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Kinetic Study of the Reaction of Bis(hydroxydimethylsilyl)benzene and Dichlorosilanes

Gaddam N. Babu* and Richard A. Newmark

Corporate I&C Research and Laboratories, 3M Company, St. Paul, Minnesota 55144

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Introduction. Silarylene–siloxane copolymers exhibit a wide range of physical properties depending on their composition and structure.[1] We have recently reported the synthesis of copolymers of silarylenes and siloxanes[1,2] and determined the sequence and composition using ^{13}C and ^{29}Si NMR spectroscopy. Alternating copolymers were obtained from the reaction of bis(hydroxydimethylsilyl)benzene (BHB) with $RR'Si(NMe_2)_2$, but random copolymers were observed with $RR'SiCl_2$. This kinetic study was undertaken to determine if the randomization occurred during the initial condensation reaction or in an equilibration of oligomers of alternating copolymers. Although NMR is frequently used to determine the structures of copolymers containing siloxanes,[2-8] no examples of kinetic analysis of silicon condensation polymers using NMR have been reported.

^{29}Si spin–lattice relaxation times (T_1) are very long [for example, $T_1 = 74$ s in poly(dimethylsiloxane) (PDMS)], and most routine silicon spectra are obtained with $Cr(acac)_3$ added to the solution to suppress the negative nuclear Overhauser enhancement (NOE) and reduce the T_1. But $Cr(acac)_3$ is not inert and perturbs the equilibria and rates of the reaction (vide supra). Doddrell[9] and West[10] pioneered the use of proton polarization transfer as an alternative means to obtain ^{29}Si spectra since the recycle time of the experiment is then determined by the relaxation time of the protons, which, for example, is 4 s for the methyl in PDMS. Brunet et al.[11] have used polarization transfer to study sol–gel polymerization of silicon tetramethoxide monomers and described the experimental method in detail.

Results and Discussion. We have obtained ^{29}Si spectra vs time for the reaction of BHB with Ph_2SiCl_2, Me_2SiCl_2, and $PhMeSiCl_2$.[12] Typical spectra are given in Figure 1 for the Ph_2SiCl_2 reaction. Ph_2SiCl_2 is observed in the first spectrum of Figure 1, but its intensity represents only 23% of the diphenylsilanes in the solution. The major absorption observed in all spectra of BHB + $RR'SiCl_2$ is observed at exactly 20.8 ppm and matches the chemical shift of reference $ClSiMe_2ArSiMe_2Cl$. Under higher resolution this absorption appears as a doublet distinguishing X = O and X = Cl in $\mathrm{Cl}\mathit{Si}\mathrm{Me_2ArSiMe_2X}$. This peak represents 45% of the silarylene silicons when the first spectrum is obtained in the Ph_2SiCl_2 reaction, approximately 60 s after mixing of the two solutions. Its intensity decreases almost 30% within 16 min after preparation of the sample. The major diphenylsilane absorption in the early spectra, at −33.0 ppm, is due to $Ph_2Si(OH)_2$.

In the early stages of the reaction absorptions are observed for $HOSiPh_2O–$ and $ClSiPh_2O–$ terminated oligomers, but no absorptions are observed in the $–OSiPh_2O–$ region. This confirms that the initial stages of the reaction are oligomerizations in accordance with the step-growth condensation process. After 30 min absorptions for monomers are no longer observed and further reaction is exclusively oligomer condensation. Slow condensation and reequilibration occur to give the expected high molecular weight condensation product with a spectrum identical to that reported for purified polymers.[2] The Ph_2SiCl_2 reaction with BHB is approximately 2-fold slower and shows no evidence for intermediate $ClSiPh_2O–$end groups in the presence of the $Cr(acac)_3$ relaxation reagent.

Similar results are observed for the reaction with $Cl_2SiMePh$, except that the rates are considerably faster. The silanediol absorption, $(HO)_2SiMePh$, at −20.6 ppm never exceeds 10% of the methylphenylsilanes, and absorption

