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Polymerization of Trialkoxysilanes. Effect of the Organic Substituent on the Formation of Gels.

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Introduction

Hydrolysis and condensation of trialkoxysilanes, R-Si(OR')$_3$, generally leads to the formation of silsesquioxane oligomers and polymers.[1] These polymers are composed of a monomer repeat unit, [R-SiO$_{1.5}$]$_n$, with a single silicon atom attached to other repeat units in the polymer through one to three siloxane bonds. The remaining substituent is an organic group attached to the silicon through a silicon-carbon single bond. Silsesquioxanes have been the subject of intensive study in the past and are becoming important again as a vehicle for introducing organic functionalities into hybrid organic-inorganic materials through sol-gel processing.[1-3] Despite all of this interest, there has not been a systematic study of the ability of trialkoxysilanes to form gels through the sol-gel process.[4] In fact, it has been noted that silsesquioxanes are generally isolated as soluble resins rather than the highly crosslinked network polymers (gels) one would expect from a tri-functional monomer.[1] In this study, we have examined the sol-gel chemistry of a variety of trialkoxysilanes with different organic substituents (R = H, Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *n*-octadecyl, n-dodecyl, cyclohexyl, vinyl, phenyl, benzyl, phenethyl), with methoxide or ethoxide substituents on silicon, at varying monomer concentrations ranging up to neat monomer, and with different catalysts (HCl, NaOH, formic acid, fluoride). Gels were prepared from tetramethoxysilane and tetraethoxysilane at identical concentrations for purposes of comparison.

$$n\ \mathrm{R{-}Si(OR')_3} + 1.5n\ \mathrm{H_2O} \xrightarrow{\mathrm{H+\ or\ OH-}} \left[\mathrm{R{-}SiO_{1.5}}\right]_n + 3n\ \mathrm{R'OH}$$

(R = H, Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *n*-octadecyl, *n*-dodecyl, cyclohexyl, vinyl, phenyl, benzyl, phenethyl

R' = Me , Et

Scheme 1. Hydrolysis and condensation of trialkoxysilanes to give polysilsesquioxanes.

The polymerization reactions were monitored for the formation of gels, insoluble precipitates, soluble polymers, or polyhedral oligosilsesquioxanes.

Experimental

General Methods. Anhydrous methanol was purchased from Aldrich. Ethanol was distilled from magnesium before use. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM400 (400 MHz) using C_6D_6 or $CDCl_3$ as solvent. Triethoxysilane, trimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, pheny-ltrimethoxysilane, phenyltriethoxysilane, vinyltrimethoxysilane, vinyl-triethoxysilane, *n*-octyldecyltrimethoxysilane, and dodecyltriethoxysilane were purchased from Aldrich. Phenethyltrichlorosilane, cyclohexyltrichlorosilane, t-butyltrichlorosilane, and benzyltriethoxysilane were purchased from Gelest. Isopropyltriethoxysilane was prepared from the Grignard reaction of isopropylmagnesium chloride with silicon tetrachloride followed by esterification with ethylorthoformate in the presence of a small quantity of ethanol. *t*-Butyltriethoxysilane and *t*-Butyltrimethoxysilane were prepared from the *t*-Butyltrichlorosilane by esterification with ethylorthoformate or methylorthoformate. Similarly, the cyclohexyl-substituted monomers were prepared from their corresponding trichlorosilane precursor. Phenethyltrimethoxysilane and Phenethyltriethoxysilane were also prepared by esterification of phenethyltrichlorosilane. Monomer purities were checked by GC and ^{1}H NMR and distilled if necessary until greater than 96% (GC).

Polymerizations. Monomers were first polymerized with 1.5 equivalents water in triplicate at 1M concentration in the appropriate alcohol (methanol for trimethoxysilanes; ethanol for triethoxysilanes). Aqueous HCl, NaOH were used as catalysts. Polymerization with formic acid or with aqueous flouride were also tried with select monomers. If gels were obtained, the monomer was then polymerized at lower concentrations to determine where the practical gelation threshold lies. If the monomer did not gel in a week or two, it was then polymerized at as high a concentration as possible (based on the molecular weight and density of the monomer). Gels were described as either colloidal (opaque white) or transluscent (blue tinted) or transparent. Soluble polysilsesquioxanes were described as resins. Precipitates were examined by microscopy to determine if they were crystalline or amorphous; ambiguous samples were then examined by powder x-ray diffraction.

Results and Discussion

Polymerizations. While hydrolysis and condensation of trialkoxysilanes readily affords oligomeric and polymeric silsesquioxanes in the form of oils or resins, gels were only observed with surprisingly small percentage of the monomers in this study. Many of the gels that did form were opaque white and colloidal in appearance. Crystalline polyhedral oligosilsesquioxanes were also observed with many of the alkyl-substituted monomers, despite the high monomer concentrations used. Under the same conditions, tetramethoxysilane and tetraethoxysilane readily form transparent or translucent silica gels.

Trimethoxysilane and triethoxysilane reacted rapidly and exothermically under acidic conditions or even with deionized water to afford insoluble gels with the hydride group intact.[5] Furthermore, gels formed even at concentrations as low as 0.1M. Under basic conditions, the monomers immediately reacted very exothermically with decomposition and loss of hydrogen to afford silica gels.[5] Methylsilsesquioxane gels have been reported elsewhere[6] and are perhaps the most studied of the silsesquioxane systems capable of gelation. With increasing length of alkyl substituents, the silsesquioxanes became less prone to form gels despite the similarity in steric bulk with the shorter alkyl substituents. Then with very long alkyl groups (dodecyl and octadecyl) gelation is again observed, presumably due to supramolecular organization of the long alkyl groups.[7] The inability of the ethyl, n-propyl, and n-butyl monomers for forming gels may be more of a physical phenomena than one of chemical reactivity. In every case, phase separation of a dense oil (that in some instances hardened into a resin) and a lighter alcoholic phase was observed. Even performing non-aqueous sol-gel polymerizations with anhydrous formic acid failed to prevent phase separation and resin formation.

