Communications to the Editor

Controlled Synthesis and Spectroscopic Characterization of Multifunctional Hybrid Silazane/Silylamine Preceramic Telechelic Oligomers

Preceramic polymer chemistry has been an area of intense interest and investigation in the recent past.[1] This field involves preparative techniques that afford the availability of soluble or fusible (i.e., processable) preceramic polymers that can be converted to materials for more recent desired applications.[1,2] The design of appropriate precursors must however meet structural and reactivity considerations and "the design of a preceramic polymer is an exercise in functional group chemistry".[3,4] One major difficulty in such a design is the inability to control polymerization reactions that often result in materials that are cross-linked or that become insoluble and/or infusible.[5] Maya has recently reported on an approach to this problem, i.e., on the feasibility of producing derivatized preformed polymers for use as ceramic precursors.[5] Even this latter approach can, however, benefit from controlled preparation of polymers to obtain appropriate functionalities that can be used for derivatization. In any case, detailed molecular-level structural characterization of precursors, which incidentally has been glaringly lacking, will be necessary to further take advantage of the preparative techniques.

We have been interested in designing polymeric precursors with desired structure and reactivity for Si–N–C/Si–C–N and Si–N–C–O ceramics and in developing a methodology for controlling the polymerization reactions. The interest in precursors for Si–N–C–O ceramics is motivated by the desire to expand the range of application of SiC and Si_3N_4 via such composite-type Si–N–C–O ceramics. Our efforts have led to the preparation of preceramic telechelic oligomers using organodichlorosilanes and ethylenediamine. The intent of this report is, therefore, mainly to communicate results on the spectroscopic characterization of these oligomers and to demonstrate how the multifunctional oligomers can serve as starting materials for further reactions with conventional di- or trifunctional monomers, multifunctional preformed oligomers, etc., to prepare molecular composites of various compositions.

Experimental Section. The details of a typical procedure for the synthesis of oligomers/polymers from ethylenediamine (EDA) and dichloromethylvinylsilane (DMVS) have been described before.[6] NMR spectra were obtained by using a Bruker WM-250 NMR spectrometer. One-dimensional ^{29}Si spectra were obtained by using the inverse-gated decoupling or the DEPT methods.[7] ^{29}Si–^{1}H 2D COSY spectra were obtained by using standard techniques.[8] FT-IR spectra were obtained on a Nicolet 730 system. Thermogravimetric analysis (TGA) was done on a Du Pont system interfaced with a thermal analysis 2000 unit. Elemental analysis was done by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion. The putative structure of a poly(organosilylethylenediamine) (POSED) that can be expected from a simple condensation, i.e., without cyclization, of organodichlorosilanes (ODS) and EDA is shown in Chart I. Also shown in Chart I is a proposed polymer structure as characterized by Kummer and Rochow[9] and recently by our group[10] for the case in which $R_1 = R_2 = CH_3$. In these cases that had been reported, the ODS to EDA feed ratio (R) was 1:2 with no other base used. In the work to be reported here, triethylamine was used as a base and the variation in microstructures and/or backbone composition was investigated by varying R.[11] R was typically varied from 0.25 to 2.5. Ratios of $R < 1$ generally gave oligomers with >NH and $-NH_2$ functional groups, and as R was increased to $R > 1.33$, Si–Cl reactive groups were obtained. The telechelic oligomers/polymers obtained in this fashion have been investigated by ^{29}Si and ^{1}H NMR and FT-IR spectroscopy and selected spectra are presented in Figures 1 and 2. From analyses of such spectra, the reactive functional groups for each ratio have been identified. The 2380–3600-cm^{-1} region of the IR spectra (Figure 1a) show >NH (3394 cm^{-1}) and $-NH_2$ (3267 and 3224 cm^{-1}) functionalities. In prototype ^{1}H NMR spectra (250 MHz), signals in the ranges 5.6–6.2 (vinyl H's), 2.6–3.2 (methylene H's), and 0.1–0.6 ppm are observed. The signals in the latter case are due to $-CH_3$ groups, and the most downfield ones (0.5–0.6 ppm) have been assigned to $>SiClCH_3$ (vide infra). Additionally, we have found ^{29}Si NMR to be extremely useful both to probe the variation in backbone structure and also to identify the Si–Cl functionality in the telechelic oligomers. This utility is demonstrated by the spectra shown in Figure 1b. Basically there are two regions in the spectra: −2 to +3 ppm and −19 to −17 ppm. Within each region, the changes in the spectral characteristics as a function of R are manifested. Specifically, there are primarily three resonances for the $R = 1$ oligomer. On the basis of comparison with previous work,[10,12] signal C is assigned to an azasilacyclopentane moiety (Figure 1b and Chart II, structure **10**) and signals F and G to acyclic and bridge moieties (Figure 1b and Chart II, structures **9** and **10**, respectively). As R increases, additional signals are observed in all regions. The unresolved four signals from −1.5 to −0.9 ppm are due to Si–Cl (D and E, Figure 1b), and the presence of this functionality in the oligomers leads to the observation of two more signals (at 1.6 (A) and 2.8 (B) ppm). The tentative assignment of these signals is shown in Chart IIA (structures **2** and **6**, respectively).

