Organic−Inorganic Polymer Hybrids Using Polyoxazoline Initiated by Functionalized Silsesquioxane

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ABSTRACT: New hybrid polyoxazolines (CubePOZO) were synthesized by ring-opening polymerization of 2-methyl-2-oxazoline initiated by functionalized polyhedral oligomeric silsesquioxane (POSS) with various feed ratios. The hybrid micelles derived from CubePOZO with both seven hydrophobic cyclopentyl groups of POSS and polyoxazoline (POZO) as a hydrophilic segment were prepared in an aqueous phase. Compared to POZO initiated by cyclohexyl iodide or methyl *p*-toluenesulfonate, increased hydrophobicity caused by the structure of POSS in CubePOZO played a major role in the micelle formation. This depended on the amount of POSS incorporated into the POZO. The CubePOZO100 and CubePOZO200 formed micelles in an aqueous phase with critical micelle concentrations (cmc) of 55 and 100 mg/L, respectively. Transparent polymer hybrids, homogeneous dispersion of hydrophobic POSS bonded covalently to POZO in the silica gel matrix at the molecular level, were obtained through hydrogen-bonding interaction between CubePOZO and silica gel. The obtained polymer hybrids from CubePOZO showed excellent solvent resistance, similar to that of polymer hybrids having an interpenetrating polymer network structure. It was concluded that the solvent-resistant property came from the size of POSS and the hydrophobic interaction between the POSS in the silica gel matrix. In addition, thermal stability of the polymer hybrids from CubePOZO was much increased compared to that of the polymer hybrids from homoPOZO and POSS.

Introduction

Considerable efforts have recently been directed toward the exploitation of new nanostructured hybrid organic−inorganic composites for their scientific interest and their industrial applications.[1−3] That is because of their utility and potential as catalysts,[4] sensors,[5] optical and electronic applications,[6] gas selective membranes,[7] etc. In general, composite materials are formed when at least two different types of materials (organic, inorganic, and metallic) are mixed. The combination of organic and inorganic materials is expected to provide remarkable and complementary properties, which cannot be obtained with a single material. Organic−inorganic nanocomposites, in which two components were mixed at the nanometer level, usually exhibit improved performance properties compared to conventional composites, in which two components were mixed on a macroscopic scale (> micrometers), owing to their unique phase morphology and improved interfacial properties.[8]

The most extensively explored synthetic approach is via the sol−gel technique for preparing inorganic oxides at ambient temperature by polymerization and coagulation of tri- or tetramethoxysilanes and other metal alkoxides. Organic phases (polymers or gels) could be incorporated without any separation into the silica matrix by using covalent bond or physical interactions between two phases or by controlling gelation of polymers and formation of silica gel through various molecular designs.[9] Organic−inorganic nanocomposites show highly optical transparency, excellent thermal, mechanical, and solvent-resistant properties.

Polyhedral oligomeric silsesquioxanes (POSS), intermediate $(RSiO_{1.5})_n$ between silica (SiO_2) and silicone (R_2-SiO), are interesting inorganic particles which can replace sol−gel-derived materials. They currently have a great impact on the field of material science because of their hybrid chemical compositions with nanosized cage structures and property enhancements via POSS to polymers.[10−12] POSS is easily incorporated into common plastics by means of copolymerization or blending, requiring little or no alteration to existing synthetic processes because POSS have an inorganic SiO_2 core surrounded by eight organic groups, which make it soluble in various organic solvents. POSS containing copolymers or blends have increased oxygen permeability, are thermoplastic or curable, have oxidation resistance, and higher thermal properties than those without the POSS moiety. We have recently explored various organic−inorganic hybrid nanocomposites based on POSS as an inorganic precursor. Such examples are hybrid gels,[13] hybrid LC polymers,[14,15] self-assembly of metal nanoparticles,[16] hydrophobic $CaCO_3$ composite particles,[17] and homogeneously transparent polymer hybrid materials combined at the molecular level.[18−20]

Here we describe the preparation of hybrid polyoxazolines initiated by new POSS having only one iodopropyl group as an initiator (CubePOZO) and also of polymer hybrids from CubePOZO utilizing the sol−gel reaction of tetramethoxysilane (TMOS). It is expected that the introduction of the hydrophobic POSS having seven cyclopentyl groups to hydrophilic POZO can induce self-association of CubePOZO, leading to the formation of hybrid micelles in an aqueous phase. This is an interesting method for preparing micelles using enhanced hydrophobicity caused by the structure of POSS even though little of POSS is incorporated into the hydrophilic polymer chain as an initiator. It is really difficult to obtain homogeneous polymer hybrids using hydrophilic POZO and hydrophobic POSS in the silica gel matrix. On the other hand, hydrophobic POSS having seven cyclopentyl groups bonded covalently to POZO could be homogeneously dispersed in the silica gel matrix at the nanometer level. We describe the properties of CubePOZO and micelle characteristics of CubePOZO in an aqueous phase. In addition, the

Scheme 1

Cube-1Cl

Cube-1I
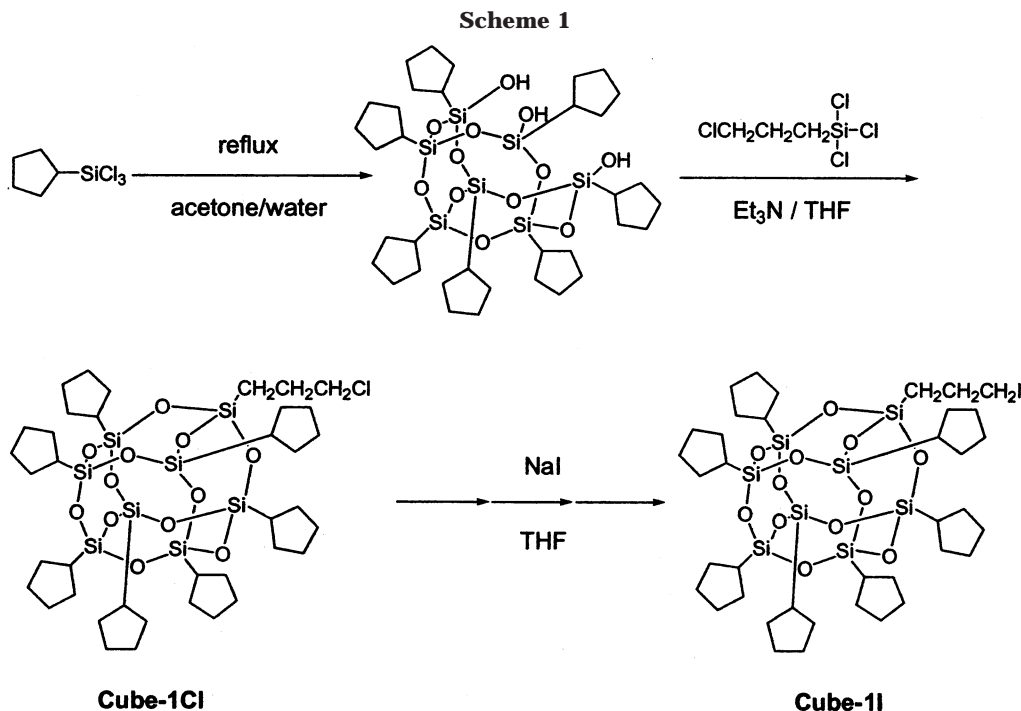
preparation of polymer hybrids from CubePOZO and TMOS utilizing the sol–gel reaction and the effect of

Figure 1. (a) DSC and (b) TGA thermograms of CubePOZO with a heating rate of 10 °C min^{-1} under nitrogen and air atmospheres, respectively. (a) DSC: (a) homoPOZO, (b) Cube-POZO50, (c) CubePOZO100, and (d) CubePOZO200. (b) TGA: (a) homoPOZO, (b) CubePOZO20, (c) CubePOZO50, (d) Cube-POZO100, (e) CubePOZO200.

the hydrophobic POSS on the pore size and solvent-resistant property of the polymer hybrids are described.

