SYNTHESIS AND CHARACTERIZATION OF VINYL-BRIDGED POLYSILSESQUIOXANE SOL-GEL MATERIALS

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ABSTRACT

Vinyl-bridged polysilsesquioxane gels were formed through the use of sol-gel polymerization methods. Acid- and base-catalyzed samples were prepared from both the pure cis-(**1**) and pure trans-(**2**) isomers of 1, 2-bis(triethoxysilyl)ethylene. Gelation times of the two isomers were compared. The trans monomer **2** formed gels within a week while the cis monomer **1** failed to gel even after several months. Gelation of **1** could be promoted by the addition of a coordinating metal such as palladium. The resulting cis- and trans- vinyl-bridged polysilsesquioxane gels were then processed either by vacuum drying to afford xerogels or by extracting with supercritical carbon dioxide to afford aerogels. These vinyl-bridged polysilsesquioxanes were characterized by SEM, nitrogen sorption porosimetry, solid state ^{29}Si and ^{13}C NMR and x-ray powder diffraction.

KEYWORDS: Sol-Gel Processing, Vinyl-Bridged Polysilsesquioxane, Aerogel / Xerogel Materials

1. INTRODUCTION

The sol-gel process is a mild method of forming an inorganic glass from a metal alkoxide solution.[1] This method is most often used in the formation of silica gels from precursors such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). More recently, there has been substantial interest in incorporating organic groups into these materials in order to extend their range of physical and chemical properties. One method involves introducing an organic substituent into the silica network by replacing one of the alkoxide groups of TEOS or TMOS with an organic group.[2] The remaining three alkoxide groups may then undergo typical sol-gel reactions with the organic group as a pendant functionality on the network *polysilsesquioxane*. If taken a step further, *bridged* polysilsesquioxanes can be formed by polymerizing a monomer in which a hydrocarbon group bridges two trialkoxysilane groups (Figure 1).[3] In this manner, an organic bridge is introduced into the

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inorganic matrix as an integral part of the network architecture. These hybrid organic-inorganic materials provide new opportunities to manipulate the nature of the architecture through the choice of the organic bridging group. Previous efforts have examined the effects of rigid aromatic- and flexible alkylene-bridging groups on the physical properties of polysilsesquioxane xerogels and aerogels.

In this study, *vinyl*-bridged polysilsesquioxane xerogels and aerogels were prepared from the cis-(**1**) and trans-(**2**) isomers of 1,2-bis(triethoxysilyl)ethylene (Figure 2). The vinyl-bridging group is a rigid organic spacer composed of a carbon-carbon double bond. The availability of the isomers **1** and **2** provides the opportunity to investigate the effects of the substitution geometry on the ability of the vinyl-bridged monomers to form gels. For example, the intra-molecular cyclization of **1** would be expected to compete with intermolecular condensation reactions, thereby retarding the onset of gelation (Figure 3). The trans-monomer, on the other hand, would be not be expected undergo intra-molecular cyclization and should more readily form gels than the cis monomer. In addition, the carbon-carbon double bond may also be used as a π-donor to metals to increase the connectivity in the three-dimensional sol-gel framework. Precedence for this has been shown with the faster gelation of 2-butenylene-bridged trimethoxysilanes when in the presence of catalytic amounts of palladium (Pd).[4]

2. EXPERIMENTAL

2.1 Monomer Preparation of cis-1,2-bis(triethoxysilyl)ethylene (1) and trans-1,2-bis(triethoxysilyl)ethylene (2). A mixture of cis- and trans-isomers of 1,2-bis(triethoxysilyl)ethylene (84% trans / 16% cis) was prepared by the metathesis of triethoxyvinylsilane (125 ml, 0.593 mol) catalyzed by $RuCl_2(PPh_3)_3$ (0.304 g, 0.317 mmol) by refluxing for 24 hours.[5] Residual triethoxyvinylsilane was distilled off at atmospheric pressure and the remaining liquid was purified by spinning band distillations (2x) under vacuum. Monomer **1** (99% by GC, yield = 6%) was collected as a clear, colorless oil at 65 °C and 15μ. Monomer **2** (98% by GC, yield = 60%) was collected around 90 °C at 15μ). ^1H and ^{13}C NMR spectra of **1** and **2** are identical to published results.[5]

