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High-Temperature Stabilization of Cross-Linked Siloxanes Glasses

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Polymers and glasses which resist high temperatures for long periods of time are used for a variety of applications such as coatings for electronic components, gaskets, sealents and flame retardant materials.[2] These materials are usually organic polyimides, polyaramids, and fluoropolymers. Polysiloxanes, however, are not used widely as high-temperature materials. It has been reported that thermal degradation of linear poly(dimethylsiloxane) occurs above 340 °C[3] and oxidation of poly(alkylsiloxanes) in air occurs above 250 °C.[4] The addition of aryl groups on silicon or carborane segments in the polymer chain does increase the thermal stability of the polysiloxane.[5]

The major thermal decompostion products of linear poly(dimethylsiloxanes) are the cyclotrisiloxane, $(Me_2SiO)_3$ (D_3), and the cyclotetrasiloxane, $(Me_2SiO)_4$ (D_4).[2] If these cyclosiloxane monomers are cross-linked into network structures, the normal degradation pathway open to the polysiloxane might be suppressed resulting in thermally stable siloxane systems. In general, polymers can be made more thermally resistant by cross-linking; this reduces the elimination of end groups or small molecules which are often responsible for low-temperature weight loss. This strategy has been used successfully to increase the char yield of preceramic polymers.[6] In this work we have examined the thermal stability of nonlinear, highly cross-linked polymers obtained from the hydrosilylation of $(Me(Vi)SiO)_4$ and $(Me(H)SiO)_4$ (where Vi is $CH_2{=}CH$).[7,8]

Cross-linking of cyclotetrasiloxane rings via Pt-catalyzed hydrosilylation was carried out using no solvent.[9] Hard, clear, low-density glasses were produced having the idealized network structure shown in I (wavy lines represent continuation of the siloxane network). Combinations of 1:1 $(MeViSiO)_4$ and $(Me(H)SiO)_4$ and 1:2 $(MeViSiO)_4$ and $(Me(H)SiO)_4$ were used. The ^{29}Si magic-angle spinning (MAS) NMR spectrum[10] of the 1:1 glass in Figure 1a shows that more than 80% of the silicon atoms are involved in the cross-linked network (peak at −21 ppm) while 18% contain un-cross-linked Si–H or Si–Vi groups (−34 peak).[11] In the 1:2 glasses, more than 70% of the silicon atoms are cross-linked which is near the theoretical

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(1) Contribution no. 6641.

(2) For a recent review see: Hergenrother, P. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1262.

(3) Kendrick, T. C.; Parbhoo, B.; White, J. W. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; Part 2, pp 1319–1340.

(4) Patnode, W.; Wilcock, D. F. *J. Am. Chem. Soc.* **1946**, *68*, 358. Scala, L. C.; Hickham, W. H.; Laeffer, M. *J. Appl. Polym. Sci.* **1959**, *2*, 297. Kuz'minskii, A. S.; Goldovskii, E. A. *Vysokomol. Soedin.* **1961**, *3*, 1054.

(5) Grassie, N.; Macfarlane, I. G.; Francey, K. F. *Eur. Polym. J.* **1979**, *15*, 415. Grassie, N.; Francey, K. F. *Polym. Degradation Stability* **1980**, 2, 53. Grassie, N.; Francey, K. F.; Macfarlane, I. G. *Polym. Degradation Stability* **1980**, *2*, 67. Papetti, S.; Schaeffer, B. B.; Gray, A. P.; Heying, T. L. *J. Poly Sci., Part A* **1966**, *4*, 1623.

(6) Wynne, K. J., Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297.

(7) Lamoreaux, H. L. US Patent 3,197,413, July 27, 1965. Zhdanov, A. A.; Andrianov, K. A.; Malykhin, A. P. *Vysokomol. Soyed.* **1974**, *A16*, 2345. Ashby, B. A. US Patent 3,159,662, Dec 1, 1964.

(8) Related work on the synthesis of oligocyclosiloxanes from cyclosiloxanes has recently appeared: Chang, P.-S.; Hughes, T. S.; Zhang, Y.; Webater, G. R.; Poczynok, D.; Buese, M. A. *J. Polym. Sci., Part A* **1993**, *31*, 891.