Experimental Section

Measurements. ^{1}H NMR spectra were recorded using a 270 MHz JEOL-JNM-GX270 NMR spectrometer. UV absorption spectra were obtained with a JASCO V-530 spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 1600 infrared spectrometer. The thermal behavior was examined with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (TG/DTA6200, Seiko Instruments) under nitrogen and air atmospheres, respectively. Gel permeation chromatography (GPC) analysis was carried out on TSK gel α-3000 by using DMF as an eluent at 40 °C after calibration with the standard polystyrene samples. The morphologies of polymer hybrids were observed by scanning electron microscopy (SEM) (JEOL JSM-5310/LV). The crystallinities of CubePOZO and polymer hybrids were determined by X-ray diffraction (XRD) (Perkin-Elmer system 2000). Fluorescence excitation spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Nitrogen absorption porosimetry was conducted with a BEL Japan Inc.
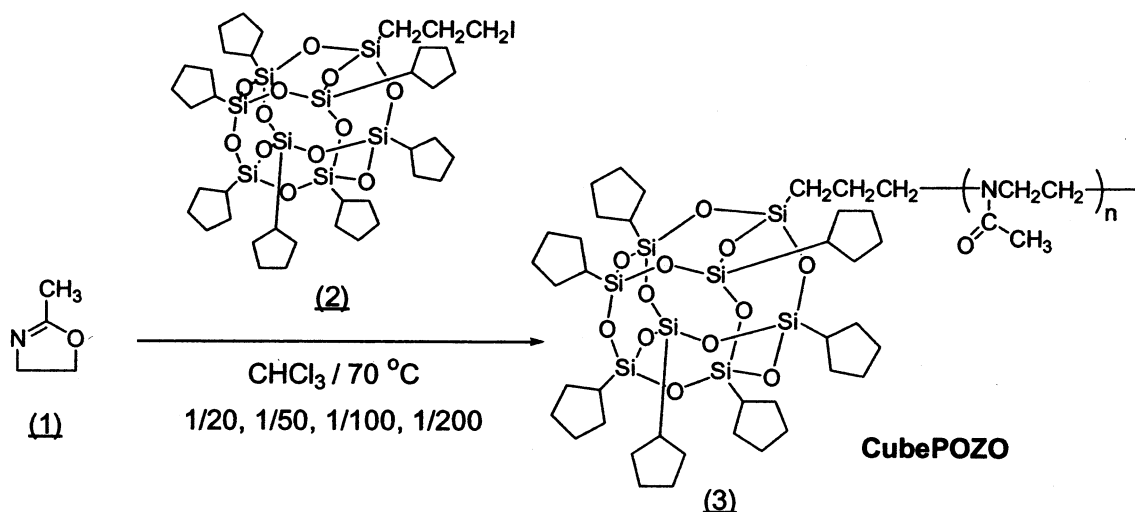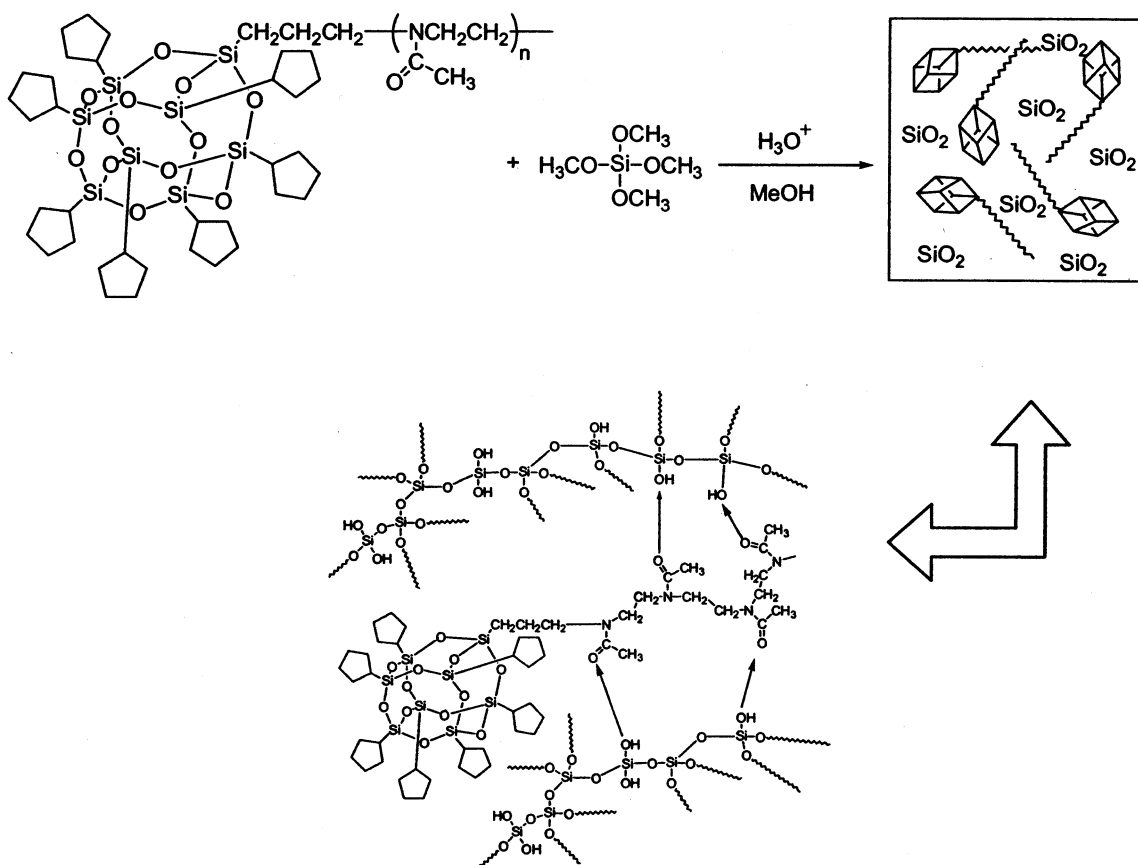
Materials. 2-Methyl-2-oxazoline (Aldrich) was distilled over potassium hydroxide and stored under nitrogen. Cyclopentyltrichlorosilane (Gelest), pyrene (Aldrich), cyclohexyl iodide (Aldrich), and 3-chloropropyltrichlorosilane (TCI) were used as received. Chloroform and acetone were dried and distilled from calcium carbonate and potassium carbonate, respectively. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled over sodium and calcium hydride, respectively. The other reagents were used as supplied without further purification.

