) that was intended to introduce 10 equivalents of ACMO units to xanthate group was 13 000. This amount was close to 18 000 of the estimated value based on the feed mole ratio. However, when 40 equivalents of ACMO were employed, the estimated M_n of the resulting PSQ (GrMP5) by GPC was 36 000. This result suggested that half amount of ACMO was polymerized and grafted. However, the M_w/M_ns of the obtained grafted PSQs were in the range of 1.59 to 1.89, which were reasonable in comparison with 1.56 of the XAPSQ. Furthermore, the graftings were performed at raised temperatures of 80 and 110 °C (GrMP6 and GrMP7). The results indicated that no obvious effect of temperature on the M_n and M_w/M_n was observed. During the use of XAPSQ2, which contained one ethylxanthate group in each silsesquioxane unit, the graft polymerization also proceeded efficiently to produce the grafted PSQ (GrMP8). The observed M_n of GrMP8 was 51 000. During the use of XAPSQ2, the expected M_ns based on the feed mole ratio of ACMO to the xanthate group and on the ^1H NMR spectral data were 54 000 and 50 000, respectively. The M_w/M_n of 1.94 of GrMP8 became slightly larger compared to 1.90 of XAPSQ2. In addition, the free radical polymerization without the PSQ macroinitiator was performed to obtain poly(ACMO) (FPMP). The M_n and M_w/M_n of the resulting FPMP became large values, such as 225 000 and 2.55. The results indicated that the presence of XAPSQs as the macroinitiators controlled the polymerization of ACMO.

The molar ratios of the xanthate group to the monomer units in the graft chain were based on ^1H NMR spectral data. As an example, the ^1H NMR spectrum of GrMP1 is shown in Figure 4. The broad signal that was assigned to the protons of the methylene group bonded to the benzene ring was detected at 4.65 p.p.m. The signals from the protons of the benzene ring, which demonstrated the presence of the PSQ backbone, appeared in the region 6.80–7.70 p.p.m. Furthermore, the signal area of the benzene protons was utilized for calculating the content of the benzyl structure on the PSQ backbone. The shoulder signal that appeared at 1.35 p.p.m. seemed to be assigned to the methyl protons of the ethylxanthate group. Methylene and methine protons of the polymerized ACMO monomer unit were exemplified by broad signals that appeared approximately 1.55 and 2.60 p.p.m. The signals from other methylene protons that are attached to nitrogen and oxygen were observed in the region 3.20–3.80 p.p.m. The calculated M_ns of the PSQs grafted poly(ACMO) were based on the ratios of those signal areas. The estimated ratios were almost in agreement with the proposed ones based on the feed mole ratios of the substrates, except for the case of GrMP5 as mentioned above.

The ^{13}C NMR spectrum of the poly(ACMO) grafted PSQs also supported the incorporation of the grafted chains. In the spectrum of GrMP1 shown in Figure 5, the signals observed at 35.4 and 36.1 p.p.m. from the methylene carbon and methine carbon demonstrate the presence of the main chain of the polymerized ACMO unit. Other signals at 42.3, 46.3 and 67.0 p.p.m. were assigned to the carbons of the methylene of morpholine ring. Although the signals that showed the presence of the PSQ backbone were difficult to observed clearly, the signals from the benzene ring were observed approximately at 130 p.p.m. The signal observed at 173.4 p.p.m. was assigned to the carbonyl carbon of the amide bond. Furthermore, the presence of monomer units in the grafted PSQs was supported by the IR spectra. In the spectra, a strong absorbance band at 1640 cm^{-1} due to the carbonyl group of the amide bond and at approximately 1100 cm^{-1} assigned to the silicon–oxygen bond of the polysiloxane backbone were clearly observed. Under the same conditions used for the grafting of poly(ACMO), poly(DMAA) and poly(NIPAM) were effectively grafted from XAPSQ1 (GrDA and GrNI). During those graft polymerizations, no formation of cross-linked product was observed. The spectral data were almost in agreement with those presented in our previous report.[23] Furthermore, in the GPC chromatograms for the grafted PSQs, an unimodal peak was observed without any unexpected peaks. As an example, the chromatograms of XAPSQ1 and GrMP1 are shown in Figure 6.

