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The chemistry of the Si–H bond with acid treated clays

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Abstract

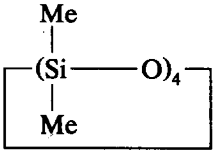
The reaction of 1,1,3,3-tetramethyldisiloxane (M^HM^H) with acid treated clays (Filtrol) gives a mixture of $HSiMe_2O$–(M^H) stopped fluids, cyclic $(Me_2SiO)_n$ oligomers and gaseous products which include H_2 and Me_2SiH_2. The reaction does not proceed with strong acid alone or with acid neutral clay.

1. Introduction

Acid- and base-catalyzed, ring opening polymerization is a well-known method for making silicone polymers [1–3]. The reaction in eqn. (1) shows a typical polymerization reaction where the product is a mixture of linear and cyclic polydimethylsilicone containing a functionalized end-group, Me_2XSiO.

$$Me_2XSiOSiXMe_2 + nD_4 \xrightleftharpoons{H^+} Me_2XSiO(Me_2SiO)_{4n}SiXMe_2(M^xD_{4n}M^x) \quad (1)$$

where D_4 =



$$D_4 = \left[(\overset{Me}{\underset{Me}{Si}}-O)_4\right]$$

The use of the M, D, T and Q shorthand notation [4] is explained in the appendix. The use of acid treated clay as the catalyst in the reaction of eqn. (1) is well known [4–7]. These clays are primarily bentonite clays [8] treated with mineral acid. Examples of the acid treated clays are the Filtrol® materials produced by the Engelhard Company. Thus, for example, preparation of Mi^{vi}-$D_{20}M^{vi}$ from $M^{vi}M^{vi}$ and 5 equiv. of D_4 requires heating the reagents in the presence of as little as 10 ppm of an acid clay such as Filtrol 13. The Filtrol 13 is a 300 m^2 g^{-1} clay treated with sufficient sulfuric acid to give a residual acidity of 15 mg KOH g^{-1} at the phenolphthalein endpoint.

Ring-chain equilibrium polymerization of octamethylcyclosiloxane with linear siloxanes has been well studied, and the ultimate equilibrium polymer molecular weight (M_n) and cyclic siloxane concentrations are observed to follow the theoretical considerations of Scott [9a], Jacobsen and Stockmeyer [9b], and others [9c]. We have observed that polymers made with M^H (Me_2HSiO–) end-groups via ring-chain equilibrium polymerization of D_4, M^HM^H with Filtrol catalysts can give dramatically higher molecular weights than expected based on the stoichiometry of polymerization and predicted theoretical values. In the course of preparing low molecular weight polymers of the type $M^HD_nM^H$, attempts to make $n \le 10$ materials often yielded $n = 20$–50 polymers, suggesting that the M^H end-group was being consumed. There is only one report in a patent by the Dow Corning group [10] describing the reaction of M^HM^H and similar SiH compounds with acid clays. The products of the reactions included $M^HD_xM^H$ polymers and the gaseous product, Me_2SiH_2. To our knowledge, no further reports have appeared describing this chemistry.

2. Results and discussion

The reaction of 9/4 equiv. of D_4 with 1 equiv. of M^HM^H was carried out in the presence of 1% by weight Filtrol 20 (acid treated clay) at 70–80°C for 8 h. After this time, the resulting oil had a viscosity of 28 centistokes (cSt). The ^1H NMR showed the presence of terminal M^H groups at 4.68 ppm, with an average degree of polymerization of the resulting $M^HD_nM^H$ polymer, $n = 47$. In addition, there was a peak at 3.76

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ppm due to Me_2SiH_2. The experiment was repeated by reacting M^HM^H with Filtrol (no D_4 present). In all cases, cyclic D_n oligomers, M^H stopped polymers and Me_2SiH_2 were produced.

The reaction between M^HM^H and Filtrol 13 was carried out by heating M^HM^H in the presence of 1 wt.% Filtrol 13 with stirring for 2 h at 80° C (eqn. (2)). The gases above the reaction were analyzed by gas chromatography mass spectroscopy (GCMS) which confirmed the presence of Me_2SiH_2. Additionally, small amounts of CH_4 and H_2 were detected as reaction products. The origin of methane was perhaps due to reaction with adventitious water causing some amount of demethylation.

$$M^HM^H + \text{acid clay} \xrightarrow{2\text{ h, }80^\circ\text{C}} Me_2SiH_2 + H_2 + CH_4 + M^HD_xM^H + \text{cyclic } D_y \tag{2}$$