2.2 Sol-Gel Sample Preparation

2.2.1 Preparation of Vinyl-Bridged Polysilsesquioxane Samples Monomers **1** or **2** (1.41 g, 3.95 mmol) were mixed in dry ethanol (4 ml). A second mixture of aqueous 1 N hydrochloric acid (0.43 ml, 23.9 mmol water) or 1 M sodium hydroxide (0.43 ml, 23.9 mmol water) and dry ethanol (4 ml) was prepared. The acid or the base catalyst mixture was then added to the monomer solution. The final volume of the resulting mixture was brought up to 10 ml with additional dry ethanol. The slightly yellow transparent solutions were then transferred to 30 ml polypropylene bottles. After gelation, the gels were aged in the closed bottles for two weeks then dried under vacuum for 24 hours at 100 °C to form xerogels or by supercritical carbon dioxide extraction to give aerogels.

2.2.2 Preparation of Vinyl-Bridged Polysilsesquioxane Samples with Palladium Monomer **1** (141 mg, 0.4 mmol) and $(PhCN)_2PdCl_2$ (77 mg, 0.206 mmol) were dissolved in tetrahydrofuran (THF, 0.60 ml). Aqueous 1 N hydrochloric acid (0.072 ml, 4 mmol) and THF (0.1 ml) was added to the solution of **1** and the final volume was brought up to 1.0 ml with additional THF. After thorough mixing, the resulting deep red solution was poured into a glass vial and sealed. Dark reddish-brown gels formed after 10 days and were allowed to age for an additional 3 days. After the aging period, the samples were repeatedly extracted with

THF until the extracts were colorless leaving dark gray gels. Xerogels were formed by drying for 24 hours at room temperature and then further drying under vacuum for 6 hours at 150 °C. Aerogels were formed by extracting the gels with carbon dioxide under supercritical conditions.

2.3 Sample Characterization Vinyl-bridged polysilsesquioxane gels prepared without palladium were characterized by the following solid state techniques: x-ray powder diffraction, scanning electron microscopy (SEM), nitrogen sorption porosimetry and solid state ^{29}Si and ^{13}C nuclear magnetic resonance spectroscopy (NMR). The gel samples prepared with palladium were characterized by the following techniques: nitrogen sorption porosimetry, solid state ^{29}Si and ^{13}C NMR and transmission electron microscopy (TEM).

2.4 Nomenclature The cis- and the trans-isomers of 1,2-bis(triethoxysilyl)ethylene are denoted by **1** and **2** respectively. Xerogel samples are denoted by an X while aerogel samples are denoted by an A. Acid-catalyzed samples were denoted by (HCl) and base-catalyzed samples were denoted by (NaOH). If the palladium complex, $(PhCN)_2PdCl_2$, was added, this is denoted by inserting -Pd after the sample type. Therefore, an example might be a base-catalyzed xerogel prepared from the trans-monomer, X**2**(NaOH). A second example might be an acid-catalyzed aerogel prepared from the cis-monomer with Pd(II), A**1**-Pd(HCl).

3. RESULTS AND DISCUSSION

Differences between the experiments using monomers **1** and **2** can be seen immediately through their gelation behavior. Both acid- and base-catalyzed samples using **1** in ethanol did not gel within 90 days. Whereas, samples prepared with **2** gelled within 20 minutes for the base-catalyzed materials and 6 days for the acid-catalyzed materials. A palladium complex, $(PhCN)_2PdCl_2$, was added during the processing of X**1** and A**1** in an attempt to shorten their gelation time. When Pd(II) was added to the acid-catalyzed **1** polymers prepared in THF, gelation occurred much faster (10 days with palladium vs. 56 days without palladium). The oxidation state of palladium, although not known for the different stages during sol-gel processing, is apparently Pd(0) in the final gel sample. The metal reduction is probably a result of exposure to ethanol which is formed as a byproduct of the sol-gel process. To test whether or not the shortened gelation time was due to the addition of the coordinating metal, a non-coordinating salt, magnesium bromide ($MgBr_2$), was added. Although these samples formed gels faster than when no metal was present, gelation was still considerably slower than if Pd(II) was added (10 days with palladium vs. 36 days with $MgBr_2$). The faster gelation rate may be attributed to the fact that $MgBr_2$ is a weak Lewis acid which might have an effect on the polymerization rate itself. The corresponding base-catalyzed **1** gels were not studied since the palladium precipitated out of the solution under basic conditions.

