Synthesis of Polystyrene and Silica Gel Polymer Hybrids Utilizing Ionic Interactions

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We investigated the synthesis of nanometer scale homogeneous polystyrene and silica gel polymer hybrids utilizing ionic interactions. The partially sulfonated polystyrene (10 mol %) was used as a starting organic polymer and (3-aminopropyl)trimethoxysilane (APTMOS) was used as a countercation as well as the precursor to the inorganic phase. The content of silica gel was controlled by the further addition of tetramethoxysilane (TMOS). The level of dispersity of the organic and the inorganic phase was found to be dependent on the amounts of APTMOS. When more than 0.5 mol equiv of APTMOS in relation to the sulfonic acid groups was incorporated in the sol−gel reaction mixture of TMOS and the polystyrene sulfonic acid, the obtained polymer hybrids became optically transparent. The homogeneity of the polymer hybrids was also found to be strongly dependent on the type of solvents. Polar solvents such as dimethyl sulfoxide yielded transparent hybrids while tetrahydrofuran or *N*,*N*-dimethylformamide caused the phase separation of the two elements. The homogeneity of the polymer hybrids was examined by scanning electron microscopy, transmission electron microscopy and nitrogen porosimetry studies. All of these results support the nanometer scale dispersion of each phase. The morphological study on the polymer hybrids was also conducted using dynamic mechanical analysis, which suggested the increase in cross-linking between the organic phases with the increase in APTMOS.

Introduction

Hybrids of organic polymers and inorganic materials characterized by the nanoscale mixing of two phases have been intensely investigated for 10 years.[1−13] The sol−gel reaction of metal alkoxides is the most practical technique for the synthesis of these hybrid materials. The method comprises initial hydrolysis of the metal alkoxides and subsequent condensation and removal of the solvent, resulting in metal oxides.[14−19] The advantage of the sol−gel technique for the preparation of composite materials is the fact that the reactions can be carried out at ambient temperature, while the conventional melt fusion technique for silica glasses requires high temperature. Thus, it enables the introduction of organic elements into inorganic materials without deteriorating their functionalities.

As previously reviewed by some authors,[20−22] these organic−inorganic hybrid materials can be generally classified into two groups based on the interactions between organic polymers and inorganic materials employed; the formation of covalent bonds among organic polymers and inorganic phases is one of them.[23−32] The other interactions are physical interac-

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tions of the two phases that are represented by the hydrogen bondings.[33−39] In our group, the organic−inorganic polymer hybrids have been prepared by utilizing various methods. The most common method for the preparation of polymer hybrids is the utilization of the hydrogen-bonding interaction between polar functional groups of organic polymers and residual silanol groups of silica gel. Organic polymers such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone), or poly(*N*,*N*-dimethylacrylamide) were incorporated homogeneously into silica gel by these interactions.[40−45] The $\pi-\pi$ interactions between phenyl rings of organic polymers and silica gel prepared from phenyltrimethoxysilane were also found to be important interactions for the synthesis of polymer hybrids. We have succeeded in the preparation of hydrophobic polystyrene and silica gel polymer hybrids by utilizing this interaction.[46]

We present here the utilization of ionic interaction as another novel method for the integration of organic and inorganic interactions. Ionic interactions are one of important interactions for the synthesis of polymer complexes. Various types of polymer complexes have been synthesized with these interactions.[47−54] The interactions were also frequently used for the intercalation of organic compounds into metal oxide layers.[55−61] However, the interactions have not been used for the synthesis of hybrid materials of organic polymers and inorganic materials, even though some reports could be found on the synthesis of hybrids between ionomer and silica gel without the ionic interactions.[62−65] Here we investigate the utilization of the interactions as another option for the synthesis of hybrids of organic polymers and silica gel. The ionic interactions are much stronger than hydrogen-bonding interactions. Thus, the interactions supposedly enable the integration of various types of organic polymers and silica gel. At the same time, concerning the isotropic nature of the interactions, the obtained hybrid materials are expected to have some advantages in mechanical properties over polymer hybrids prepared by using covalent bondings.[66]

We used partially sulfonated polystyrene (PSSA), prepared by reacting polystyrene with chlorosulfonic acid, and (3-aminopropyl)trimethoxysilane (APTMOS) to introduce countercation groups in silica gel. The polymer hybrids were prepared by mixing PSSA, APTMOS, and tetramethoxysilane (TMOS), followed by the sol−gel reaction of these alkoxysilanes.

Experimental Section

Materials. TMOS was used after distillation under nitrogen. Tetrachloroethane was distilled under nitrogen with calcium hydride. APTMOS, dimethyl sulfoxide (DMSO), chlorosulfonic acid, 0.1 M HCl, hexane, and polystyrene ($n = 1000-1200$) were used as supplied.

Synthesis of Poly(styrenesulfonic acid). Poly(styrenesulfonic acid) (PSSA) was prepared by the reaction of polystyrene with chlorosulfonic acid in tetrachloroethane under nitrogen atmosphere at 0 °C. Polystyrene (10 g) was dissolved in tetrachloroethane (100 mL) under nitrogen. To the solution, was added chlorosulfonic acid (1.12 g) diluted in 10 mL of tetrachloroethane dropwise at 0 °C in nitrogen while the solution was stirred with a magnetic stirrer. After 20 h of stirring, the solution was diluted with additional 100 mL of tetrachloroethane and was added dropwise to 2000 mL of hexane. White precipitates were collected by filtration and washed with 200 mL of hexane. The PSSA was dried and kept in a desiccator until the preparation of polymer hybrids. The ratio of sulfonated phenyl groups in polystyrene was calculated to be 10.4% from ^{1}H NMR and the elemental analysis. Elemental analysis: H, 7.15; C, 82.22; S, 3.00. ^{1}H NMR: δ7.5−6.2 broad peak with two maxima at δ 7.1 and 6.5 (48.2 H), δ 2.2−0.8 broad peak with two maxima at δ 1.8 and 1.5 (28.9 H).[67] The molarity of the sulfonic groups is abbreviated as “*y*”, which is calculated by the weight of polystyrene (g) × 0.966 mmol/g.

