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Amphiphilic Telechelics Incorporating Polyhedral Oligosilsesquioxane: 1. Synthesis and Characterization

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ABSTRACT: Well-defined amphiphilic telechelics incorporating polyhedral oligosilsesquioxane (POSS) were synthesized by direct urethane linkage between the diol end groups of poly(ethylene glycol) (PEG) homopolymers and the monoisocyanate group of POSS macromers. The hydrophobicity of the amphiphilic telechelics was varied by using a series of PEG homopolymers of increasing molecular weight, resulting in control over molecular architecture by hydrophilic/hydrophobic balance. The synthesized amphiphilic telechelics were characterized by ^{1}H NMR, FT-IR, GPC, DSC, and TGA, showed a relatively narrow and unimodal molecular weight distribution ($M_w/M_n < 1.1$) that had close to 2.0 end groups per PEG chain, and revealed strongly modified thermal behavior. Amphiphilic telechelics with POSS contents of 19.8, 23.6, 40.7, 52.7, and 68.1% depending on the molecular weights of PEG homopolymers could be obtained. Modification to crystallization behavior is observed and attributed to the bulkiness of POSS groups with respect to crystalline lamellae dimensions.

Introduction

In general, when amphiphilic block copolymers are dissolved in a solvent that is selective for only one of the blocks, nanosized aggregates can form due to the self-assembly of the less soluble segment. The term “water-soluble associating polymer” is given to those polymers constituted by a hydrophilic skeleton that bears some hydrophobic groups either randomly distributed along the chain (grafted or comblike) or fixed at one or two extremities (telechelic).[1] Telechelic polymers are linear chains containing associating “sticker” groups only at the chain ends and are analogous to the triblock copolymers.[2] The difference is in the shortness of the aliphatic “tail” group compared to the block size of typical triblocks. A telechelic polymer, therefore, bears features of both surfactants and block copolymers; it contains two surfactant-sized hydrophobic groups attached to a polymer-sized hydrophilic one. Telechelic polymers developed to date are most often based on poly(ethylene oxide) (PEO). Hydrophobic groups can be either aliphatic (with a number of methylene units ranging from 8 to 20), aromatic, or fluorinated.[3−6] Such novel architectures lead to significant alteration of solution properties, often with water as solvent. In particular, it is well-known that aqueous solutions exhibit shear-thickening and shear-thinning behaviors because hydrophobic groups associate pairwise or into larger nanodomains, which act as temporary cross-links or chain extensions.[7−12] Such self-assembly behavior of block copolymers and of hydrophobically modified polymers has been extensively studied as a building block approach to the processing of nanostructured materials beginning at the molecular level.[13−16]

Recently, Eisenberg et al. described[17−20] several morphologies found in crew-cut aggregates made from two families of diblock copolymers, polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) and polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO), in dilute solution. As the soluble PAA or PEO blocks are made progressively shorter, the morphology of the aggregates changes from spherical to rodlike to lamellar or vesicular and finally to large compound vesicles (LCVs) and large compound micelles (LCMs). Winnik et al. reported[2−4,10] the synthesis, characterization, and rheological behavior of a concentration series of PEG end-capped with hydrophobic fluorocarbon groups. Using an approach similar to the present work, Frey et al. reported[21] the synthesis and first data on the aggregation of silsesquioxane-based amphiphiles: the cubic-shaped spherosilsesquioxane, 1-(1,ω-propylenemethoxy)oligo(ethylene oxide)-3,4,7,9,-11,13,15-heptahydridopentacyclo[9.5.1$^{3.9}$.1$^{5.15}$.1$^{7.13}$]-octasiloxane. However, these silsesquioxane-based amphiphiles were monosubstituted. As far as we know, there is no prior report on amphiphilic telechelics incorporating polyhedral oligosilsesquioxane (POSS) macromers. Indeed, POSS macromers can represent interesting building units for the construction of organic−inorganic hybrid structures[22−27] compared to other hydrophobic groups, such as the linear aliphatic, aromatic, or fluorinated groups previously explored. We should note that these amphiphilic telechelics have a hydrophobic, bulky, and well-defined dimensional property such that both end groups contribute to self-assembly while contributing steric hindrance properties in the solution and melt state. Moreover, the partially inorganic composition offers the potential for conversion to ceramic (SiO_2/SiC) nanostructures.

In this study, the objective was first to synthesize and characterize a series of amphiphilic telechelics incorporating POSS macromers as an end group of PEG homopolymers. We used several PEG homopolymers of varying molecular weight to control the molecular architecture by hydrophilic and hydrophobic balance. Initial characterization efforts have examined discrete macromolecular structures (NMR, GPC, FT-IR) and solid-state thermal behavior of the semicrystalline materials (TGA, DSC). A detailed study of association behavior of these amphiphilic telechelics in the solution and melt states is in progress.

