Synthesis of Sulfonated Polystyrene–Silica Hybrids and Their Application As Ion Exchange Materials

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ABSTRACT: The first synthesis of poly(styrene-*co*-styrylethyltrimethoxysilane)[P(ST-STMS)]–silica hybrid materials has been achieved via the acid-catalyzed sol-gel reactions of P(ST-STMS) with tetraethyl orthosilicate. New sulfonated polystyrene–silica hybrid materials have been prepared by sulfonation of P(ST-STMS)–silica and poly[-styrene-*co*-3-(trimethoxysilyl)propyl methacrylate]–silica hybrids with concentrated or fuming sulfuric acid. The sulfonated materials exhibit cation exchange capacities ranging from 0.33 to 1.27 meq/g depending on the composition of the hybrid materials and on the sulfonation conditions. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1893–1902, 1997

Key words: ion exchangers; organic–inorganic hybrid materials; sol-gel; sulfonation

INTRODUCTION

Silica and cross-linked polystyrene gels are among the most widely used stationary phases in modern chromatography. The polymers prepared from copolymerization of styrene and divinyl benzene followed by sulfonation are commonly known cation exchange resins in either bead or membrane form.[1] These resins can be employed as reaction catalysts[2,3] and stationary phase in high-performance liquid ion chromatography.[4–6] Membranes of the sulfonated polystyrene can also be applied as solid polymer electrolyte materials in the fabrication of electronic and electro-optical devices.[7] On the other hand, inorganic silica-based ion exchangers have been developed by bonding ionically modified polymers to porous silica microparticles.[8,9] This type of ion exchangers have been demonstrated to be advantageous for the separations of large organic ions, such as polypeptides, vitamins, and nucleotides, because of their porous structures with high surface area and large pore sizes.

In the past decade or so, the preparation of inorganic or organic–inorganic hybrid materials via the sol-gel reactions has been exploited extensively.[10–16] We have been interested in the synthesis of new polymer–inorganic hybrid sol-gel materials and their applications in dental restorative materials, coatings, membranes, catalysts or catalyst supports, reaction templates, and lithography.[17–26] A general methodology has been developed for the preparation of vinyl polymer sol-gel precursors containing the sol-gel reactive alkoxysilyl groups via chain copolymerization of 3-(trimethoxysilyl)propyl methacrylate or other alkoxysilyl vinyl monomers with conventional vinyl monomers (e.g., methyl methacrylates, acrylonitrile, styrene, etc.). The polymer precursors were then chemically or photochemically hydrolyzed and cocondensed with inorganic precursors such as alkoxides of silicon, titanium, aluminum, and/or zirconium to afford monolithic, transparent hybrid materials without macroscopic phase separation. We have also demonstrated that the vinyl polymer components in the inorganic matrices

could be modified further to give new hybrid materials or nanocomposites, taking advantage of the microporous nature of the sol-gel silica materials. For example, we have successfully transformed the nitrile groups chemoselectively to amide or carboxyl groups in the polyacrylonitrile–silica hybrid materials without destroying the covalent bonding between the polymer chains and silica network.[26]

In this article, we report the synthesis and sulfonation of polystyrene–silica hybrid materials via the acid-catalyzed sol-gel reactions of poly-[styrene-*co*-3-(trimethoxysilyl)propyl methacrylate] [P(ST-MSMA)] or poly(styrene-*co*-styrylethyltrimethoxysilane) [P(ST-STMS)] with tetraethyl orthosilicate (TEOS) followed by treatment with concentrated sulfuric acid. All the polymer precursors and the hybrid materials before and after sulfonation have been characterized by ^{1}H NMR, Fourier transform infrared (FTIR), and thermogravimetric analysis (TGA). It should be noted that the synthesis of P(ST-STMS)–silica hybrid materials has not been reported in the literature. The cation exchange properties of the new sulfonated polystyrene–silica hybrid materials have been investigated.

EXPERIMENTAL

Materials and Instrumentation

Styrene (ST, Aldrich) was washed with 5% NaOH aqueous solution to remove inhibitors, dried over anhydrous calcium chloride and distilled under a reduced pressure. 3-(Trimethoxysilyl)propyl methacrylate (MSMA, Aldrich) was distilled under vacuum. Benzoyl peroxide (BPO, Fisher) was recrystallized from alcohol twice. Styrylethyltrimethoxysilane (STMS, United Chemical Technologies and Gelest 95%) was purified either by column chromatography over silica gel or by distillation under a reduced pressure. Tetraethyl orthosilicate (TEOS, Aldrich), concentrated sulfuric acid (98%, Fisher), and fuming sulfuric acid (Fisher) were used as received. All other reagents and reaction media were purified by the standard procedures. Infrared spectra of the samples in free standing film or KBr powder pressed pellet form were recorded on a Perkin-Elmer 1610 FTIR spectrophotometer. TGA was performed on a DuPont 9900 TA system equipped with 951 TGA module at a heating rate of 20°C/min in a temperature range of 30–800°C under air atmosphere. Before

recording each thermogram, the sample powder was held isothermal at 120°C for 20 min to remove any volatile compounds. Proton nuclear magnetic resonance (NMR) spectra of the monomers and copolymers in CDCl$_3$ solutions were taken on an IBM Bruker WM250 FT-NMR spectrometer operating at 250 MHz. The chemical shifts were referenced to the proton signal (7.26 ppm) of residual CHCl$_3$ in the solvent.

