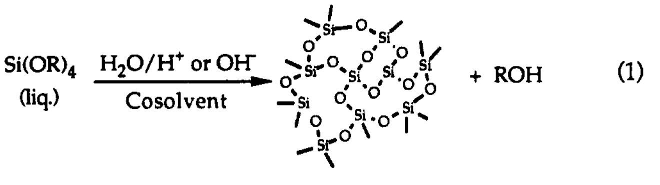
Macromolecules 1991, *24*, 5481-5483

"Inverse" Organic–Inorganic Composite Materials. 2.[1] Free-Radical Routes into *Nonshrinking* Sol–Gel Composites

We,[1,2] as well as others,[3] have been interested in exploring the reverse side of traditional glass-fiber-reinforced, organic polymer composites[4] by developing methods for uniformly embedding organic polymers within inorganic glass matrices. Although "inverted", the basic composite principles remain intact,[5] but now the advantages (and occasionally synergistic) relationship can result from the combination of a high-modulus organic polymer (providing high tensile strength) or an amorphous elastomer (providing improved impact resistance) with a three-dimensionally cross-linked, inorganic matrix (providing high compressive strength). The realization of these inverted organic–inorganic materials requires formation of the inorganic matrix under conditions in which the organic polymers will survive. We herein report the synthesis of optically transparent, simultaneous interpenetrating composites[6] through the synchronous formation of both the inorganic and organic components. This is accomplished by the hydrolysis and condensation of tetraalkenyl orthosilicates (the sol–gel process)[7] to form an inorganic SiO_2 matrix while simultaneously eliminating unsaturated alcohols which are polymerized in situ using free-radical techniques. This simultaneous approach utilizing polymerizable alkoxides circumvents the insolubility problem often associated with organic polymers in the sol–gel precurser solutions, while at the same time it eliminates the ubiquitous shrinkage problem associated with drying of sol–gel derived xerogel materials.

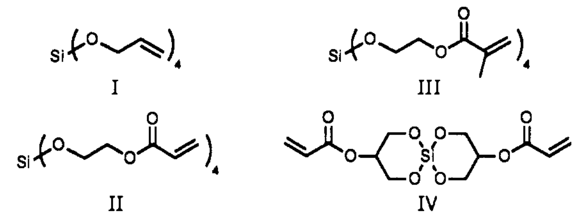
The sol–gel process for the preparation of glasses under mild conditions has received much attention with respect to the formation of highly uniform monolithic glasses and inorganic ceramic composites.[7,8] The sol–gel process is based on the homogeneous hydrolysis and condensation of metal alkoxides in the presence of cosolvents to form highly cross-linked, solvent-swollen networks. Under controlled drying conditions, the excess water, liberated alcohol, and cosolvents can slowly be removed to yield large-scale, optically transparent monolithic samples. The simplest sol–gel process is the formation of ramified SiO_2 gels from the hydrolysis of tetraethyl orthosilicate (TEOS) (eq 1).



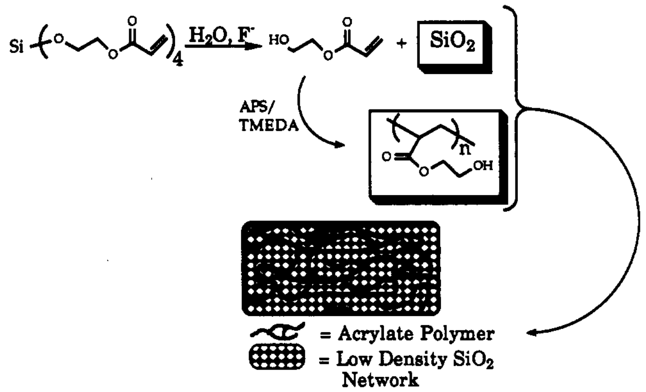
The mild conditions offered by the sol–gel process make it attractive for application in the formation of composite materials.[1-3] The most common approach involves dissolving a preformed organic oligomer or polymer in the sol–gel solution and then allowing the hydrolysis and condensation of the inorganic network to proceed. Under the appropriate conditions, the polymer remains uniformly embedded within the inorganic gel throughout the synthesis and drying steps.

In spite of its attractive features, the application of the sol–gel process in the synthesis of new composite materials is limited by the insolubility of many important engineering polymers within the sol–gel solution. In addition, the extraordinary shrinkage which occurs upon drying the solvent-swollen gels (shrinkages of $>$50–75% are common)[9] precludes most molding processes and introduces considerable stress within these materials. The former problem can be circumvented by the in situ formation of both the inorganic and organic components.[1,2,3e,f] In order to address the latter problem, we have synthesized a series of tetraalkenyl orthosilicates possessing polymerizable groups (Table I) in place of the standard ethoxide or methoxide groups commonly used in the sol–gel process.[3] The hydrolysis and condensation of these siloxane derivatives to form the inorganic network liberate a polymerizable alcohol. In the presence of the appropriate catalyst and by using a stoichiometric amount of water and the corresponding alcohol as cosolvent, all components of these derivatives are polymerized. Since both the cosolvent and the liberated alcohol polymerize, gel drying is unnecessary and no gel shrinkage occurs. This overall process is illustrated in Scheme I.

Table I
Candidate Polymerizable Monomers for Nonshrinking Composites



Scheme I



Siloxane derivatives I–IV (Table I) are readily synthesized in high yields (typically $>$95%) by allowing the free alcohols to react with $SiCl_4$ in the presence of a base.[10] Modifying the alkoxide groups in siloxane sol–gel precursors is not without potential complications. Specifically, the rate of hydrolysis is known to be inversely related to the steric bulk of the alkoxide moieties.[11] We have therefore studied the NaF (10–25 μM) catalyzed hydrolysis kinetics of siloxane II with excess D_2O in acetone-d_6 or DMSO-d_6 and have measured a pseudo-first-order rate constant of 14.4 s^{-1} for this derivative at 27 °C. This value compares favorably with the hydrolysis rate we measured for the simple ethoxide derivative, TEOS, under similar conditions.