Increasing the steric hinderance at the silicon with branched alkyl groups effectively prevented polymerizations of trialkoxysilanes from forming gels. ^{29}Si NMR reveals that hydrolysis and condensation occurs in most of these systems, but that soluble resins are favored rather than gel-forming network polymers. t-Butyltrialkoxysilanes are sterically hindered enough that while hydrolysis occurs, condensation reactions are inhibited such that even oligomers form only slowly.

Aryl substituents (phenyl, benzyl, and phenethyl) also formed resinous oligomers with molecular weights under 10K. Even with heating to 200 °C, the molecular weights (M_w) remained under 20K.

Table 1. Gelation results from the hydrolysis and condensation of methoxysilane monomers. Monomer concentration is in parentheses (tr. bl. = translucent blue, trp. = transparent, op. = opaque, prcp = precipitate, vsc oil = viscous oil, crst. = crystals).

Monomer	Polymerization Results Acid-Catalyzed	Base-Catalyzed	Water
Si(OMe)$_4$	tr.bl. gel (1M)	trp. gel (0.8M)	tr.bl.gel (1M)
(MeO)$_3$SiH	tr.bl. gel (1M)	tr. bl. gel (1M)	tr.bl. gel (1M)
MeSi(OMe)$_3$	gel (5.8M)	tr.bl. gel (1M)	vsc oil
EtSi(OMe)$_3$	resin	resin/crst.(1M)	resin
n-PrSi(OMe)$_3$	crst./resin	resin	vsc oil
n-BuSi(OMe)$_3$	vsc oil	resin	crst.
i-BuSi(OMe)$_3$	crst.	resin	soln.
t-BuSi(OMe)$_3$	prcp	crst.	prcp
octadecylSi(OMe)$_3$	op. gel(0.1M)	op.gel (0.5M)	____
vinylSi(OMe)$_3$	op.gel (5.5M)	op.gel (0.8M)	resin
phenylSi(OMe)$_3$	resin	precp	vsc oil
phenethylSi(OMe)$_3$	vsc oil	resin	vsc oil

The main difference between the *trimethoxysilyl* and *triethoxysilyl* monomers (Tables 1 and 2) is that the methoxide monomers reacted faster and so exothermically (methyltrimethoxysilane) that the reaction solutions would explosively boil upon mixing. For every trimethoxysilyl monomer that reacted to form gels, the corresponding triethoxysilylmonomer would also afford gels, but generally under a more limited set of reaction conditions.

Table 2. Gelation results from the hydrolysis and condensation of ethoxysilane monomers. Monomer concentrations at which gels were obtained are given in parentheses (tr. bl. = translucent blue, trp. = transparent, op. = opaque, prcp = precipitate, vsc oil = viscous oil, crst. = crystals).

	Polymerization Results		
Monomer	Acid-Catalyzed	Base-Catalyzed	Water
$Si(OEt)_4$	tr. gel (4M)	prcp	vsc soln
$(EtO)_3SiH$	tr. gel(0.5M)	gel(0.5M)	——
$MeSi(OEt)_3$	crst/resin	gel (1M)	vsc soln
$EtSi(OEt)_3$	crst/resin	precip/resin	vsc oil
n-$PrSi(OEt)_3$	vsc oil	resin	vsc oil
i-$PrSi(OEt)_3$	vsc soln	prcp	vsc soln
n-$BuSi(OEt)_3$	vsc soln	resin	vsc oil
i-$BuSi(OEt)_3$	crst	crst/vsc oil	vsc oil
t-$BuSi(OEt)_3$	crst	prcp	soln
cyclohex$Si(OEt)_3$	vsc oil	prcp	vsc oil
dodecyl$Si(OEt)_3$	op. gel (1M)	op. gel (1M)	——
vinyl$Si(OEt)_3$	crst/gel (4M)	op. gel (0.8M)	vsc oil
phenyl$Si(OEt)_3$	prcp/vsc soln	resin	resin
benzyl$Si(OEt)_3$	vsc oil	resin	vsc oil
phenethyl$Si(OEt)_3$	vsc oil	resin	vsc soln

Conclusions

Formation of gels from trialkoxysilanes is significantly hindered by sterically bulky organic substituents and by phase separation of oligomeric or polymeric silsesquioxanes. Gels were obtained from trimethoxysilane, triethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, dodecyltriethoxysilane, octadecyltrimethoxysilane, vinyltrimethoxysilane, and vinyltriethoxysilane. The rest formed oligomers and polymers in the form of oils and resins. Crystalline products were obtained, despite the high monomer concentrations used, from a few alkylsubstituted trimethoxysilanes and a variety of triethoxysilyl monomers under acidic conditions.

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(1) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.
(2) Schubert, U.; Husing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.
(3) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007.
(4) Slinyakova, I. B.; Kurennaya, L. I. *Vysokomol. Soedin., Ser. B.* **1972**, *14*, 889.
(5) Pauthe, M.; Phalippou, J.; Corriu, R. J. P.; Leclercq, D.; Vioux, A. *J. Non-Cryst. Solid* **1989**, 113, 21.
(6) Chen, K. C.; Tsuchiya, T.; MacKenzie, J. D. *J. Non-Cryst. Solid* **1986**, *81*, 227.
(7) Shimojima, A.; Sugahara, Y.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2847.

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