The results mentioned above showed that the xanthate group on PSQ was an effective chain transfer species during the RAFT/MADIX process and enabled the controlled grafting of the acrylamide

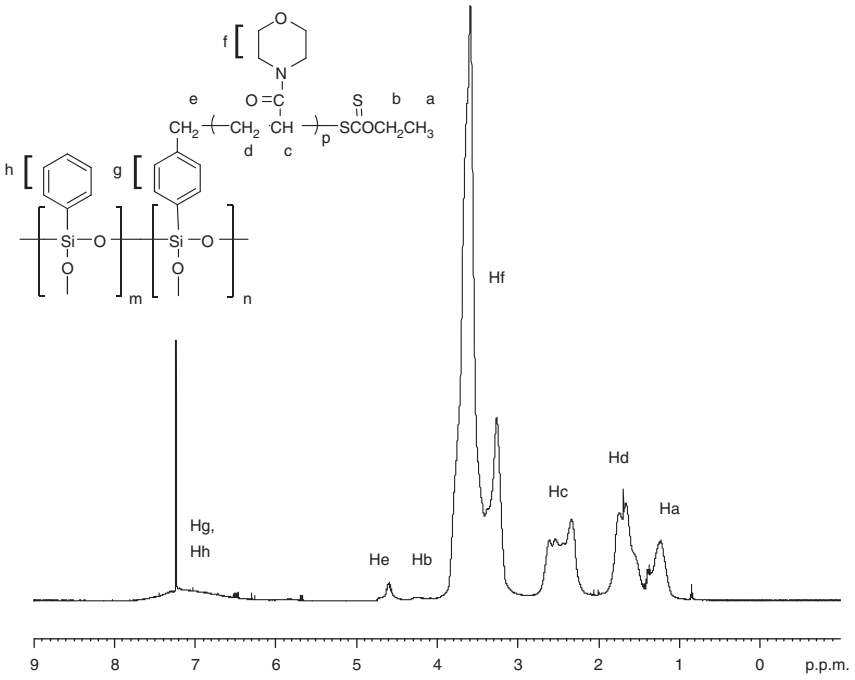

Figure 4 ^{1}H NMR spectrum of GrMP1.

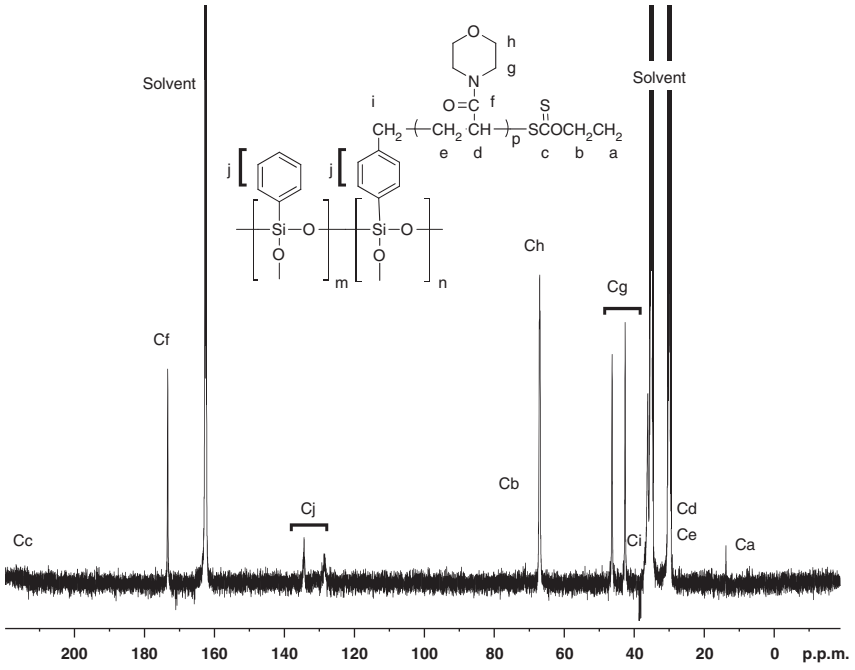

Figure 5 ^{13}C NMR spectrum of GrMP1.