Synthesis of Polymer Precursors

The detailed synthesis and characterization of P(ST-MSMA) and the P(ST-MSMA)–silica hybrid sol-gel materials were reported in our previous article.[25] The copolymer P(ST-MSMA) samples contained 90 and 70 mol % ST units as determined by TGA and ^{1}H NMR spectroscopy.[25] Similar to the preparation of P(ST-MSMA), the synthesis of poly(styrene-*co*-styrylethyltrimethoxysilane) [P(ST-STMS)] was carried out by the free radical copolymerization of styrylethyltrimethoxysilane with styrene using benzoyl peroxide as initiator in benzene at temperatures of 60–80°C under nitrogen for 3 h. The [ST]/[STMS] molar ratios were 9 : 1, 8 : 2, and 7 : 3 in the comonomer feeds. As a typical procedure, 9.36 g (89.9 mmol) of distilled styrene and 2.67 g (10.6 mmol) of styrylethyltrimethoxysilane were dissolved in 40 mL of dry benzene in a three-necked 100 mL flask, which was equipped with a condenser, thermometer, and nitrogen gas inlet/outlet. To this solution was added 0.242 g (1.00 mmol) of BPO. After heating at 60–80°C for 3 h under a nitrogen atmosphere, the reaction mixture was poured dropwise into 200 mL dry *n*-hexane with stirring. The precipitate was collected by filtration and dissolved again in benzene followed by another precipitation in *n*-hexane. The final precipitate was filtered and dried in a vacuum oven for 24 h to afford 2.6 g of the copolymer P(ST-STMS).

Preparation of Hybrid Materials

The alkoxysilyl-containing polymer precursors were hydrolyzed and cocondensed with tetraethyl orthosilicate with aqueous HCl as catalyst to yield hybrid sol-gel materials, following the previously reported general procedures.[17–25] Thus, the polymer precursor P(ST-STMS) or P(ST-MSMA) was dissolved in a solvent (e.g., THF) to give a solution denoted as Sol A. A mixture of TEOS, aqueous HCl, and the solvent (THF) was stirred for 10
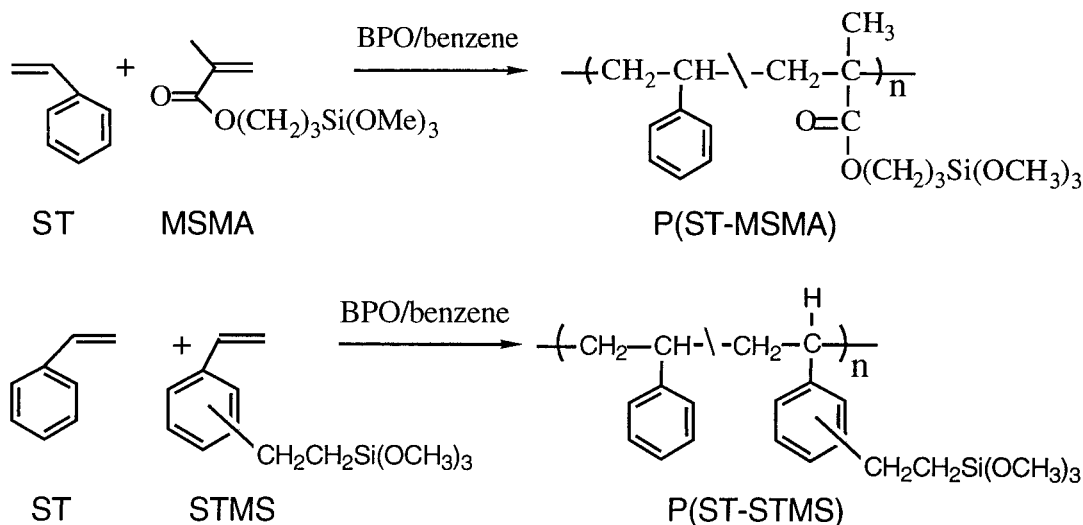
Scheme 1.

to 30 min at room temperature to yield a clear homogeneous solution denoted as Sol B. In some cases, the solution (Sol B) was further refluxed for 30 to 120 min to facilitate the sol-gel reactions. Combination of Sol A and Sol B with stirring resulted in a homogeneous solution. This solution

Figure 1 IR spectra of poly(styrene-*co*-styrylethyltrimethoxysilane) containing (a) 70 and (b) 90 mol % of styrene units.

was allowed to stand at room temperature for about 20 days without stirring to evaporate the solvent (i.e., THF) and the low-molecular-weight products of hydrolysis and condensation (i.e., MeOH, EtOH, and H_2O) to afford the polystyrene–silica hybrid gels. Further thermal treatment of the hybrid materials was performed in an oven under N_2 atmosphere at 100°C for 2 h or at 60°C for 12 h.