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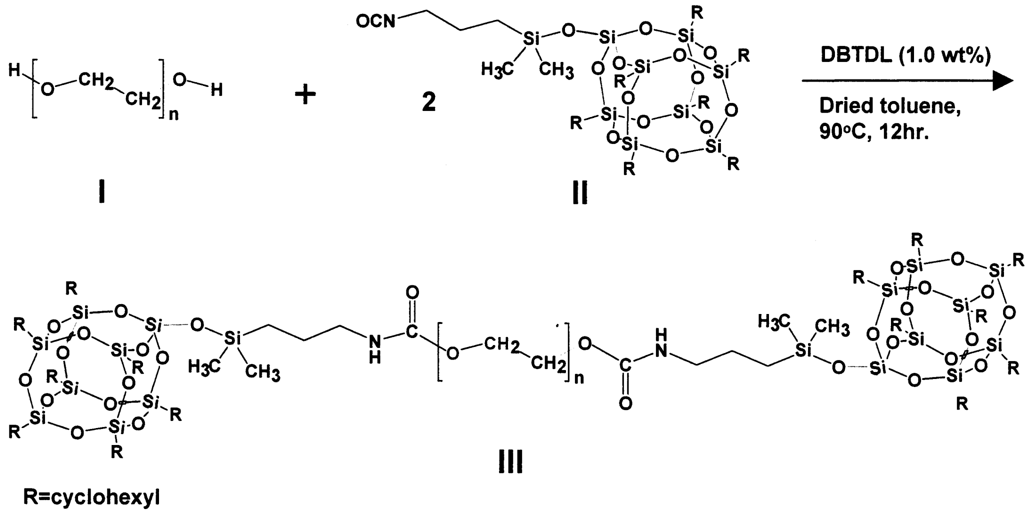
Scheme 1. Reaction Scheme of the Amphiphilic Telechelics Incorporating Polyhedral Oligosilsesquioxane (POSS)



I: Poly(ethylene glycol) (PEG); MW=1k, 2k, 3.4k, 8k, 10k g/mol.
II: Isocyanatopropyldimethylsilycyclohexyl-POSS (POSS macromer).
III: Amphiphilic telechelics incorporating POSS.

Experimental Section

Materials. Poly(ethylene glycol) (PEG) specimens with a molecular weight (MW) = 1000, 2000, 3400, 8000, and 10 000 g/mol, designated as PEG1K, PEG2K, PEG3.4K, PEG8K, and PEG10K, respectively, were obtained from Aldrich. All PEGs were purified by twice repeating the process of precipitation into *n*-hexane from chloroform solutions, followed by drying under vacuum overnight. Isocyanatopropyldimethylsilylcyclohexyl-POSS (POSS macromer) was provided by Air Force Research Lab, AFRL/PRSM, and its chemical structure was confirmed by ^{1}H NMR spectroscopy. Dibutyl tin dilaurate (DBTDL; Aldrich, 95% purity) as a catalyst for urethane formation was used as received. Toluene and tetrahydrofuran (THF) were dried over CaH_2 and then distilled under nitrogen prior to use.

Synthesis. Solutions of PEG homopolymer and POSS macromer were prepared separately in dried toluene. The PEG solution was charged in a four-necked flask, equipped with a stirrer, a nitrogen inlet, an outlet, and a thermometer. A mixture of PEG and toluene was further predried by azeotropic distillation, and the concentration was controlled to approximately 10% (w/v). Subsequently, the mixture was cooled to 90 °C and POSS macromer (0.69 g, 0.60 mmol) solution, containing 1.0 wt % of catalyst (DBTDL) based on the weight of the reactant, was added slowly via syringe within 20 min into a flask containing a preweighted amount of PEG (MW = 10K, 3.00 g, 0.30 mmol). These reactants were miscible throughout the synthesis as indicated by the clarity of the solution. The reaction mixture was kept at 90 °C under a nitrogen atmosphere for about 12 h. Then the reaction mixture was microfiltered (0.45 μm), precipitated in an excess amount of *n*-hexane, and washed with fresh *n*-hexane several times to remove the unreacted POSS macromer and catalyst, and then the precipitated telechelic was filtered. The isolated product was subsequently washed with deionized water to remove unreacted homopolymer PEG as a precautionary measure; however, no PEG was detected in the wash water. Various amphiphilic telechelics with different MWs of PEO segments were also synthesized following this procedure. It is noted that other reaction conditions were explored (including POSS:PEG molar ratio and THF as solvent) but proved inferior with respect to the level of disubstitution. The resulting products were dried under vacuum for at least 2 days to remove residual solvent. Products in the physical form of a white powder could be obtained. The product yield in all cases was more than 90%, within experimental error. A schematic depiction of the synthetic procedure for amphiphilic telechelic formation is shown in Scheme 1.

Characterization. To identify the chemical structures of the product polymers, FT-IR spectra were recorded with a Nicolet MAGNA-IR 560 spectrometer using neat films cast from $CHCl_3$ solution upon KBr windows. All measurements were made at room temperature within several minutes after drying the film KBr window under vacuum. Special care was also taken to avoid absorption of moisture while transferring samples from the oven to the spectrometer. To further establish their chemical structures, ^{1}H NMR spectra were recorded with a Bruker 500 MHz DMX500 high-resolution spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC, Waters Associates, 150-C Plus) with a PL-ELS 1000 control detector (Polymer Laboratories) was used to obtain molecular weights (MWs) and molecular weight distributions (MWDs). The samples, dissolved in THF, were injected at 35 °C with THF as an eluent and at a flow rate of 1.0 mL/min. The sample concentration was about 0.1 wt %. GPC data reported for the MWs and MWDs of the synthesized amphiphilic telechelics are relative to a calibration based on monodispersed polystyrene standards (472, 982, 4000, 6930, 43 000, 200 000, 400 000, and 824 000 g/mol; Polymer Standards Service-USA, Inc.).