polymers. In previous work, DTC group was employed as the chain transfer species for the grafting of NIPAM and DMAA.[23] During the use of DTC, a few GPC chromatograms showed the formation of a small amount of by-product, which showed an unexpectedly higher M_n. In comparison with the previous phenomenon, the xanthate group is thought to be a preferable chain transfer species for the fine control of the graft polymerization from the PSQ backbone, although the case using the larger molar ratio of ACMO to the xanthate group, such as 40 equivalents, may show a limitation of the designed polymerization. The observation of controlled polymerization also suggested that the terminating process through the coupling reaction between the radical species of the chain ends was effectively retrained by

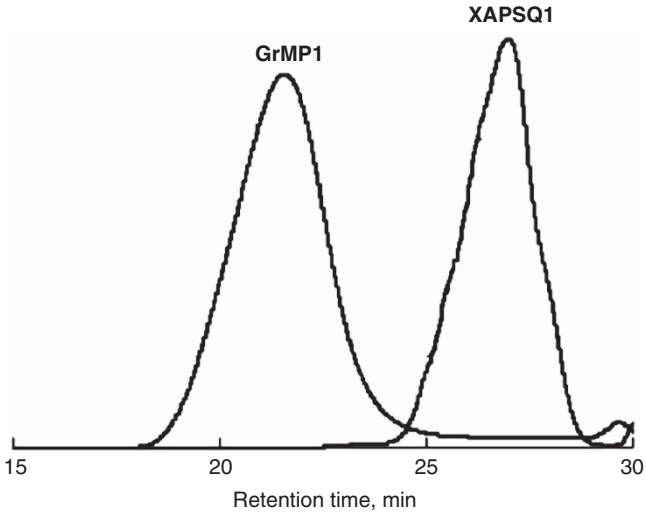

Figure 6 GPC chromatograms of XAPSQ1 and GrMP1.

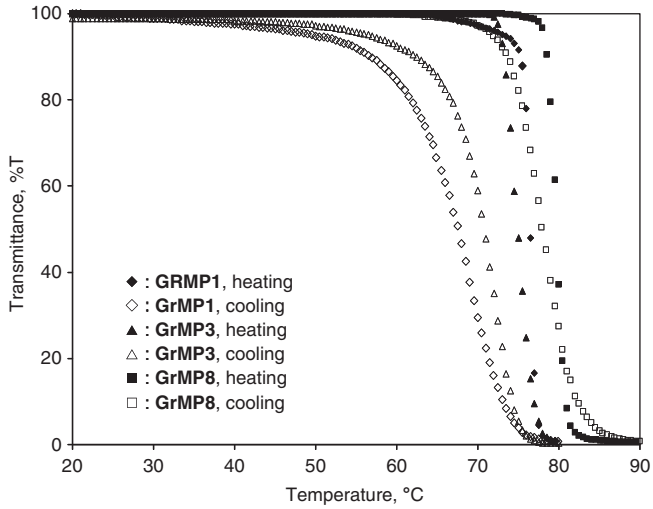

Figure 7 Temperature dependence of %T at 800 nm for a 1-wt% aqueous solution of the grafted PSQs under heating and cooling (1 °C per min).

a temporary bond formation with the xanthate group. This observation seems to result in no formation of cross-linked by-products.

Thermoresponsive property of the PSQ containing poly(ACMO)

The introduction of polymeric ACMO and DMAA was an effective procedure to transform the hydrophobic PSQ to the amphiphilic hybrid. Similarly, poly(NIPAM) is known to show an amphiphilc property. However, the PSQ designed to contain ca. 20 NIPAM monomer units to one xanthate initiator species exhibited insufficient solubility in water. Our previous examinations showed that the grafting of approximately 30 equivalents of NIPAM to one initiator species was required to obtain the amphiphilic PSQ and to measure the thermoresponsive aggregation behavior in a 1-wt% aqueous solution.[23] Therefore, in this study, the thermoresponsive behavior was examined on PSQs containing poly(ACMO) or poly(DMAA) components, which have been scarcely reported as being thermoresponsive materials. The examinations were performed by measuring the turbidity indicated as %T at 800 nm under heating and cooling at a rate of 1 °C per min.

