SAND2000-0835C

POLYMETHYLSILSESQUIOXANES THROUGH BASE-CATALYZED REDISTRIBUTION OF OLIGOMETHYLHYDRIDOSILOXANES

Kamyar Rahimian and Roger A. Assink*

*Organic Materials Department, Sandia National Laboratories, Albuquerque, NM 87185-1407

Douglas A. Loy

Catalysis and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM 87185-1407

Introduction

There has been an increasing amount of interest in silsesquioxanes and polysilsesquioxanes. They have been used as models for silica surfaces[1] and have been shown to have great potential for several industrial applications.[2] Typical synthesis of polysilsesquioxanes involves the hydrolysis of organotricholorosilanes and/or organotrialkoxysilanes in the presence of acid or base catalysts, usually in the presence of organic solvents (reaction 1).

$$\begin{matrix}RSiCl_3 \text{ or} \\ RSi(OR')_3\end{matrix} + 3H_2O \longrightarrow -[RSiO_{1.5}]_n- + \begin{matrix}3HCl \\ \text{or } 3R'OH\end{matrix} \qquad (1)$$

There have also been reports of titanium-catalyzed redistribution alkoxysilanes and oligomethylhydridosiloxanes to produce methylsilane and polymethylsilsesquioxane.[3] We have recently demonstrated that alkylammonium hydroxides catalyze the ring-opening polymerization of disilaoxacyclopentanes to form highly crosslinked siloxane networks, that behave as traditional sol-gel materials.[4] One of the advantages to using these bases is their thermal decomposition to volatile species during the heat curing of the resulting product, thus providing an end product which has no residual catalyst or impurities. In this paper, we report on the catalytic, as well as stoichiometric, redistribution of oligomethylhydridosiloxanes to produce polymethylsilsesquioxanes $(MeSiO_{1.5})_n$, as well as its copolymer with dimethylsiloxane $(Me_2SiO)_n$ and hydridosiloxane $(MeHSiO)_n$.

Experimental Section

Oligomethylhydridosiloxane (PMHS) (MW = 1500-1900, puchased from Gelest and used as received), or its copolymer with dimethylsiloxane (PDMS) (with various mole % of MeHSiO, purchased from Gelest and used as received) was weighed out in a flask and catalytic amounts of tetrabutylammonium hydroxide (TBAH) (0.1N solution in MeOH/toluene, purchased from Acros and used as received) were added to known weights of the oligosilane. The reaction, performed both under argon atmosphere and repeated in air, is exothermic and immediate generation of $MeSiH_3$ was observed. As more $MeSiH_3$ is generated, the product gets more viscous and within one minute, the reaction solidifies. The resulting gels were analyzed by IR and solid state NMR spectroscopy. The reaction is also performed in THF solvent under argon atmosphere.

Caution: At high catalyst concentrations, the reaction is very exothermic, violent and can blow out of the reaction vessel.

Results and Discussion

The general scheme for the reactions of PMHS and its PDMS copolymer with TBAH are shown in scheme 1.

Scheme 1

$$-[MeHSiO]_n- \xrightarrow{Bu_4NOH} 0.33n\, MeSiH_3 + -[MeSiO_{1.5}]_n-$$

$$-[MeHSiO]_n-[Me_2SiO]_m- \xrightarrow{Bu_4NOH} 0.33n\, MeSiH_3 + -[MeSiO_{1.5}]_n-[Me_2SiO]_m-$$

The reaction is exothermic and very rapid. As the amount of TBAH catalyst is increased, so do the exothermicity of the reaction and the rate of the reaction. The reaction solidifies within one minute of TBAH addition. As $MeSiH_3$ gas is produced during the reaction (confirmed by ^1H NMR spectroscopy of the gas evolved), the resulting material foams under neat conditions and can discharge out of the reaction vessel. Under these conditions not all of the SiH groups are converted to $MeSiH_3$, as the reaction is so rapid that it solidifies before the redistribution reaction has a chance to reach completion. However, the reaction can be driven to completion when enough solvent is used (0.012M solution in THF based on repeating units, 2.0 mol% TBAH based on r.u.) and the mixture is allowed to react long enough (overnight). Still, if the solution is more concentrated (0.30 M in THF based on r.u.), upon addition of the TBAH catalyst (1.0 mol% TBAH based on r.u.), the solution gels and the reaction does not reach completion. Products of the reaction of PMHS with TBAH are all white brittle solids. When the reaction is performed under conditions which it gels, the resulting gel is colorless and clear, which upon drying results in the same type of materials.

