Chem. Mater. 1993, 5, 839–844

"Inverse" Organic–Inorganic Composite Materials. 3.[1] High Glass Content "Nonshrinking" Sol–Gel Composites via Poly(silicic acid esters)

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Received March 19, 1993

A critical challenge in the design of inorganic–organic composites is control over the mixing between the two chemically dissimilar phases. The sol–gel process has been utilized for the homogeneous incorporation of organic polymers into an inorganic matrix. One major limitation in the synthesis of sol–gel composites is the ubiquitous shrinkage that results from the evaporation of excess solvents and water. In our research, we have attempted to address this issue by developing *in* situ synchronous polymerization routes into these hybrid materials through the use of tetraalkoxysilanes possessing polymerizable alkoxides. Since our initial reports on the use of these new sol–gel precursors for the production of nonshrinking sol–gel composites, we have focused our efforts toward the synthesis and application of poly(silicic acid esters) bearing the same polymerizable alkoxides. This new approach allows for the synthesis of nonshrinking sol–gel composites with higher glass content than was previously possible with the tetraalkoxysilane derivatives. Furthermore, the use of poly(silicic acid esters) provides a new means for controlling composite morphology through the size and shape of the poly(silicic acid ester). Molecular weights for these poly(silicic acid esters) can be varied from 3000 to 30 000 simply by increasing the reaction time of the silicic acid synthesis. Also, particle shape can be controlled by the pH of the reaction solution. A modified esterification process using THF or benzene for azeotropic removal of water has been developed for synthesizing poly(silicic acid esters) with thermally unstable unsaturated alcohols. These substituted poly(silicic esters) have been used to produce transparent nonshrinking composites with a wide range of glass/polymer ratios.

Introduction

The properties of composite materials are greatly influenced by the degree of mixing between the two phases. This is especially important in the area of inorganic–organic composites where failure at the inorganic–organic interface can seriously diminish the mechanical performance of a material.[2] Composites with a high degree of mixing have been achieved through the use of the sol–gel process. The application of the sol–gel process[3] to the formation of optically transparent, organic–inorganic composite materials has received a great deal of attention in recent years.[4–9] On the basis of the homogeneous hydrolysis and condensation of metal alkoxides to form the three-dimensional inorganic network, the sol–gel process proceeds at temperatures under which incorporated organic polymers survive. Depending upon their morphologies, phase behavior, and organic–inorganic ratios, these composite materials comprise a continuum ranging from glass reinforced organic polymers to polymer-modified glasses.[7a,10] Ideally, one would like to be able to enter this continuum at any given point, thus gaining access to new, precision tailored materials.

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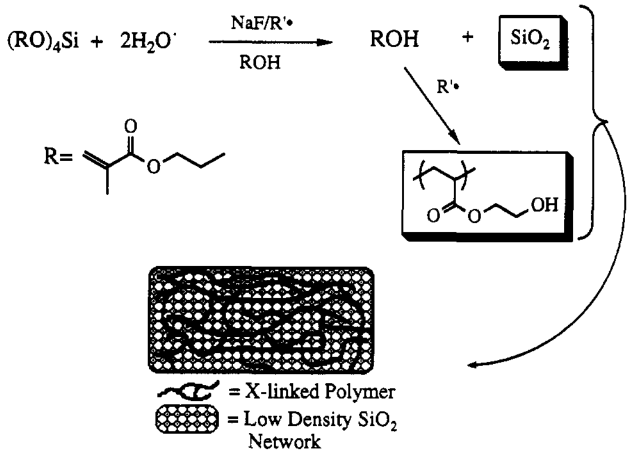
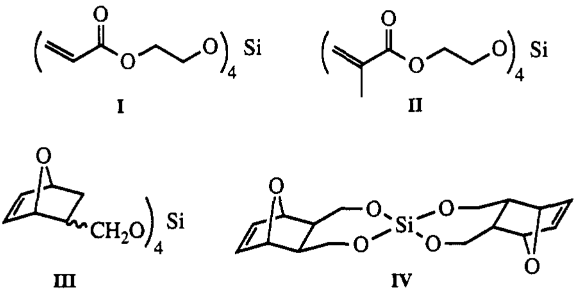
Scheme I