The PSQs grafted with poly(ACMO) showed reversible phase separation behavior, whereas those containing poly(DMAA) did not show lowest critical solution temperature (LCST) under 90 °C. The behaviors caused by the presence of the poly(ACMO) component are depicted in Figure 7. In the 1-wt% aqueous solution of GrMP1, which contained approximately 20 monomer units of ACMO to one benzyl structure as the grafted chain and showed an M_n of 34 000, the phase separation started at 65 °C and reached 0%T at approximately 78 °C under heating. Under cooling, the transmittance began to increase at 77 °C and a transparent solution was recovered at 45 °C. The aggregation of GrMP3, with an M_n of 20 000, showed a LCST at 72 °C. In comparison with the grafted PSQs obtained from XAPSQ1, GrMP8, which contained a poly(ACMO) component in each silsesquioxane unit, showed a relatively good responsive property to temperature. The aggregation began at 78 °C and recorded 100%T at 82 °C. Under cooling, the change in the transmittance from 0%T to 100%T was reached within 17 °C. However, poly(ACMO) without the PSQ structure, FPMP, did not show LCST under 90 °C, which reflected a good hydrophilic property. The results suggested that the combination of poly(ACMO) with a benzyl structure and/or xanthate group presented the thermoresponsive property. Namely, the balance of the hydrophilic poly(ACMO) grafted chain with the hydrophobic benzene ring and/or ethylxanthate group contributed to the appearance of this property. The observation of lower LCSTs in the cases of GrMP1 and GrMP3 suggested that the presence of the hydrophobic phenyl groups, in addition to the benzyl structure, also affected the temperature to enhance the hydrophobic aggregation. The somewhat high LCST of GrMP8, which only contained a benzyl xanthate structure and lacked hydrophobic phenyl groups, seemed to be explained by the above-mentioned speculation. Therefore, the PSQ with grafted poly(ACMO) was found to present thermoresponsive reversible aggregation in aqueous solution, although the LCST was higher than the usually reported temperatures that are favorable for medical usages.

CONCLUSIONS

An ethylxanthate group on the PSQ backbone was utilized for the grafting of polymeric acrylamides using the RAFT process. The results demonstrated that the effective graft polymerization using the xanthate group under thermal-polymerization conditions proceeded without the formation of cross-linked product. Through the use of the grafting procedure called MADIX, the PSQs incorporated the designed number of monomer units into the grafted chains and showed reasonable M_n values. The graft polymerization resulted in the efficient preparation of amphiphilic organic–inorganic hybrids based on the PSQ structure. In addition, the PSQ containing poly(ACMO) graft chain was found to show thermoresponsive properties in aqueous solution. The observed LCST was approximately 80 °C, which was higher compared with the temperatures that usually attract attention.[36–40] This property may make the direct utilization of PSQ difficult in the medical fields. However, combination with a hydrophobic PSQ unit or copolymerization with the monomer, which shows appropriate hydrophobic properties, seems to enable control of the LCST depending on the purpose.

Further applications of the RAFT/MADIX process for developing a new adhesive material containing the PSQ structure with designed block copolymers as the graft chains have been continued, and the results will be presented elsewhere.

