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Tuning of Properties of POSS-Condensed Water-Soluble Network Polymers by Modulating the Cross-Linking Ratio between POSS

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ABSTRACT: We describe the synthesis and characteristics of the water-soluble network polymers consisting of POSS. When $[ClH_3N(CH_2)_3]_8Si_8O_{12}$ and $[HO_2C(CH_2)_2CONH(CH_2)_3]_8Si_8O_{12}$ were condensed in the aqueous solutions, a series of the POSS polymers with the different cross-linking ratios between POSS can be synthesized by changing the monomer concentrations in the reaction solutions. The hydrophobicity inside the POSS polymers and the mobility of the entrapped molecules into the polymers significantly depend on the cross-linking ratio of the polymers. The refractive indices of the thin films obtained from the aqueous solutions of the polymer were examined, and it was revealed that the decrease of the cross-linking ratio can significantly lift up the refractive indices from 1.51 to 1.58 due to the effect of the different amount of polar substitution groups such as amino and carboxylate groups. We demonstrate one example for modulating the properties of the POSS-based material via the small conditional change in the synthesis.

Introduction

New classes of hybrid materials with organized structures often lead to interesting chemical or physical properties distinctly different from those of their component parts.[1] Development of general methods for building 2-D or 3-D nanostructures is a critical process and an important goal in materials chemistry for practical applications in nanotechnology as they provide a molecular-level control over the macroscopic properties.[2] Polyoctahedral oligomeric silsesquioxanes (POSS) have paid attention not only as a platform for the combination of organic and inorganic materials at the molecular scale but also as a building block for constructing 3-D network structure.[3]

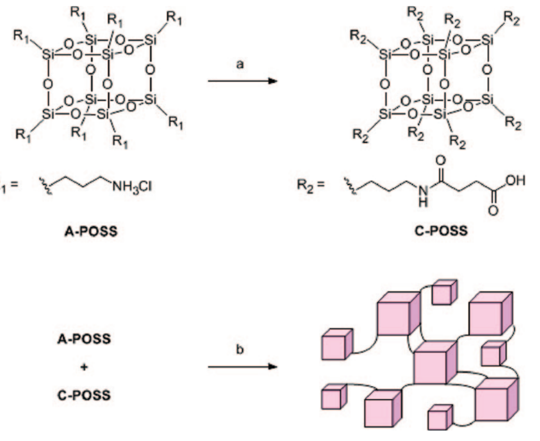
The incorporation of POSS moieties into the side or main chains of conventional polymers can greatly enhance thermal and chemical stability due to the rigidity of the inner silicon and oxygen framework.[4] The incorporation of POSS into materials can reduce the refractive index due to lower density of the cubic structure, and as applications, stimuli-responsive optical polymers containing modified POSS species have been reported.[5] The POSS-based molecules can show good dispersion state in solvents or materials, and a variety of the POSS derivatives have been used as a filler to improve the thermal or mechanical properties of conventional polymers.[6] In particular, the POSS-core dendrimers which have hydrophilic distal groups can produce distinct special space in aqueous solutions.[7] As applications, the encapsulation of lipophilic molecules or nucleic acids for drug delivery and the scaffolds for the functional MRI contrast agents have been reported.[8,9] Therefore, we can expect that POSS-assembling materials have large potential to present interested characteristics in addition to the intrinsic properties of single POSS molecules.

We herein report the synthesis and characteristics of the water-soluble network polymers containing POSS. Octaammonium and octacarboxy POSS[11] were synthesized and condensed in the aqueous solutions. The cross-linking ratio between POSS in the polymers can be modulated by changing the monomer concentrations in the polymerization reaction. The hydrophobicity inside the POSS polymers and the mobility of the entrapped molecules into the polymers significantly depend on the cross-linking ratio of the polymers. In addition, the refractive indices of the thin film obtained from the aqueous solutions of the polymer were also tunable by the cross-linking ratio. We can demonstrate the simple method for controlling polymer properties by the small conditional change in the polymer synthesis.