The preparation of these hybrid materials, however, can be challenging on both the synthetic and processing levels. First, only a limited number of preformed polymers are soluble in the sol–gel solutions.[11] Furthermore, large-scale shrinkages (50% or more) arise from the necessary evaporation of excess water, cosolvents, and liberated alcohols from the ramified, three-dimensional SiO_2–polymer gels.[3] Shrinkage on this scale precludes many molding applications and can introduce a high degree of stress in sol–gel monolithic composites. Earlier, we found that the solubility problem can be solved in part through simultaneous formation of the inorganic and organic phases.[1,11] During the development of synthetic routes into these mutually interpenetrating organic and inorganic networks, we became interested in finding solutions to the ubiquitous shrinkage problem, which has long plagued sol–gel derived materials. To this end, we examined the hydrolysis and condensation of tetraalkenyl orthosilicates to form an inorganic SiO_2 matrix, while simultaneously eliminating unsaturated alcohols which are then polymerized *in situ* to form the organic phase (Scheme I). In the presence of an appropriate catalyst (free radical or ROMP) and by using the tetralkenyl orthosilicate, a polymerizable monomer as the cosolvent, and a stoichiometric quantity of water, all components in the reaction mixture contribute to the inorganic network or the organic polymer. Since both the cosolvent and the liberated alcohol polymerize, gel drying is unnecessary, and no gel shrinkage associated with evaporation occurs.[1,11] One major limitation to the polymerizable precursor approach outlined above is that the maximum glass content of the product composites is low (ca. 10–18%) and is governed by the internal stoichiometry of the tetraalkenyl orthosilicate. Using a similar approach, we would now like to report the synthesis of nonshrinking materials possessing high glass contents, using preformed polysiloxanes possessing polymerizable alkoxides.

Table I. Tetraalkenyl Orthosilicates for the Synthesis of Nonshrinking Sol–Gel Composites



Results and Discussion

In our previous work using discrete molecular species, the maximum glass content of composites generated from tetraalkenyl orthosilicates was ca. 10% (compounds **I**, **II**, and **III**, Table I). Glass contents can be increased to ca. 18% by forming spiral bis-diolates typified by compound **IV**. In all cases, these materials are best classified as glass reinforced polymers.

To increase the glass content within this "nonshrinking" polymerizable-alkoxide motif, we considered synthesizing soluble, branched silicate particles possessing variable levels of polymerizable alkoxides. In contrast to the aforementioned composite precursors, preformed polysiloxanes offer two adjustable parameters for controlling glass content: the first being the number of Q^3 and Q^4 branch points, and the second being the degree of alkoxide substitution. From a practical standpoint, however, the former is the more appropriate parameter for controlling glass content (*vide infra*). Neglecting endgroup effects, the weight percent of glass in composites derived from these appropriately substituted polysiloxanes is given by

$$\% \text{ glass} = \left[\frac{1}{n}\left(1 + x\left(\frac{2\text{MW}}{60.1}\right)\right)\right]^{-1} + \left[\frac{1}{m}\left(1 + x'\left(\frac{\text{MW}}{60.1}\right)\right)\right]^{-1} + p \quad (1)$$

where MW is the molecular weight of the liberated alcohol, n, m, and p are the percent of Q^2, Q^3 and Q^4 silicon centers respectively, and x and x' are the fractional alkoxide substitutions on the Q^2 and Q^3 moieties, respectively. In general, this equation shows that by switching from small molecules to branched, highly three-dimensional particles, the glass content of the final composite can be increased. Furthermore, control over the Q ratios should allow for the formation of inorganic particles with structures ranging from highly three-dimensional (high percentage of Q^4) to more linear (high percentage of Q^2 and Q^3 relative to Q^4) particles.

1. **Silicic Acid Synthesis.** Poly(silicic acid) can be generated *in situ* by the hydrolysis and condensation of sodium metasilicate (Na_2SiO_3) in acidic aqueous solution (3.6 M HCl) and extracted into organic solvent (THF) by the addition of salt to the aqueous layer.[12] The literature method for increasing the molecular weight of poly(silicic acid) involves allowing a solution of the oligomers to condense at room temperature or at elevated temperatures in organic solvent.[12] We found that a more