Preparation of Polymer Hybrids. PSSA (0.5 or 0.1 g) was dissolved in 8 or 1.6 mL of DMSO (or other solvents discussed in the text) with the prescribed amounts of TMOS, APTMOS, and 0.1 M HCl (or water). After being stirred at room temperature for 1 h, the mixture was heated initially at 60 °C in a vessel covered with aluminum foil having a few pinholes for 12 h. The samples were further heated at 80 °C for 12 h and at 100 °C for 7 days.

Films for DMA Measurement. PSSA (1 g) was dissolved in 1.6 mL of DMSO and 0.4 mL of water. To the solution were

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Table 1. Effect of APTMOS Contents on the Homogeneity

	poly(styrene-sulfonic acid)		3-aminopropyl TMOS (mol)(mg)		TMOS					ceramic yield	
run[a]	y^b (mol)	wt (g)	y (mol)	wt (mg)	y (mol)	wt (g)	DMSO (mL)	0.1 M HCl (mL)	appearance	obs %[c]	cal %
1	1.0	0.5	0		20.0	1.47	8	2	turbid	53.3	53.7
2	1.0	0.5	0.1	8.66	19.9	1.46	8	2	translucent	52.0	53.6
3	1.0	0.5	0.3	26.0	19.7	1.46	8	2	translucent	52.0	53.3
4	1.0	0.5	0.5	43.3	19.5	1.43	8	2	transparent	51.6	53.1
5	1.0	0.5	0.7	60.6	19.3	1.42	8	2	transparent	51.0	52.9
6	1.0	0.5	1.0	86.6	19.0	1.40	8	2	transparent	50.4	52.5

[a] Each mixture was heated at 60−100 °C in a vessel covered with pin-holed aluminum foil. [b] The number of sulfonated styrene units. y = poly(styrenesulfonic acid) (g) × 0.966 mmol/g. [c] Calculated from TGA.

added the prescribed amounts of APTMOS and TMOS. The mixture was cast in a polypropyrene container and heated at 60 °C for 12 h and further heated at 80 °C for 12 h and at 100 °C for 7 days. The obtained sample was cut into a film (length 25 mm × width 9 mm × thickness 0.05 mm).

Measurement. Thermogravimetric analysis (TGA) was performed on a Shimadzu TG-30, TGC-30 with a heating rate of 10 °C/min in air for the measurement of ceramic yield. The ceramic yield was calculated at 900 °C. Scanning electron microscope (SEM) measurement was conducted with a JEOL JSM-5200 at 15 kV. The sample for transmission electron microscopy (TEM) was sectioned at room temperature from the polymer hybrid contained in an epoxy resin with a ultramicrotome, giving a film with 30 nm thickness. The thin film was dyed with RuO_4 to improve the contrast. TEM was performed with a JEOL JEM-2000FX microscope at 200 kV. Nitrogen absorption porosimetry was conducted with a BEL Japan INC instrument. The powder of the hybrids was heated at 600 °C under ambient atmosphere to remove the organic parts. The samples were then dried at 200 °C for 2 h at reduced pressure under nitrogen atmosphere. Surface areas were calculated with the BET equation[68] equipped on the apparatus in the range of 0.05−0.30 (p/p_0), and the pore size distribution was calculated by the BJH method[69] equipped on the apparatus. Dynamic mechanical analysis (DMA) was conducted on a DMS 210 (Seiko Instruments Inc.). The sample was measured at 2 Hz. The temperature for the measurement was ramped from 30 to 250 °C at the rate of 2 °C/min.

Results and Discussion

Effect of APTMOS Content on the Homogeneity. The effect of APTMOS content on the homogeneity of polymer hybrids was initially investigated. The prescribed amounts of APTMOS were added to a solution of PSSA with TMOS. The molarity of sulfonic groups in the total, represented by "y", is calculated by the weight of PSSA (g) × 0.966 mmol/g. The total molarity of two alkoxysilanes were fixed at y = 20 mol. The solution was mixed at room temperature for 1 h and was heated initially at 60 °C. The temperature was gradually ramped to 100 °C. The solvents were evaporated, resulting in glassy materials. The samples were kept at this temperature for 1 week to remove the solvent completely.

As shown in Table 1, without APTMOS, the obtained sample became optically turbid, indicating the phase separation of the organic and inorganic phases at a scale larger than the wavelength of visible light. When y = 0.1 mol of APTMOS was added to the mixture of PSSA and TMOS, the homogeneity was found to be much improved and the sample became translucent. With further addition of APTMOS above y = 0.5 mol of APTMOS, the homogeneity of the sample was improved drastically. The optical appearance of the samples was all transparent with the introduction of APTMOS greater than this amount. These results suggest that the organic and the inorganic phases were mixed at the level smaller than the length of visible light, that is, 200 nm.