The glass transition temperatures (T_g) and melting temperatures (T_m) were determined using a TA Instruments differential scanning calorimeter (DSC 2920) equipped with a liquid nitrogen cooling accessory (LNCA) unit under a continuous nitrogen purge (50 mL/min). The samples were first heated from room temperature to 150 °C at a fast heating rate of 40 °C/min to remove any previous thermal history and then quenched to −150 °C with liquid nitrogen or cooled to −50 °C at a cooling rate of 10 °C/min after isothermal treatment at 150 °C for about 30 min. Data were gathered on the second heating runs with scan rates of 10 °C/min. All of samples were dried under vacuum overnight before measurement. A sample of pure indium was used to calibrate the measurements of temperature and latent heat. Reported T_g values are defined as the temperatures corresponding to the midpoints of heat capacity change.

The thermal stability of the synthesized amphiphilic telechelics was analyzed by thermogravimetry (TGA) using a TA Instruments TGA 2950 under a continuous nitrogen purge of 50 mL/min. The samples were heated from room temperature to 800 °C with a uniform heating rate of 20 °C/min. The residual char mass percentage, m_{ch}, was taken as the mass percentage remaining at $T = 700$ °C.

Results and Discussion

Synthesis of Amphiphilic Telechelics Incorporating POSS Macromers. The synthesis of the amphiphilic telechelics incorporating POSS macromers was achieved by forming the urethane bond between a monoisocyanate group of POSS macromer and each hydroxyl group of PEG homopolymer (Scheme 1). Using linear PEG homopolymers of different MWs, thus controlling the molecular architecture by hydrophobic/hydrophilic balance, varied the hydrophobicity of the synthesized amphiphilic telechelics. Here, we should also note that the physical spacing between both hydrophobic end groups of the amphiphilic telechelics might have an important role in both the liquid-state aggregation and solid-state morphological behavior. Accordingly, various amphiphilic telechelics were synthesized by using the PEG homopolymers of different molecular weight MW = 1K, 2K, 3.4K, 8K, and 10K g/mol. The weight percentages of POSS macromers in the amphiphilic telechelics were thereby controlled to be 18.7, 22.3, 40.3, 53.5, and 69.7% in the feed, respectively. As a result, while PEG homopolymers are soluble in H_2O and POSS macromers are soluble in hexane, the synthesized amphiphilic telechelics could not dissolve in either H_2O or hexane, suggesting that incorporation of the hydrophobic POSS macromers onto PEG homopolymers gave rise to dramatically altered solubility. It is noted that while the wide breadth in POSS weight percentage affords significant variation in hydrophobic/hydrophilic balance, we anticipate that the most desired composition will depend on the end application.

The synthesized amphiphilic telechelics were characterized by ^{1}H NMR, GPC, and FT-IR spectroscopy. Figure 1 shows ^{1}H NMR spectra of the POSS macromer and the synthesized amphiphilic telechelic for PEG10K: POSS macromer (Figure 1a), ($CDCl_3$) δ 3.27 ppm ($-CH_2-NCO$), δ 1.73 ppm (cyclohexyl ring, $-CH_2-$), δ 1.2 ppm (cyclohexyl ring, $-CH_2-CH-$ and $-CH_2-CH_2-NCO$), δ 0.76 ppm (cyclohexyl ring, $-CH_2-C(CH_2)H-$), δ 0.63 ppm ($-O-Si(CH_3)_2-CH_2-$), δ 0.16 ppm ($-O-Si(CH_3)_2-CH_2-$); the synthesized amphiphilic telechelic for PEG10K (Figure 1b), ($CDCl_3$), δ 4.2 ppm ($-NH-COO-$), δ 3.6 ppm ($-CH_2-$), δ 3.15 ppm ($-CH_2-NH-COO-$), δ 1.73 ppm (cyclohexyl ring, $-CH_2-$), δ 1.2 ppm (cyclohexyl ring, $-CH_2-CH-$ and $-CH_2-CH_2-NCO$), δ 0.76 ppm (cyclohexyl ring, $-CH_2-C(CH_2)H-$), δ 0.63 ppm ($-O-Si(CH_3)_2-CH_2-$), δ 0.16 ppm ($-O-Si(CH_3)_2-CH_2-$). Evidence for the formation of urethane linking groups comes from the emergence of a weak proton signal at about 4.2 ppm, accompanied by the disappearance of a proton signal of the $-CH_2-NCO$ group (3.27 ppm). This clearly indicates the formation of the urethane bond, even though the urethane signals are too small to be analyzed quantitatively. The level of incorporation of POSS macromers in the amphiphilic telechelics could be determined quantitatively by the monitoring of the resonances for the cyclohexyl groups of POSS macromer.[28] They were obtained by comparing the ratio of the PEG $-CH_2-$ (δ = 3.5 ppm; "h" in Figure 1b) integration value, normalized to that for a single proton, to the average integration value for the POSS macromer $-O-Si(CH_3)_2-CH_2-$ (δ 0.16 ppm; "e" in Figure 1b) integral. The compositions of our amphiphilic telechelics thus calculated by ^{1}H NMR are detailed in Table 1. The calculated concentration of POSS macromers in the products was quite consistent with the feed ratio. The well-defined amphiphilic telechelics with chain end functionality >95% (~ a degree of end functionalization of more than 1.9) could be obtained, as calculated by ^{1}H NMR spectroscopy. It is also quite noteworthy that the amphiphilic telechelics of PEG1K (POSS content = 68.1%, as calculated by ^{1}H NMR spectroscopy) and PEG2K (POSS content = 52.7%) show a similar copolymer sequence structure to that of an ABA triblock copolymer, on a weight percentage basis, where A and B represent hydrophobic POSS and hydrophilic PEO sequences, respectively.