As a typical procedure for the preparation of P(ST-STMS) (Sample SG4D), 0.05 g (0.1 mmol) of 2.0M HCl was added to a mixture of 1.77 g (8.50 mmol) of TEOS, 1.8 g of THF (Aldrich, HPLC grade), and 0.61 g of H_2O. The mixture was stirred at the ambient temperature for 10 min followed by refluxing for 2 h under nitrogen to afford a homogeneous solution (Sol B), which was then combined with a solution (Sol A) of 1.20 g (10.0 mmol based on the repeating units) of the copolymer P(ST-STMS) containing 90 mol % of styrene units in 11 g of THF. The resultant mixture was stirred at room temperature for 30 min to form a homogeneous solution. This solution was kept at room temperature in a 50 mL beaker covered with a paraffin film having a number of holes made with a syringe needle. After drying for about 20 days at room temperature, a transparent, monolithic disc of the hybrid product was obtained. The gel product was heated in an oven at 60°C for 12 h and was ground into a fine powder for the subsequent sulfonation process. The silica content of the product was 34 wt % as determined from TGA measurement.
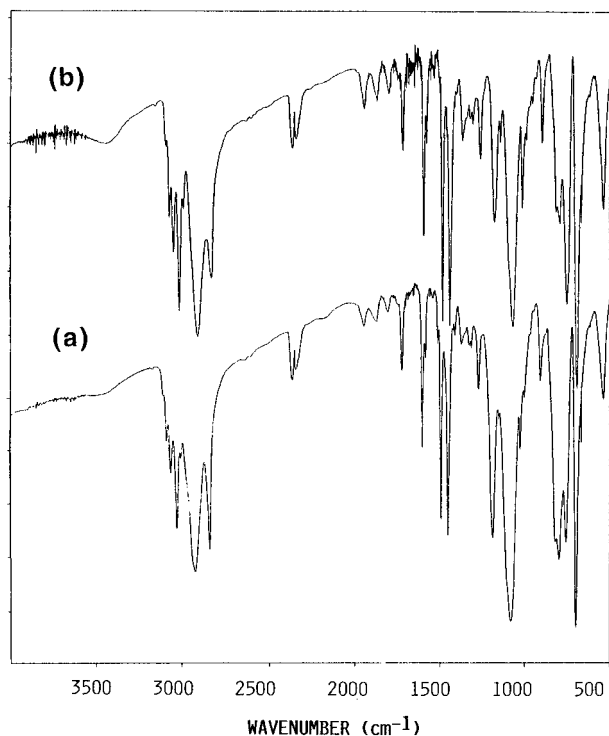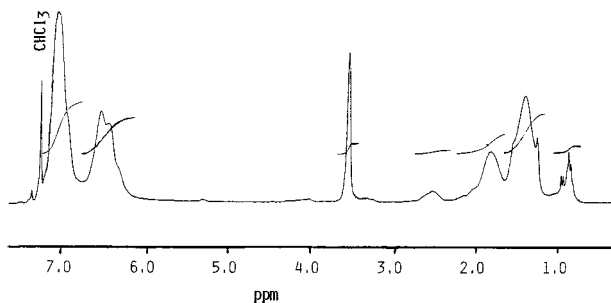
Figure 2 Proton NMR spectrum of poly(styrene-*co*-styrylethyltrimethoxysilane) containing 90 mol % of styrene units.

Sulfonation of the Hybrid Materials

Preparation of the sulfonated polystyrene–silica hybrid materials was achieved by following the well-established procedures for the sulfonation of cross-linked polystyrene resins.[27–29] As a typical procedure for the sulfonation of P(ST-STMS)–silica hybrid materials, to 25 mL of concentrated sulfuric acid (98%) in a 100 mL round bottom flask was added 0.1 g of the finely ground powder of the hybrid sample (SG4D) with the silica content of 34 wt %. The mixture was heated to 90°C in an oil bath under nitrogen and maintained at this temperature for 2.5 h with stirring. The mixture was then carefully added, with stirring, to 100 mL of 6M sulfuric acid precooled in an ice bath. Upon cooling to room temperature, the solid product was filtered through a sintered glass filter and washed with at least five 20 mL portions of distilled water until the filtrate became neutral as checked with pH paper to ensure a complete removal of sulfuric acid from the product. The sulfonated hybrid product was further rinsed with two 20 mL portions of methanol, followed by drying at 105°C for 2 h in a vacuum oven. In a typical procedure for the sulfonation of P(ST-MSMA)–silica hybrid materials, 2.0 g of the hybrid sample (SG3B) was suspended in 50 mL of fuming sulfu-
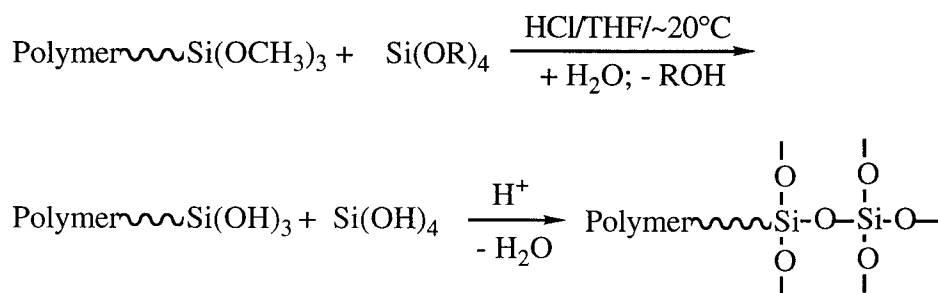
ric acid in a 100 mL round bottom flask for 4 h with stirring at room temperature. The mixture was poured slowly into a 1-L beaker that contained 250 mL of 50% sulfuric acid precooled in an ice bath. The solid product was filtered, washed with water until the filtrate became neutral in pH, and dried at 100°C for 4 h in an vacuum oven.