The dispersity of the two phases was also examined by SEM. As shown in Figure 1a, the sample prepared without APTMOS showed phase separation of silica and the organic polymer. Bright spots indicate silica, from which the size of silica domain could be estimated to be around 100 μm at largest. On the other hand, when a sample was prepared with y = 0.5 mol of APTMOS, the bright spots disappeared (Figure 1b). The same result was obtained in the sample prepared with y = 1.0 mol of APTMOS, even though the surface of the sample was partially rough, that did not indicate the phase separation (Figure 1c). These results also demonstrate the improvement of the homogeneity with the increase in APTMOS. The distribution of two phases will be discussed more specifically later.

The improvement of the dispersity of the two elements in the samples with the increase in APTMOS was supposedly caused by the increase in interactions at the interfaces. As described in Scheme 1, the proton transfer was supposed to occur from sulfonic acid groups of PSSA to amino groups of APTMOS at the moment APTMOS was added to the solution of PSSA. Then the ionic interactions between the sulfonate ion and the ammonium ion would be induced and PSSA and APTMOS linked via the ionic pairs. The coupling of PSSA and APTMOS was followed by the sol−gel reaction of alkoxyl groups of APTMOS and TMOS. The ionic interactions are assumed to be strong enough to tie APTMOS to PSSA during the sol−gel reaction. Therefore, the ionic pairs are supposed to function as linkers between the organic polymer and the silica gel. As a consequence of the increased interactions between the interfaces of two elements, the organic polymers and silica gel obtained from APTMOS and TMOS would be integrated homogeneously.

Effect of Solvents and Water on the Homogeneity: Suppression of the Ionic Aggregation. The solvents used for the synthesis of polymer hybrids were THF, DMF, and DMSO, all of which can dissolve PSSA. The same synthetic methods as described in the above section were utilized. The results are listed in Table 2. It was found that the type of solvent has a great influence on the homogeneity of the polymer hybrids produced. When THF was used as a solvent, white

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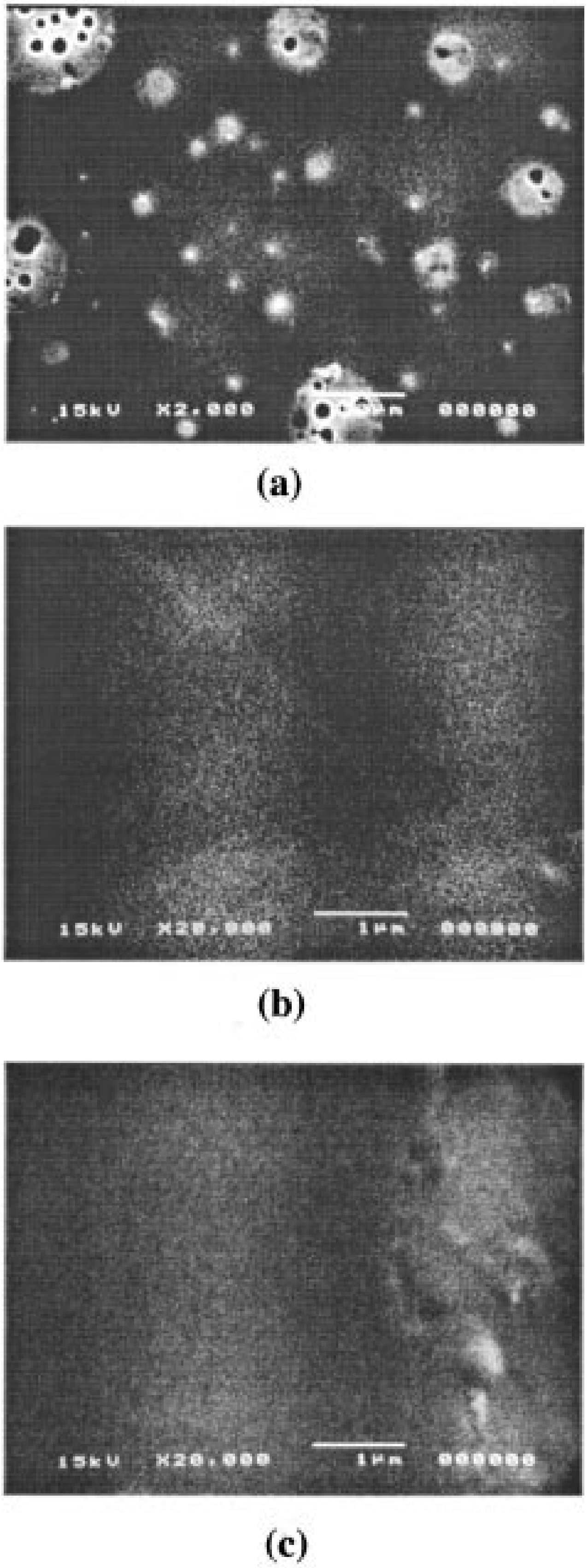
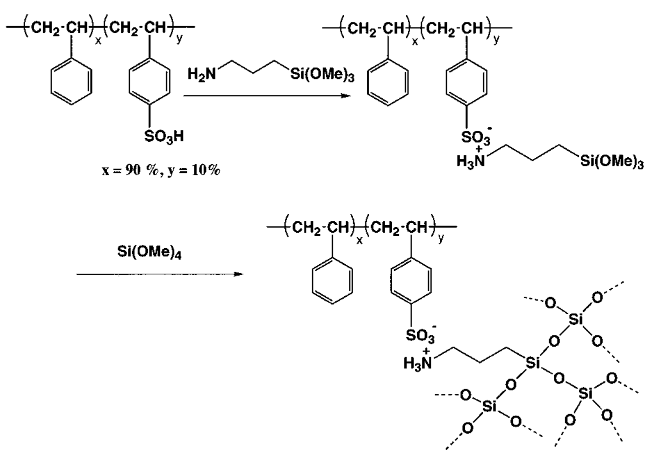


Figure 1. SEM images of the polymer hybrids. Bright spots indicate the silica gel and the dark part represents the organic polymer. (a) Without APTMOS. Silica gel domains 100 μm in size are observed. (b) $y = 0.5$ mol of APTMOS and $y = 19.5$ mol of TMOS. (c) $y = 1.0$ mol of APTMOS and $y = 19.0$ mol of TMOS.