Results and Discussion

Octaaminopropyl POSS (A-POSS) was prepared according to the previous reports.[10] Scheme 1 illustrates the synthesis of the POSS polymers. A-POSS was reacted in the methanolic solution with excess succinic anhydride in the presence of triethylamine at 25 °C for 2 h, followed by washing with chloroform, and then octa-substituted carboxy-termini POSS (C-POSS) was successfully obtained in good yield (79%). C-POSS was identified with ^{1}H, ^{13}C, and ^{29}Si NMR and MS spectroscopy. For the next condensation, A-POSS and C-POSS were used as the monomer without further purification. The polymerizations with A-POSS and C-POSS (0.85 mmol) were carried out in the presence of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride[9] (DMT-MM, 8.5 mmol, 10 equiv)

Scheme 1. Synthetic Scheme of the POSS Monomers and Polymers[a]



[a] Reagents and conditions: (a) succinic anhydride, triethylamine, methanol, 25 °C, 2 h, 79%; (b) DMT-MM, triethylamine, water, 25 °C, 24 h.

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Table 1. Physicochemical Properties of the POSS Polymers

run	solvent (mL)	yield (%)	cross-linking ratio (%)[a]	M_n[b]	PDI[b]	r_H (nm)[c]	T_d (5%, °C)[d]	n_D[e]
1	10	99	97	3500	22.5	187 ± 21	210	1.51
2	20	90	76	3500	17.6	174 ± 21	190	1.55
3	50	90	58	3800	18.2	154 ± 21	176	1.58
4	100	68	52	3000	16.1	159 ± 21	147	

[a] All values were determined from the ^{1}H NMR spectra. [b] M_n and polydispersity index (PDI = M_w/M_n) of the polymers were determined by the GPC analysis using poly(ethylene glycol) standards. [c] The values were determined from the DLS analysis. [d] Thermal decomposition temperature of 5% mass loss. [e] Refractive indices were measured with the thin films of the POSS polymers.

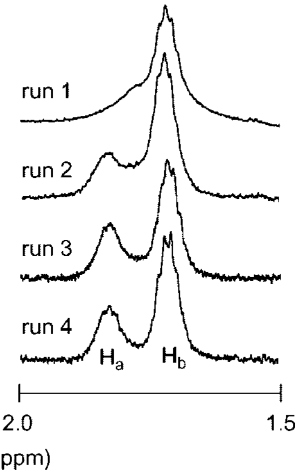

Figure 1. ^{1}H NMR spectra (400 MHz, D_2O) of the polymerization products. The signal peaks were assigned as the 2-position of the hydrogen atoms at the aminopropyl linker. After the amide bond formation of the amino groups in A-POSS, the peak was shifted from 1.7 to 1.6 ppm. The cross-linking ratio was calculated from the integral ratio of these peaks.

known as an effective water-soluble condensation agent and triethylamine (1 mL) in various volumes of water (10, 20, 50, and 100 mL) as a solvent at 25 °C. Less gelation or precipitation was observed after 24 h stirring. After finishing the reaction, the resulting mixtures were passed through the size-exclude membrane to eliminate unreacted monomers and miscellaneous salts. The water-soluble, white powders were obtained after drying in vacuo.

GPC analysis for the POSS polymers showed reaction yields and molecular weights compared to poly(ethylene glycol) standards in the aqueous solvent system (Table 1). Large M_w/M_n values, typical of the condensation polymerization, were observed for all samples. In addition, from the DLS measurements with aqueous solutions of the POSS polymers (1 mg/mL), the hydrodynamic radii r_H of the corresponding POSS polymers were determined to be larger than those of the plural monomers, A-POSS and C-POSS (25 ± 6 and 11 ± 1 nm, respectively). These results indicate that the water-soluble polymers were synthesized.

The structures of the POSS polymers were analyzed by ^{1}H NMR and IR absorption spectra. Figure 1 shows the ^{1}H NMR spectra of the POSS polymers. The signal peak from the 2-position of the hydrogen atoms at the aminopropyl linker shifts upfield from 1.7 to 1.6 ppm on the formation of amide bonds with C-POSS in the NMR spectra. Consequently, the conversion of the amino group of A-POSS can be evaluated from the ^{1}H NMR integral ratio. The conversion of the amino group was varied from 97% (run 1) to 52% (run 4). From the IR spectra, we confirmed the cross-linking between A- and C-POSS. The broad peak at 3300 cm^{-1} assigned as the amide bond appeared in samples from runs 1 and 2 (Figure 2). In contrast, the peak at 2200 cm^{-1} was observed in samples from runs 3 and 4. These data represent good agreement with the amount of the amino group evaluated from the NMR data. The concentrations of the POSS monomers and the condensation agent in the reaction solutions were lowered by increasing the solvent volume; therefore, the percentages of unreacted amino and carboxyl groups in the polymers should increase. These results suggest that the cross-linking ratio between the POSS moieties should be tunable by changing the solvent volume in the polymerization, and the amounts of residual ionic functional groups such as ammonium of A-POSS and carboxylate of C-POSS in the polymer could be modulated by the condensation reaction.