After drying, the X**2** samples prepared in ethanol were small white granular insoluble, intractable solids. The A**2**(HCl) materials were in the form of translucent cracked pieces while the corresponding A**2**(NaOH) materials were opaque white monoliths. All of the samples were amorphous as there was no evidence of peaks in the x-ray powder diffraction patterns. The X**1**-Pd(HCl) materials formed small black granular solids. The A**1**-Pd(HCl) materials were dark gray colored monolithic fragments. All of the palladium containing samples were also found to be amorphous.

Through the solid state ^{29}Si NMR studies, the extent of reaction for samples under differing processing conditions can be compared. All of the gels in this study show degrees of condensation in the range of 65-85 % (Table 1). The X2(NaOH) and A2(NaOH) polymeric materials were found to be more highly condensed than the corresponding acid-catalyzed materials. This observation is consistent with previous studies.[6] Higher degrees of condensation suggests that these materials have fewer surface silanols and therefore are more hydrophobic. The X1-Pd(HCl) and A1-Pd(HCl) samples were found to have reasonably comparable degrees of condensation to those of X2(HCl) and A2(HCl).

The solid state ^{13}C NMR spectroscopy gives further information as to the molecular structure of the gels (Table 2). For example, the vinyl-bridge was found to be intact in all of the gels formed from **1** and **2** after processing. This is evidenced by the single resonance found at 146 ppm. The spectra also show evidence of residual ethoxy groups (58 and 17 ppm) except for in the X2(NaOH) materials. This is as expected since X2(NaOH) samples also shows the highest degree of condensation.

Porosimetry studies on the vinyl-bridged polysilsesquioxane materials were carried out to further characterize the material's porosity and surface areas (Table 3). All of the materials were determined to be mesoporous, having mean pore diameters between 20 and 500 Å. The surface areas of the materials ranged from 300 and 1100 m^2/g. Comparisons of the surface areas for X1(HCl) and A1(HCl) to the corresponding surface areas for X2(HCl) and A2(HCl) shows that they are approximately the same. On the other hand, the mean pore diameters for X1(HCl) and A1(HCl) are shown to be much higher than those for X2(HCl) and A2(HCl).

Finally, the morphology of the gel samples and the presence of the palladium particles was observed through electron microscopy. SEM micrographs of the A2(HCl) and A2(NaOH) materials (Figure 4) revealed a rough surface composed of packed particles with no porosity between the particles. The micrographs of X2(HCl) and X2(NaOH) (Figure 4) on the other hand revealed a much smoother surface with much smaller particle size. There was no apparent difference between acid- and base-catalyzed gels which is characteristic of bridged polysilsesquioxanes. In addition, TEM micrographs of X1-Pd(HCl) and A1-Pd(HCl) (Figure 5) revealed a range of dispersed palladium particles embedded in an amorphous gel matrix. The palladium particle size in the xerogel samples varied greatly depending on whether or not the samples were extracted with THF prior to drying. Small dispersed palladium particles (1-2 nm in diameter) were seen in the unwashed samples whereas the washed samples contained a variety of much larger particles (10-100 nm in diameter).

4. CONCLUSIONS

The 1,2-bis(triethoxysilyl)ethylene isomers show differing gelation behaviors. Samples prepared with monomer **1** failed to gel while the monomer **2** samples gelled with both acid- and base-catalysis The acid-catalyzed polymerization of **1** formed gels more rapidly after the addition of a coordinating metal species, in this case Pd(II). The faster gelation times seen for the gels prepared from **1** were found not to just be due to a salt effect. The palladium is thought to coordinatively bind in such a manner as to form a template which promotes the formation of a three-dimensional polymeric gel network. In addition, polysilsesquioxane gels containing palladium particles with sizes dependent upon the processing conditions are formed during sol-gel processing. Characterization of all of the gel

samples show that the highest degrees of condensation were found with the base-catalyzed samples and that the vinyl-bridge remained intact during the processing. The samples were all amorphous with high surface areas and porosity in the mesoporous range.

5. ACKNOWLEDGMENTS

The authors would like to thank Ed Russick for the supercritical carbon dioxide extraction of the aerogel samples, Gary Zender for the SEM work, Linda McLaughlin for the use of the Autosorb6 porosimeter, Roger Assink for the solid state ^{29}Si and ^{13}C NMR studies, Mary Gonzales for the x-ray diffraction studies and Tom Headley and Celeste Drewien for the TEM work.