Scheme 1



precipitates appeared at the moment APTMOS was added to the solution containing PSSA, and this mixture resulted in largely phase-separated sample. When other solvents were used for the reaction, no precipitate appeared at the initial stage. However, the polymer hybrids obtained in DMF became optically translucent after the removal of the solvent. In contrast to these results, the polymer hybrids obtained in DMSO were optically transparent, even after completion of the gelation. Therefore, in the polymer hybrids prepared in these solvents, the organic and the inorganic parts were expected to be homogeneously integrated. The difference in homogeneity of the polymer hybrids could be attributed to the different dielectric constants of the solvents. The dielectric constants of THF, DMF, and DMSO were 7.58, 36.71, and 48.9, respectively.[70] The solvents with high dielectric constant can solvate ionic pairs via stronger electrostatic interaction, thus preventing the ionic aggregation of ionic pairs. The uniform and one-phase solution is a prerequisite for the synthesis of homogeneous polymer hybrids. However, in this synthetic method the ionic bonds between the organic polymers and silica gel should be formed for the homogeneous dispersion of the organic and the inorganic phases. The solvents should suppress the ionic aggregation but should not hinder the formation of ionic interaction itself between the sulfonates and the ammmonium. Judging from the results obtained, it is expected that the moderate solvation of the ionic pairs was manifested in this system.

Water was also found to have a profound effect on the homogeneity of the polymer hybrids. Even when DMSO was employed for the reaction, the organic and the inorganic elements were separated into two distinct phases without water (Table 2). Only when the reactions were conducted in the presence of water were the optically transparent polymer hybrids obtained. HCl incorporated as a catalyst for the sol–gel reaction did not seem to interrupt the interactions. The effect of water could be also explained in relation with the strong dielectric constant of the molecule.[71]

Evidence of the Ionic Interactions. The change of peak position of S=O stretching vibration observed

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Table 2. Effect of Solvents on the Homogeneity

	poly(styrene-sulfonic acid)		3-aminopropyl TMOS		TMOS					
run	y^c (mol)	wt (g)	y (mol)	wt (g)	y (mol)	wt (g)	solvent [mL]	cosolvent [mL]	appearance	dielectric constant (25 0c)
1[a]	1.0	0.1	1.0	19.4	19.0	0.279	THF [1.6]	0.1M HCl [0.4]	precipitated[d]	7.58
2[a]	1.0	0.1	1.0	19.4	19.0	0.279	DMF [1.6]	0.1M Hcl [0.4]	translucent	36.71
3[b]	1.0	0.1	1.0	19.4	19.0	0.279	DMSO [1.6]	0.1M HCl [0.4]	transparent	48.9
4[b]	1.0	0.1	1.0	19.4	19.0	0.279	DMSO [1.6]	H_2O [0.4]	transparent	48.9
5[b]	1.0	0.5	1.0	19.4	19.0	0.279	DMSO [1.6]	none	turbid	48.9

[a] The mixture was heated at 60−80 °C in a vessel covered with pin-holed aluminum foil. [b] The mixture was heated at 40−100 °C in a vessel covered with pin-holed aluminum foil. [c] The number of sulfonated styrene units. y = poly(styrenesulfonic acid) (g) × 0.966 mmol/g. [d] White precipitates appeared immediately after an addition of aminoTMOS.

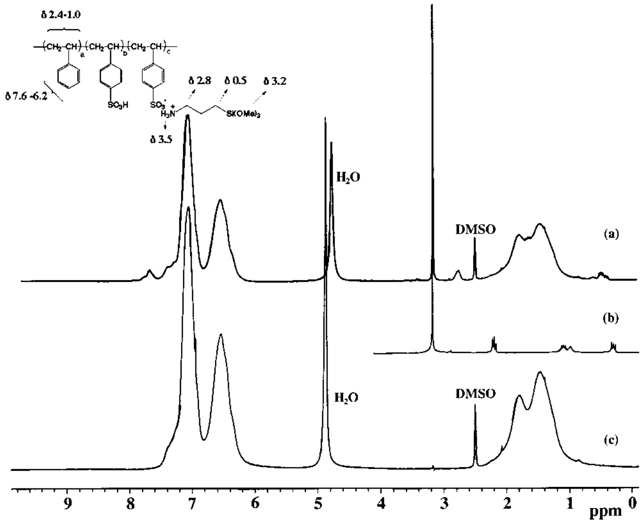
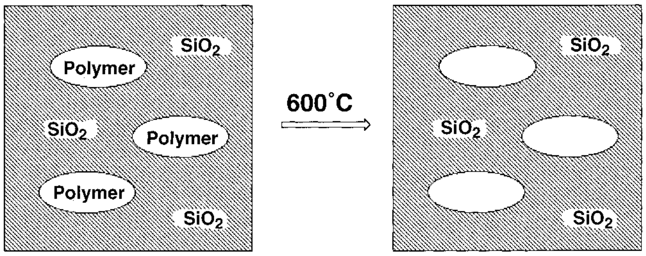