^{29}Si NMR has been used to further characterize the microstructure of the telechelic oligomers.[13] As an example, ^{29}Si–^{1}H 2D COSY spectra are presented in Figure 2.[15] Upon comparison of the 1D proton spectra for $R = 1.1$ and 2.5 (Figure 2), it is evident that the signals at about 0.5 ppm are not observed for $R = 1.1$ (Figure 2A). These signals, which are observed in the 1D proton spectrum of Figure 2B, correlate with signals D and E (Figure 1b).[16] Further examination of the ^{29}Si NMR spectra in Figure 1 shows that, of the signals in the Si–Cl region, two (D) are associated with signal A and the other two (E) with signal B. We have tentatively assigned signals A and B to segments **2** and **6** shown in Chart IIA. The assignments of signals A and B (Figure 1b) to Si atoms A and B in Chart IIA (**2** and **6**, respectively) are reasonable since the Cl atoms in segments **2** and **6** should lead to a

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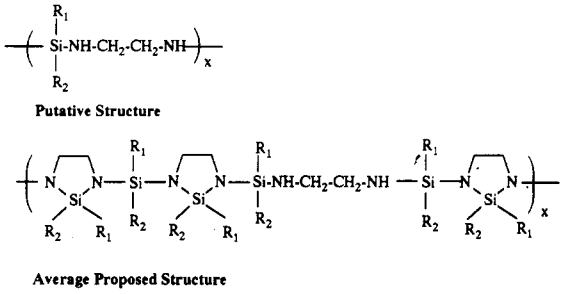
Chart I
Proposed Structure of POSED



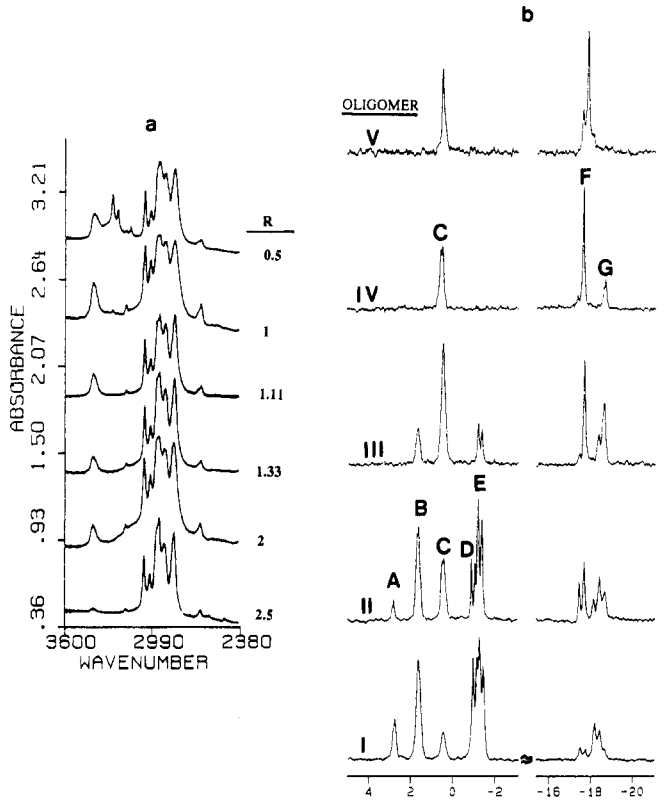


Figure 1. (a) 2380–3600-cm^{-1} region of the IR spectra for various R's. (b) 49.69-MHz ^{29}Si NMR spectra obtained by the DEPT technique with recycling time = 3 s, a spectral width of 2000 Hz, a delay of 0.0125 s, and the NS (number of transients) varied from 48 to 160. Observation and decoupling 90° pulse widths were about 23 and 48 μs, respectively. R values for I–V are 2, 1.67, 1.33, 1, and 0.5, respectively.