Determination of Ion-Exchange Capacity

Cation exchange capacity of the sulfonated polystyrene–silica hybrid materials was determined following the standard procedure for the cross-linked polystyrene cation exchange resins.[30] As a general procedure, the sulfonated hybrid powder was treated with an excess amount of aqueous 1N HNO$_3$ to ensure that the sulfonate groups in the materials were in the free acid form. The materials were then washed to neutrality with distilled, deionized water and dried at 60°C for 4 h. An exactly weighed sample (e.g., 1.000 g) was allowed to stand overnight in 250 mL Erlenmeyer flask containing 50 to 100.00 mL of standardized 0.100 N NaOH solution. Of the supernatant solution in the Erlenmeyer flask, 25.00 mL was back-titrated to a pH of 7.0 with a standardized 0.100 N HCl solution using phenolphthalein as indicator. An average of four titration results was used. The cation exchange capacity was reported as milliequivalent per gram (meq/g) of the dry sample.

RESULTS AND DISCUSSION

The sol-gel reactive polymer precursors, poly[styrene-*co*-3-(trimethoxysilyl)propyl methacrylate] and poly(styrene-*co*-styrylethyltrimethoxysilane), were prepared in various copolymer compositions by a free radical copolymerization of styrene (ST) with 3-(trimethoxysilyl)propyl methacrylate (MSMA) and with styrylethyltri-

Polymer〜〜Si(OCH$_3$)$_3$ + Si(OR)$_4$ $\xrightarrow[\text{+ H}_2\text{O; - ROH}]{\text{HCl/THF/~20°C}}$

Polymer〜〜Si(OH)$_3$ + Si(OH)$_4$ $\xrightarrow[\text{- H}_2\text{O}]{\text{H}^+}$ Polymer〜〜$\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}$-O-$\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}$-O—

Scheme 2.

Table I   Synthesis of Polystyrene–Silica Hybrid Materials Derived from the Sol-gel Reactions of Tetraethyl Orthosilicate (TEOS) with Poly[styrene-*co*-3-(trimethoxysilyl)propyl methacrylate] [P(ST-MSMA)] or Poly(styrene-*co*-styrylethyltrimethoxysilane) [P(ST-STMS)]

Sample Code	SG1A	SG1B	SG1C	SG3A	SG3B	SG4A	SG4B	SG4C	SG4D
Sol A composition:									
P(ST-MSMA) (g)	7.28	7.00	4.00	3.64	2.10				
P(ST-STMS) (g)						4.92	0.50	0.70	1.20
ST content (mol %)	70	70	70	90	90	81	90	90	90
THF (g)	29.1	28.0	16.0	14.6	8.7	19.7	4.5	5.0	10.8
Sol B composition:									
TEOS (g)	8.27	22.60	32.36	4.14	6.78	5.50	4.06	2.43	1.77
THF (g) 150%	5.8	15.2	21.8	2.9	4.6	3.7	4.2	2.5	1.8
$0.2M$ HCl (g)	2.00	5.42	7.77	1.00	1.63	1.32	1.00[a]	0.66[b]	1.50[a]
[Copolymer]/[TEOS]	1.24	0.44	0.17	1.55	0.54	1.41	0.22	0.51	0.35
[HCl]/[TEOS] ($\times 10^2$)	1.0	1.0	1.0	1.0	1.0	1.0	0.68	0.86	2.3
SiO$_2$ content (wt %) in the hybrid materials:									
Calc[c]	37	58	77	30	52	33	73	54	35
Expt (TGA)[d]	37	59	77	29	49	31	67	51	34

[a] [HCl] = 0.13M. [b] [HCl] = 0.15M. [c] The calculated SiO$_2$ contents in the hybrid materials were from the stoichiometry of the reactants based on 1 mol of TEOS or MSMA or STMS unit yielding 1 mol of SiO$_2$. [d] The experimental SiO$_2$ contents in the hybrid materials were determined from the TGA curves at 750°C under air.

methoxysilane (STMS), respectively, with benzoyl peroxide as initiator in benzene, as depicted in scheme (1).