Generally, hydrophobic ethoxylated urethane (HEUR) polymers which are prepared by a chain extension reaction of an oligomeric PEO with a diisocyanate followed by end-capping with an aliphatic alcohol are characterized by a relatively broad MWD ($M_w/M_n \approx 2$), and not all of the polymer molecules contain two hydrophobic end groups.[2,29] In contrast, GPC analysis of the present amphiphilic telechelic of PEG1K (as an example) shows a very narrow and unimodal molecular weight distribution ($M_w/M_n < 1.1$), as shown in Figure 2, indicating that the diol groups of PEG homopolymers had completely reacted with the monoisocyanate groups of POSS macromers. We note that a small high molecular weight (low retention time) peak appears in the POSS−isocyanate trace, but this "impurity"—perhaps POSS dimer—does not persist in the end-capped polymers. Moreover, there was no evidence of unreacted PEG homopolymers and POSS macromers. The GPC chromatograms of the amphiphilic telechelics (not shown) also reveal systematic increases in MW afforded by covalent linkage of PEG homopolymers with POSS macromers. However, MWs of the amphiphilic telechelics of PEG 3.4K and PEG8K did not exactly coincide with the calculated values. Surprisingly, the measured molecular weight for the amphiphilic telechelic of PEG8K was about 1.5 times larger than calculated one. Although these observations are not fully understood, we hypothesize the formation of small aggregates in organic elution solvent, THF, even though it is good solvent. That is, because the retention time depends on the hydrodynamic volume of the eluting species, this suggests that the aggregated structures possess similar size, resulting in the higher average MW.[30] These facts will be studied in more detail by the viscometric measurements in other reports.

Figure 3 shows the FT-IR spectra of the PEG3.4K homopolymer (Figure 3a), the POSS macromer (Figure 3b), and the synthesized amphiphilic telechelic for PEG3.4K homopolymer (Figure 3c). For the case of the amphiphilic telechelic for PEG3.4K homopolymer (Figure 3c), new carbonyl ($-C{=}O$) and amine ($-NH$) bands appear at 1720 and 3350 cm^{-1}, respectively. The telechelic spectra also show strong absorption bands in the 2800−3000 cm^{-1} range assignable to the aliphatic (asymmetric and symmetric) C−H stretching vibrations; at 1530 cm^{-1}, the N−H bending vibration; at 1467 cm^{-1}, the $-CH_2-$ bending vibration in aliphatic hydrocarbon; in the 1000−1300 cm^{-1} range, the strong C−O and Si−O stretching vibrations; in the 1200−1400 cm^{-1} range, $Si-CH_3$ and $Si-CH_2$ bending vibrations; at 963 and 843 cm^{-1}, the characteristic bands of the crystalline phase of PEG segments;[31] and at 895 and 848 cm^{-1}, the rocking vibration of cyclohexyl ring structure. We found