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Table II. Molecular Weight Data for Benzyl Silicic Acid Esters (GPC Relative to Polystyrene)

rxn time, h	[HCl], M	M_w	M_n	PDI	yield, %
1	3.0	5 044	3 041	1.66	80–90
1	4.5	25 925	15 275	1.70	75–80
1	6.0	24 907	13 082	1.90	75–80
24	3.0	19 742	7 163	2.76	80–85
48	3.0	88 450	14 407	6.14	75–80
72	3.0	1 685 299	19 531	86.3	50–60
72	3.0	insoluble particles			

Table III. Q Values Determined by ^{29}Si NMR for Silicic Acid Oligomers

entry	M_n	[HCl], M	Q^1, %	Q^2, %	Q^3, %	Q^4, %
1	3 041	3.0	0.7	11.0	49.3	39.0
2	7 163	3.0	<0.1	10.2	55.0	34.8
3	14 407	3.0	<0.1	10.0	50.0	40.0
4	19 531	3.0	<0.1	11.0	50.0	50.0
5	15 275	4.5	<0.1	3.0	26.1	70.8
6	13 082	6.0	<0.1	4.8	33.0	62.2

convenient approach to increasing molecular weight was simply to increase the reaction time of the acidic hydrolysis and condensation reaction. As can be seen in Table II, the molecular weight (M_n) of these poly(silicic acid) polymers can be varied from *ca.* 3000 to greater than 20 000 by controlling reaction time. The molecular weights of the poly(silicic acid) samples were determined by gel permeation chromatography (GPC) analysis after converting them into the corresponding poly(silicic acid benzyl ester) (ca. 50% substituted) through the reaction of benzyl alcohol, and then endcapping the residual silanol groups with trimethylsilyl chloride (TMSCl).[12] The decreasing yields of soluble polymers throughout the course of the reaction is paralleled by increasing amounts of insoluble silicates. Under these low-pH conditions, the degree of cross-linking becomes extensive after approximately 72 h, and insoluble gels are produced.

Increasing the hydrolysis reaction time increases the molecular weight of the silicic acid polymers, but the increased reaction time does not have a substantial effect on the Q ratios (Table III, enties 1–4). The degree of branching in these poly(silicic acids) can be readily determined using ^{29}Si NMR.[13] In an effort to find an alternative method for increasing the number of Q^4 species, we examined varying the pH of the sodium metasilicate reaction. We found this reaction to be quite sensitive to solution pH, as insoluble gels are formed under dilute acids (pH ≈ 6) and neutral conditions (NaF catalyst), and insoluble silicates are formed under basic conditions. This pronounced pH dependence can be related to the relative rates of hydrolysis and condensation of silicic acid monomers. At higher pH values, condensation is fast relative to hydrolysis, resulting in highly branched structures with increased crosslink densities. At low pH these relative rates reverse, and the resultant percentage of Q^3 and Q^4 branching points (i.e., cross-links) is decreased to a point at which ramified, soluble polymers are obtained.[14] The number of Q^4 species can be increased by conducting the silicic acid synthesis at even lower pH (i.e., 6.0 M HCl).

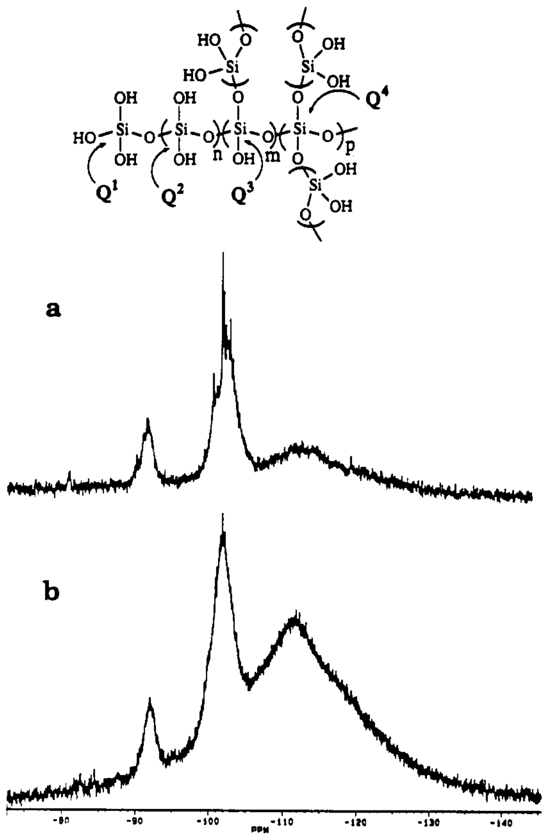

Figure 1. ^{29}Si NMR spectra of poly(silicic acid): (a) 3 M HCl, 1-h reaction; (b) 6 M HCl, 1-h reaction. Assignments: δ −81, Q^1; δ −92, Q^2; δ −103, Q^3; δ −112, Q^4.