Synthesis of Cube-1Cl. Incompletely condensed trisilanol (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ was prepared in 29% yield by the hydrolytic condensation reaction of cyclopentyltrichlorosilane in reflux aqueous acetone, according to the procedure reported before.[21] The obtained trisilanol (3.05 g, 3 mmol) and triethylamine (1.23 g, 12 mmol) were dissolved in THF. The solution was cooled in an ice bath, and 3-chloropropyltrichlorosilane (0.74 g, 3 mmol) in THF was added slowly to the mixture. The resulting solution was stirred overnight at room temperature. After removal of insoluble salts by filtration, the filtrate was concentrated to 5 mL and poured into acetonitrile. The white precipitate was collected by filtration and dried in vacuo to produce a white solid (2.50 g, 64%). ^{1}H NMR (CDCl$_3$): δ 3.54 (t, 2H), 1.87 (m, 2H), 1.48–1.80 (m, 56H), 0.97 (m, 7H), 0.74 (m, 2H). ^{29}Si NMR (CDCl$_3$): −66.52, −67.11.
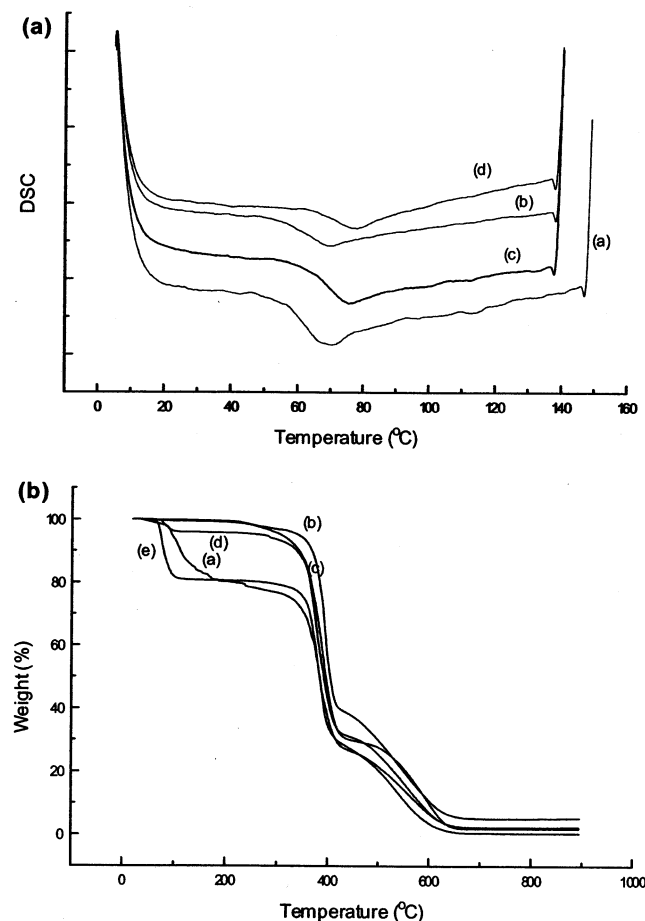
Scheme 2

Scheme 3

Synthesis of Cube Initiator (Cube-1I). A mixture of Cube-1Cl (2.20 g, 2 mmol) and sodium iodide (11.7 g, 78 mmol) was added in THF (120 mL) and acetone (40 mL) cosolvent under a nitrogen atmosphere. The mixture was refluxed for 24 h, cooled to room temperature, and evaporated. A fine solid of sodium chloride formed during the mixture was refluxed. The white mixture was extracted with methylene chloride, and the insoluble parts were removed by filtration. After evaporation of methylene chloride and drying in a vacuum, the raw product was again reacted with sodium iodide in THF and acetone cosolvent. The workup procedure was repeated three times, and then the product was obtained as a yellow solid (1.20 g, 58%). ^{1}H NMR (CDCl$_3$): δ 3.22 (t, 2H), 1.89 (m, 2H), 1.40−1.80 (m, 56H), 0.97 (m, 7H), 0.72 (m, 2H). ^{29}Si NMR (CDCl$_3$): −66.52, −67.93.

Synthesis of Polyoxazoline Initiated by Cube-1I (Cube-POZO). The polymerization of 2-methyl-2-oxazoline using POSS as an initiator ([monomer]/[initiator] = 1/20, 1/50, 1/100, 1/200) was carried out in dry chloroform at 70 °C for 7 days under nitrogen. As a representative example, the hybrid polymer, CubePOZO100, which has 100 molar ratio of 2-methyl-2-oxazoline to Cube-1I, was synthesized by the following procedure: To a solution of 2-methyl-2-oxazoline (0.80 g, 9 mmol) in chloroform (6 mL) was added Cube-1I (0.1 g, 0.09 mmol) at room temperature under nitrogen. The reaction mixture was heated at 70 °C for 7 days. The resulting yellow solution was diluted with 15 mL of chloroform. This polymer solution was poured into ca. 200 mL of diethyl ether to precipitate the polymeric product. The white precipitate was collected by filtration and dried in a vacuum (0.73 g, 81%).
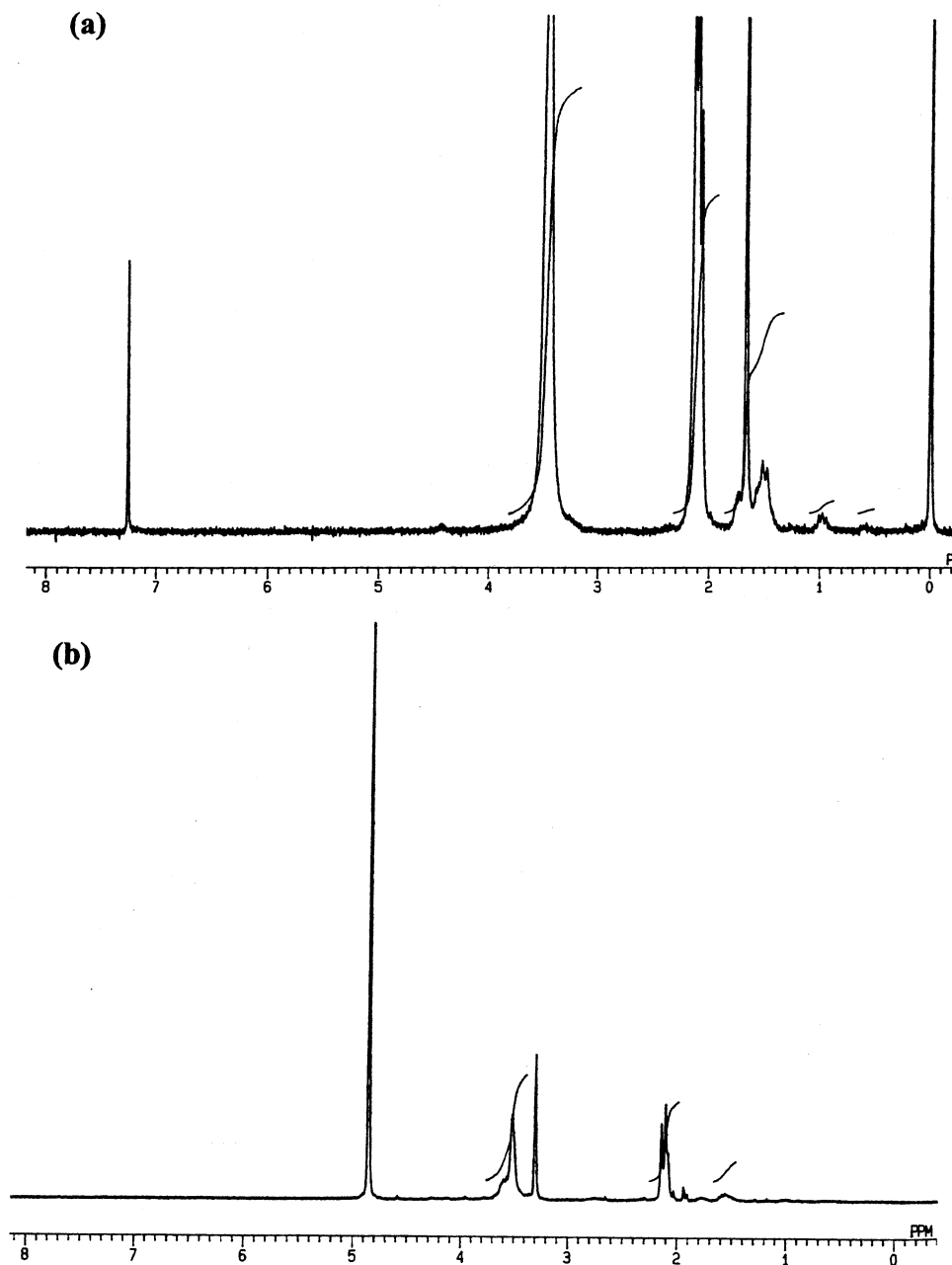
Figure 2. ^{1}H NMR spectra of CubePOZO100 in CDCl$_3$ (a) and CD$_3$OD (b).