The amount of the sol-gel reactive trimethoxysilyl groups in the copolymers was controlled by the initial comonomer compositions. Since we would like to have the properties of the copolymers as close to those of polystyrene as possible, the amounts of MSMA and STMS in the copolymers were kept low (e.g., 10 to 30 mol %). It should be noted that if the MSMA and STMS contents are too low (e.g., <10 mol %), a macroscopic phase separation often occurs during the subsequent sol-gel reactions of the copolymers with the inorganic precursor TEOS, leading to the formation of translucent products. The copolymers were characterized by infrared (IR) and ^{1}H NMR spectroscopy. The results are consistent with the proposed copolymer structures. For example, the representative IR and ^{1}H NMR spectra of the P(ST-STMS) copolymers are shown in Figures 1 and 2, respectively. The IR spectra of the copolymer samples (Fig. 1) exhibit the characteristic absorption bands of both the styrene units, e.g., 1493 and 1451 cm^{-1}, for aromatic ring stretching, and the alkoxysilyl groups, e.g., 1086 and 1192 cm^{-1}, for Si—O stretching.[31,32] As the amount of STMS units is increased from 10 mol % [Fig. 1(b)] to 30 mol % [Fig. 1(a)] in the copolymer, the intensities of the bands at 1086 and 1192 cm^{-1} become higher relative to those at 1493 and 1451 cm^{-1}. In the ^{1}H NMR spectrum (Fig. 2), the singlet at 3.6 ppm is attributed to the trimethoxysilyl protons in the STMS units. The peaks at ca. 2.7 and 0.9 ppm are assigned to the methylene groups attached to the phenyl and silyl groups, respectively. All the aromatic protons appear as two groups of signals at ca. 6.5 and 7.0 ppm. Two broad peaks at ca. 1.4 and 1.8 ppm are assigned, respectively, to the methylene and methine protons in the polymer backbone. In addition, the vinyl proton signals (e.g., 2 doublets at 5.7 and 5.2 ppm for =CH$_2$) for the ST and STMS monomers disappeared. The spectral data are consistent with the proposed copolymer structures. The copolymer composition (i.e., the ratio of ST to STMS units in the copolymer) was determined from the integration ratio of the trimethoxysilyl to the aromatic signals (Fig. 2) to be approximately 9 : 1, which is about the same as the comonomer composition.

To prepare the polystyrene–silica hybrid sol-gel materials, the polymer precursors P(ST-MSMA) and P(ST-STMS) were allowed to undergo the HCl (aq.) catalyzed hydrolysis and poly-
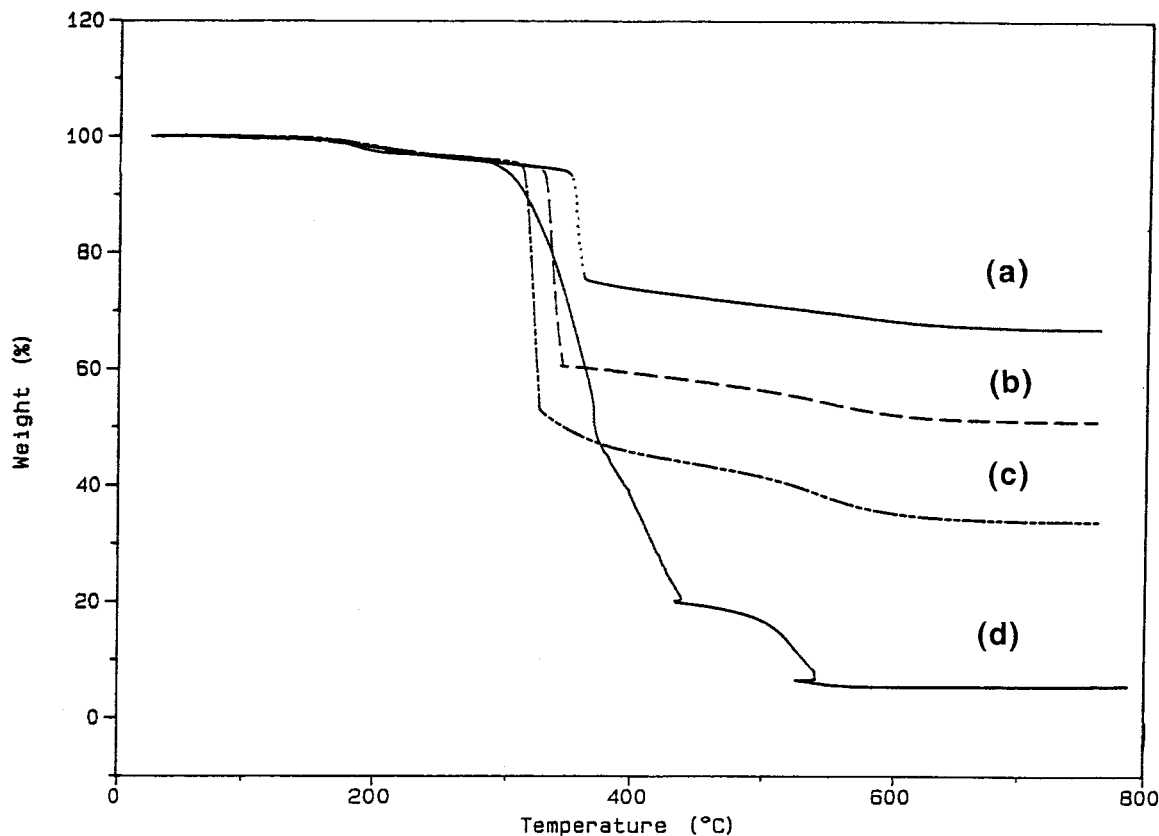
Figure 3 TGA curves of the poly(styrene-*co*-styrylethyltrimethoxysilane)–SiO$_2$ hybrid materials with the SiO$_2$ content of (a) 67 (SG4B), (b) 51 (SG4C), and (c) 34 wt % (SG4D); and (d) the TGA curve of precursor polymer containing 90 mol % of styrene units. All the measurements were done in air at a heating rate of 20°C/min.