(9) A typical preparation of the 1:1 glass is as follows: to a mixture of 2.95 g (8.56 mmol) of $(MeViSiO)_4$ and 2.09 (8.69 mmol) of $(Me(H)SiO)_4$ was added 3 drops of platinum divinylsiloxane complex (3–3.5% Pt concentration in xylene). After mixing, the clear solution was allowed to cure at room temperature for 70 h and then heated to 110 C in argon for 2 h producing a hard, transparent glass. The 1:2 glasses were synthesized using the same method. No unusual hazards related to this synthesis were found.

(10) The NMR spectra were taken on a Bruker CXP300 spectrometer with 10- or 20-min delay time between 90° pulses. The T_1 relaxation times were <1 min in the unheated glasses and <5 min in the heated materials.

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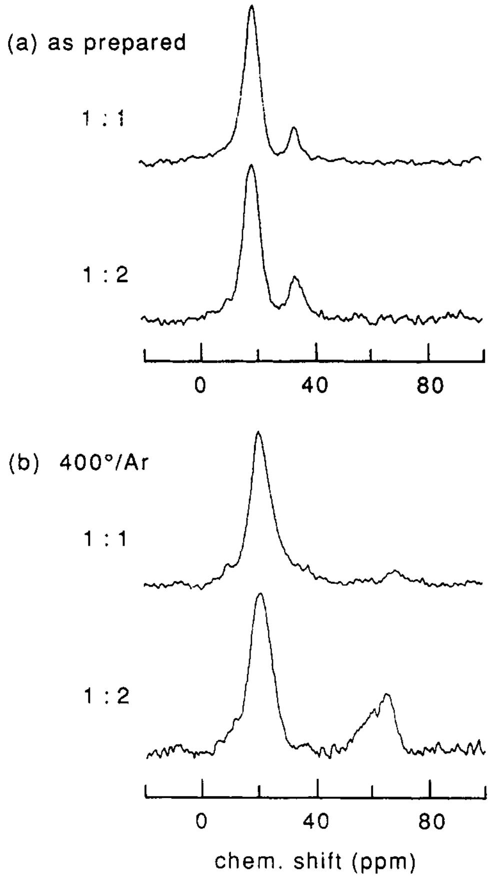
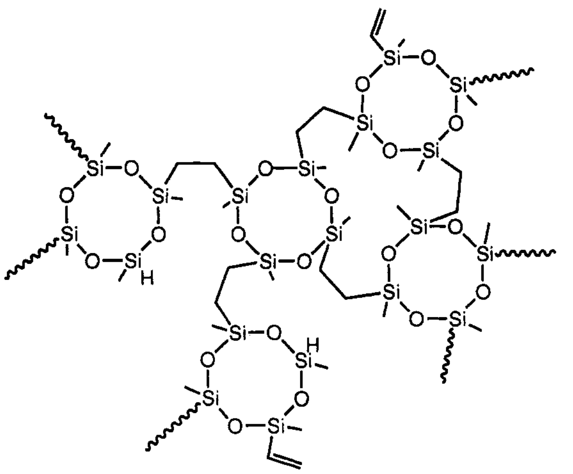


Figure 1. ^{29}Si MAS NMR spectra of the $(Me(Vi)SiO)_4/(Me(H)SiO)_4$ network glasses: (a) the 1:1 and 1:2 glasses as prepared; (b) the 1:1 and 1:2 glasses after heating to 400 °C for 1 h under Ar.



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limit of 67% assuming only hydrosilylation reactions. No evidence for Si–Si dehydrocoupling was found in the spectra of these glasses, or in spectra of $(Me(H)SiO)_4$ in toluene-d_8 heated with the Pt catalyst under similar conditions.