This research was supported by United States Department of Energy under contract # DE-AC04-94AL85000.

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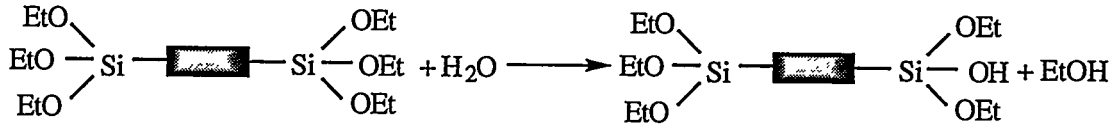
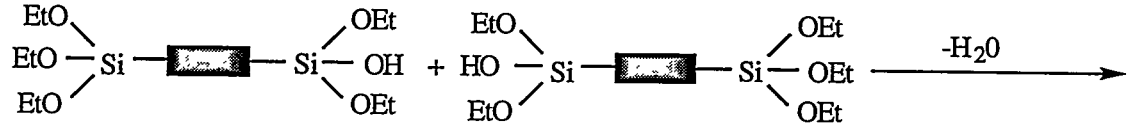
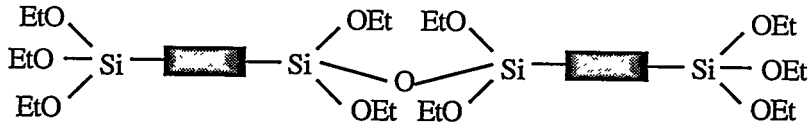
Hydrolysis



Condensation





= alkylene, arylene, acetylene

Figure 1. Sol-Gel Reactions for *Hydrocarbon-Bridged* Polysilsesquioxanes.

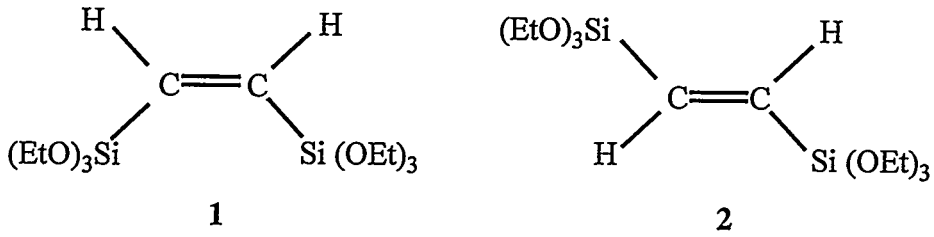


Figure 2. The Cis-(**1**) and Trans-(**2**) Isomers of 1,2-bis(triethoxysilyl)ethylene.

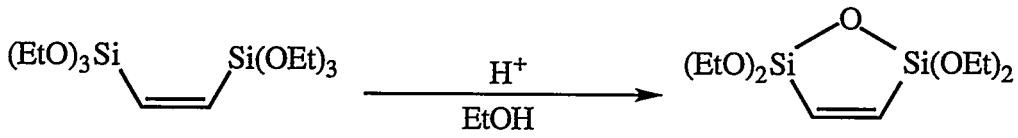
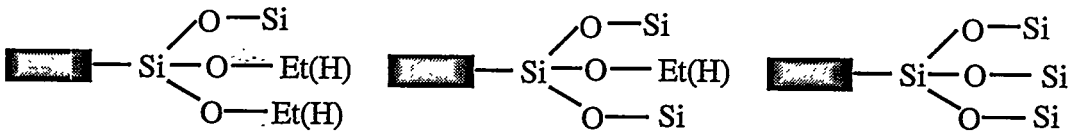


Figure 3. Formation of Cyclic Species from Cis-1,2-bis(triethoxysilyl)ethylene (**1**).