Preparation of Hybrid Micelles from CubePOZO. For the measurement of fluorescence spectra, pyrene solution was prepared following a literature procedure.[22] The pyrene solution was mixed with CubePOZO in a distilled water to obtain CubePOZO concentration from 2×10^{-4} to 2.5 g/L. The pyrene concentration of the samples was 6×10^{-7} M. All the samples were sonicated for 1 h and were allowed to stand for 1 day in a dark place before fluorescence measurements.

Preparation of Polymer Hybrids from CubePOZO. The obtained polymer having POSS moiety (CubePOZO20, 50, 100, 200) was dissolved in methanol, and the resulting mixture was stirred for 1 h. To the solution was added TMOS and 0.1 M aqueous HCl as a catalyst for sol−gel reaction. The weight of CubePOZO was fixed to 0.05 g. The weight of TMOS was varied to that of CubePOZO (4/1, 10/1, 20/1). Four equivalents of aqueous HCl to TMOS was added. The resulting mixture was stirred at room temperature for 1 h in a sealed bottle. Then, the mixture was placed in a container covered with a paper towel and left in air to evaporate the solvent. After the complete removal of the solvent, the polymer hybrids were obtained as a glassy material.

Soxhlet Extraction of Polymer Hybrids. The powders of polymer hybrids were put in a cellulose timber and extracted with methanol or chloroform using a Soxhlet apparatus for 14 days. The powders in a timber were dried in a vacuum for the TGA measurement and nitrogen absorption porosimetry.

X-ray Diffraction Measurement of CubePOZO and Polymer Hybrids. All the measurements were made in $\theta/2\theta$ mode at room temperature. The 2θ scan data were collected at 0.02° interval, and the scan speed was 2° (2θ)/min.

Nitrogen Absorption Porosimetry. The preparation of samples for nitrogen absorption porosimetry was made by two methods to remove the organic parts in the silica matrix. One is that the powders of polymer hybrids are heated at 600 °C under an ambient atmosphere. The other is solvent extraction of the powders of polymer hybrids with methanol using a Soxhlet apparatus for 14 days. The samples were then heated to 150 °C for 2 h and dried at 150 °C for 2 h at reduced pressure under a nitrogen atmosphere. Surface areas were calculated with the BET equation[23] in the range of 0.05−0.30 (p/p_0), and the pore size distribution was calculated by the BJH method.[24]

Table 1. Preparation of CubePOZO Initiated by Silsesquioxanes

run	$[1]/[2]^a$	time (days)	temp (°C)	M_n	M_w	PD^b	yield (%)	T_d^c
1	20	7	70	3 000	10 000	3.45	62	367
2	50	7	70	5 200	12 000	2.30	64	342
3	100	7	70	10 000	21 000	2.13	81	335
4	200	7	70	20 000	42 000	2.03	83	

^{a} Feed ratio of 1 to 2. ^{b} Polydispersity. ^{c} Temperature at which a 10% weight loss was observed under air.

Results and Discussion

Synthesis of Hybrid CubePOZO Initiated by POSS. POSS as an initiator (Cube-1I) were prepared by corner-capping reaction of incompletely condensed trisilanol with a coupling reagent followed by nucleophilic substitution with sodium iodide, as shown in Scheme 1. In the ^{29}Si NMR, two resonances were shown at −67.93 and −66.52 ppm with a ratio of 1 to 7. The ^{1}H NMR spectra of Cube-1I showed the chloromethylene group ($\delta = 3.54$ ppm) derived from Cube-1Cl completely shifted to the iodomethylene group ($\delta = 3.22$ ppm). The structure of Cube-1I, in which POSS has seven cyclopentyl groups and only one iodopropyl group for polymerization, was thus characterized by ^{1}H NMR, ^{29}Si NMR, and FT-IR.

The new hybrid polyoxazolines using POSS as an initiator were synthesized by varying the feed ratio of 2-methyl-2-oxazoline to Cube-1I (Scheme 2). The hybrid polymers were denoted as CubePOZO20, CubePOZO50, CubePOZO100, and CubePOZO200, which have 20, 50, 100, and 200 molar ratios of 2-methyl-2-oxazoline to Cube-1I, respectively. The results of the preparation of hybrid polymers are summarized in Table 1. Long reaction times around 7 days were necessary for 60−80% conversion in this polymerization, unlike the system using methyl *p*-toluenesulfonate as an initiator. This result is due to the steric hindrance, that is, the decreased initiation activity of the iodopropyl group surrounded by bulky cyclopentyl groups of POSS. Figure 1 represents DSC and TGA thermograms for CubePOZO. The hybrid CubePOZO show an increase in glass transition temperature (T_g) except CubePOZO50, compared to that of homoPOZO initiated by methyl *p*-toluenesulfonate. This can be attributed to the reduction of segmental mobility of POZO in CubePOZO, which was caused by the incorporation of the hard, compact POSS moiety (Figure 1a). In the case of CubePOZO50, no increase in T_g was observed because the real molecular weight of CubePOZO50 was too small to reveal the effect of POSS on the mobility of POZO. The thermal stabilities of CubePOZO increased as the weight percent of POSS was increased (Figure 1b). This is a measure of the effect of the inorganic POSS unit on polymer thermal properties. CubePOZO show the strong reflections ($2\theta = 17°−19°$) indicative of crystallinity of Cube-1I, which confirm the formation of CubePOZO consisting of POSS and POZO moieties.