At extremely high acid concentrations, hydrolysis and condensation rates become almost equal.[14] Consequently, smaller, soluble, highly three-dimensional particles are formed.[14] Table III (entries 5 and 6) shows the relative Q values for lower pH reactions. Two typical ^{29}Si NMR spectra of poly(silicic acid) for 1-h reactions in 3.0 M and 6.0 M HCl are shown in Figure 1.

2. Silicic Acid Esterification. Poly(silicic acid) oligomers thusly formed are only metastable in solution and eventually undergo further condensation to form crosslinked gels. As in the benzyl alkoxide case above, tractable poly(silicic acid ester) materials with varying degrees of substitution (DS) can be formed through an esterification reaction with added alcohols, which is driven by the azeotropic distillation of the liberated water with excess alcohol.[12] This method for silicic acid esterification is not applicable to our polymerizable alkenyl alcohols for several reasons: first, these alcohols are not volatile enough for azeotropic distillation at standard pressure; second, the unsaturated alcohols are thermally unstable and will polymerize or decompose at elevated temperatures and reduced pressures; and finally, some of these alcohols are synthetically valuable, and the large excesses needed for azeotropic distillation are difficult and expensive to obtain.

We have designed two alternative methods for silicic acid esterification which avoid the need for high reaction temperatures and large excesses of alcohol (Scheme II).

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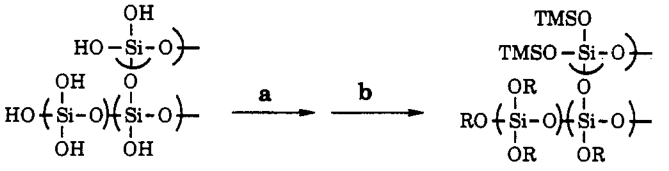
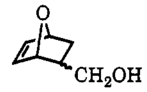
Scheme II



Method I: a) +ROH/-THF•H_2O b) TMSCl
Method II: a) +ROH/C_6H_6 Dean-Stark Trap b) TMSCl

V ROH =



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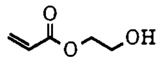
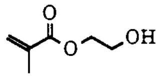
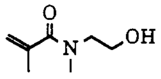


VII ROH =



VIII ROH =



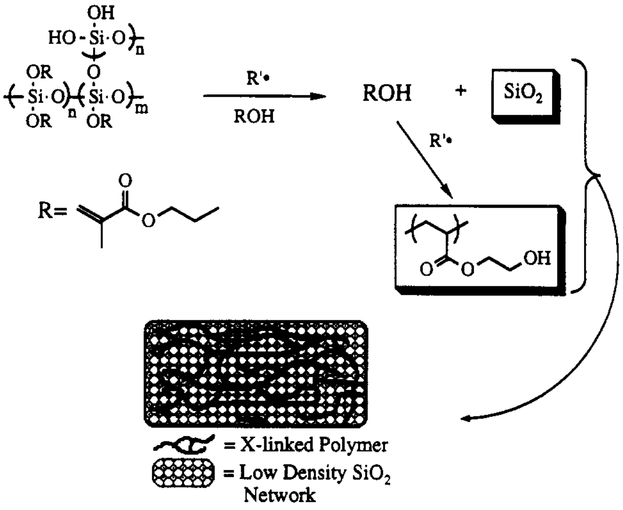
The first method involved the azeotropic removal of water with THF at 80 °C. The second method used benzene for the azeotropic removal of water and a Dean–Stark trap to recover the water as it was removed. Since the solvents used for these azeotropic distillation methods are volatile, elevated temperatures and reduced pressures were not necessary. More importantly, much less alcohol was required to carry out the esterification since inexpensive and readily available solvents were used for the distillation. The degree of substitution was conveniently controlled by varying the reaction time to achieve DS values from 25% to 80%. Unreacted silanol moieties in these poly(silicic acid ester) materials are also capable of further crosslinking reactions. We have found, however, that subsequent reactions in the solution are slow, and that these partially substituted poly(silicic acid esters) can be stored in THF or acetone for longer than 1 month without appreciable changes in their solubilities. Again, endcapping the residual silanol groups with TMSCl provides nonreactive polymers suitable for further characterization. Through application of this simple strategy, a variety of precursor materials have been synthesized using 7-oxanorbornenemethanol, poly-V, 2-hydroxyethyl acrylate, poly-VI, 2-hydroxyethyl methacrylate poly-VII, and (2-hydroxyethyl)-*N*-methyl methacrylamide, poly-VIII.