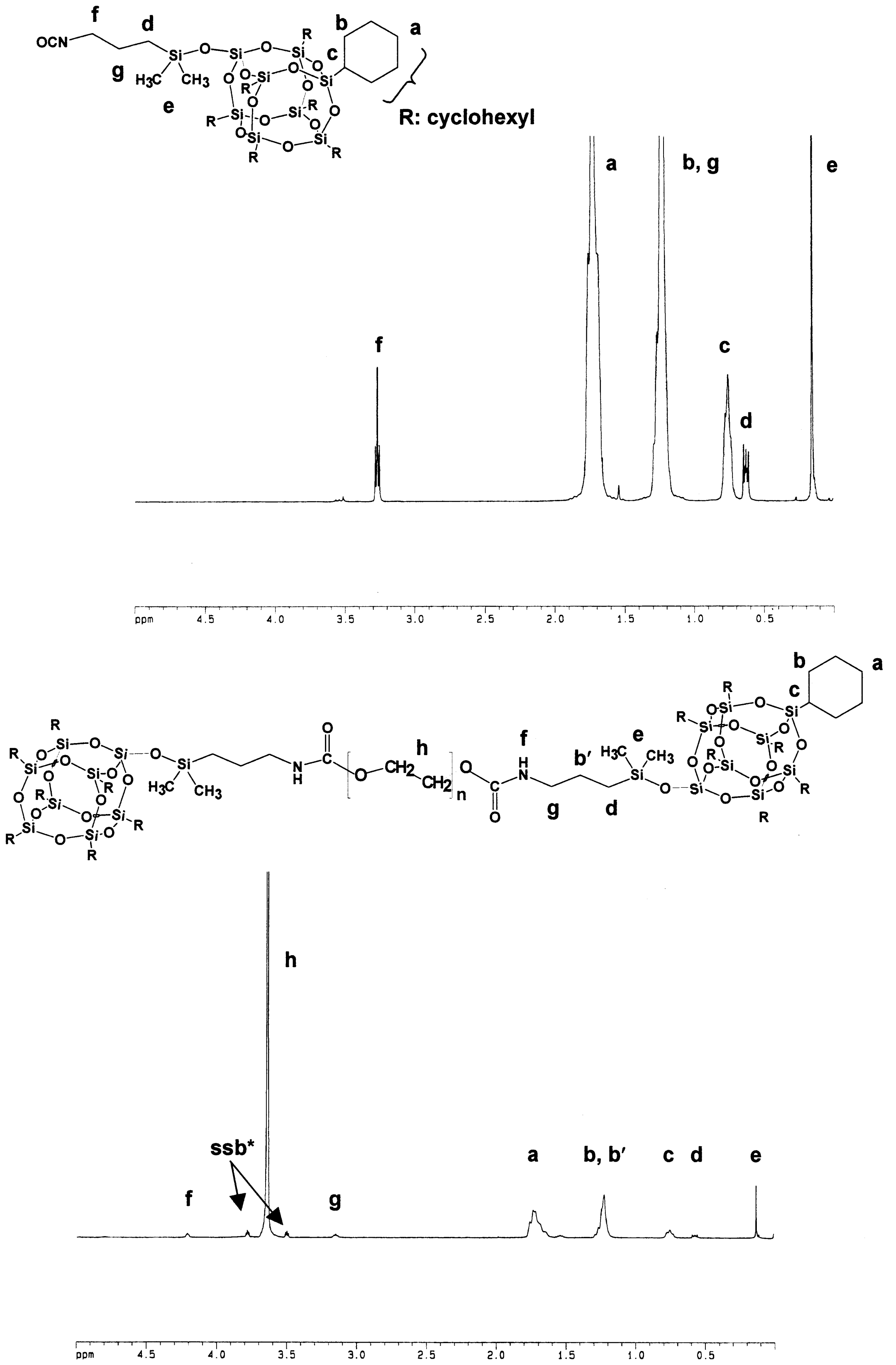


Figure 1. (a, top) ^{1}H NMR spectrum of POSS macromer. (b, bottom) ^{1}H NMR spectrum of the amphiphilic telechelic of PEG8K. *ssb indicates a spinning sideband.

the disappearance of the weak broad absorption band at 3400 cm^{-1} attributed to the H-bonded hydroxyl end groups (−OH) of PEG homopolymer (Figure 3b) and characteristic strong absorption band at 2260 cm^{-1} attributed to the isocyanate group (−NCO) of POSS macromer (Figure 3c), together proving the urethane

Table 1. Molecular Characteristics of the Amphiphilic Telechelics

$(POSS)_a/(EO)_b/(POSS)_a$ [a]	[PEG]/[POSS] by NMR	calcd MW[b]	M_w by NMR	POSS composition[c] (wt %)	M_n by GPC	M_w/M_n[d]
1/22/1	1/2.15	3300	3472	68.1	3355	1.02
1/44/1	1/2.16	4300	4484	52.7	4798	1.08
1/74/1	1/2.03	5700	5734	40.7	7257	1.02
1/174/1	1/1.94	10300	10231	23.6	15642	1.03
1/217/1	1/1.86	12300	12139	19.8	11496	1.04

[a] POSS = propyl dimethyl silyl cyclohexyl polyhedral oligosilsesquioxane. EO = ethylene oxide. The numbers indicate block length; e.g., 1−22−1 indicates a ethylene oxide block length of 22 units attached to the both POSS materials. [PEG]/[POSS] = 1/2 in feed. [b] Calculated using the following equation; MWs of amphiphilic telechelics = MWs of PEGs + 2MW of POSS macromer. [c] Determined by ^{1}H NMR. [d] Determined by GPC.