Preparation of Hybrid Micelles of CubePOZO. CubePOZO self-assembled in an aqueous solution to form a novel hybrid micelle structure by serving POSS segments as a hydrophobic core and POZO segments as a surrounding hydrophilic outer shell. The micelle formation of CubePOZO was confirmed by NMR spectroscopy, a fluorescence technique, and SEM.[25,26] Figure 2 shows the ^{1}H NMR spectra of CubePOZO100 in CDCl$_3$ (a) and CD$_3$OD (b). While the whole peaks from both
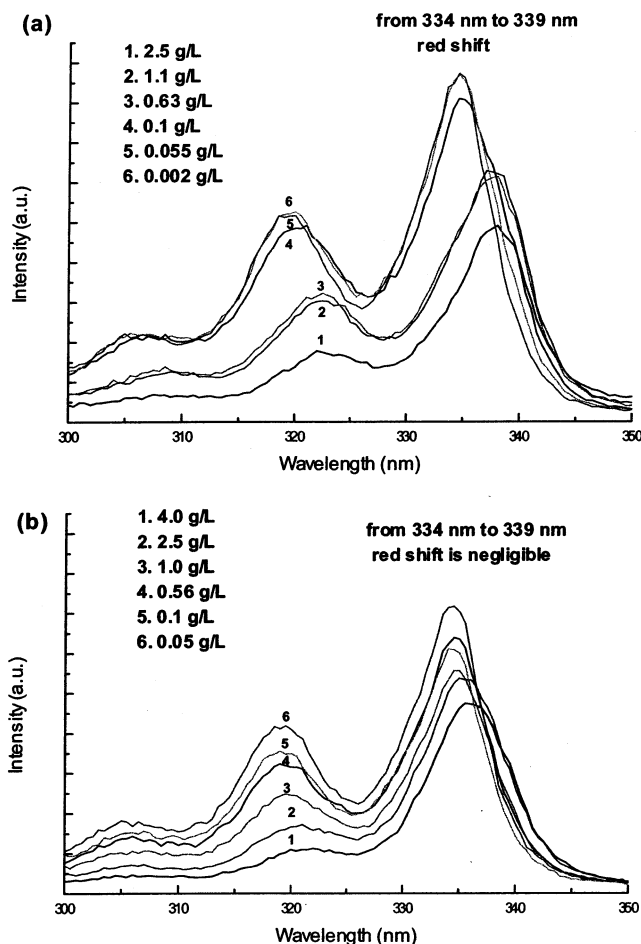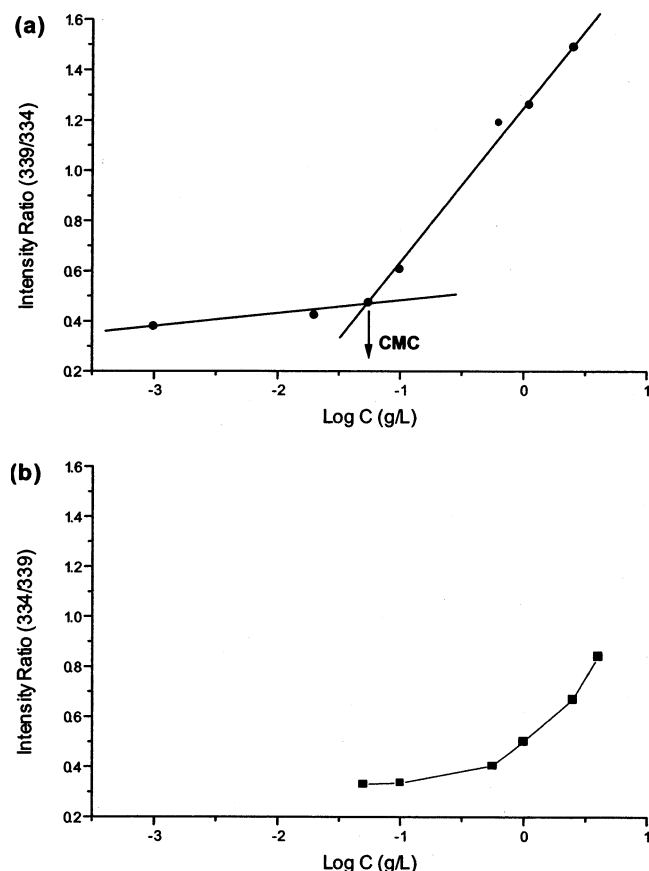
Figure 3. Excitation spectra of pyrene as a function of (a) CubePOZO and (b) cyclohexylPOZO concentration in aqueous solution.

POSS (0.7, 0.9, and 1.3−1.8 ppm) and POZO (2.1 and 3.5 ppm) moieties were clearly observed in CDCl$_3$, the peaks of POSS disappeared in CD$_3$OD, which indicated the limited molecular motion of hydrophobic POSS surrounded by the hydrophilic POZO. The critical micelle concentration (cmc) of CubePOZO micelles was determined by using pyrene as a fluorescence probe, which partitioned into the hydorphobic POSS core of micelles above the cmc value.

Excitation spectra of pyrene are shown at varying concentrations of CubePOZO100 and POZO initiated by cyclohexyl iodide (cyclohexylPOZO100) (Figure 3). Above the critical concentration region, the remarkable shift of pyrene spectra from 334 to 339 nm was observed, reflecting the change in vibrational structure of pyrene emission (Figure 3a). On the other hand, with increasing concentration of cyclohexylPOZO100, the distinct red shift from 334 to 339 nm was not observed in cyclohexylPOZO100 (Figure 3b). This means that enhanced hydrophobicity of cyclopentyl groups derived from the structure of POSS leads to form the POSS core of hybrid micelles. The fluorescence intensity ratio at the two excitation wavelengths (I_{339}/I_{334}) was used to determine the cmc value of CubePOZO.

Figure 4 shows the intensity ratio (I_{339}/I_{334}) of pyrene excitation spectra depending on the concentration of CubePOZO100 and cyclohexylPOZO100. The cmc value was determined from the threshold concentration, where the intensity ratio I_{339}/I_{334} begins to increase markedly (Figure 4a), whereas there was no distinctly increased

(a)

(b)

Figure 4. Intensity ratio (I_{339}/I_{334}) of pyrene in the excitation spectra as a function of logarithm of (a) CubePOZO100 and (b) cyclohexylPOZO concentration.

intensity ratio I_{339}/I_{334} despite the increase of cyclohexyl-POZO100 concentration (Figure 4b). No cmc value in methylPOZO initiated by methyl *p*-toluenesulfonate was observed alike. The cmc values of CubePOZO200 and CubePOZO100 were 55 and 100 mg/L, respectively. CubePOZO having a higher POSS moiety, CubePOZO20 and CubePOZO50, could not form the micelle formation in an aqueous phase, which might be ascribed to their rather poor dispersion caused by the increased POSS moiety in aqueous media. The micelles of CubePOZO were visualized as the spherical shape by SEM as shown in Figure 5. The cmc and the micelle size of CubePOZO were higher and larger than those of other amphiphilic block copolymers.[27,28] This phenomenon indicated that high concentration of CubePOZO was necessary to make micelle formation because of weaker hydrophobicity of CubePOZO than that of normal amphiphilic block copolymer. Any precipitation or aggregation was not observed even after the micelle solution of CubePOZO was left in air for 1 month, indicating the high stability of hybrid micelles from CubePOZO in an aqueous phase.

