CHEMISTRY of MATERIALS

VOLUME 2, NUMBER 4 JULY/AUGUST 1990

Communications

Synthesis of New Organic–Inorganic Hybrid Glasses

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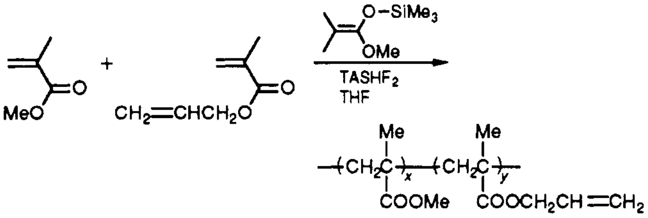
Received February 15, 1990

We have successfully synthesized new hybrid glasses that covalently incorporates acrylate polymers into a SiO_2 inorganic glass network via a sol–gel approach. The acrylate polymers were prepared with controlled molecular weights by group-transfer polymerization (GTP) of allyl methacrylate (AMA) and by copolymerization of allyl methacrylate with methyl methacrylate (MMA). The allylic vinyl groups in these polymers were converted to triethoxysilyl groups by hydrosilylation. The polymers with triethoxysilyl groups were then co-condensed with tetraethoxysilane (TEOS) via the sol–gel route to yield the new hybrid materials.

In the search for novel materials that meet the technological requirements of modern society, the sol–gel process was developed to make ceramic materials and inorganic glasses with superior optical properties and control of the chemical compositions at a relatively low temperatures.[1] Recently, many organic groups, polymers or oligomers,[2-6] such as poly(tetramethylene oxide)[3,4] and poly(dimethylsiloxane),[3,5,6] were incorporated into silicon and/or titanium glass networks by the sol–gel process. The properties of these organic–inorganic hybrid materials could be controlled by the choice of the inorganic component (i.e., metal alkoxides) and functionalized polymers or oligomers.[2-6] From these exciting developments, we envisioned that if an organic glass such as poly(methyl methacrylate) (PMMA) could be covalently combined with an inorganic glass such as SiO_2 at the molecular level, we would obtain a new hybrid glass that would have tailored combinations of the hardness of the inorganic glass and the toughness of the organic glass while retaining the good optical properties of both. Since the two components are covalently bonded and uniformly distributed in the materials, there would be no problems at the interfaces as exist in the conventional polymer composites.

Therefore, poly(allyl methacrylate) (PAMA) and poly(allyl methacrylate-*co*-methyl methacrylate) (PA-MMA) were prepared by the GTP method, which has been demonstrated to be a living polymerization process and to polymerize only the carbonyl conjugated vinyl groups in the monomers but leave the allyl vinyl groups intact:[7,8]



PAMA ($x = 0$) or PA-MMA

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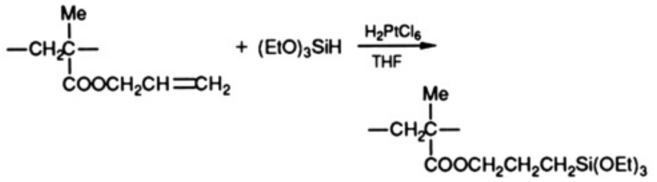
Table I. Group-Transfer Polymerization of Allyl Methacrylate (AMA) and Copolymerization of Allyl Methacrylate with Methyl Methacrylate (MMA) in THF at Room Temperature with MTDA as Initiator and $TASHF_2$ as Catalyst

						exptl[b]		
entry	[AMA], mmol	[MMA], mmol	[MTDA], mmol	yield, %	theoret[a] $\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	4.0	0	0.33	99	1510	1000	1220	1.2
2	4.0	0	0.27	96	1890	1470	1740	1.2
3	4.0	0	0.17	94	3020	3090	4300	1.4
4	4.0	0	0.095	87	5340	4360	6170	1.4
5[c]	4.0	4.0	0.50	90	1810	1800	2440	1.4
6[c]	4.0	4.0	0.33	68	2710	2390	2800	1.2

[a] Calculated from the molar ratio of the monomer to initiator as for a living polymerization. [b] Determined by gel-permeation chromatography (GPC) with THF as solvent and calibrated with monodispersed polystyrene standards. [c] The copolymer compositions were estimated to be approximately 0.5 for entries 5 and 6, from the ^1H NMR integrations of allylic methylene protons (4.4 ppm) of the AMA units and the ester methyl protons (3.6 ppm) of the MMA units in the copolymers.

The polymerizations were carried out in dry tetrahydrofuran (THF) with methyltrimethylsilyl dimethyl ketene acetal (MTDA) as initiator and tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) as catalyst in an argon atmosphere at room temperature.[7,8] As shown in Table I, good yields were generally achieved in the polymerizations, and the molecular weights of the polymers were controlled by the use of appropriate molar ratios of monomer to initiator.[7] The polymers were found to undergo cross-linking[9] through the pedant allylic vinyl groups upon exposure to air. A small amount of hydroquinone was added to the polymers for stabilization. The polymers were further characterized by elemental analysis (anal. calcd: C, 66.67; H, 7.94; found: C, 66.24; H, 7.94) and ^1H and ^{13}C NMR (in $CDCl_3$), and IR spectroscopies. The diagnostic feature of ^1H NMR spectrum of PAMA revealed the presence of allylic vinyl protons at 5.3–5.4 and 5.95–6.1 ppm with signal integrations accounting for three protons. The ^{13}C NMR spectrum also showed the presence of allyic double-bond carbons at 119 and 134 ppm. In the NMR spectrum of PA-MMA, both the vinyl and α-methyl signals were observed. All the results supported the proposed structures for the polymers and demonstrated that only the acrylic double bond has undergone polymerization in the GTP process.