3. Composite Synthesis. Solubility and processability limitations with these poly(silicic acid) esters limit the minimum DS to approximately 50%. For this reason, Q ratios are the primary factor in determining the glass/polymer ratio. The percent glass in the final composite is controlled by the weight percent glass from the silicic ester and the amount of cosolvent used. Low silicic ester concentrations (<50% w/v) produce high polymer content composites, while solutions with high silicic ester concentrations (>50% w/v) produce high glass content composites. Furthermore, highly branched silicic esters (high Q^4 ratio) can be used to produce even higher glass content composites owing to the higher weight percentage of glass in the silicate precursor (Table IV).

Table IV. Weight Percent SiO_2 as a Function of Molecular Weight and Percent Q^4

M_n	Q^4, %	DS, %	% SiO_2
3 041	39.0	49.6	52.1
19 531	50.0	50.1	64.1
13 082	62.2	50.8	75.0

Scheme III



Composites were synthesized by dissolving either benzoyl peroxide (free radical polymerization catalyst) or $K_2RuCl_5{\cdot}H_2O$ (aqueous ROMP catalyst) into the silicic ester/polymerizable cosolvent solution. Water was not necessary for composite synthesis since the free silanol groups were able to undergo condensation to form the inorganic network. The composite solution was then poured into a mold and purged with nitrogen. Heating at 60 °C initiated both the organic polymerization (free radical or ROMP) and the inorganic condensation polymerization. After 2–3 h, the composite solution solidified and the partially polymerized composite was removed from the mold. Further heating at 80 °C for 24 h completed the polymerization, and homogeneous transparent inorganic–organic composites were obtained (Scheme III).

As is the case with the tetraalkenyl orthosilicate systems, all the components in the silicic ester composite solution contribute to either the inorganic network or the organic polymer. Since there are no volatile alcohols or cosolvents to remove, gel drying is unnecessary, and no shrinkage associated with drying occurs. It is important to note, however, that this is a bulk polymerization, and small-scale shrinkages (*ca.* 10%) do occur when going from the precursor solution to the final solid. This is common to almost all bulk polymerizations, and the important factor in our systems is the elimination of the large scale shrinkages and long drying times associated with traditional sol–gel composites. Figure 2 shows the difference between a conventional sol–gel glass and a nonshrinking composite. Both samples were set in the same size mold, but the conventional sol–gel glass lost 70–80% of its initial volume in drying.

Conclusion

The use of silicic acid esters provides a convenient method for producing sol–gel composites with minimal shrinkage and a wide range of glass/polymer ratios. The glass content and the microstructure of the composite can be uniquely adjusted by the controlled synthesis of the poly(silicic acid) composite precursors. A variety of polymerizable alcohols and polymerizable cosolvents can be used to produce composites with different mechanical and physical properties. By eliminating the large-scale

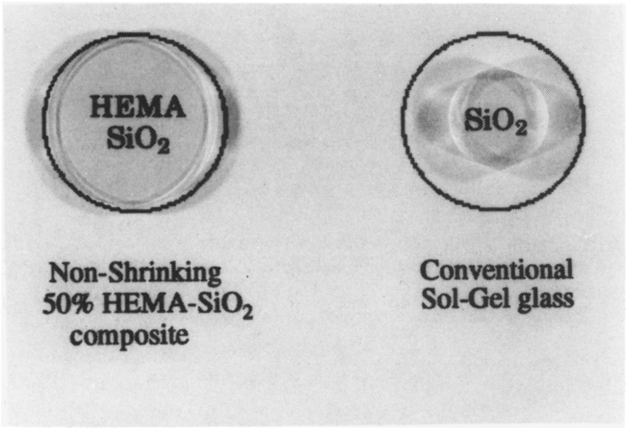


Figure 2. Comparison of a nonshrinking composite (left) with a conventional sol–gel glass (right). Circles show the approximate size of the mold the samples were cast in.

shrinkages and long drying times associated with conventional composites, these new nonshrinking materials may lead to new and important applications.