Figure 2. ^{1}H NMR spectra in DMSO-d_6: (a) PSSA with y = 0.5 mol of APTMOS; (b) APTMOS; (c) PSSA.

in FT-IR could be an effective tool to examine the ionic interactions between PSSA and APTMOS.[48] Unfortunately in the present samples, it was not easy to observe the shift of S═O peak due to some overlap from strong Si−O stretching vibration bands positioned also around 1100 cm $^{-1}$. Therefore ^{1}H NMR was utilized to evaluate the ionic interactions between the sulfonic groups of PSSA and the amino groups of APTMOS. As shown in Figure 2, APTMOS has peaks at 3.2, 2.2, 1.1, 1.0, and 0.28 ppm in DMSO-d_6, which are due to methyl protons of the trimethoxysilyl group, 1-methylene protons, 2-methylene protons, amine protons, and 3-methylene protons, respectively. These methylene peaks shifted to lower field with the introduction of PSSA, as was observed in other ionomeric blends.[67] Especially the peak for the methylene protons closest to the amine nitrogen shifted by 0.6 ppm. The shift of the peak could be attributed to the transfer of the proton from the sulfonic groups to the amino groups. The results indicate the formation of ionic bonds.

Nitrogen Porosimetry Study and TEM Measurement. The homogeneity of the polymer hybrids was quantitatively examined on the nanoscale level using a nitrogen porosimetry method.[72] SEM studies on these samples indicated the homogeneous dispersion at a micrometer level. However, the results did not give information on the integration at much smaller scale. Thus, it is required to conduct other methods for the elucidation of the real image of the polymer hybrids.

Scheme 2



The nitrogen porosimetry method was found to be a quite useful technique to investigate the dispersity of organic polymers inside polymer hybrids.[43] The calcination of the polymer hybrids at 600 °C removes the organic elements effectively, resulting in porous silica (Scheme 2). The size of the pores was found to correspond well to the size of organic polymer domains in the polymer hybrids. Thus, the dispersity of organic phases inside the organic polymers can be determined by measuring the pore size of the porous silica.

The polymer hybrids prepared with y = 0, 0.5, and 1.0 mol of APTMOS were calcinated, and the resulting porous silicas were subjected to the nitrogen porosimetry study. The porous silicas obtained from these polymer hybrids were abbreviated as porous silica 0, 0.5, and 1.0, respectively. The total amount of APTMOS and TMOS was y = 20 mol. The adsorption isotherm curves obtained from nitrogen porosimetry studies on the polymer hybrids are illustrated in Figure 3. In contrast to porous silica 0, which shows a type II isotherm curve, porous silicas 0.5 and 1.0 show type IV curves, which indicates the presence of ultramicropores.[73] Surface areas and pore volumes were calculated by the BET method[68] equipped on the apparatus. The results are listed in Table 3. As indicated by the isotherm curves of the porous silica, porous silica 0 was found to have the lowest pore volume and surface area, which are 246 m^2/g and 56.5 mL/g, respectively. With the increase in the content of APTMOS, both pore volume and surface area increased. With the incorporation of y = 1.0 mol of APTMOS, the surface area and pore volume reached the value of 425 m^2/g and 97.9 mL/g, respectively. The pore size of the porous silica was also calculated by applying the BJH method,[69] equipped with the apparatus, to the desorption curve of each porous silica. The results are shown in Figure 4 and Table 3. As shown in Figure 4, porous silicas 0.5 and 1.0 exhibit sharp peak around 1.8 nm in the pore size distribution plot. On the contrary, porous silica 0 shows little peaks

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(72) Gregg, S. J.; Sing, K. S. W. *Adsoption, Surface Area and Porosity*; 2nd ed. New York, 1982.

(73) Kondo, S.; Ishikawa, T.; Abe, I. *Science of Adsorption (Kyutyaku no Kagaku)*; 1st ed.; Maruzen: Tokyo, 1991; p 228.

Table 3. Pore Volume and Surface Area of Porous Silica[a]

	poly(styrene-sulfonic acic)		3-aminopropyl TMOS		TMOS				
run[a]	*y* (mol)	wt (g)[c]	*y* (mol)	wt (mg)	*y* (mol)	wt (g)	pore volume[d] (mL/g)	surface area[d] (m^2/g)	pore radius[e] (nm)
1	1.0	0.5	0		20.0	1.47	56.5	246	1.8, 3.5
2	1.0	0.5	0.5	43.3	19.5	1.43	87.2	380	1.7
3	1.0	0.5	1.0	86.6	19.0	1.40	97.9	425	1.8

[a] The porous silicas were obtained by calcinating the polymer hybrids at 600 °C for 24 h. [b] The number of sulfonated styrene units. y = poly(styrenesulfonic acid) (g) × 0.966 mmol. [c] The amount of the polymer. [d] Calculated by the BET method. [e] Calculated by the BJH method from the desorption curve.