condensation (i.e., the sol-gel reactions)[10–17] in the presence of various amounts of the inorganic precursor TEOS at room temperature, as illustrated in scheme (2).

The synthetic parameters and conditions are summarized in Table I. The polymer precursors employed were at two copolymer compositions, i.e., 70 and 90 mol % of styrene units in P(ST-MSMA) and 81 and 90 mol % of styrene units in P(ST-STMS). The silica contents in the hybrid materials were designed to be 29 to 77 wt % by employing appropriate amounts of the starting materials. Upon gelation and drying at room temperature, the hybrid materials with various silica contents were all monolithic and transparent. The good transparency to the visible light suggests there is no macroscopic organic-inorganic phase separation in the materials.[15–17] The silica contents in the hybrid products were determined by TGA at 750°C performed in air atmosphere. As shown in Figure 3, the organic components in the P(ST-STMS)–silica hybrid materials began to

decompose at 300 to 350°C. The onset decomposition temperature appears to increase with the silica content. All the organic components became completely decomposed at 750°C, leaving only the inorganic silica. The silica contents calculated from the stoichiometry of the starting materials are very close to those obtained from the TGA measurements (Table I).

The hybrid materials were further characterized by IR spectroscopy. Figure 4 shows representative IR spectra of P(ST-STMS)–silica samples. All the characteristic bands of the copolymer component are in good agreement with those for the copolymer precursor (Fig. 3). For example, the bands at 1493 and 1451 cm^{-1} for the aromatic ring in the styrene units are present in all the spectra. In addition, the presence of two strong and broad absorption bands in the 1000–1200 cm^{-1} region in the spectra of the hybrid materials (Fig. 4), which can be assigned to the stretching vibrations of Si—O bonds,[31,32] indicates the formation of the silica network. As expected, the rel-
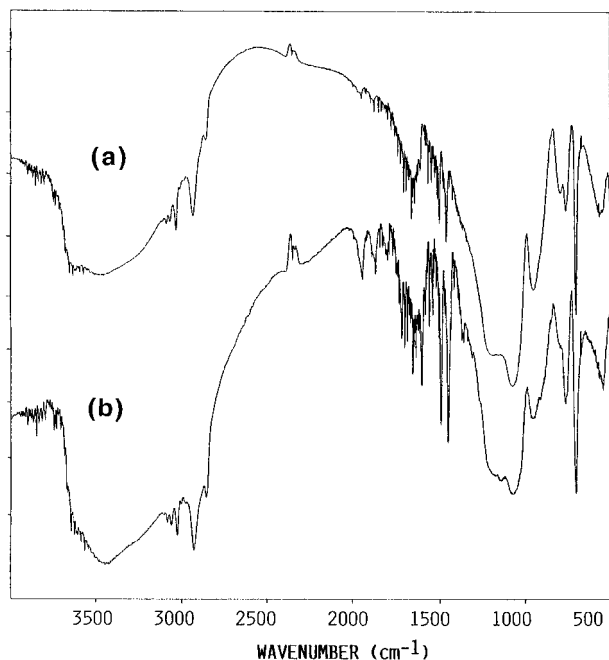
Figure 4 IR spectra of the poly(styrene-*co*-styryleth-yltrimethoxysilane)–SiO$_2$ hybrid materials with the SiO$_2$ content of (a) 67 (SG4B) and (b) 34 wt % (SG4D).

ative intensities of the bands at 1000–1200 cm^{-1} to those at 1493 and 1451 cm^{-1} increase when the silica content in the hybrid materials is increased.

As illustrated in scheme (3), sulfonation of the polystyrene components in the hybrid materials was achieved by treating the materials with fuming or concentrated (98%) sulfuric acid following the similar procedures for the sulfonation of conventional polystyrene.[27–29] Before the sulfonation, the polystyrene–silica hybrid samples were heated at 100°C for 2 h or 60°C for 12 h in an inert atmosphere and were ground into a fine powder. The sulfonation was performed at various temperatures for 2 to 24 hours. Upon sulfonation, the materials were isolated by filtration as yellow to brownish powder and were washed thoroughly with water until the filtrate became neutral in pH value.