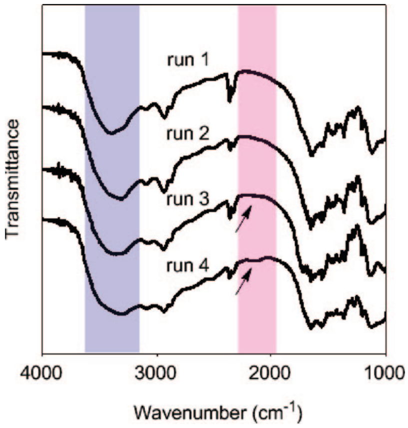

Figure 2. FTIR spectra of the POSS polymers.

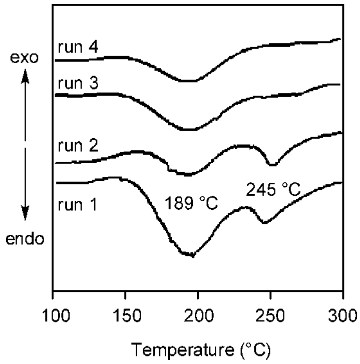

Figure 3. DSC profiles of the POSS polymers from 100 to 300 °C.

We investigated the thermal stability of the POSS polymers with TGA. The decrease of the T_{5d} values which mean the temperature taking place weight loss of 5% were observed from run 1 to run 4. This result is likely because the formation of the cross-linking can enhance the thermal stability of the network structure. In the DSC profiles of the run 1 and run 2 samples, two endothermic peaks were observed at 189 and 245 °C (Figure 3). On the other hand, the endothermic peak at higher temperature was not detected in the samples of run 3 and run 4. These data support that the cross-linking between POSS has an ability to stabilize the network structure.

The polarity inside the POSS polymers in aqueous solutions was investigated by the photochemical approach. We used 6-(dimethylamino)-2-naphthaldehyde (DAN) known as a microenvironment-sensitive fluorescent probe (Figure 4a and Table 2).[12] The irradiation at 300 nm wavelength to the DAN solution gave fluorescence emission at the peak of 530 nm, which can represent the polarity of the local microenvironment as the position of the peak top (Figure 4b).[12a] The samples containing 1 mg/mL of the POSS polymers and 10 μM DAN in 50 mM sodium phosphate buffer (pH = 7.0) were sonicated for 15 min at 25 °C for entrapping DAN into the polymers. From the run

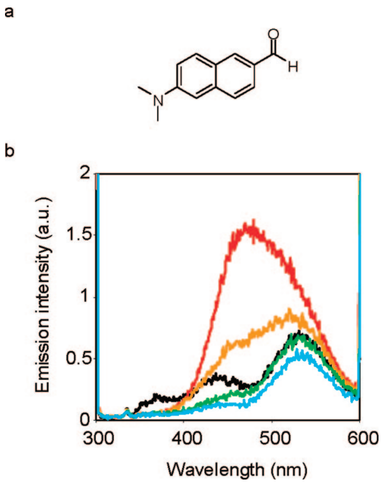

Figure 4. (a) Chemical structure of DAN. (b) Fluorescence spectra of the sample containing 10 μM DAN (black line) and 1 mg/mL of the POSS polymers from run 1 (red line), run 2 (yellow line), run 3 (green line), and run 4 (blue line) in 50 mM sodium phosphate buffer (pH = 7.0), measured at 25 °C with the excitation at 300 nm.

Table 2. Optical Properties of the Fluorophores Entrapped into the POSS Polymers

	DAN		CCVJ	
run	λ_{em} (nm)[a]	Φ_F[a] ($\times 10^{-2}$)	emission intensity (au)[b]	Φ_F[b] ($\times 10^{-2}$)
1	475	0.137	2990	0.004
2	521	0.081	2660	0.004
3	530	0.049	2000	0.002
4	530	0.036	1830	0.002
fluorophore	532	0.057	1380	0.002

[a] Emission peaks and quantum yields were obtained from the solution containing 10 mM DAN with or without 1 mg/mL the POSS polymers in 50 mM sodium phosphate buffer with the excitation at 300 nm at 25 °C. [b] Emission intensities at 500 nm and quantum yields were obtained from the solution containing 10 mM CCVJ with or without 1 mg/mL the POSS polymers in 50 mM sodium phosphate buffer with the excitation at 430 nm at 25 °C.