The triethoxysilyl functional groups were introduced into the polymers PAMA and PA-MMA by hydrosilylation of the allylic vinyl groups with triethoxysilane in the presence of Speier's catalyst[10] as shown in the following equation:



As a representative procedure, a solution of PAMA (0.7 g) in 10 mL of dry THF, the Speier's catalyst H_2PtCl_6 (5 mg), and 1 mL of triethoxysilane was combined at room temperature under argon with magnetic stirring. The reaction was allowed to continue for 4 h. The volume of the solution was then reduced to ca. 2 mL by evaporating the solvent under reduced pressure. The product was precipitated in and washed with hexane. Upon drying in vacuo at room temperature overnight, a white powder was obtained (0.69 g, 43%). This material was found to become insoluble in THF and other common organic solvents on exposure to air and moisture, owing probably to a condensation of ethoxysilyl groups.[1] Proton NMR spectra of the hydrosilylated polymers showed the absence of vinyl proton signals, and a triplet at 1.2 ppm and a quartet at 3.8 ppm for the methyl and methylene protons in the ethoxysilyl group, respectively. Strong Si–O and C=O stretching bands were observed in the FTIR spectra at 1100 and 1735 cm^{-1}, respectively. All the spectroscopic data indicate a successful hydrosilylation.

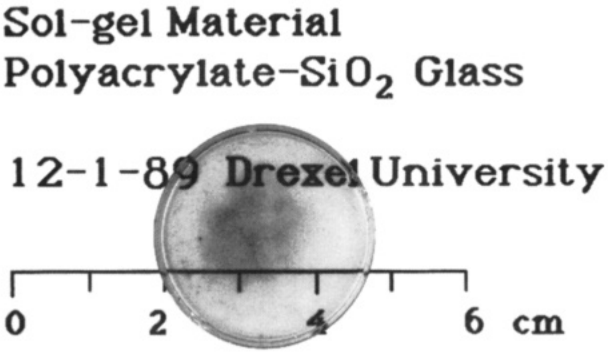
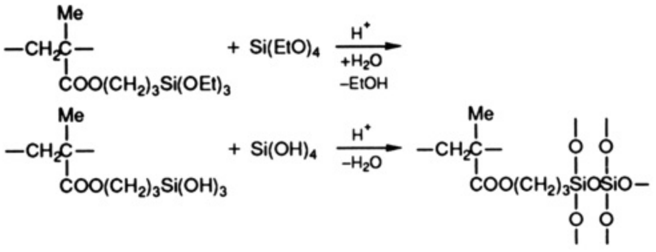


Figure 1. Representative photograph of monolithic polyacrylate-SiO_2 sol–gel glass derived from hydrosilylated poly(allyl methacrylate) (39% by mole based on the repeat unit) and tetraethoxysilane (61% by mole). The sol–gel synthesis was carried out in THF at room temperature with the molar ratios of water and HCl to TEOS being 1.53 and 0.1, respectively.

An acid-catalyzed hydrolysis and polycondensation of the hydrosilylated polyacrylates and tetraethoxysilane to produce the new hybrid sol–gel glasses is illustrated in the following scheme:



It has been shown that control of the reaction parameters in the sol–gel process such as the structures and concentrations of all the reactants and catalysts, solvents, and reaction temperature, etc., could be very important in order to obtain a monolithic and transparent material.[3,5,6] Experiments were carried out with a variety of compositions of the hydrosilylated polyacrylates, TEOS, water, and acid catalysts including HCl and methanesulfonic acid at different temperatures. In general, transparent and monolithic hybrid materials as shown in Figure 1 were obtained at room temperature by a slow evaporation of the solvent (THF), and the small-molecule products (e.g., EtOH and