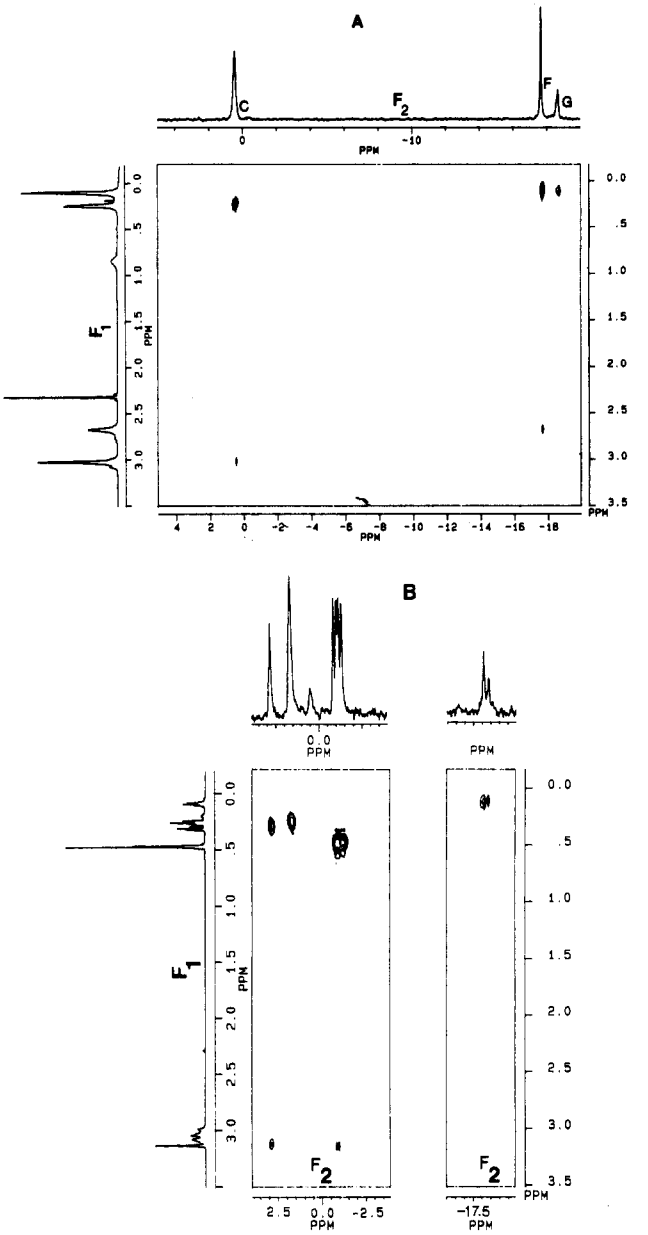
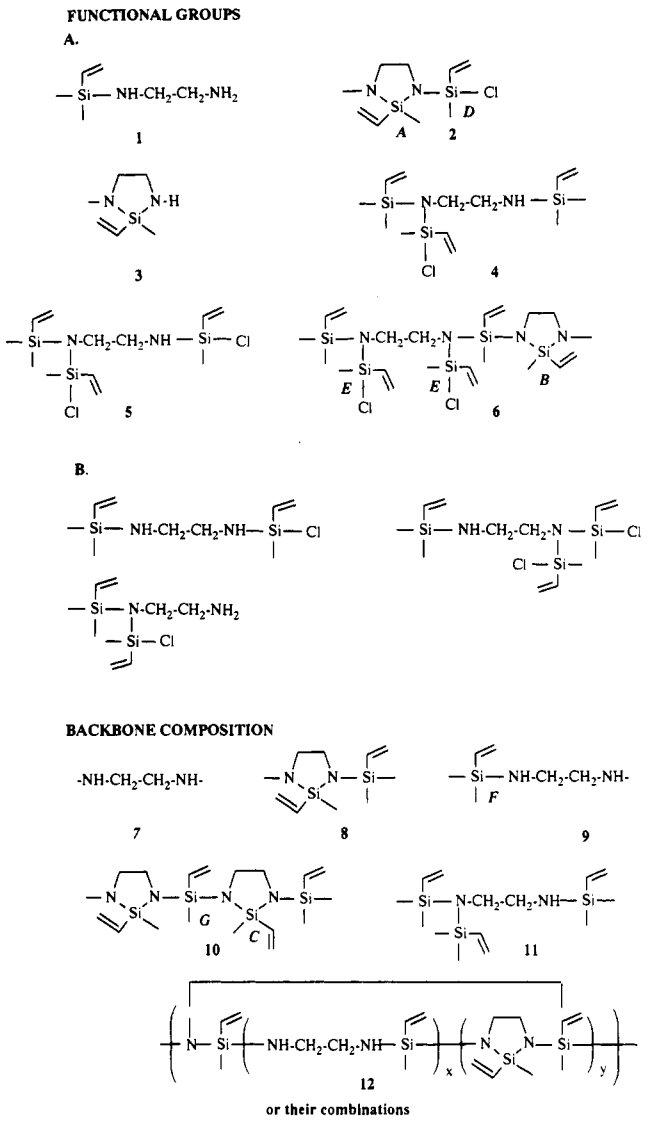