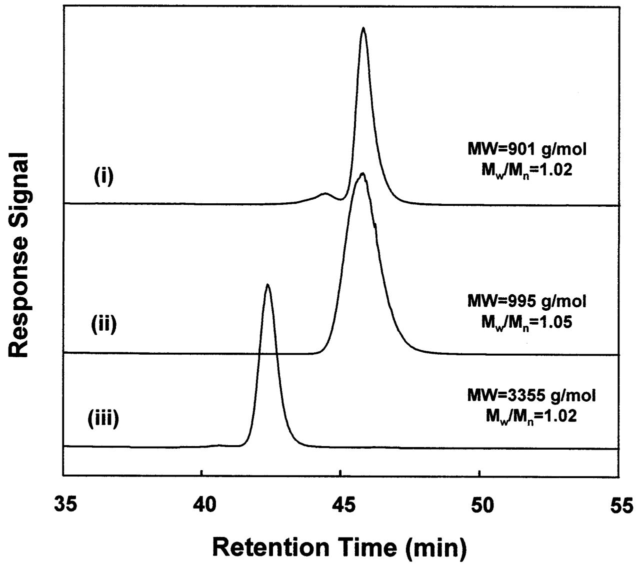


Figure 2. GPC chromatograms of (i) POSS macromer, (ii) PEG1K homopolymer, and (iii) amphiphilic telechelic of PEG1K.

bond formation between the terminal hydroxyl group of PEG homopolymers and the isocyanate group of POSS macromers. In addition, even though it is not shown here, as the POSS content increased, the intensities of the absorption bands at 1720, 1530, 895, and 848 cm^{-1} attributed to the C=O stretching, N−H bending, and cyclohexyl ring rocking vibrations also increase. On the other hand, the intensities of the absorption bands at 963 and 843 cm^{-1}, which are the characteristic bands of the crystalline phase of PEO segments, decrease. We also found that the absorption intensity at 1467 cm^{-1} attributed to the $-CH_2-$ bending vibration in aliphatic hydrocarbon decreases with the increase of POSS content, while the absorption intensity at 1447 cm^{-1} attributed to the $-CH_2-$ bending vibrations in strained cyclohexyl ring increases. Considering all of our molecular characterization data discussed above, we are satisfied that the structures drawn in Scheme 1 are quite accurate.

Thermal Properties of Amphiphilic Telechelics Incorporating POSS Macromers. On the basis of high thermal stability of POSS macromers,[28,32,33] the thermal stability of the synthesized amphiphilic telechelics incorporating POSS is expected to be improved over unmodified PEG homopolymers. Figure 4 shows the TGA results for the synthesized amphiphilic telechelics. As shown in Figure 4a, the thermal decomposition behavior of the amphiphilic telechelics was altered compared to the pure PEG homopolymers, the latter showing one sharp decomposition event. In particular, for the case of the amphiphilic telechelic of PEG1K, quite different thermal decomposition behavior was shown; that is, thermal decomposition occurred over a broad temperature range, suggesting the suppression of thermal decomposition due to the incorporation of POSS macromers. In addition, the degradation patterns of the amphiphilic telechelics in nitrogen are different from PEG homopolymers. While PEG homopolymers exhibit one-step decomposition behavior, amphiphilic telechelics show two-step decomposition behavior (Figure 4b). The first derivative peak is attributed to the decomposition of the organic PEO fraction, while the second peak is attributed to the inorganic POSS fraction, probably cyclohexyl ring cleavage from the incorporated POSS macromers.

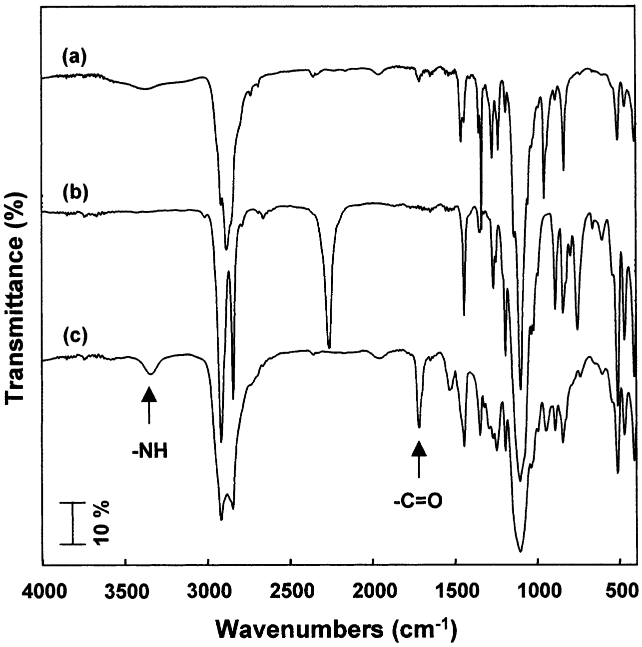


Figure 3. FT-IR spectra of (a) PEG3.4K homopolymer, (b) POSS macromer, and (c) amphiphilic telechelic of PEG3.4K.

PEG oligomers have been studied for their melting behavior in the previous reports,[34,35] revealing the sensitivity of the melting point to polydispersity, even at small levels. Thus, we have anticipated dramatic alteration in melting behavior of the present telechelics. Figure 5 represents the DSC thermograms (second scans) of the PEG homopolymers and the amphiphilic telechelics with various PEO contents, respectively. In the case of PEG homopolymers, as shown in Figure 5a, narrow melting points (T_m) of PEG homopolymers were clearly observed, T_m following an inverse relationship with molecular weight (inset in Figure 5a). The double melting transition for PEG3.4K is attributed to the existence of folded-chain lamellae with different fold numbers.[36] On the other hand, distinct melting patterns were found in the synthesized amphiphilic telechelics.