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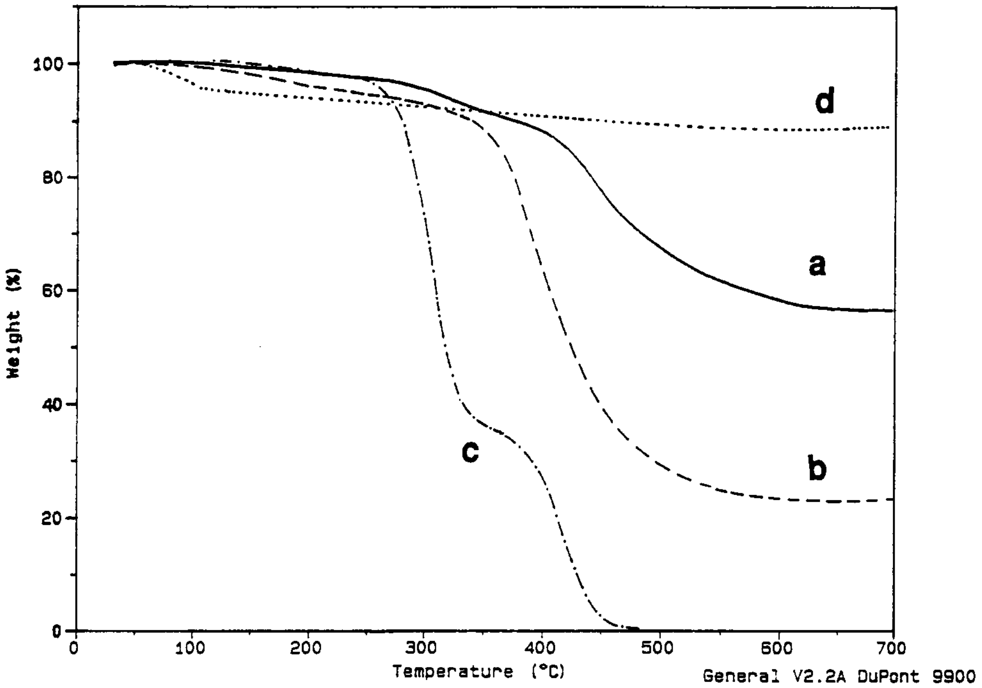

Figure 2. TGA thermograms of (a) the hybrid material derived from the hydrosilyated poly(allyl methacrylate) (39% by mole, based on the repeat unit) and TEOS (61% by mole), (b) hydrosilylated poly(allyl methacrylate), (c) poly(allyl methacrylate), $\bar{M}_n$ = 4360, and (d) a pure SiO_2 sol–gel glass derived from TEOS. The heating process for the TGA runs was performed at a rate of 20 °C/min in a nitrogen atmosphere.

H_2O) resulted from the further hydrolysis and polycondensation.

For a typical example, TEOS (8.6 mmol), distilled water (13.2 mmol), and HCl (0.086 mL of 10 M aqueous solution) were added simultaneously to a solution of freshly prepared poly(triethoxysilylpropyl methacrylate) (5.5 mmol, based on the repeat unit) in 10 mL of dry THF at room temperature in an argon atmosphere with magnetic stirring. After stirring at room temperature for 24 h, the homogeneous and viscous solution was poured into a glass beaker (4.0-cm diameter), which was then covered with a paraffin film having a number of holes made with a syringe needle for the evaporation of the volatiles. After this stood at room temperature for 25 days, a polyacrylate–SiO_2 glass was obtained (Figure 1). Both FTIR (C=O, 1735; C–H, 2950; Si–O, 1100 cm^{-1}) and elemental analysis demonstrated the presence of the polyacrylate components in the SiO_2 network.

The material were further characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Figure 2a, the hybrid material has a major weight loss at ca. 415 °C, which is assigned to a decomposition of the polyacrylate components in the hybrid material. This decomposition temperature is higher than those of poly(triethoxypropyl methacrylate) (Figure 2b) and poly(allyl methacrylate) (Figure 2c). At ca. 700 °C, the weight loss is ca. 42% for the hybrid material (Figure 2a), which is comparable to the calculated value of 45% organic content assuming that the residue at ca. 700 °C consists of only SiO_2. A sol–gel glass derived from TEOS alone under the same conditions retained ca. 90% of it original weight upon heating to 700 °C (Figure 2d). In the differential scanning calorimetry analysis of the hybrid material, no well-defined glass transition for the polyacrylate component was observed, suggesting a good dispersion of the polymer chains in the glass network.[3] The preliminary Izod tests demonstrated that the hybrid materials are tougher than the pure SiO_2 sol–gel glass. Further investigation is in progress to characterize these hybrid materials by Raman and ^{29}Si NMR spectroscopies, small-angle X-ray scattering, and electron microscopy, etc., and to study the mechanical and optical properties of these materials. In addition, further work is being conducted to synthesize the hybrid materials from the polyacrylates with higher molecular weights and telechelic PMMA with triethoxysilyl end groups.

Acknowledgment is made to the Office of Sponsored Research Projects, Drexel University, for the support of this research. We also thank Eastman Kodak Co. for a grant in support of the synthesis of polyacrylates. Many useful suggestions from Dr. Robert O. Hutchins are gratefully acknowledged.

Registry No. SiO_2, 60676-86-0; 2-propenoic acid, 79-10-7.

Near-Infrared Dyes. An Air-Stable Radical Anion

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Received March 19, 1990

Dyes that absorb in the near-infrared region (NIR, 0.8–2.0 μm) have received limited attention.[1] NIR optical phenomena are of importance, however. Fiber optic transmission in silica is best performed at 1.3 or 1.55 μm, inexpensive semiconductor lasers operate throughout the NIR, and there is an interest in NIR dyes for optical storage.[2]

Recently, we described several anion radicals that absorb NIR light.[3,4] These ions are composed from two or more

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