1 Baney, R. H. & Cao, X. *In Silicon-Containing Polymers* (eds Johns, R.G., Ando, W. & Chojnowski, J.) (Kluwer, Dordrecht, 2000).
2 Sprung, M. M. & Guenther, F. O. The hydrolysis of n-amyltriethoxysilane and phenyltrimethoxysilane. *J. Polym. Sci.* **28,** 17–34 (1958).
3 Brown, Jr J. F., Vogt, Jr L. H., Katchman, A., Eustance, J. W., Kaiser, K. M. & Krantz, K. W. Double chain polymers of phenylsilsesquioxane. *J. Am. Chem. Soc.* **82,** 6194–6195 (1960).
4 Roy, D. A. & Shea, K. J. Bridged polysilsesquioxanes. Highly porous hybrid organic-inorganic materials. *Chem. Rev.* **95,** 1431–1442 (1995).
5 Lee, J-K., Char, K., Rhee, H-W., Ro, H. W., Y. Yoo, D. & Yoon, D. Synthetic control of molecular weight and microstructure of processible poly(methylsilsesquioxane)s for low-dielectric thin film applications. *Polymer* **42,** 9085–9089 (2001).
6 Chang, C-L. & Ma, C-C. M. Synthesis, characterization, and properties of novel ladderlike phosphorus-containing polysilsesquioxanes. *J. Polym. Sci. Part A* **41,** 1371–1379 (2003).
7 Yamamoto, S., Yasuda, N., Ueyama, A., Adachi, H. & Ishikawa, M. Mechanism for the formation of poly(phenylsilsesquioxane). *Macromolecules* **37,** 2775–2778 (2004).
8 Gunji, T., Iizuka, Y., Arimitsu, K. & Abe, Y. Preparation and properties of alkoxy (methyl)silsesquioxanes as coating agents. *J. Polym. Sci. Part A* **42,** 3676–3684 (2004).
9 Khiterer, M., Loy, D. A., Cornelius, C. J., Fujimoto, C. H., Small, J. H., Mcintire, T. M. & Shea, K. J. Hybrid polyelectrolyte materials for fuel cell applications: design, synthesis, and evaluation of proton-conducting bridged polysilsesquioxane. *Chem. Mater.* **18,** 3665–3673 (2006).
10 Fina, A., Tabuani, D. & Camio, G. Polypropylene-polysilsesquioxane blends. *Euro. Polym. J.* **46,** 14–23 (2010).
11 Qin, Y., Ren, H., Zhu, F., Zhang, L., Shang, C., Wei, Z. & Luo, M. Preparation of POSS-based organic-inorganic hybrid mesoporous materials networks through shiff base chemistry. *Euro. Polym. J.* **47,** 853–860 (2011).
12 Chuang, W-P., Sheen, Y-C., Weit, S-M., Teng, C-C., Yen, M-Y. & Ma, C-C. M. Phase segregation polymethylsilsesquioxane in antireflection coatings. *Macromolecules* **44,** 4872–4878 (2011).
13 Pyun, J. & Matyjaszewski, K. Synthesis of nanocomposite organic/inorganic hybrid materials using controlled/"living" radical polymerization. *Chem. Mater* **13,** 3436–3448 (2001).
14 Kim, K-M., Keum, D-K. & Chujo, Y. Organic-inorganic polymer hybrids using polyoxazoline initiated by functionalized silsesquioxane. *Macromolecules* **36,** 867–875 (2003).
15 Fu, B. X., Lee, A. & Haddad, T. S. Styrene-butadiene-styrene triblock copolymers modified with polyhedral oligomeric silsesquioxanes. *Macromolecules* **37,** 5211–5218 (2004).
16 Kessler, D., Teutsch, C. & Theato, P. Synthesis of processable inorganic-organic hybrid polymers based on poly(silsesquioxanes): grafting from polymerization using ATRP. *Langmuir* **209,** 1437–1446 (2008).
17 Wang, R., Wang, W-Z., Lu, S. & Liu, T. Controlled radical synthesis of fluorene-based blue-light-emitting coplymer nanospheres with core-shell structure via assembly. *Macromol. Chem. Phys* **42,** 4993–5000 (2009).
18 Belon, C., Chemtob, A., Crouyxé-Barghorn, C., Righholet, S., Le Houérou, V. & Gauthier, C. Combination of radical and cationic photoprocesses for the single-step synthesis of inorganic hybrid films. *J. Polym. Sci. Part A* **48,** 4150–4158 (2010).
19 Yoshitake, H., Nakajima, H., Oumi, Y. & Sano, T. Control of spacing between aminoalkyl functions by mesostructural transition in a polysilsesquioxane lamellar assembly. *J. Mater. Chem.* **20,** 2024–2032 (2010).
20 Chaikittisilp, W., Kubo, M., Moteki, T., Sugawara-Narutaki, A., Shimojima, A. & Okubo, T. Porous siloxane-organic hybrid with ultrahigh surface area through simultaneous polymerization-destruction of functionalized cubic siloxane cages. *J. Am. Chem. Soc.* **133,** 13832–13835 (2011).