Figure 2. (A) ^{29}Si–^{1}H 2D correlated NMR spectrum for R = 1.1. Conditions: pulse sequence, D1–90°(^{1}H)–D0–180°(^{29}Si)–D0–D3–90°(^{1}H),90°(^{29}Si)–D4 detection with D0 = 3 μs, D1 = 3 s, and D3 and D4 being 12.5 and 6.25 ms, respectively. F_1 = ±950.6 Hz; F_2 = 2000 Hz; NS = 48 scans (accumated over 128 t_1 increments); LB = 2 (F_2 dimension only); data matrix = 1024 × 128 (with one level of zero-filling in the F_1 dimension during processing). Magnitude spectra were obtained with the sine bell window function applied in both dimensions prior to FT. (B) As in A but the spectrum for R = 2.5 and NS = 208.

Si signal downfield from that for atom C in segment 10. The assignment of signals E to Si atoms E in segment 6, which does not have any N–H functionality, is also reasonable because, as is evident in the IR spectra (Figure 1a), there is essentially no N–H functionality in the polymer structure for R = 2.5. For R in the range $1 < R < 2.5$, other functional groups represented by segments 4 and 5 as well as those under Chart IIB should form but the N–H functionalities in these structures should react further in an intra- and/or intermolecular fashion, leading to other functional groups and/or backbone structures (the details of this interpretation will be presented elsewhere).[17]

The ^{29}Si NMR and IR spectra in Figure 1 manifest the qualitative similarities and/or differences among the backbone structures and the functional groups of the oligomers (I–V, Figure 1b). The variations in backbone structure and functional group can be accounted for, by and large, by a combination of the structural segments shown in Chart II. For example, structural segment 2 (Chart II) is absent in III–V; segment 6 is present in I–III; segments 8–10 probably constitute the backbone structure of IV; V can be characterized by a combination of segments 8 and 9, etc. In the latter case (for V), only isolated rings are present in the backbone chain since signal G (Figure 1), which arises from a structural segment represented by structure 10, is not observed in the spectrum for V. Oligomer IV has very little, if any, $-NH_2$ end groups, suggesting that the end group for this system should be >NH. The end group in this case may be represented by structure 3. It is also possible that larger ring moieties represented by structure 12 may be present. Structure 1 is primarily observed in oligomer V. The data, as a whole, clearly demonstrate how the microstructures of the telechelic oligomers can be controlled by varying the monomer feed ratio.

Chart II
Possible Functional Groups and Backbone Composition



Another way of controlling the microstructure can be accomplished by starting with a certain monomer feed ratio R, which results in an oligomer of a specific functionality, and reacting the resulting oligomer with the appropriate monomer (in a stepwise manner). Figure 3 illustrates two such cases. The bottom spectrum in Figure 3A is for the starting oligomer (R = 1). When this oligomer (with N–H functionality) is reacted (stepwise) with ODS, the backbone structure and functional groups of the oligomer, as can be gleaned from the spectra, resemble that shown in Figure 1 (for oligomers I and/or II). Figure 3B shows the results obtained when a starting oligomer of R = 2.5 is reacted (stepwise) with EDA. The microstructure of the final oligomer in this case resembles that shown in Figure 1 (oligomer IV). It is thus evident from the data in Figure 3 that an oligomer akin in structure to that for R = 1 can be converted to an oligomer with structure akin to that for R = 2.5 and vice versa.[18]