The silicone portion of the products from eqn. (2) were also analyzed. At the early stages of the reaction, analysis by GC showed the presence of unreacted M^HM^H, Me_2SiH_2 (after about 1 h) and $M^HD_xM^H$, $x = 0$–18. ^{1}H and ^{29}Si NMR analysis confirmed that M^H stopped oligomers were present; however, the ratio of M^H/D (Si*H*/Si*Me* ratio by ^{1}H NMR and *Si*H/Me_2*Si*O ratio by ^{29}Si NMR) was very low. After 2 h, M^HM^H was consumed (as shown by GC and ^{1}H and ^{29}Si NMR). Careful analysis by GCMS showed that the major silicone products were cyclic oligomers D_x, with lesser amounts of $M^HD_xM^H$. The trimer, M^HDM^H, was observed at an early stage of the reaction (about 1 h) by ^{29}Si NMR. The trimer had a D chemical shift at −17.8 ppm and a GC retention time consistent with three silicon atoms. This and other short-chain M^H stopped fluids were presumably consumed as the reaction proceeded. The final resting state mixture from eqn. (2) had a ^{29}Si NMR spectrum where M^HM^H and M^HDM^H were not observed. A resonance at −6.95 was assigned to an M^H end, the end of an oligomer, while three resonances at −19.18, −19.94 and −21.97 were assigned, respectively, as D_4, $M^HDD_xDM^H$ and either D_n ($n \geq 5$) and/or $M^HDD_xDM^H$. The M stopped, linear polymers such as MD_xM are ruled out by the absence of an M resonance. Overlap of cyclic D_n ($n \geq 5$) resonances with D chain resonances of $M^HD_xM^H$ made accurate determination of x by ^{29}Si NMR impossible. Clearly, significant loss of SiH occurs with release of Me_2SiH_2.

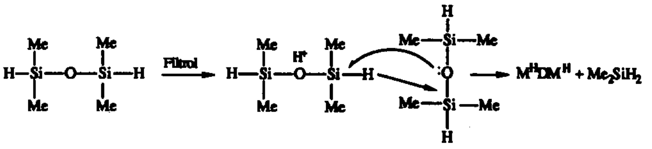
The reaction of M^HM^H with 1% by weight Filtrol 13 as in eqn. (2) gave a product with an average degree of polymerization (dp) of 24 as determined by ^{1}H and ^{29}Si NMR integration. In the ^{29}Si NMR, a ratio of $M^HD'D_xD'M^H$, $M^H:D':D$ of 1:0.98:11.7 was found. The calculated dp from this ratio for the polymer rewritten as $M^HD_xM^H$ is $x = 24$. In addition, 1 equiv. of D_4 was found as determined by ^{29}Si NMR. Because ^{29}Si NMR does not distinguish all of the D groups from each other, gel permeation chromatography (GPC) was employed to determine the length of the $M^HD_xM^H$ polymers by using an IR detector set at the SiH resonance. The GPC analysis, using silicone standards, of the $M^HD_xM^H$ polymer showed $M_n = 841$ which would correspond to an average dp of 12. Thus, about half of the observed D resonance is due to cyclic-D_n, average $n = 12$.

Higher consumption of SiH was noted when 1% by weight Filtrol 20 was used in place of Filtrol 13 in the reaction of eqn. (2). ^{29}Si NMR analysis showed an $M^H:D':D$ ratio of 1:0.94:46.9. This ratio corresponded to an average dp for $M^HD_xM^H$, $x = 94$. In addition, 2 equiv. of D_4 were observed. The GPC analysis of this product showed $M_n = 7461$ corresponding to a dp of 101. Thus, the product from the Filtrol 20 catalyzed rearrangement had a low yield of D_n and was primarily composed of long chain $M^HD_xM^H$.

Both Filtrol 13 and Filtrol 20 reactions were monitored by GC in order to determine qualitatively the relative catalyst activity. Under nearly identical conditions at 1 h reaction time, nearly all of the low molecular weight species were consumed in the Filtrol 20 catalyzed reaction, whereas significant low molecular weight material was present in the Filtrol 13 catalyzed reaction. These results suggest that D_n is consumed by combination with $M^HD_xM^H$, eqn. (3).

$$M^HM^H \xrightarrow[\text{Filtrol 20}]{\text{Filtrol 13 or}} M^HD_xM^H + D_n \xrightarrow{\text{Filtrol}} M^HD_{x+n}M^H \tag{3}$$

The differences between Filtrol 20 and Filtrol 13 are minor. According to product information available from Engelhard [11], Filtrol 20 has a slightly higher level of residual acidity *vs.* Fitrol 13 as measured by mg KOH g^{-1} at phenolphthalein endpoint (18 *vs.* 15). Thus, the reaction in eqn. (2) must be extraordinarily sensitive to pH. In a control experiment employing acid neutral clay, Filtrol 2C, no reaction occurred when M^HM^H was heated for 2 h at reflux in the presence of 1% by weight Filtrol 2C. Additionally, the reaction of eqn. (2) was run with either concentrated sulfuric acid (free of clay) or triflic acid which gave no reaction at all, no change in the integrated intensity of H *vs.* Me in ^{1}H NMR was observed, and there was no formation of Me_2SiH_2. Finally, M^HM^H was treated with concentrated sulfuric acid in the presence of carbon black. After reflux for several hours, no change was observed in the M^HM^H. Thus, the acid clay alone is responsible for the observed reaction.



Scheme 1.