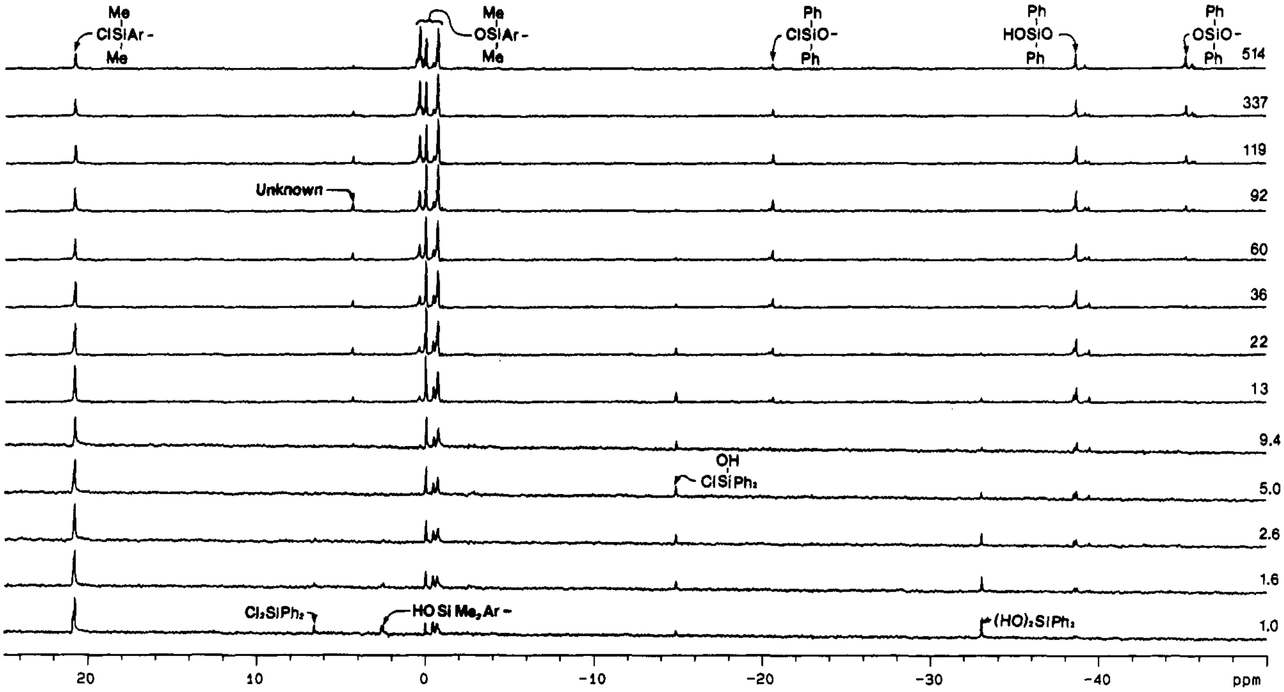

Figure 1. ^{29}Si NMR spectra vs time (in minutes) for the reaction of 1 mol of BHB and 1 mol of dichlorodiphenylsilane. The first spectrum was obtained 1 min after mixing the reaction. Spectra between 1 and 13 min are the average of 4 transients accumulated in 16 s; spectra between 22 and 60 min are the average of 61 transients accumulated in 5 min; spectra at longer times are from 122 transients accumulated in 10 min. Times are given for the first transient of each spectrum.

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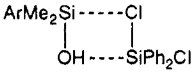
for HOSiMePhO– end groups is observed in the first spectrum. After 15 min 50% of the methylphenylsilane intensity is in siloxane units, whereas 9 h are required for 50% conversion to diphenylsiloxane units in the analogous reaction with Cl_2SiPh_2. With Me_2SiCl_2 the reaction is too fast to follow with NMR in a 1:1 solution at +22 °C; the first spectrum shows over 90% conversion to dimethylsiloxane units. In summary, the rate of reaction of chlorosilanes with diol is $Cl_2SiMe_2 \gg Cl_2SiMePh \gg Cl_2SiPh_2$.

The reaction products are unchanged when the Ph_2SiCl_2 + BHB reaction is carried out at −15 °C, but the initial rates are slower and it is possible to observe in real time the initial oligomerization of BHB. Spectra for the reaction of bis(chlorodimethylsilyl)benzene (BCB) and diphenylsilanediol are very similar to those for BHB + Ph_2SiCl_2, except that no absorption is observed at +6.5 ppm for Ph_2SiCl_2 in the former reaction. However, hydroxydimethylphenyl end groups are observed at +2.3 ppm with intensities vs time similar to those shown in Figure 1.

The formation of $(HO)_2SiPh_2$ during the early stages of the reaction suggests that the reaction is driven toward the formation of a diol which is thermodynamically more stable than Cl_2SiPh_2. The reaction probably proceeds through a four-membered transition state such as



$$\begin{array}{lcl} \mathrm{ArMe_2Si} & \text{-----} & \mathrm{Cl} \\ | & & | \\ \mathrm{OH} & \text{----} & \mathrm{SiPh_2Cl} \end{array}$$

where the cyclic structure promotes the initial formation of $Ph_2SiClOH$ and, after reaction with a second $ArMe_2SiOH$, $Ph_2Si(OH)_2$. The OH–Cl exchange reaction must proceed much faster than the condensation polymerization. The reaction of Me_2SiCl_2 with BHB probably proceeds similarly, but $Me_2Si(OH)_2$ is unstable in the presence of acid in the medium.

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(12) All ^{29}Si INEPT spectra were obtained at 80.8 MHz on a Varian XL-400 NMR spectrometer. The best signal/noise was obtained with delays corresponding to coupling constants of 14–18 Hz even though the Si–H coupling constant in a typical CH_3Si group is only 7 Hz. The optimum value is a compromise between the true coupling constant and transverse relaxation which causes an exponential decrease in the signal for long delay times. Samples of the dichlorosilane and diol were prepared as 50% solutions in THF (distilled over CaH_2) in a drybox. They were mixed under nitrogen using septa-covered vials and NMR tubes in the NMR laboratory. One minute was required for mixing and transfer to the spectrometer.