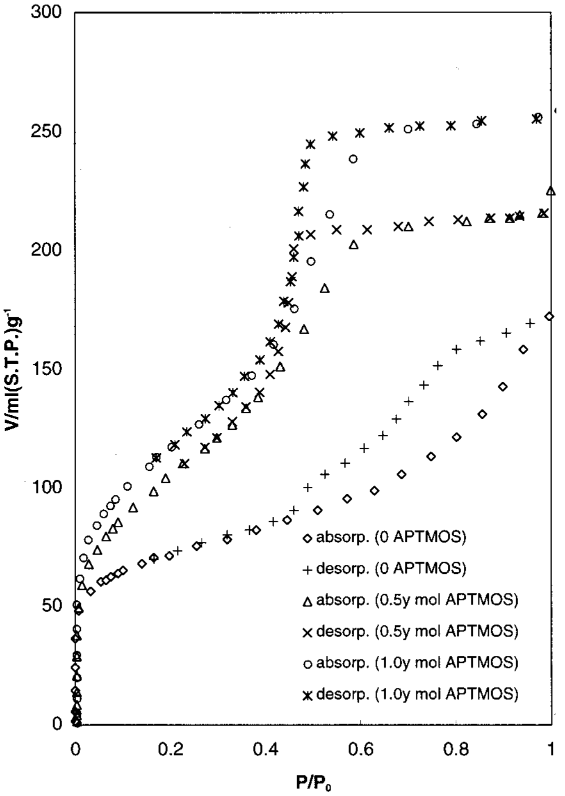

Figure 3. Adsorption isotherm curves of porous silica obtained from polymer hybrids.

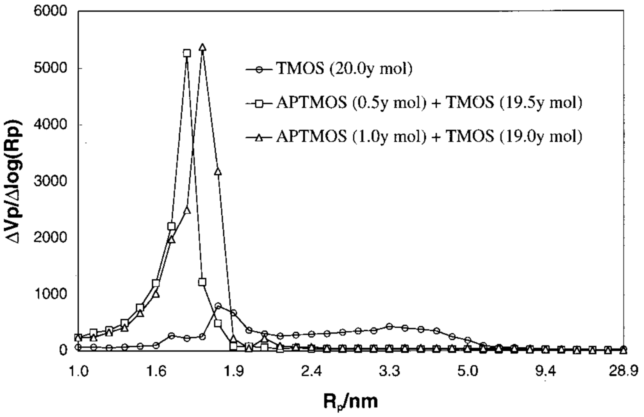

Figure 4. Pore size distribution plots of the porous silica obtained from the polymer hybrids.

in the region smaller than 30 nm. Combining with the results of SEM, it is assumed that in the polymer hybrids prepared without APTMOS, the organic and the inorganic elements resulted in the phase separation on a micrometer scale. On the other hand, the polymer hybrids prepared with more than y = 0.5 mol of APTMOS resulted in quite homogeneous integration of the organic and the inorganic elements. Especially from the results of nitrogen porosimetry studies, the size of the organic polymer domain in the polymer hybrids was found to be less than 2 nm. Therefore, each phase was expected to be entangled at a molecular level, forming one phase rather than two phases with distinct interfaces.

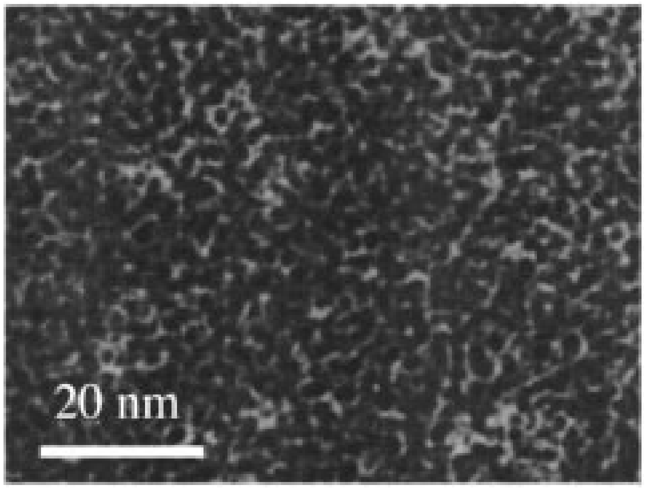

Figure 5. TEM image of the polymer hybrid prepared with y = 1.0 mol of APTMOS and y = 19.0 mol of TMOS. Bright spots and dark spots correspond to silica gel and PSSA, respectively.

The homogeneity of the polymer hybrids was further confirmed by TEM. In Figure 5, the TEM image of a thin-sliced section of the polymer hybrid prepared with y = 1.0 mol of APTMOS is shown. The bright spots correspond to silica gel and the dark spots represent the organic part. As confirmed by the nitrogen porosimetry method, silica gel and the organic polymer were also observed to integrate as a few nanometers. The image also gave information about the distribution pattern of the dark spots, i.e., the organic polymer, in the polymer hybrids. The result indicates the homogeneous distribution of each phase.