Table 1. Solid State ^{29}Si CP MAS NMR Data for Monomer **1** and Monomer **2** Sol-Gel Samples

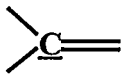
Sample	T Distribution			Degree of Condensation
	T^1	T^2	T^3	
A2(HCl)	13.62	61.15	25.21	0.71
X2(HCl)	11.49	67.02	21.48	0.70
A2(NaOH)	12.70	40.46	46.82	0.78
X2(NaOH)	6.94	35.62	57.43	0.84
A1-Pd(HCl)	23.20	55.67	30.28	0.69
X1-Pd(HCl)	0	84.00	36.38	0.77



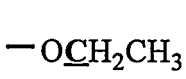
T^1 T^2 T^3

Table 2. Solid State ^{13}C CP MAS NMR Data for Monomer **2** Sol-Gel Samples

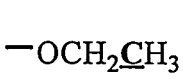
Sample ID	Relative Intensities for the Following Peaks:		
	146 ppm	58 ppm	17 ppm
A2(HCl)	68.7	16.3	15.0
X2(HCl)	70.9	15.6	13.5
A2(NaOH)	73.3	10.1	16.6
X2(NaOH)	100	-	-



146 ppm



58 ppm



17 ppm

Table 3. Nitrogen Sorption Porosimetry Data for Monomer **1** and Monomer **2** Sol-Gel Samples

Sample	BET Surface Areas (m^2/g)	Average Pore Diameter (Å)
A2(HCl)	782	42
X2(HCl)	329	24
A2(NaOH)	1104	159
X2(NaOH)	600	23
A1-Pd(HCl)	775	154
X1-Pd(HCl)	405	244