Polymer Hybrids from CubePOZO and TMOS Utilizing the Sol−Gel Reaction. Transparent and homogeneous polymer hybrids were prepared in a wide range of compositions utilizing hydrogen-bonding interaction between CubePOZO and silica gel (Scheme 3). In other words, hydrophobic POSS was homogeneously dispersed with POZO in the silica gel matrix. Initial contents of CubePOZO and TMOS were varied as shown in Table 2. The mixing of homoPOZO, Cube-1I, and TMOS resulted in the phase separation between hydrophilic POZO and hydrophobic POSS in the silica gel
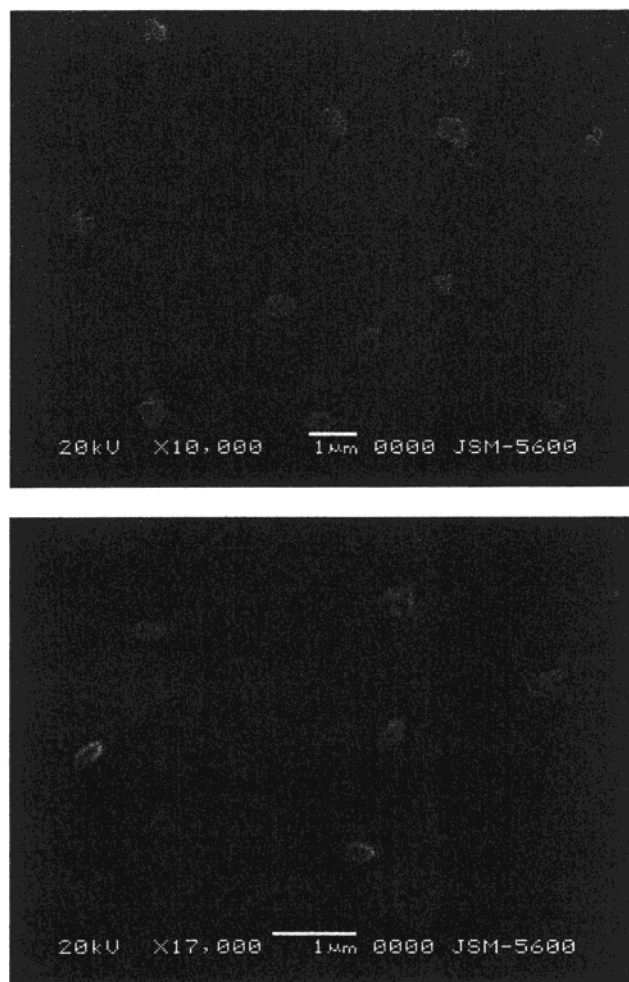
Figure 5. Scanning electron micrographs of hybrid Cube-POZO100 micelles.

Table 2. Preparation of Polymer Hybrids from CubePOZO

run[a]	materials[b] (g)	TMOS (g)	HCl (0.1 M) (mL)	appearance[c]	polymer content calcd	polymer content obsd[d]
1	homoPOZO Cube-1I (0.01)	0.24	0.12	turbid		
2	CubePOZO20	0.2	0.1	transparent		
3	CubePOZO50	0.2	0.1	transparent	38.7	38.5
4	CubePOZO100	0.2	0.1	transparent	38.7	37.4
5	CubePOZO200	0.2	0.1	transparent		
6	CubePOZO20	0.5	0.24	transparent		
7	CubePOZO50	0.5	0.24	transparent		
8	CubePOZO100	0.5	0.24	transparent	20.2	23.2
9	CubePOZO200	0.5	0.24	transparent		
10	CubePOZO20	1.0	0.47	transparent		
11	CubePOZO50	1.0	0.47	transparent		
12	CubePOZO100	1.0	0.47	transparent	11.2	17.4
13	CubePOZO200	1.0	0.47	transparent		

[a] Methanol was used as a solvent. [b] CubePOZO and homoPOZO were fixed at 0.05 g. [c] Homogeneity was observed optically. [d] Measured by TGA.

matrix (run 1). The optically transparent polymer hybrids were obtained in most cases except run 1. This methodology can be effectively used to prepare polymer hybrids from hydrophilic and hydrophobic materials with TMOS, whose polymer hybrids have been thought to be prepared with difficulty.

FT-IR measurement of polymer hybrids confirms the shift of amide carbonyl peaks caused by hydrogen-
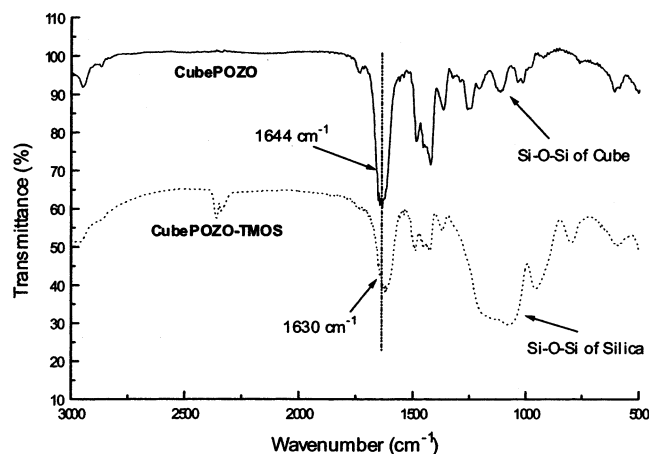
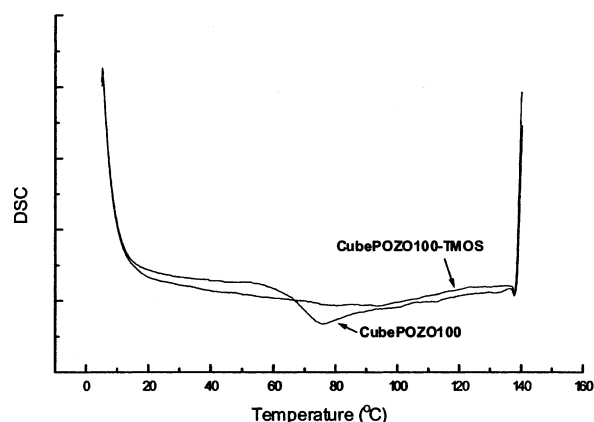**Figure 6.** FT-IR spectra of polymer hybrids from CubePOZO.

**Figure 7.** DSC thermograms of polymer hybrids from Cube-POZO.

bonding interaction between CubePOZO and silica gel. Figure 6 is representative IR spectra of CubePOZO and CubePOZO and TMOS hybrid. The amide carbonyl peaks of CubePOZO were downshifted from 1644 to 1630 cm^{-1} with the formation of hydrogen-bonding interaction. The disappearance of T_g of the polymer hybrids using CubePOZO was determined by DSC (Figure 7). These results indicate the complete and homogeneous mixing of CubePOZO and inorganic phase.