Effects of TMOS Content on the Homogeneity. By the introduction of enough APTMOS in the mixture of PSSA and TMOS, the integration of the organic phase and the inorganic phase on the nanometer scale could be obtained. Here the effect of TMOS content on the homogeneity of the polymer hybrids was examined. The mechanical properties are affected by varying the ratio of inorganic element in the polymer hybrids. Therefore, it is important to obtain homogeneous polymer hybrids having various inorganic contents. The content of APTMOS was fixed at y = 1.0 mol, and the content of TMOS was varied from y = 1.0 to 49.0 mol. Interestingly, as shown in Table 4, the obtained polymer hybrids became optically transparent with all TMOS contents, indicat-

Table 4. Effect of TMOS Contents on the Homogeneity

	poly(styrenesulfonic acid)		3-aminopropyl TMOS		TMOS		DMSO	0.1 M HCl		ceramic yield	
run[a]	y^b (mol)	wt (g)	y (mol)	wt (g)	y (mol)	wt (g)	(mL)	(mL)	appearance	(obs %)[c]	(cal %)
1	1.0	0.5	1.0	86.6	1.0	0.0735	8	2	transparent	11.2	10.0
2	1.0	0.5	1.0	86.6	19.0	1.40	8	2	transparent	50.4	52.5
3	1.0	0.5	1.0	86.6	49.0	3.60	8	2	transparent	66.3	73.4

[a] Each mixture was heated at 60−100 °C in a vessel covered with pin-holed aluminum foil. [b] The number of sulfonated styrene unit. y = poly(styrenesulfonic acid) (g) × 0.966 mmol/g. [c] Calculated from TGA.

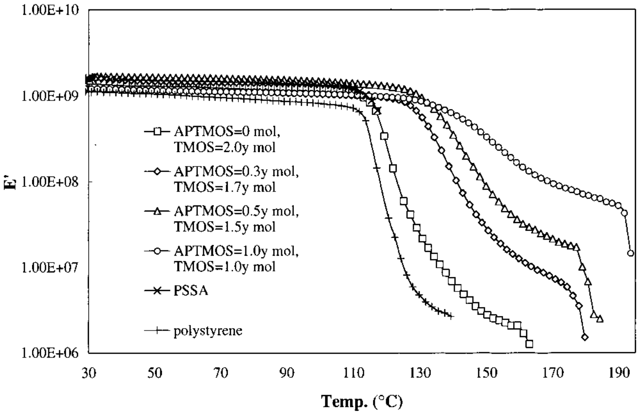

Figure 6. Dynamic viscoelasticity measurement of the polymer hybrids at 2 Hz. Storage moduli obtained from DMA were plotted against temperature.

ing the homogeneous dispersion of the organic phase and the inorganic phase. The content of silica gel inside the polymer hybrids was confirmed by TGA. The results are also listed in Table 4. The ceramic yields were found to be 11% and 66% for the polymer hybrid prepared with $y = 1.0$ mol of TMOS and with $y = 49.0$ mol of TMOS, respectively. With the lowest incorporation of TMOS, the obtained polymer hybrids were much like base PSSA, exhibiting some degree of flexibility, and with the highest incorporation of TMOS, the polymer hybrids became glasslike, hard materials, as expected. More specific mechanical studies will be conducted soon. It was at least confirmed that the ratio of the organic element and the inorganic element in the polymer hybrids could be controlled in a wide range when the ionic interactions were utilized.

Morphological Studies of the Polymer Hybrids: Evaluation of Cross-Linking in the Polymer Hybrids. The dynamic viscoelasticity of the polymer hybrids was investigated using dynamic mechanical analysis (DMA) to evaluate the effect of APTMOS content. The polymer hybrids were prepared starting from TMOS and APTMOS as the precursors for silica gel. The total content of the alkoxysilanes was fixed at $y = 2$ mol and APTMOS contents were $y = 0$, 0.3, 0.5, and 1.0 mol. The DMSO solution of the mixture was cast on polypropylene container and the film with about 0.05 mm thickness was obtained by heating the solution at 100 °C. As found in the polymer hybrids prepared with a total of $y = 20$ mol of alkoxysilanes, the homogeneity of the polymer hybrids was found to be improved with an increase in APTMOS contents. In this case, transparent polymer hybrids were obtained with more than $y = 0.3$ mol of APTMOS, at which content the polymer hybrids were translucent in the experiment with $y = 20$ mol of alkoxysilanes. The difference in the homogeneity could be simply attributed to the difference in the total amount of alkoxysilanes.

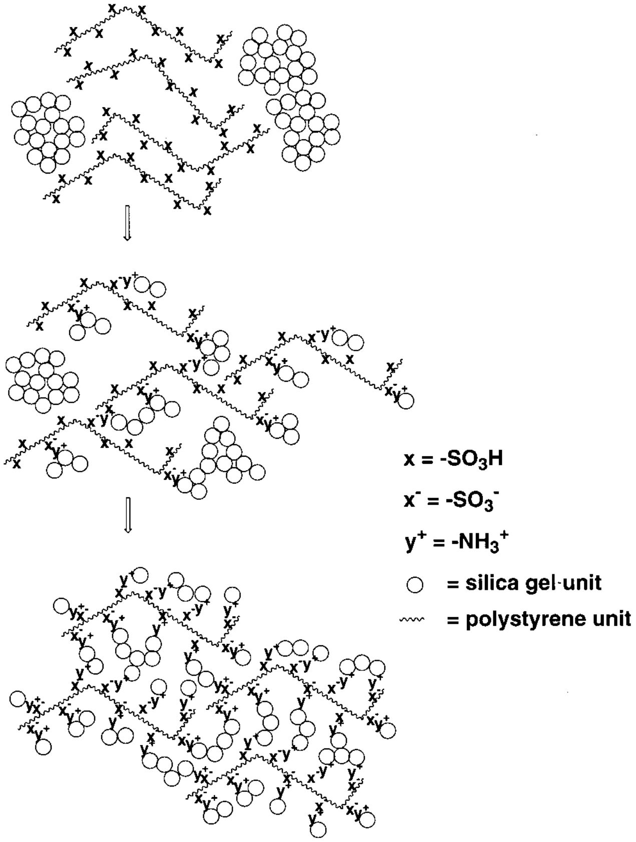

Figure 7. Schematic representation of the ionic interactions. The cross-linking via the ionic bonds is expected to increase with the increase in APTMOS.