Corriu and co-workers [12] have described a mechanism by which $HSiO_{1.5}$ can decompose to give SiH_4 and SiO_2. The formation of Me_2SiH_2 in acid catalyzed polymerization can be explained utilizing arguments which describe the mechanism by which SiH is converted to SiO (Scheme 1).

The high activity of acid supported clay *vs.* free acid may be related to the higher electrophilicity of the acid on the clay. The effect of higher activity of the acid clay is similar to the higher activity of oxide supported metal catalysts *vs.* homogeneous analogs [13]. In both cases the support plays an important role in the observed reactivity. The clay may help to anchor/activate the siloxane for acid attack at Si–O–Si oxygen.

Further studies are under way to understand the details of clay structure *vs.* reactivity.

3. Experimental

^1H NMR spectra were recorded on a GE QE-300 instrument (300.15 MHz) in $CDCl_3$, all shifts, δ, relative to TMS = 0 internal standard. ^{29}Si NMR were recorded on a Varian XL 300 NMR spectrometer (59.3 MHz) using $Cr(acac)_3$ as a relaxation agent and all shifts, δ, relative to TMS = 0 internal standard. Gas chromatography was performed using an HP model 5890 gas chromatograph employing a 1.8-m 3% OV 101 column and a thermal conductivity detector. GCMS data for light gases (H_2, CH_4, *etc.*) were collected by employing a JEOL SX-102 model GCMS instrument. Gas analyses were carried out using a gas syringe injected into molecular sieve PLOT column (Chrompack 10 m × 0.32 mm) run isothermally. The instrument was tuned for H_2 and then after detection of H_2 retuned to observe the high molecular weight species. The high vapor pressure portion of the liquid was analyzed using a DB-1 (30 m × 0.32 mm) run at -70°C isothermally for 4 min then ramped at 10°C min^{-1}. Finally, the conventional liquid portion of the reaction was analyzed by injecting into a DB-5 (30 m × 0.32 mm) run from 10°C at 10°C min^{-1}.

In a typical reaction M^HM^H (10 ml) and Filtrol 13 (0.1 g) were combined and heated at 80°C and the reaction was then monitored by GC and ^1H NMR. In the experiment where the gases were analyzed, M^HM^H (1 g) was placed in a Schlenk tube with Filtrol 20 (10 mg) and the contents were thoroughly degassed. The tube was then immersed in a 100°C oil bath and the contents were stirred for 2 h. After this time, the liquid portion was frozen in liquid nitrogen and then the gases overhead were sampled by GCMS. In addition, the contents of the reaction were analyzed by both analyzing the liquid portion of the reaction and the high vapor pressure components not observed above, *e.g.* to confirm the presence of Me_2SiH_2.

Acknowledgements

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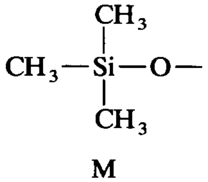
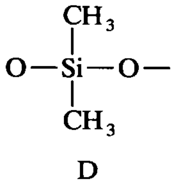
Appendix A: Nomenclature and shorthand for silicones



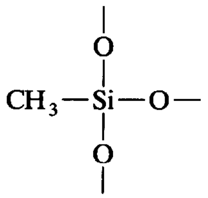
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-$$

M



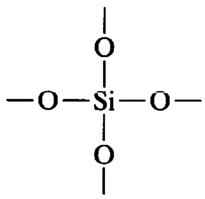
$$O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-$$

D



$\mathrm{CH_3{-}Si(O{-})_2{-}O{-}}$

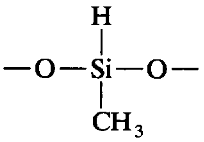
T



$\mathrm{{-}O{-}Si(O{-})_2{-}O{-}}$

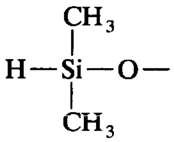
Q

Superscripts R are used to designate functional groups other than CH_3.



$\mathrm{{-}O{-}Si(H)(CH_3){-}O{-}}$

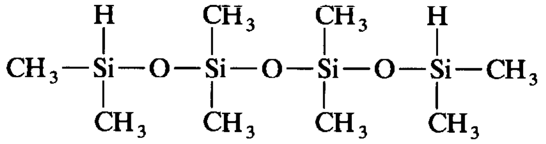
D^H



$\mathrm{H{-}Si(CH_3)_2{-}O{-}}$

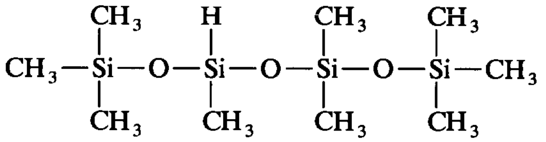
M^H

Subscripts are used to indicate stoichiometry; for example, $M^HD_2M^H$ is shorthand for



$\mathrm{CH_3{-}Si(H)(CH_3){-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}O{-}Si(H)(CH_3){-}CH_3}$

while MD^HDM is shorthand for



$\mathrm{CH_3{-}Si(CH_3)_2{-}O{-}Si(H)(CH_3){-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}CH_3}$