3 and 4 samples, the emission spectra were less significantly changed from the DAN solution. On the other hand, the run 2 sample showed the peak broadening toward shorter wavelength, and the run 1 sample had the larger emission band at the peak of 460 nm which was the similar emission band observed from the acetonitrile solution of DAN. These data represent that the POSS polymers can provide hydrophobic spaces to DAN in water, and the increase of the cross-linking ratio could enhance the hydrophobicity inside polymers.

In order to examine the interaction with POSS in the polymers, the molecular rotor, 9-(2-carboxy-2-cyanovinyl) julolidine (CCVJ), was entrapped with same manner as above, and the emission from each sample with the excitation at 430 nm was monitored (Figure 5).[13] The CCVJ derivatives can show strong emission under higher viscosity circumstances due to the suppression of nonradiative process via internal molecular rotation; therefore, in this experiment, we can evaluate the motility of CCVJ inside the POSS polymers from fluorescence intensity. The emission bands at the peak of 500 nm from the run 3 and 4 samples were enhanced slightly compared to the CCVJ solution. On the other hand, the run 1 and 2 samples showed ~2.5-fold larger emission intensities than the CCVJ solution. These data suggest that the molecular rotation is restricted due to the rigid structure of the POSS moiety and the amide cross-linkers. The peak position of CCVJ derivatives was reported to be less dependent on solvent polarity, while the changes in Stokes shifts were observed in the run 3 and 4 samples.[14] These results imply that the high numbers of ammonium and carboxylate groups in their samples might generate strong interactions with the CCVJ fluorophore.

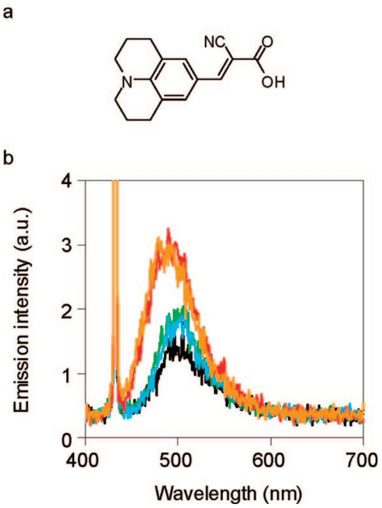

Figure 5. (a) Chemical structure of CCVJ. (b) Fluorescence spectra of the sample containing 10 μM CCVJ (black line) and 1 mg/mL of the POSS polymers from run 1 (red line), run 2 (yellow line), run 3 (green line), and run 4 (blue line) in 50 mM sodium phosphate buffer (pH = 7.0), measured at 25 °C with the excitation at 430 nm.

Refractive indices (n) are increased in the presence of carboxylate anions inside glass materials.[15] We expected that we could tune the n values by controlling the cross-linking ratios of the POSS polymers. We prepared thin films cast from the aqueous solutions of the POSS polymers. The POSS polymers (10 mg) were dissolved in 1% triethylamine solution, followed by casting onto the silicon wafer. After 24 h at ambient temperature, submicron-thick films were obtained (0.5 μm). The n values were determined using an Abbe refractometer at 580 nm at 25 °C. As we expected, the n values increased in the wide range from 1.51 (run 1) to 1.58 (run 3) by addition of the cross-linking ratios. These results represent that the tuning of the refractive index can be realized by the regulation of the solvent volume in the polymerization.