Experimental Section

General Methods. All synthetic operations were carried out under dry nitrogen except where noted. Acrylate monomers were washed with 10% sodium bicarbonate and distilled to remove the inhibitor. Tetrahydrofuran and benzene were distilled from sodium benzophenone immediately prior to use. All other reagents and solvents were of commercial grade and used without further purification. Scintillation vials for nonshrinking composite synthesis were immersed in 25% TMSCl/toluene solution at 60 °C for 24 h before use. ^1H NMR spectra were recorded at 500 MHz on a Bruker AM-500 spectrometer. ^{13}C NMR spectra were recorded at 125.7 MHz on the same instrument. Chemical shifts are reported in δ values with tetramethylsilane (TMS) as the interal reference. ^1H NMR data are tabulated by chemical shift, multiplicity, number of protons, and coupling constants in Hz. All ^{13}C NMR spectra are proton decoupled. ^{29}Si NMR were recorded at 99.5 MHz on a Bruker AM-500 spectrometer using a 10-mm broad-band probe. Q values for poly(silicic acid) were determined by integration after subtracting the residual resonance from the glass tube. Integrals were standardized by using a known concentration of TMS as an internal reference. Mass spectra were obtained with Atlas MS-12, Consolidated 12-110B, or Kratos MS50 spectrometers. Mass spectral data are reported as *m/e* (intensity expressed as percent total ion current). Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform infrared spectrometer. Gel permeation chromatography was performed on a Hewlett-Packard 1050 Series HPLC with $CHCl_3$ as the eluant at 1.0 mL/min with Waters Ultrastyragel columns. Elemental analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley, CA.

7-Oxabicyclo[2.2.1]hept-5-ene-2-methanol (V). To a suspension of 2.80 g (74.0 mmol) of $LiAlH_4$ in 250 mL of THF was added dropwise 9.28 g (60.20 mmol) of 2-(carbomethoxy)-7-oxabicyclo[2.2.1]hept-5-ene (the Diels–Alder adduct of furan and methyl acrylate[15]) in 50 mL of THF. The solution was allowed to stir overnight to ensure complete reaction. In sequence 3.0 mL of water, 3.0 mL of 15% NaOH, and 9.0 mL of water were added to the reaction solution. The resulting white precipitate was filtered and the filtrate concentrated. The precipitate was washed by Soxhlet extraction with CH_2Cl_2 for 24 h. The CH_2Cl_2 solution was concentrated, and the combined residues were distilled under vacuum to afford 7.35 g (96.9% yield) of a clear liquid: bp 45–47 °C/0.007 mmHg; IR (neat) 3400–3200, 2821, 2796, 1491, 946, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.31 (d, J_{HH} = 5.89 Hz, C(6)*H*, endo isomer), 6.24 (s, C(5) C(6) *H*, exo isomer), 6.20 (d, J_{HH} = 5.89 Hz, C(5)*H*, endo isomer), 4.94 (d, J_{HH} = 4.10 Hz, C(1)*H*, exo isomer), 4.85 (m, C(4)*H*, 4.78 (s, C(1)*H*, endo isomer), 3.60 (quintet, J_{HH} = 4.55 Hz, CH_2OH, exo isomer), 3.44 (m, CH_2OH, endo isomer), 3.19 (bs, CH_2OH, exo isomer), 3.05 (m, CH_2OH, endo isomer), 1.85 (m, C(2)*H*, endo isomer), 1.69 (m, C(2)*H*, exo isomer), 1.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 136.2, 135.7, 134.6, 131.9, 79.43, 79.29, 78.14, 64.87, 64.63, 40.32, 39.66, 27.99, 27.58; MS *m/e* 127 (3.70), 126 (3.26), 108 (41.24), 95 (51.77), 68 (63.36), 58 (73.89). Anal. Calcd for $C_7H_{10}O_2$: C, 66.69; H, 7.93. Found: C, 67.15; H, 8.15.