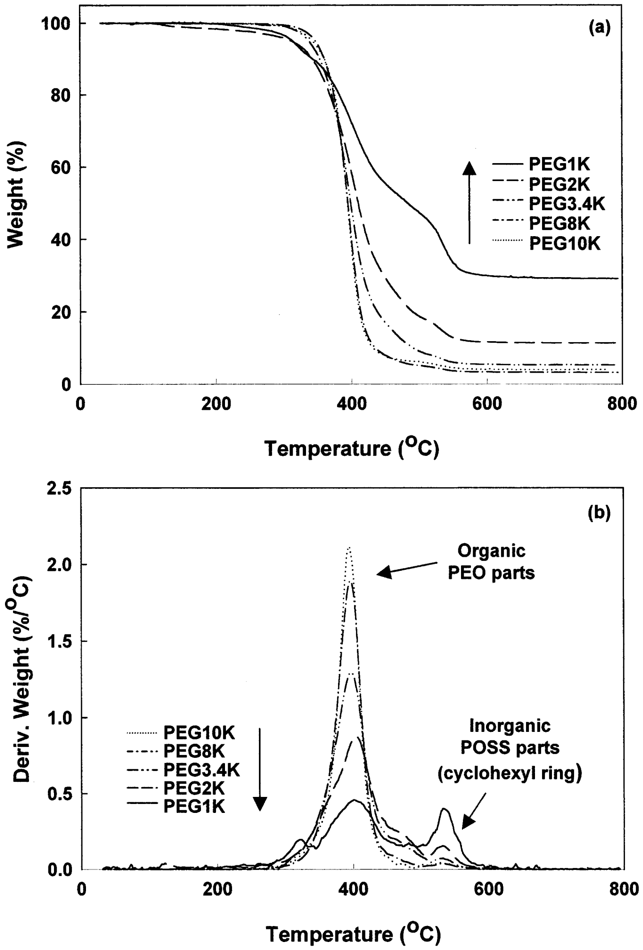


Figure 4. (a) Thermogravimetric analysis of the amphiphilic telechelics. A heating rate of 20 °C/min was applied to samples in a nitrogen environment. (b) Thermogravimetric analysis of the amphiphilic telechelics. Here d(wt %)/dT is plotted to reveal a two-step decomposition process. Conditions same as in (a).

That is, T_m for the amphiphilic telechelics of PEG10K and PEG8K were observed at 50 and 53 °C, respectively, which are both slightly lower temperatures compared to the melting point of PEG homopolymer. Remarkably, T_m of the amphiphilic telechelic of PEG3.4K was shifted to a lower temperature, observed at the around of the room temperature (20 °C), while the peak is broadened. These results suggest that an increased disturbance in ordering attributed to the large steric hindrance of amorphous rigid POSS blocks results in less intermolecular or intramolecular interaction between PEO segments during crystallization. Accordingly, a small decrease in ΔH_m is found as the POSS macromers are incorporated. T_g values of the soft PEO segments in the amphiphilic telechelics of PEG10K, PEG8K, and PEG3.4K were progressively shifted to higher temperature with an increase of POSS content,[25] although the magnitude of this shift is difficult to quantify. Such a result, nonetheless, demonstrates that direct incorporation of the rigid POSS macromers onto PEO chains may retard the chain movement and alter amorphous chain dynamics due to its large tethered mass. On the other hand, in the case of the amphiphilic telechelics of PEG1K and PEG2K, we could not find any sharp endothermic peaks (Figure 5b) unlike the PEG1K and PEG2K homopolymers. The absence of such melting endotherms is probably due to complete disruption of the orderly lamellar folding pattern of the PEO crystals by the presence of the bulky POSS moieties. Thus, the amphiphilic telechelics of PEG1K and PEG2K feature suppression of PEO crystallization. T_g values of the soft PEO segments in the case of the amphiphilic telechelics of PEG1K and PEG2K are contrary to expectation, a little decreased with an increase of POSS content, suggesting that the amorphous properties of PEO segments were remarkably enhanced by incorporating the POSS macromers. The detailed results of thermal analysis are summarized in Table 2. Further structural investigations are currently underway.