The homogeneity of polymer hybrids was confirmed by SEM. As shown in Figure 8, the polymer hybrids from CubePOZO and TMOS with various ratios showed a homogeneous dispersion of CubePOZO in the silica gel matrix at the molecular level (Figure 8b−d). On the other hand, an aggregation of homoPOZO and Cube-1I in the silica gel matrix brought about the phase separation (Figure 8a).

The solvent-resistant property by the effect of POSS in the hybrid system was estimated by means of solvent extraction experiments. The results are shown in Table 3. Surprisingly, very little CubePOZO component was extracted with CH$_3$OH and CHCl$_3$, while 70−80% of homoPOZO initiated by methyl p-toluenesulfonate was extracted with CH$_3$OH. This excellent solvent resistance is similar to that of polymer hybrids having an interpenetrating polymer network structure. It is likely that the hydrophobic interaction between two or three Cube-POZO with hydrophobic POSS moiety, which is poorly soluble in methanol itself, results in the strong resistance against solvent extraction.
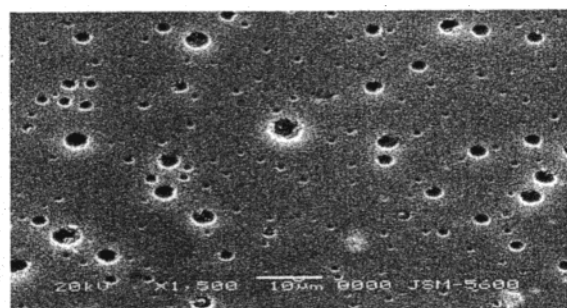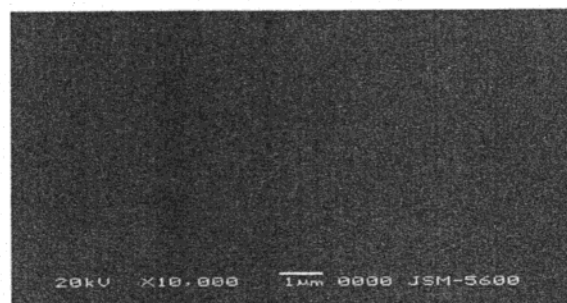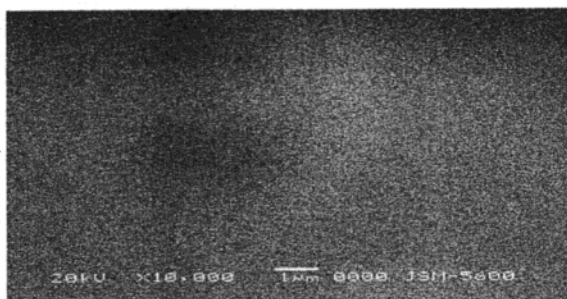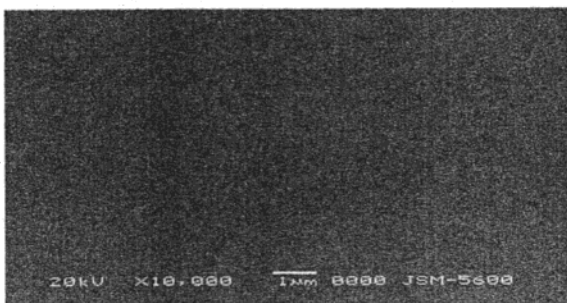

Figure 8. SEM images of polymer hybrids from CubePOZO: (a) homoPOZO/Cube-1I/TMOS = 0.05 g/0.01 g/0.24 g; (b) CubePOZO20/TMOS = 0.05 g/0.5 g; (c) CubePOZO100/TMOS = 0.05 g/0.2 g; (d) CubePOZO200/TMOS = 0.05 g/1.0 g.

The quantity and the size of organic domain were evaluated by nitrogen absorption porosimetry as compared with calcined hybrids (Figure 9a) and Soxhlet extraction hybrids (Figure 9b). The pore size distribution of calcined hybrids had a maximum at 1.7 nm, while Soxhlet extraction hybrids had very few quantity of pore and more larger pore size of 2.9 nm, compared to those of calcined hybrids. This result of nitrogen absorption porosimetry is consistent with that of solvent extraction experiments. It was considered that calcined hybrids had a smaller pore size by the transformation from

**Table 3. Solvent-Resistant Property of Polymer Hybrids from CubePOZO[a]**

run	solvent	solvent extraction efficiency (%)	polymer content (wt %)[c]	
			P_a	P_b
1	methanol	3.5	33.	33.8
2	chloroform	5.7	32.5	33.8
3[b] (homoPOZO)	methanol	70.7	17.4	41.8

[a] The polymer content in polymer hybrids before (P_b) and after (P_a); solvent extraction efficiency E was calculated according to the equation $E = 100(P_b - P_a)/P_b(100 - P_a)$. [b] Polymer hybrids from homoPOZO and TMOS. [c] Measured by TGA.
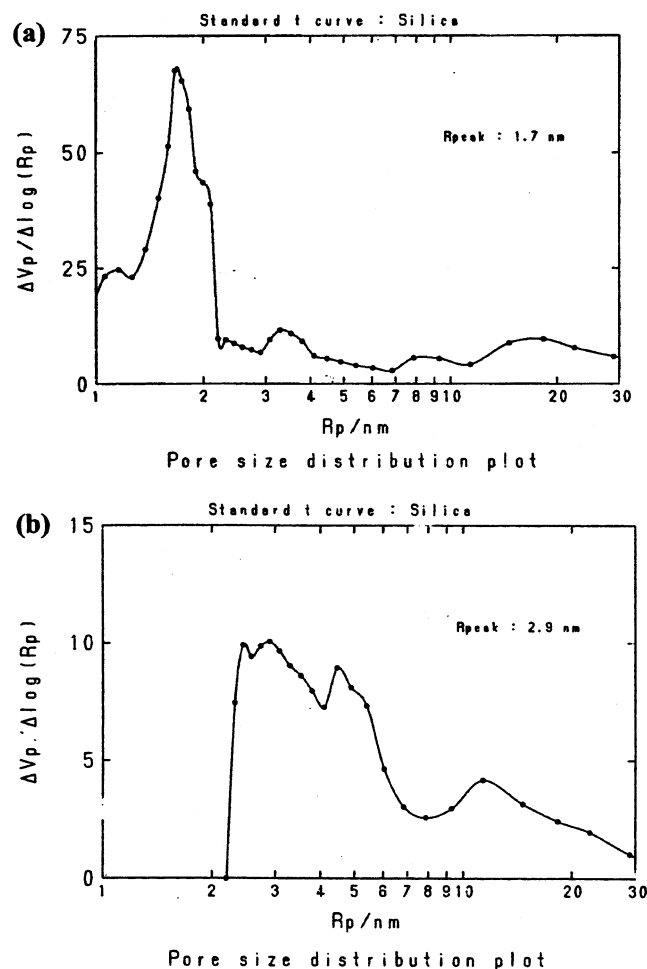
Figure 9. Pore size distribution of (a) calcined and (b) Soxhlet extraction CubePOZO/silica polymer hybrids.