***N*-(2-Hydroxyethyl)-*N*-methyl Methacrylamide (VIII).** To a solution of 5.0 mL (62.2 mmol) of 2-(methylamino)ethanol in 30 mL of acetone was added dropwise 3.04 mL (31.1 mmol) of methacryloyl chloride in 20 mL of acetone. After complete addition, the reaction mixture was allowed to stir for 1 h. The acetone solution was separated from the HCl salt of 2-(methylamino)ethanol and concentrated. The residue was purified by Kugelrohr distillation (80 °C, 60 mTorr) to yield 3.92 g (88.1% yield) of clear oil. IR (thin film) 3400–3200, 2934, 1608, 1492, 1400, 1114, 1054, 915 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.19 (d, J = 33 Hz, 1H), 5.03 (s, 1H), 4.42 (bs, 1H), 3.71 (d, J = 33 Hz, 2H), 3.50 (s, 2H), 3.11 (d, J = 67 Hz, 3H), 1.96 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 173.2, 140.2, 115.4, 114.9, 59.8, 52.4, 49.5, 37.5, 32.2, 20.3, 19.6. MS (*m/e*) 143(60), 112(100), 100(40), 74(32). Anal. Calcd for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.85; H, 9.06, N, 9.50.

Synthesis and Extraction of Poly(silicic acid). Sodium metasilicate (8.5 g, 70 mmol) was dissolved in 50 mL of water. The solution was added dropwise to 50 mL of 3.0 M HCl at 0 °C with stirring. After complete addition, the reaction mixture was allowed to stir at 0 °C for 1, 24, 48, or 72 h. Increased reaction times produce higher molecular weight poly(silicic acid) (see text). The silicic acid was extracted into THF by the addition of 30 g of sodium chloride and 100 mL of THF. The two-phase mixture was stirred vigorously for 1 h. The aqueous layer was removed and the THF solution was dried over 20 g of anhydrous sodium sulfate to give an approximately 0.5 M silicic acid/THF solution (3.5 g of silicic acid; 89.1% SiO_2; 50 mmol of SiO_2). The same general procedure was used for the 4.5 and 6.0 M HCl reactions. The extraction was performed with 10 mL of 25% NaOH, 30 g of sodium chloride, and 100 mL of THF.

Representative Esterification of Poly(silicic acid) (Method I): Poly(silicic acid benzyl ester). To the poly(silicic acid) solution from above was added 50 mL of benzyl alcohol (52.3 g, 0.48 mol). The reaction mixture was subjected to azeotropic distillation of THF/H_2O at 80 °C. After removal of approximately 75 mL of THF/H_2O, dry THF was added to the reaction mixture at the same rate THF/H_2O was removed. Removal of approximately 600 mL of THF/H_2O resulted in a DS = 40–50% as evaluated by TMSCl endcapping. The reaction mixture was concentrated *in vacuo* and the residue redissolved in 100 mL of dry THF. To this solution was added 30 mL of TMSCl, and the reaction mixture was heated at reflux for 1 h. The reaction mixture was concentrated *in vacuo* and the residue redissolved in 100 mL of methanol. The polymer was isolated by pouring the solution into 250 mL of water. The solid was collected by filtration and dried *in vacuo* to yield a white powder. *Representative analysis*: Poly(silicic acid benzyl ester), 5.6 g (57 mmol SiO_2, 81.0% yield) of white powder. IR (thin film from $CHCl_3$) 3600–3200, 2981, 2921, 1200–1000, 755, 691 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.3 (bs, Ar–H), 4.8 (bs, ArCH_2O), 0.1 (bs, $(CH_3)_3$-Si). DS = 43.6%. Analysis found: C, 32.88; H, 4.86; SiO_2 residue, 62.1.

Representative Esterification of Poly(silicic acid) (Method II): Poly(silicic acid 2-ethoxyethyl methacrylate ester) VII. To a solution of poly(silicic acid) in THF was added 60 mL of HEMA and 5 mg of monomethoxyhydroquinone. The THF was removed by rotary evaporation and the remaining solution was diluted with 10 mL of dry benzene. This solution was poured into a three-necked flask fitted with a Dean–Stark trap and an air or O_2 bubbler. The reaction mixture was heated to 80 °C with stirring and rapid air or O_2 bubbling, and water was collected in the Dean–Stark trap. Removal of approximately 5 mL of water resulted in a DS = 40–50% as evaluuated by TMSCl endcapping.

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(15) (a) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595. (b) Moore, J. A.; Partain, E. M. *J. Org. Chem.* **1983**, *48*, 1105. (c) Dauben, W. G.; Krabbenhoft, H. O. *J. Am. Chem. Soc.* **1976**, *98*, 1992.