An important note to these reactions is that no hydrogen is generated during the reaction. The catalytic redristribution of alkoxysilanes, $(RO)_3SiH$, with nucleuphilic catalysts[5] or TBAH[6] does produce hydrogen gas. The volatiles in the reactions above were trapped in C_6D_6 and solution ^1H NMR spectroscopy confirmed the presence of only $MeSiH_3$.

The reactions can be followed by both NMR and IR spectroscopies. By IR spectroscopy, disappearance of the SiH stretching frequency at 2170 cm^{-1} can easily be followed (Figure 1). IR data are semi-quantitative since the intensity of the SiH stretching frequency seems to depend on the extent of redistribution. Figure 2a displays the IR spectrum of starting PMHS, while 1b is that of the reaction of neat PMHS with 1.20 mol% TBAH and figure 1c is the reaction of PMHS in THF (0.14 M solution) with 4.9 mol% TBAH.

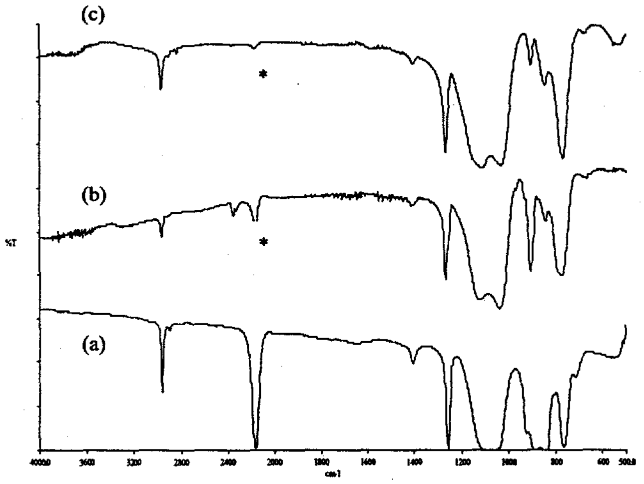

Figure 1. IR spectra of: (a) starting PMHS; (b) after reaction with catalytic TBAH under neat conditions; (c) the reaction in THF. SiH stretching frequency is denoted by *.

In the ^{29}Si NMR spectra of the reactions, the loss of SiH can be followed by the disappearance of its corresponding resonance in PMHS, at –35 ppm. Based on these data, it is clear that in the neat reactions, the amount of redistribution to $MeSiH_3$ is independent of the amount TBAH catalyst used (Figure 2b, c), except for when only enough TBAH is used to induce slow gelation (Figure 2a). When the reaction is performed in solvent under dilute conditions, all of the SiH groups are converted and the final product has a formula of $(MeSiO_{1.5})_n$, methylsilsesquioxane, provided that the reaction is allowed to react for sufficient length of time (about 24 hours). Solid State ^{29}Si spectrum of the product displays only resonance of T^3 silicons (Figure 2d). This is also confirmed by the almost absence of the SiH stretching frequency in the IR spectrum of the final product (Figure 1c).