When the 1:1 glasses were heated to 400 °C for 1 h under Ar, weight losses of 2–4% were observed. Similar weight losses were observed in the 1:2 glass. TGA/MS results on the 1:1 glass are shown graphically in Figure 2. The TGA/MS (10 °C/min) shows at least two chemically distinct weight loss events (Figure 2b).[12] Over the range 300–450 °C, CH_4 (*m/e* 16,15) and C_2H_4 (*m/e* 28, 27, 26) are the most prominent evolved gases. These molecules would be expected products from Si–C bond cleavage reactions at Si–CH_3 sites, and residual vinyl endgroups respectively. Similar Si–CH_3 cleavage is proposed in the thermal degradation of highly cross-linked poly(dimethylsiloxane).[13] The evolution profiles for the C_1 and C_2 fragments are not identical. It appears that the C_2 fragments, represented by *m/e* 27 in Figure 2, have a lower temperature onset and a distinct intensity maximum at around 400 °C. This might result from the expected lower dissociation energy for the Si–vinyl vs Si–CH_3 bond. From the ^{29}Si NMR data showing at least 20% un-cross-linked end groups in this sample, the expected weight loss if all of the available vinyl ends evolved as C_2H_4 would be 3.5%. The weight losses observed on annealing in Ar at 400 °C (2–5%) are similar to this and their variability can be understood from the TGA/MS as a variability in the amount of trapped solvent with synthesis and drying conditions. Above 450 °C the gas evolution becomes more complex. Clear evidence for the onset of degradation of the siloxane ring network can be seen in the sharp appearance of *m/e* 59 and 73 at 525 °C. These are significant fragments in the electron impact (EI) mass

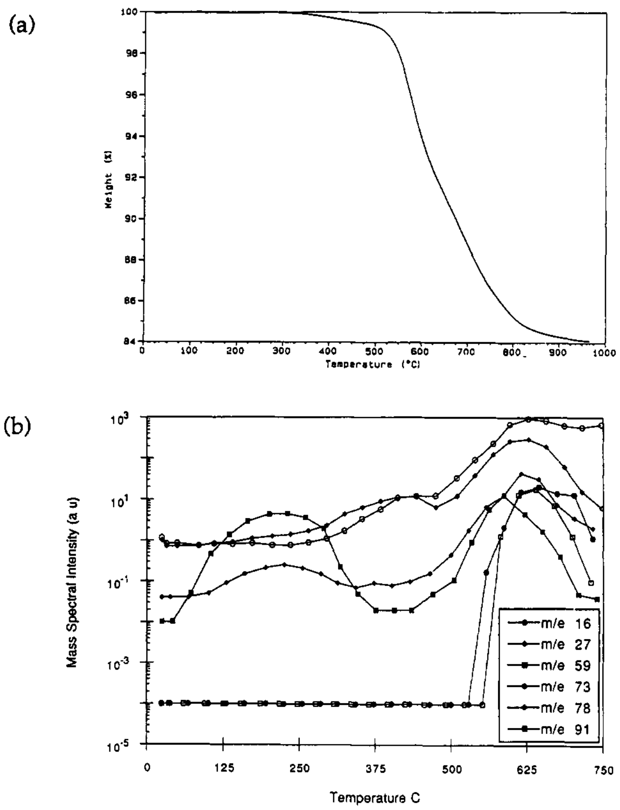

Figure 2. TGA/MS results of 1:1 $(Me(Vi)SiO)_4/(Me(H)SiO)_4$ network glass: (a) TGA of the glass in N_2 from 25 to 950 °C; (b) MS of fragments obtained from volatile decomposition products upon heating the glass from 25 to 750 °C.

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(11) In our hands using the ^{29}Si MAS NMR spectrometer both $(Me(H)SiO)_4$ and $(Me(Vi)SiO)_4$ are observed to have chemical shifts of −32.7 ppm. The $^1J_{Si-H}$ coupling in $(Me(H)SiO)_4$ is observed to be 245 Hz.

(12) The low temperature range (50–300 °C) is characterized by fragments due to small amounts of residual toluene and/or xylene (*m/e* 78, 91) from the Pt catalyst solution which is apparently trapped in the glass network.

(13) Li, D.; Hwang, S.-T. *J. Appl. Polym. Sci.* **1992**, *44*, 1979.

spectra of both monomers $(Me(Vi)SiO)_4$ and $(Me(H)SiO)_4$. The results obtained from the 1:2 glass are consistent with the observations above.