The reaction mixture was cooled and the polymer isolated by pouring the reaction solution into 1 L of vigorously stirring toluene or CH_2Cl_2. The solid was collected by filtration and immediately dissolved in 100 mL of acetone or THF. This solution was used for composite synthesis. A sample for analysis was obtained by removing a 10-mL aliqout of the solution. To this solution was added 3.0 mL of TMSCl and the reaction was heated at reflux for 1 h. The reaction mixture was concentrated and the residue redissolved in 5 mL of methanol. The polymer was isolated by pouring the solution into 25 mL of water. The solid was collected by filtration and dried *in vacuo* to yield a white powder. The same procedure was used for 7-oxanorbornenemethanol, poly-V, 2-hydroxyethyl acrylate, poly-VI, and *N*-(2-hydroxyethyl)-*N*-methyl methacrylamide, poly-VIII. *Representative analysis*: Poly(silicic acid 2-ethoxyethyl methacrylate ester) VII, 4.8 g (50 mmol SiO_2, 75% yield) of white powder. IR (thin film from THF) 3600–3200, 2959, 1702, 1636, 1454, 1200–1000 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.15 (bs, $\mathit{H}_2C{=}C$), 5.61 (bs, $\mathit{H}_2C{=}C(CH_3)$), 4.26 (bs, $CO_2C\mathit{H}_2CH_2$), 4.09 (bs, $CO_2CH_2C\mathit{H}_2O$), 1.90 (bs, $H_2C{=}C(C\mathit{H}_3)$), 0.10 (bs, $(C\mathit{H}_3)_3Si$). DS = 50.6%. Analysis: Found C, 34.44; H, 4.63; SiO_2 residue, 59.9.

Representative Nonshrinking Composite Synthesis: A 33-mL aliquot (1.6 g of HEMA silicic ester) was taken from a solution containing 4.8 g of HEMA silicic ester in 100 mL of THF. To the aliquot solution was added 0.4 g of HEMA containing 2% ethylene diacrylate and 20 mg of benzoyl peroxide. The solution was concentrated by rotary evaporation until a viscous solution formed. The solution was poured into a scintillation vial with a magnetic stir bar and the vial was evacuated with stirring to remove any remaining volatile solvents. When the solution became too viscous to stir, the stir bar was removed and the sample placed under vacuum again. After 2–3 h, the vial was purged with N_2 and placed in a 60 °C bath for 3 h. The solidified sample was removed by crushing the vial. The composite sample was then placed in a vacuum oven at 80 °C for 24 h after which a 2.0-g transparent composite containing approximately 50% glass and 50% polymer was obtained. Table V lists formulations for a range of glass/polymer ratios. The same exact procedure was used for 2-hydroxyethyl acrylate, poly-VI, and (2-hydroxyethyl)-*N*-methyl methacrylamide, poly-VIII. The same general procedure was used for 7-oxanorbornenemethanol, poly-V, with $K_2RuCl_5{\cdot}H_2O$ as the polymerization catalyst. IR (thin film) 3400–3200, 2950, 1754, 1200–1000 cm^{-1}. Analysis: Found C, 30.41; H, 4.78, SiO_2 residue, 51.1.

Table V. Formulations for Composites with Various Polymer/Glass Ratios[a]

solution, mL (g of silicic ester)[b]	HEMA,[c] g	wt % SiO_2
33 (1.6)	0.4	50
27 (1.3)	0.7	40
21 (1.0)	1.0	30
15 (0.7)	1.3	20
8 (0.4)	1.6	10

[a] In all cases, 20 mg of benzoyl peroxide was used. [b] Values calculated for a 4.8 g/100 mL HEMA silicic ester solution in acetone. Weight percent SiO_2 = 60.1% for the HEMA silicic ester. [c] HEMA containing 2% tetraethyleneglycol dimethacrylate.

Acknowledgment. We gratefully acknowledge financial support for this work from the National Science Foundation, Presidential Young Investigator Award; The Alfred P. Sloan Foundation; the Office of Naval Research; The Center for Advanced Materials, Materials Science Division, Lawrence Berkeley Laboratory; E. I. du Pont Nemours and Co., the Exxon Foundation; Amoco; Chevron Research; and Dow Corning Corp. M.W.E. acknowledges the Department of Education for a Graduate Student Fellowship.