POSS to Si_8O_{16} than Soxhlet extraction hybrids by no change of CubePOZO (even little CubePOZO was extracted), as demonstrated in Figure 10.

From these results, the excellent solvent resistance can be explained to stem from the hydrophobic interaction between the POSS in CubePOZO and the increased size of POSS domain in silica gel matrix derived from close distance between the POSS by hydrophobic interaction. It is of interest to note that this unique method for high solvent resistance not using any cross-linking material in the hybrid system may find applications in the industrial area. Thermal stabilities of polymer hybrids from CubePOZO were much increased with increasing feed ratio of TMOS to CubePOZO, indicating homogeneous dispersion of the CubePOZO in the thermally stable inorganic matrix.
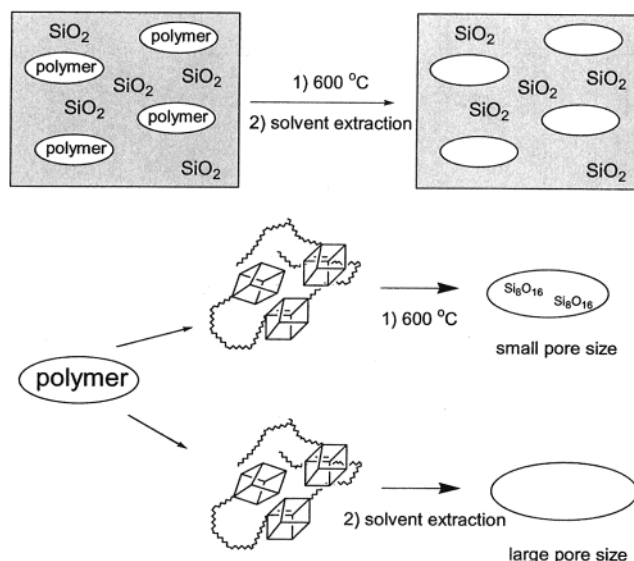
Figure 10. Schematic illustration for hydrophobic interaction between CubePOZO having hydrophobic POSS moiety themselves in the silica gel matrix.

Conclusion

A new class of hybrid POZO initiated by POSS (CubePOZO) with various feed ratios was synthesized. CubePOZO composed of POSS as a hydrophobic portion and POZO as a hydrophilic portion formed the hybrid micelles in an aqueous phase, indicating that enhanced hydrophobicity caused by the structure of POSS participated in the formation of the micelle structure. No aggregation of hybrid CubePOZO micelles in an aqueous solution for long period indicated that their self-assembling tendency was stable enough. Transparent polymer hybrids from CubePOZO and TMOS utilizing sol–gel reaction were prepared and characterized by DSC, TGA, FT-IR, SEM, and nitrogen absorption porosimetry. Hydrophobic POSS bonded covalently to POZO were homogeneously dispersed in the silica gel matrix at the nanometer level. The obtained polymer hybrids from CubePOZO showed the high solvent resistance, similar to that of polymer hybrids having an interpenetrating polymer network structure. This novel method for preparing hybrid micelles and polymer hybrids from hydrophobic and hydrophilic materials with TMOS can be potentially used to enlarge the pathways for new organic–inorganic polymer hybrids.

References and Notes

(1) Giannelis, E. P. *Appl. Organomet. Chem.* **1998**, *12*, 675.
(2) Innocenzi, P.; Brusatin, G. *Chem. Mater.* **2001**, *13*, 3126.
(3) Pyun, J.; Matyjaszewski, K. *Chem. Mater.* **2001**, *13*, 3426.
(4) Chandrasekhar, V.; Athimoolam, A. *Org. Lett.* **2002**, *4*, 2113.
(5) Panusa, A.; Flamini, A.; Poli, N. *Chem. Mater.* **1996**, *8*, 1202.
(6) Kim, H. K.; Kang, S. J.; Choi, S. K.; Min, Y. H.; Yoon, C. S. *Chem. Mater.* **1999**, *11*, 779.
(7) Tamaki, R.; Chujo, Y.; Kuraoka, K.; Yazawa, T. *J. Mater. Chem.* **1999**, *9*, 1741.
(8) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.
(9) (a) Chujo, Y.; Saegusa, T. *Adv. Polym. Sci.* **1992**, *100*, 11. (b) Tamaki, R.; Chujo, Y. *Chem. Mater.* **1997**, *7*, 1719. (c) Tamaki, R.; Samura, K.; Chujo, Y. *Chem. Commun.* **1998**, 1131. (d) Tamaki, R.; Naka, K.; Chujo, Y. *Polym. Bull. (Berlin)* **1997**, *39*, 303. (e) Ogoshi, T.; Itoh, H.; Kim, K. M.; Chujo, Y. *Macromolecules* **2002**, *35*, 334.
(10) Schwab, J. J.; Lichtenhan, J. D. *Appl. Organomet. Chem.* **1998**, *12*, 707.

(11) Fu, B. X.; Hsiao, B. S.; Pagola, S.; Stephens, P.; White, H.; Rafailovich, M.; Sokolov, J.; Mather, P. T.; Jeon, H. G.; Phillips, S.; Lichtenhan, J. D.; Schwab, J. *Polymer* **2001**, *42*, 437.

(12) Choi, J. W.; Harcup, J.; Yee, A. F.; Zhu, Q.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 11420.

(13) Kim, K. M.; Chujo, Y. *J. Mater. Chem.*, submitted.

(14) Kim, K. M.; Chujo, Y. *Polym. Bull. (Berlin)* **2001**, *46*, 15.

(15) Kim, K. M.; Chujo. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 4035.

(16) Itoh, H.; Naka, K.; Chujo, Y. *Polym. Prepr. Jpn.* **2001**, *50*, 307.

(17) Keum, D. K.; Kim, K. M.; Naka, K.; Chujo, Y. *J. Mater. Chem.* **2002**, *12*, 2449.

(18) Kim, K. M.; Chujo, Y. *Polym. Bull. (Berlin)* **2001**, *46*, 351.

(19) Kim, K. M.; Adachi, K.; Chujo, Y. *Polym. Prepr. Jpn.* **2000**, *49*, 1757.

(20) Kim, K. M.; Adachi, K.; Chujo, Y. *Polymer* **2002**, *43*, 1171.

(21) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526.

(22) Lee, S. C.; Chang, Y.; Yoon, J. S.; Kim, C.; Kwon, I. C.; Kim, Y. H.; Jeong, S. Y. *Macromolecules* **1999**, *32*, 1847.

(23) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(24) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.

(25) Wilhelm, M.; Zhao, C.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 1033.

(26) Kim, C.; Lee, S. C.; Kang, S. W.; Kwon, I. C.; Kim, Y. H.; Jeong, S. Y. *Langmuir* **2000**, *16*, 4792.

(27) Jeong, J. H.; Park, T. G. *Bioconjugate Chem.* **2001**, *12*, 917.

(28) Kim, C.; Lee, S. C.; Kwon, I. C.; Chung, H.; Jeong, S. Y. *Macromolecules* **2002**, *35*, 193.

MA021303B