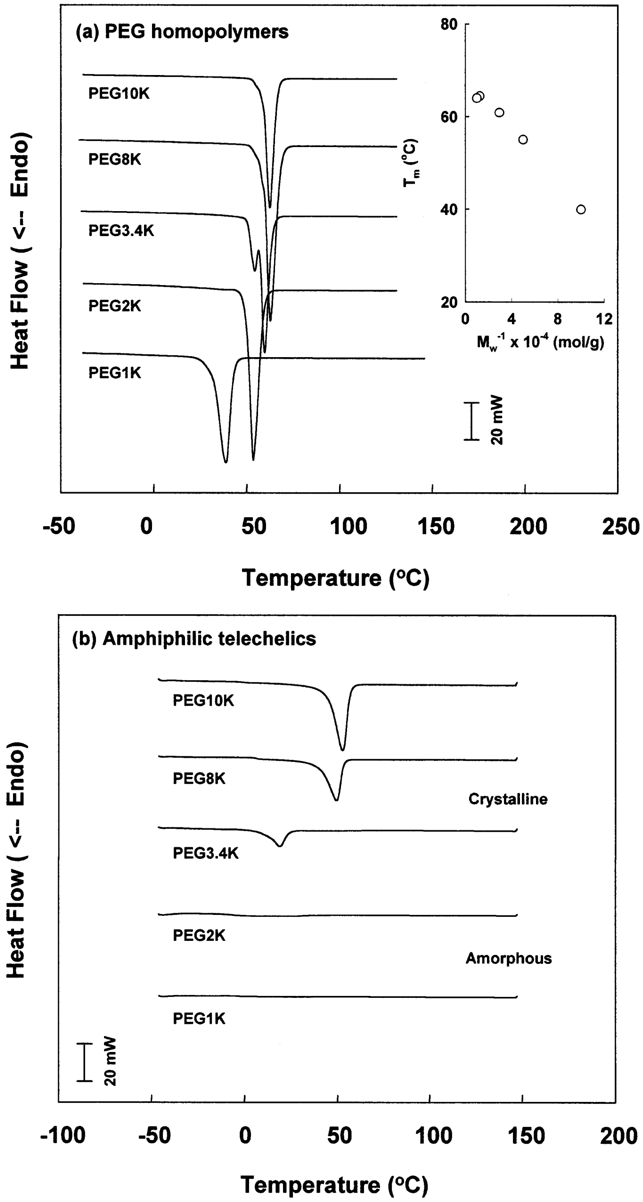


Figure 5. (a) Differential scanning calorimeter (DSC) analysis of the PEG homopolymers. (b) DSC analysis of the amphiphilic telechelics.

From the measured values of ΔH_m due to melting of the amphiphilic telechelics of PEG3.4K, PEG8K, and PEG10K, the percentages of PEO crystallinity were approximated by integrating the endothermal peak and normalizing the resulting latent heat by a reference value for 100% crystalline poly(ethylene oxide) (198 J/g).[37] The crystallinity of amphiphilic telechelics of PEG3.4K, PEG8K, and PEG10K were thus determined to be 19.1, 50.6, and 51.8%, respectively. This result also indicates that the crystallinity of PEO segments is

Table 2. Thermal Properties of the Amphiphilic Telechelics

$(POSS)_a/(EG)_b/(POSS)_a$	POSS[a] (wt %)	$T_m(\Delta H_m)$ of pure PEG homopolymers (°C, J/g)	$T_m(\Delta H_m)$ of amphiphilic telechelics (°C, J/g)	$T_c(\Delta H_c)$ of amphiphilic telechelics (°C, J/g)	T_g of PEG segments[b](°C)	residual char yield[c] (m_{ch}, %)
1/22/1	68.1	39.1 (180.4)	none	none	−50.0	29
1/44/1	52.7	53.8 (176.2)	none	none	−57.7	11
1/74/1	40.7	59.8 (176.5)	20.6 (37.8)	−13.2 (37.5)	−42.8	5
1/174/1	23.6	63.0 (178.8)	49.7 (100.1)	16.2 (94.6)	−47.3	3
1/217/1	19.8	62.8 (126.8)	53.0 (102.6)	29.6 (100.8)	−50.9	4

[a] Calculated by ^{1}H NMR. [b] Data were gathered on the second heating curve with a heating rate of 10 °C/min on the quenched samples with liquid nitrogen. [c] Residual char yield was taken as the mass percentage remaining at $T = 700$ °C.

dramatically decreased when the POSS content in the amphiphilic telechelic is 40.7 wt % and becomes amorphous beyond about 50 wt %. Concerning the level of POSS ordering, per se, that exists in the telechelic materials, thermal analysis inadequately addresses this issue; instead, we have turned to wide-angle X-ray scattering to investigate the details of this ordering, and the results will be presented in a future publication.

Conclusion

Well-defined amphiphilic telechelics incorporating polyhedral oligosilsesquioxane (POSS) were synthesized by direct urethane linkage between diol end groups of poly(ethylene glycol) (PEG) homopolymer and monoisocyanate group of POSS macromer. We found that the synthesized amphiphilic telechelics showed a relatively narrow and unimodal molecular weight distribution ($M_w/M_n < 1.1$) and had close to 2.0 end groups per PEG chain. Amphiphilic telechelics with the POSS contents of 19.8, 23.6, 40.7, 52.7, and 68.1% depending on the molecular weights of PEG homopolymers could be obtained. The crystallinity of PEO segments in the amphiphilic telechelics is dramatically decreased when the POSS content in the amphiphilic telechelic is 40.7% and becomes amorphous beyond about 50%. As a result, we were obtained several amphiphilic telechelics with different thermal and morphological properties by controlling the balance of the hydrophilic PEG homopolymer and hydrophobic and bulky POSS macromers. The detailed association behavior of these amphiphilic telechelics in the solution and melt state is presently under investigation. It is expected that these unique materials will offer strong alterations in solution rheological behavior (i.e., associative thickening) and provide novel preceramic assemblies for the creation of controlled nanostructures via a building-block approach.

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