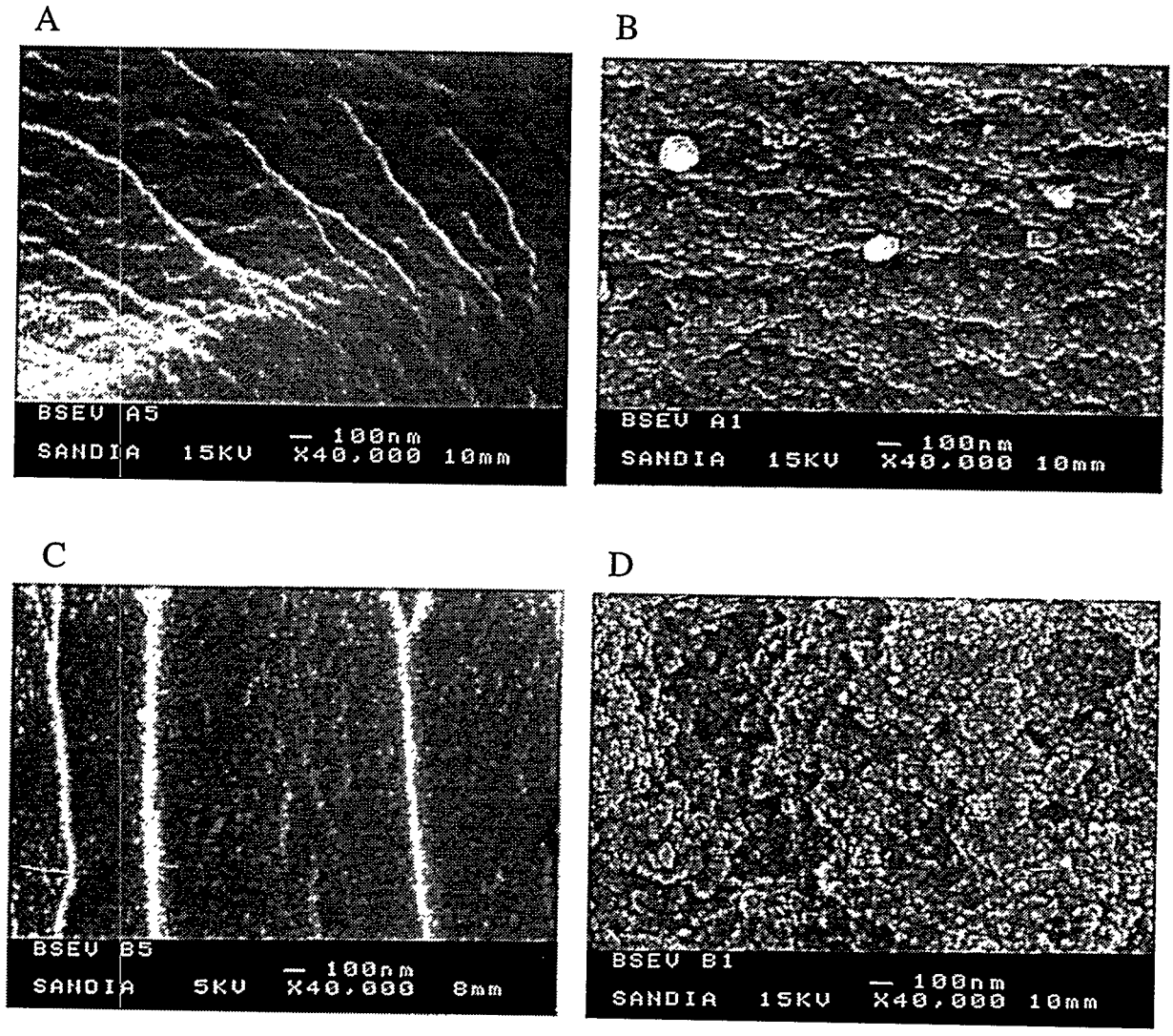


Figure 4. SEM Micrographs of the Monomer 2 Aerogels and Xerogels Prepared in Ethanol. A) Acid-catalyzed xerogel. B) Acid-catalyzed aerogel. C) Base-catalyzed xerogel. D) Base-catalyzed aerogel

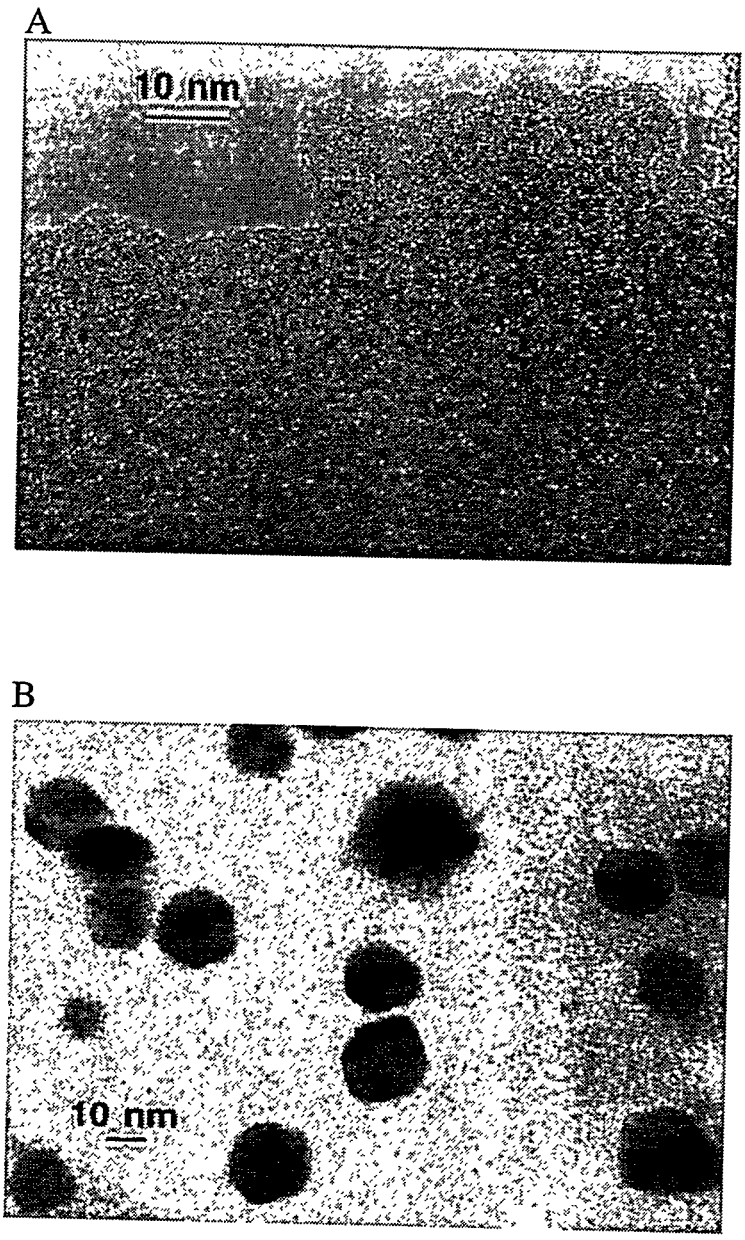


Figure 5. TEM Micrographs of Monomer 1 Xerogels Prepared with Pd. A) Sample dried without further washing. B) Sample dried after extracting with THF.