Conclusion

In conclusion, a new series of water-soluble POSS-containing polymers were synthesized, and the cross-linking ratio between the POSS molecules can be tuned by small changes in synthetic conditions such as the solvent volume. The cross-linking ratio between POSS in the polymer can create microenvironments with distinct properties in the solution and with a wide-range of tunable refractive indices in this film. Water solubility and the simple tuning of the properties of the POSS polymers described here could be beneficial not only for developing new materials with less environmental burden but also for developing biochemical matters. We can demonstrate one example of a POSS assembly that includes large potentials to represent interesting characteristics due to their structural specificities.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were measured with a JEOL EX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer. ^{29}Si NMR spectra were measured with a JEOL JNM-A400 (80 MHz) spectrometer. Coupling constants (J value) are reported in hertz. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using residual chloroform (δ = 7.24 in ^{1}H NMR, δ = 77.0 in ^{13}C NMR) as an internal standard. The samples for TGA measurements and elemental analysis were isolated from dispersed solutions by centrifugation and purified by repeated washing with acetonitrile, followed by drying in vacuo at room temperature for 24 h. The refractive indices were determined with an Abbe refractometer at 580 nm at 25 °C. The polymers (10 mg) were dissolved in 1% triethylamine solution, followed by the mixtures casting of the silicon wafer. For the measurements of fluorescence spectra, samples containing the polymers (1 mg/mL) and 10 μM fluorophores were sonicated for 30 s in 50 mM sodium phosphate buffer (pH = 7.0) and allowed to equilibrate in darkness overnight. Emission from the samples was monitored using a Perkin-Elmer LS50B at 25 °C using 1 cm path length cell. The quantum yields were determined as the absolute value using the integral sphere. The excitation bandwidth was 3 nm. The emission bandwidth was 3 nm. The DLS measurements were carried out at 90° scattering angle and 25 ± 0.2 °C using a FPAR-1000 particle analyzer with a He−Ne laser as a light source. The CONTIN program was used for data analysis to extract information on the average hydrodynamic size. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1600 infrared spectrometer. Gel permeation chromatography (GPC) was carried out on a UV-8020 and RI-8020 (TSK-GEL g-3000) using water as an eluent after calibration with standard poly(ethylene glycol). Differential scanning calorimetry (DSC) thermograms were carried out on a SII DSC 6220 instrument by using ~10 mg of exactly weighed samples at heating rate of 10 °C/min. MASS spectra were obtained on a JEOL JMS-SX102A.

A-POSS (1). (3-Aminopropyl)triethoxysilane (100 mL, 0.427 mol) and 35−37% HCl (135 mL) in MeOH (800 mL) produced **1** as a white precipitate after 2 days at room temperature. The crude product was obtained after filtration, washing with cold MeOH, and drying. The product was spectroscopically pure in 30% yield (18.8 g). Recrystallization from hot MeOH afforded **1** (4.29 g, 3.66 mmol, 7%) as a white solid. ^{1}H NMR ($(CD_3)_2SO$, 25 °C): δ 8.23 (s, 24H), 2.76 (t, 16H), 1.71 (m, 16H), 0.72 (t, 16H). ^{13}C NMR ($(CD_3)_2SO$, 25 °C): δ 40.53, 20.13, and 7.96. ^{29}SiNMR($(CD_3)_2SO$, 25 °C): δ −66.4 (s).

C-POSS (2). To a solution of POSS **1** (1.0 g, 0.85 mmol) and triethylamine (1 mL, 7.2 mmol) in methanol (20 mL), succinic anhydride (1.5 g, 15.0 mmol) was added, and the reaction mixture was stirred at room temperature. After stirring for 2 h, chloroform was poured into the reaction solution, and white precipitation was collected via filtration and washing with chloroform as a white powder C-POSS (1.1 g, 0.67 mmol, 79%). ^{1}H NMR (DMSO, 400 MHz): δ 0.59 (br, 2H), 1.44 (br, 2H), 2.30 (br, 2H), 2.41 (br, 2H), 3.02 (br, 2H). ^{13}C NMR (DMSO, 100 MHz): δ 8.74, 22.48, 29.15, 29.98, 41.00, 170.92, 173.89. ^{29}Si NMR (D_2O, 80 MHz): δ −65.3. LRMS (NBS) $[(M + H)^+]$: calcd 1680, found 1680. HRMS (NBS) $[(M + H)^+]$: calcd 1680.4081, found 1680.4041.

Polymerization. To a solution of A-POSS (1.00 g, 0.85 mmol), C-POSS (1.43 g, 0.85 mmol), and triethylamine (1 mL, 7.2 mmol) in methanol (20 mL), 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM, 85%) (2.77 g, 8.5 mmol) was added, and the reaction mixture was stirred at room temperature. After stirring for 24 h, the resulting mixture was directly dialyzed in distilled water, following evaporation gave the POSS polymers as a white powder. The yields and the results of GPC analysis are shown in Table 1 in the content.

Determination of the Cross-Linking Ratio. From ^{1}H NMR spectra of the polymerization products in D_2O, the integral ratio was determined from the peaks at 1.7 and 1.6 ppm assigned as the 2-position of the hydrogen atoms before (H_a) and after (H_b) the amide bond formation, respectively. The cross-linking ratio was calculated according to the following equation:

$$\text{cross-linking ratio (\%)} = (H_b - H_a)/H_b \times 100 \qquad (1)$$

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