21 Moriya, O., Yamamoto, S., Kumon, S., Kageyama, T., Kimura, A. & Sugizaki, T. Synthesis of graft copolymer from polysilsesquioxane initiated by photoiniferter. *Chem. Lett.* **33,** 224–225 (2004).
22 Sugizaki, T., Kashio, M., Kimura, A., Yamamoto, S. & Moriya, O. Graft polymerization of polysilsesquioxane containing chloromethylphenyl groups by atom transfer radical polymerization. *J. Polym. Sci. Part A* **42,** 4212–4221 (2004).
23 Masuda, T., Yamamoto, S., Moriya, O., Kashio, M. & Sugizaki, T. Preparation of amphiphilic polysilsesquioxane by grafting of block copolymer of acrylamide monomers. *Polym. J.* **39,** 220–229 (2007).
24 Masuda, T., Yamamoto, S., Moriya, O., Kashio, M. & Sugizaki, T. Preparation of stimuli-responsive polysilsesquioxane grafted block copolymer of acrylamide monomers. *Polym. J.* **40,** 126–136 (2008).
25 Kashio, M., Sugizaki, T., Yamamoto, S., Matsuoa, T. & Moriya, O. Ring-opening polymerization of ε-caprolactone by base catalyst for synthesis of grafted polysilsesquioxane. *Polymer* **49,** 3250–3255 (2008).
26 Kashio, M., Sugizaki, T., Tanaka, Y., Yamamoto, S., Moriya, O. & Nishikubo, T. Synthesis of grafted polysilsesquioxane by ring-opening polymerization of lactide and trimethylene carbonate. *Polym. J.* **43,** 525–530 (2011).
27 Ninomiya, A. & Yoshimura, H. Synthesis and photosensitivity of acryloylmorpholine copolymers with a pendant (meth)acryloyl group. *J. Appl. Polym. Sci.* **87,** 684–692.
28 Rivas, B. L., Villegas, S. & Ruf, B. Water-insoluble polymers containing amine, sulfonic acid, and carboxylic acid groups: synthesis, characterization, and metal-ion-retention properties. *J. Appl. Polym. Sci.* **99,** 3266–3274.
29 Jo, Y. S., van der Vlies, A. J., Gantz, J., Antonijevie, S., Demurtas, D., Velluto, D. & Hubell, J. A. RAFT homo- and copolymerization of n-acryloyl-morpholine, piperidine, and azocane and their self-assembled structures. *Macromolecules* **41,** 1140–1150 (2008).
30 Takahashi, A. & Hisatomi, H. Hydrophilic monomers surpress the adsorption of plasma protein onto a poly(vinylidene fluoride) membrane. *Mol. Med. Rep* **2,** 749–752 (2009).
31 Chiefari, J., Chong, Y. K., Ercole, F., Krstina, J., Jeffery, J., Le, T. P. T., Mayadunne, R. T. A., Meijs, G. F., Moad, C. L., Moad, G., Rizzardo, E. & Thang, S. H. Living free-radical polymerization by reversible addition-fragmentation chain transfer: the raft process. *Macromolecules* **31,** 5559–5562 (1998).
32 Charmot, D., Corpart, P., Adam, H., Zard, S. Z., Biadatti, T. & Bouhadir, G. Controlled radical polymerization in dispersed media. *Macromol. Sym* **150,** 23–32 (2000).
33 Perrier, S. & Takolpuckdee, P. Macromolecular design via reversible addition-fragmentation chain transfer (raft)/xanthates (madix) polymerization. *J. Polym. Sci, Part A: Polym. Chem* **43,** 5347–5393 (2005).
34 Smith, A. E., Xu, X. & McCormick, C. L. Stimuli-responsive amphiphilic (co)polymers via RAFT polymerization. *Prog. Polym. Sci.* **35,** 45–93 (2010).
35 Beija, M., Marty, J. -D. & Destarac, M. RAFT/MADIX polymers for the preparation of polymer/inorganic nanohybrids. *Prog. Polym. Sci.* **36,** 845–886 (2011).
36 Chen, G. H. & Hoffman, A. S. Graft copolymers that exhibit temperature-induced phase transitions over a wide range of pH. *Nature* **373,** 49–52 (1995).
37 Kikuchi, A. & Okano, T. Pulsatile drug release control using hydrogels. *Adv. Drug. Deliver. Rev* **54,** 53–77 (2002).
38 Sugihara, S., Kanaoka, S. & Aoshima, S. Double thermosensitive diblock copolymers of vinyl ethers with pendant oxyethylene groups: unique physical gelation. *Macromolecules* **38,** 1919–1927 (2005).
39 Meyer, S. & Richtering, W. Influence of polymerization conditions on the structure of temperature sensitive poly(N-iso-propylacrylamid) (PNiPAM) microgels. *Macromolecules* **38,** 1517–1519 (2005).
40 Skrabania, K., Kristen, J., Laschewsky, A., Akdemir, O., Hoth, A. & Lutz., J-F. Design, synthesis, and aqueous aggregation behavior of nonionic single and multiple thermoresponsive polymers. *Langmuir* **23,** 84–93 (2007).