The sulfonation of P(ST-STMS)–silica hybrid materials was performed at about 90°C. The sulfonated hybrid materials were characterized by IR spectroscopy and TGA. As shown in Figure 5, there are a number of new absorption bands for the sulfonated hybrid materials [Fig. 5(b)] in comparison with those before the sulfonation [Fig. 5(a)]. The bands at 1010 and 1175 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of the sulfonate groups, re-

spectively.[33] The formation of aryl-sulfone bonds is further evidenced by the absorption band at 1038 cm^{-1} upon sulfonation.[34] In addition, the intensity of the aromatic C—H bending vibration band at 760 cm^{-1} is decreased because of the substitution of the aromatic hydrogen atoms by the sulfonate groups. On the other hand, all the characteristic bands for the hybrid materials (e.g., the broad Si—O absorption bands at 1050–1200 cm^{-1}) before the sulfonation are retained, suggesting that the structure of the materials changed little during the sulfonation except for the introduction of the sulfonate groups. Similar spectral results were obtained for the sulfonated P(ST-MSMA)–silica hybrid materials, which were prepared by sulfonation at room temperature.

The extent of sulfonation could be estimated from the TGA experiments by comparing the percentage of silica contents before and after the sulfonation. In all the cases, the percentage silica content became lower after sulfonation. For example, the silica content in the hybrid material containing 29 wt % silica and 62 wt % polystyrene units before sulfonation (Sample SG3A) decreased to 24 wt % after the sulfonation for 24 hours at room temperature. With an assumption that the difference (i.e., 5 wt %) resulted solely from the introduction of the organic sulfonate groups, the extent of sulfonation was found to be approximately 45% (i.e., approximately every other phenyl ring was sulfonated in the hybrid materials). This value is quite close to that obtained from elemental analysis (40%). All the above described results are indicative of the achievement of sulfonation of the polystyrene component in the hybrid materials.

Cation exchange capacity of the sulfonated polystyrene–silica hybrid materials was determined by following the standard procedures for cross-linked polystyrene cation exchangers.[30] Thus, the hybrid materials were treated with 1 N HNO$_3$ to ensure the free sulfonic acid form of the materials. The acid form was then neutralized with a standardized base solution (i.e., 0.100 N NaOH) in excess. Upon back-titration with a standardized acid solution (i.e., 0.100 N HCl), the cation exchange capacity could be evaluated. Our preliminary results are summarized in Table II. In general, the hybrid materials exhibit the cationic exchange capacity to various extents ranging from 0.33 to 1.27 meq/g. The exchange capacity of the hybrid materials was found to increase with the polystyrene content in the materials pre-

Scheme 3.
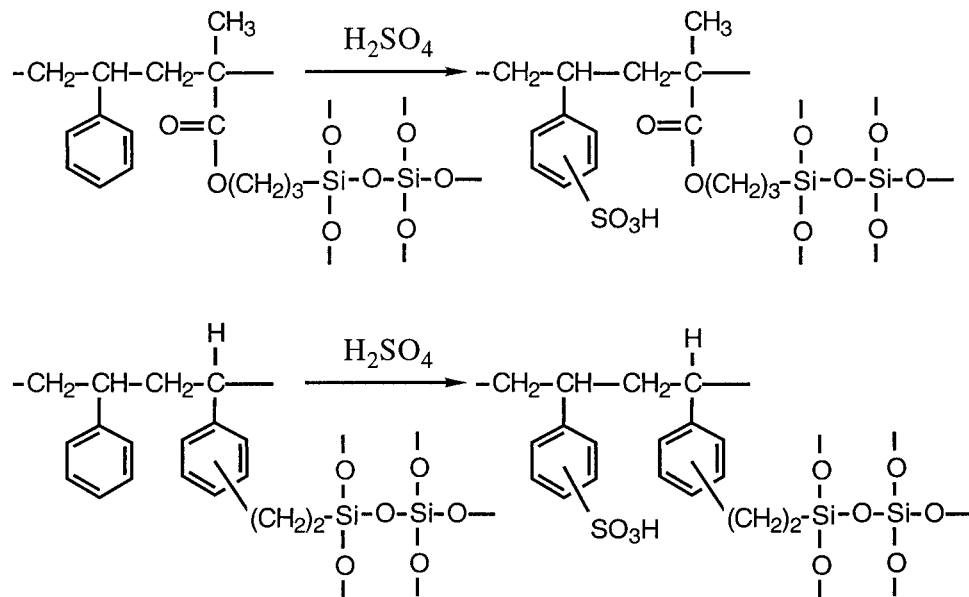
pared under the same sulfonation conditions. For example, the sample containing 42 wt % of polystyrene (SG1A) has a capacity value of 0.86 meq/g, which is appreciably higher than that (0.33 meq/g) for the sample containing 15 wt % polysty-