RECEIVED
APR 10 2000
OSTI

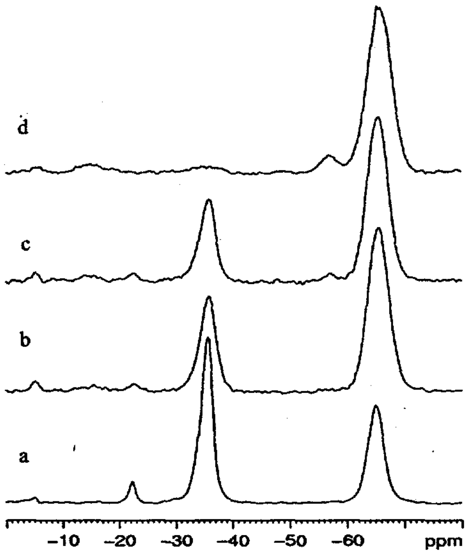

Figure 2. Selected solid state ^{29}Si NMR spectra of reaction of PMHS (starting PMHS has one resonance, at −35 ppm, by solution ^{29}Si NMR spectroscopy) with TBAH: (a) neat PMHS with 0.024 mol% TBAH; (b) neat PMHS with 0.24 mol% TBAH; (c) neat PMHS with 1.20 mol% TBAH; (d) 0.0 14 M PMHS/THF solution with 4.9 mol% TBAH (all values are based on "MeHSiO" repeating units).

Catalytic redistribution reaction of PMHS/PDMS copolymer follows the same pathway and displays the same trend as the PMHS reactions. As the amount of TBAH catalyst is increased, more $MeSiH_3$ is produced and all of the SiH portion of the copolymers can be converted when the reaction is performed in solvent and allowed to reach completion, or when enough catalyst is added (figure 3). The linearity content in the final product can be varied by simply varying the amount of the PDMS portion of the starting oligomer.

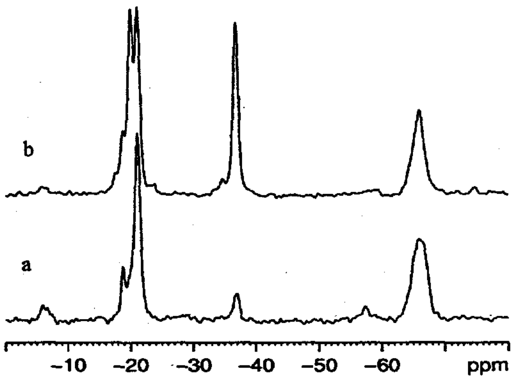

Figure 3. Solid state ^{29}Si NMR spectra of the products of catalytic reaction of PMHS/PDMS copolymer (50-55% PMHS) with TBAH: (a) neat copolymer with 0.04 mol% TBAH ; (b) neat copolymer with 4.0 mol% TBAH (values based on "MeHSiO" repeating unit).

Conclusions

Oligomethylhydridosiloxane and its copolymer with dimehtylsiloxane undergo redistribution chemistry with catalytic tetrabutylammonium hydroxide to produce methylsilane and polymethylsilsesquioxanes. The rate and extent of redistribution reaction can be controlled by the amount of TBAH added, as well as use of solvent. The extent of reaction can be followed by both IR and solid state NMR spectroscopy, following the disappearance of the SiH in the starting oligosiloxane.

Acknowledgement. We would like to thank David P. Lang (NMR spctroscopy), and Arturo Sanchez (IR spectroscopy) for their assistance. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

References

(1) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.*, **1989**, *111*, 1741.
(2) (a) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.*, **1982**, *102*, 199. (b) Frye, C. L.; Klosowski, J. M. *J. Am. Chem. Soc.*, **1971**, *93*, 4599.
(3) (a) harrod, J. F.; Xin, S.; Aitken, C.; Mu, Y; Samuel, E. *Can. J. chem.*, **1990**, *68*, 471. (b) Laine, R. M.; Rahn, J. A.; Youngdahl, K. A.; Babonneau, F.; Hoppe, M.L.; Zhang, Z.-F.; Harrod, J. F. *Chem. Mater.*, **1990**, *2*, 464.
(4) Loy, D. A.; Rahimian, K.; Samara, M. *Angew. Chem. Int. Ed.*, **1999**, *35*, 555.
(5) Corriu, R. P. J.; Perz, R.; Reye, C. *Tetrahedron*, **1983**, *39*, 999.
(6) Loy, D. A.; Schneider, D. A. Manuscript in preparation.