The TGA/MS results show that loss of the un-cross-linked end groups occurs in small amounts throughout the heating of the glass, while the cyclosiloxane network decomposition does not occur until above 525 °C.[14] This observation led us to examine high temperature curing of the 1:1 glass under argon. By controlling the curing time at a given temperature, one should be able to burn off the un-cross-linked end groups while keeping the glass properties intact. ^{29}Si MAS spectra taken of the glasses after annealing at 400 °C for 1 h (Figure 1b) show loss of the un-cross-linked signal at −34 ppm and the appearance of a new broad resonance centered at −68 ppm. This new signal represents about 7% of the spectral intensity in the 1:1 glass and 28% in the 1:2 glass. An increase in the area of the −21 ppm peak from 80% to 93% is also observed which most likely implies further hydrosilylation cross-linking upon heating. This is supported by the observation that the −21 ppm peak intensity for the 1:2 glass remains nearly the same during heating. The new −68 ppm resonance most likely corresponds to a "T-type" silicon atom, one surrounded by three oxygens and one carbon.[15] The rearrangement which occurs within the glass to form this "T-type" silicon may be related to similar redistributions of siloxanes bearing SiH groups using Pt-, Ir-, and Rh-based catalysts.[16] We do observe a higher intensity of T silicons in the NMR spectra of the less cross-linked 1:2 system. The production of T resonances may be the result of chemistry involving the Pt catalyst and the un-cross-linked Si–H sites in the glass.

Samples of the 1:1 glass were next cured for longer periods of time. Heating the glasses at 400 °C in Ar for 1–18 h produced weight losses in the range 2–5%. When these cured samples were subjected next to conditions of 300 °C in air for 1 h, a linear decrease in the observed weight loss in air was found as a function of increased argon cure time. In fact, the sample cured for 18 h in Ar did not change weight when heated at 300 °C in air for 1 h. Some surface oxidation was found on the sample when it was removed from the furnace; however, the bulk of the sample was intact with complete shape retention. In the absence of curing, the 1:1 glass had a 10% weight loss when heated at 300 °C in air for 1 h. If high-temperature air stability of cross-linked polysiloxanes is needed, this curing method provides a possible solution.

The TGA ceramic yields of the 1:1 glass at 950 °C were 84% (N_2) and 82% (air).[17] Some air oxidation of the glass occured above 200 °C leading to 0.4% weight gain. Analysis of the white ceramic produced at 1000 °C in Ar gave $Si_{1.2}C_{1.4}O_{1.0}$, roughly stoichometric silicon oxycarbide.[18]

In conclusion, we have demonstrated that highly cross-linked cyclotetrasiloxane inorganic/organic hybrid networks can be stabilized at elevated temperatures. We have recently shown that similar networks can be formed from the hydrosilylation of $(MeViSiO)_4$ and $(MeHSiO)_n$ as well as from tetravinylsilane and $[(Me_2Si)(Me(H)Si)]_n$; these highly cross-linked glasses (75% by ^{29}Si MAS NMR) also show no observable weight loss when heated at 400 °C for 1 h under argon.

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(14) Thermal ring opening of cyclic polydimethylsiloxanes, catalyzed by glass surfaces, is reported to occur near 350 °C; Clarson, S. J.; Semlyen, J. A. *Polymer* **1986**, *27*, 91.

(15) The chemical shift of the "T-type" silicon in $(Me_3SiO)_3SiMe$ was found to be −64.4 ppm; Engelhardt, G.; Jancke, H.; Radeglia, R.; Kriegsmann, H.; Larin, M. F.; Pestunovich, V. A.; Dubinskaja, E. I.; Voronkov, M. *Z. Chem.* **1977**, *17*, 376.

(16) Curtis, M. D., Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213. The redistribution of cyclic siloxanes has been reported to occur readily in platinum boats at temperatures above 350 °C; see ref 13.

(17) TGA conditions: 25–950 °C at 10 °C/min.

(18) See: Belot, V.; Corriu, R. J. P.; Leclecq, D.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids*. **1992**, *147, 148*, 52. Renlund, G. M.; Prochazka, S.; Doremus, R. H. *J. Mater. Res.* **1991**, *6*, 2716.