rene (SG1C). Such a trend could be attributed to the presence of more sulfonate groups when there are more phenyl rings available for the sulfonation. It was also observed that an increase in the reaction time for the sulfonation resulted in a
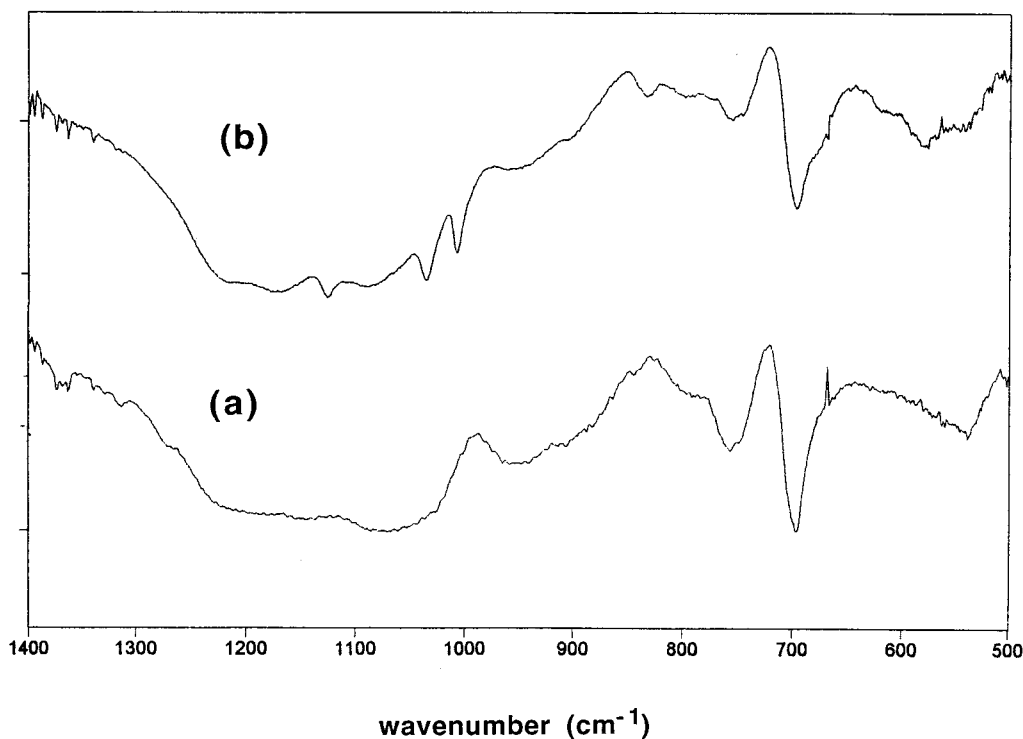

wavenumber (cm^{-1})

Figure 5 IR spectra of the poly(styrene-*co*-styrylethyltrimethoxysilane)−SiO$_2$ hybrid materials with the SiO$_2$ content of 34 wt % (a) before and (b) after sulfonation.

Table II Sulfonation of the Polystyrene–Silica Hybrid Sol-gel Materials and The Cation Exchange Capacity of the Sulfonated Hybrid Materials

Sample Code	ST Content (wt %)	SiO$_2$ Content (wt %)	Sulfonation Time (h)	Cation Exchange [Capacity (meq/g)]	Extent (%) of Sulfonation[a]
SG1A	42	37	4.0	0.86	32
SG1B	27	59	4.0	0.54	
SG1C	15	77	4.0	0.33	
SG3A	62	29	5.0	0.83	45
SG3A	62	29	24	1.27	50
SG3B	42	49	5.0	0.84	
SG3B	42	49	24	1.14	50
SG4A	52	31	24	1.19	40
SG4D	57	34	2.5	—	15

[a] The mol % of styrene units sulfonated as estimated from the TGA curves at 750°C under air with the assumption that the difference in weight of the sample before and after sulfonation resulted solely from the introduction of the organic sulfonate groups.

higher ion exchange capacity because of the greater extent of sulfonation. Thus, the exchange capacity values of sample SG3A were 0.83 and 1.27 meq/g at the sulfonation times of 5.0 and 24 hours, respectively. It should be noted that the ion exchange capacity of a polymer system is dependent on many chemical and physical factors. Further investigation is in progress in our laboratory to evaluate these new hybrid materials for the ion exchange applications.

CONCLUSIONS

The first synthesis of poly(styrene-*co*-styrylethyltrimethoxysilane)–silica hybrid materials has been achieved via the acid-catalyzed sol-gel reactions of P(ST-STMS) with TEOS. The P(ST-STMS)–silica and poly[styrene-*co*-3-(trimethoxysilyl)propyl methacrylate]–silica hybrid materials have been successfully sulfonated by treatment with concentrated or fuming sulfuric acid. All the polymer precursors and the hybrid materials before and after sulfonation have been characterized by ^{1}H NMR, FTIR, and TGA, and the results are consistent with the proposed structures. The new sulfonated polystyrene–silica hybrid materials exhibit cation exchange capacities ranging from 0.33 to 1.27 meq/g, depending on the composition of the hybrid materials and on the sulfonation conditions.

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