The organic free-radical polymerization of siloxane II can be initiated photochemically by using UV light (medium-pressure Hanovia Hg lamp through quartz) with or without azobis(isobutyronitrile) (AIBN), thermally ($>$60 °C under N_2), ammonium persulfate (APS), and sodium metabisulfite as redox initiators at room temperature and finally with APS and *N,N,N′,N′*-tetramethylethylenedi-

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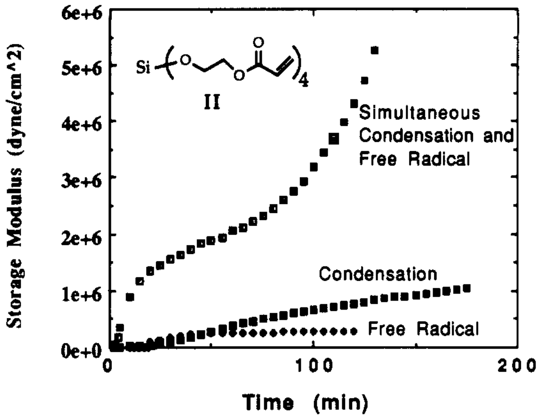

Figure 1. Dynamic storage modulus, G' (at 5% strain), as a function of time for the independent free-radical polymerization of HEA (Free Radical), the independent hydrolysis condensation of siloxane II (Condensation), and the simultaneous condensation and free-radical polymerization of II (Simultaneous Condensation and Free Radical).

amine (TMEDA) at room temperature. The latter system is highly efficient and provides the greatest control and is therefore the preferred method. Quantitative polymerization of the acrylate moieties of II is obtained under actual composite-forming conditions using the APS/TMEDA initiator as evidenced by IR spectroscopy. In preliminary experiments, we discovered that TMEDA is a potent catalyst for sol–gel condensation; thus, it influences the rate of polymerization of the organic *and* the inorganic components of the system. As a result, polymerization of each monomer type is not independently initiated/catalyzed; this makes kinetic studies difficult. Nevertheless, it is possible to "tune" both polymerizations to proceed at similar rates by varying the amount of APS present in the system. Matching the two rates is important for the formation of optically transparent composites where scattering losses must be minimized. Systems with inorganic condensation rates much greater than the organic polymerization rates produce opaque, brittle glasses that shrink (due to the evaporation of unreacted monomer), while uncontrolled polymer precipitation (phase separation) occurs in systems with fast (dominant) organic polymerization rates.

The actual inorganic condensation and hydrolysis process and the organic polymerizations under reaction conditions can be studied both independently and simultaneously by measuring the dynamic storage modulus, G', as a function of time (Rheometrics RMS-705 mechanical spectrometer configured in a parallel-plate geometry). The modulus–time plots for the independent free-radical polymerization of 2-hydroxyethyl acrylate (HEA) (labeled Free Radical; ambient temperature, 1.2 equiv of H_2O relative to HEA, 6 mM APS and 31 mM TMEDA in HEA), the independent hydrolysis/condensation of siloxane II (labeled Condensation; ambient temperature, 2.7 equiv of H_2O relative to II, 21 mM NaF, 29 mM TMEDA in II), and the simultaneous hydrolysis/condensation and free-radical polymerization of II (ambient temperature, 2.8 equiv of H_2O relative to II, 18 mM NaF, 7.6 mM APS, 29 mM TMEDA in II) are shown in Figure 1.

As can be seen in Figure 1, poly-HEA under these bulk polymerization conditions forms a gel which displays the behavior expected of a relatively weak hydrogen-bonded three-dimensional network. Likewise, the nascent inorganic matrix has a low modulus. In contrast, however, the composite material obtained from the simultaneous polymerization of both organic and inorganic components displays synergistic, nonadditive behavior.

Materials with even greater moduli can be prepared by incorporating varying amounts of cross-linking agents into the organic phase. The composites formed as described above from the synchronous polymerization of tetravinylalkoxy orthosilicates are semiinterpenetrating networks composed of linear organic polymers and the three-dimensional SiO_2 network. These materials can be converted into simultaneous interpenetrating three-dimensional cross-linked networks (SIPNs) by incorporating small amounts of divinyl monomers into the reaction mixture prior to polymerization. For example, cross-linking of the organic component of materials formed from the reaction of II can be accomplished by using ethylene diacrylate (EDA) (5:1 mole ratio II/EDA, 20:1 vinyl/divinyl moieties). The dynamic storage modulus of these fully cross-linked SIPNs increases rapidly and enters the glassy regime within minutes of initiation.

Acknowledgment. We gratefully acknowledge financial support for this work from UC Berkeley "Startup Funds"; 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; and Chevron Research. C.D. acknowledges the Eastman Kodak Co. for a Graduate Student Fellowship.

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(6) The interpenetrating network nomenclature used herein conforms to that introduced for polymer–polymer systems. See: Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981. The actual phase behavior and morphology of these materials are unknown and still under investigation. Scanning electron microscopy (SEM) studies (JEOL-35C instrument at 20 kV) on these composite materials show them to be highly uniform, as they exhibit no discernible phase separation at the ca. 10^2-nm level.

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Received April 25, 1991
Revised Manuscript Received July 16, 1991