In Figure 6, the results of DMA on the polymer hybrids are illustrated along with the results of polystyrene and PSSA. The difference between the polymer hybrids and the base organic polymers was apparent. First, the difference in values of the storage modulus after transition state can be recognized. With polystyrene, PSSA, and even the polymer hybrids prepared without APTMOS, the drastic decrease in the storage modulus after the transition state was observed, implicating absence of the elastic state. In the case of PSSA, the film was extended beyond the capacity of the apparatus; thus, the storage modulus after the transition could not be measured. However the polymer is expected to behave like polystyrene. The content of APTMOS was found to have a profound effect in this region. With an increase in APTMOS content, the decrease in the storage modulus after the glass state was gradually suppressed. With more than $y = 0.5$ mol of APTMOS, the distinct plateau region could be observed above 150 °C, indicating the presence of the

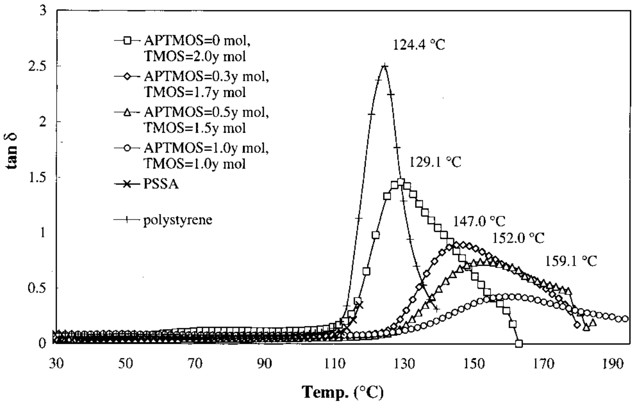

Figure 8. Dynamic viscoelasticity measurement of the polymer hybrids at 2 Hz. tan δ obtained from DMA was plotted against temperature.

elastic state. The increase in the storage modulus in the elastic state could be attributed to the increase in cross-linking between PSSA chains.

As illustrated in Figure 7, without APTMOS the organic polymer and silica gel are expected to exist in two independent phases, as confirmed by the above spectroscopic observation, since there is little interaction between the two phases. Therefore, the presence of silica gel did not affect the mechanical property of the organic polymer. On the contrary, with the incorporation of APTMOS, silica gel obtained from TMOS and APTMOS would be intercalated into the organic polymers and the cross-linking, based on ionic bonds, would be formed in some part that contribute to the increase in the storage modulus. With $y = 1.0$ mol of APTMOS, the complete integration of the organic polymer and silica gel could be attained and at the same time all sulfonic groups would participate in the cross-linking between the polymers with the formation of ionic bonds between the amino groups of APTMOS. This state was confirmed as the drastic increase in the storage modulus compared with that of the other polymer hybrids.

It is also worth mentioning that there was a further increase in storage modulus, even though the homogeneity of the polymer hybrids did not change above $y =$ 0.3 mol of APTMOS. The results indicate that even after formation of the homogeneous integration of the organic and the inorganic phase, some part of silica gel did not participate in the cross-linking. In other words, this silica gel is assumed to be just physically blended without any chemical bonds (covalent bondings between silica gel and ionic bonds via amino groups). However the DMA results confirmed the further increase in the ionic bonds, i.e., the cross-linking in these transparent polymer hybrids with an increase in APTMOS content.

As another feature of these DMA results, the shift of transition state to higher temperature was observed. Without APTMOS, the transition to elastic state began around 110 °C, as in the base organic polymers (Figure 6). On the contrary, the initiation temperature shifted to around 130 °C, indicating the reduced mobility of the organic polymer chains due to the increase in cross-linking. The change can be clearly seen in the plot of tan δ against temperature that suggests the glass transition temperature (Figure 8). Without APTMOS, the glass transition temperature (T_g), exhibited by tan δ, was observed at 129 °C and the temperature shifted to higher temperature with an increase in APTMOS content. With $y = 1.0$ mol of APTMOS, T_g could be observed at 159 °C, which is 30 °C higher than that of the polymer hybrid without APTMOS.

Conclusion

We have demonstrated the synthesis of homogeneous polystyrene and silica gel polymer hybrids utilizing the ionic interactions between the sulfonic groups of the organic polymer and the amino groups of APTMOS. As a consequence of APTMOS incorporation to the hybrids system, the interactions between the organic polymers and silica gel were profoundly improved, resulting in the homogeneous dispersion of each phase on a nanometer level. At the same time, the incorporated siloxane linkage works as cross-linkers between the organic polymer chains that increase the storage modulus in elastic state. These results suggest that the increase in APTMOS content resulted in the increase in the interfaces of two phases as well as the enhanced bondings via ionic interactions. APTMOS behaves like silane coupling agents such as 3-(trimethoxysilyl)propyl methacrylate used for the synthesis of polymer hybrids.[28] Both reagents act as cross-linker between organic polymers and silica gel. The content of APTMOS, though, is not necessarily equivalent to the content of the counteranionic groups. Therefore, the density of cross-linking can be controlled easily by adjusting the content of APTMOS, starting as the same as the organic polymers. At the same time, as the content of APTMOS is less than that of counteranions, the polymer hybrids are expected to have some ionic properties. The properties will be examined soon.

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