What has been illustrated here is that a rather simple approach that involves controlled conventional condensation reactions can be available for the synthesis of ceramic precursors and for the development of a "data base" for precursor chemistry. Some of the advantages of this approach are as follows: (a) one can vary the composition of the precursor almost essentially at will; (b) the methodology may maximize the probability for obtaining char yields with uniform composition; (c) the methodology is suitable for maximizing the molecular weight of the polymer precursor; (d) the ability to control the reactions and/or the microstructures of the oligomers can enable the preparation of suitable and processable precursors for composite ceramic powders/fibers; i.e., the pendant, intrachain and end-reactive (α,ω-difunctional) oligomers should prove useful in the preparation of block and/or graft copolymers, in modification and/or crosslinking reactions, etc. In the case discussed here, the data indicate that the oligomer microstructures are best described by multifunctional hybrid silazane/silylamine segments. The data reported also illustrate that a combination of IR and ^{29}Si and ^{1}H NMR techniques can be extremely valuable for unraveling structural information that will be needed to develop a "data base" for precursor chemistry. Further work is currently in progress on some of these above aspects of the precursor chemistry and will be reported elsewhere.

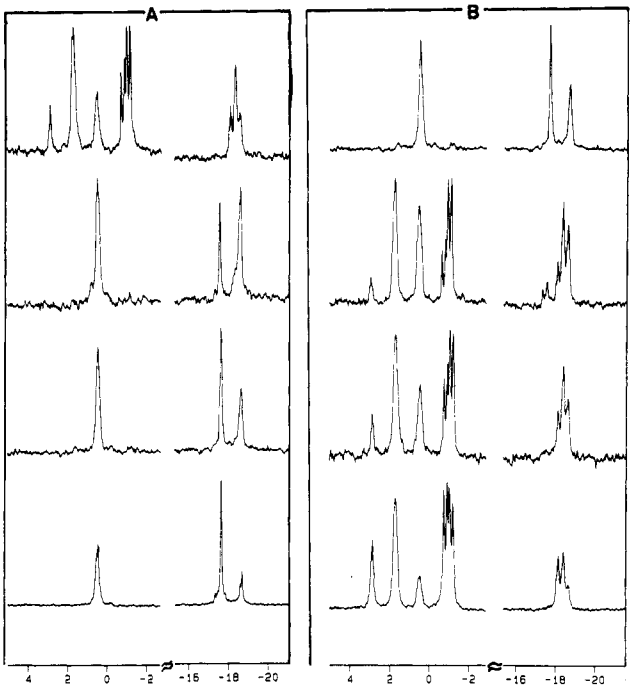


Figure 3. 49.69-MHz ^{29}Si NMR spectra obtained by the inverse-gated decoupling technique with recycling time = 90 s, spectral width = 5000 Hz, 8K data points, and pulse width = 22 μs. Samples were run in $CDCl_3$ solutions, using TMS as either an internal or external reference. (See text for reaction details.)

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References and Notes

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(11) Char yields at 1000 °C as determined by TGA (10 °C/min) varied from 34 to 64% (for various ratios R). For $R = 1$, the results of one elemental analysis gave Si = 42.51%, C = 33.04%, N = 20.04%.
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(13) We have found ^{29}Si NMR to be extremely useful in this work because of its sensitivity to microenvironmental electronic factors (structural entities, ring strain, bonding, hydrolysis, etc.).[14]
(14) Marsmann, H. In *NMR: Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1981.
(15) The data in Figure 2A (for $R = 1.1$) indicate that the $-CH_3$ signal(s) at 0.23 (0.24) ppm correlate with signal C. Signal C also correlates with the $-CH_2CH_2-$ signal at 3.02 ppm, which has been assigned to the ring moiety based on previous work on similar systems.[10] The signal at 2.67 ppm (F_1 dimension) correlates with signal F, which has been assigned to an acyclic moiety. Signal G (F_2 dimension) is due to the bridge moiety (Chart II, structure 10), and both signals F and G correlate with the unresolved ^{1}H signals at 0.09 and 0.1 ppm.
(16) The 0.5 ppm proton signals are observed only when $R > 1$. Furthermore, we had determined that when the oligomers prepared using R of 2 or 2.5 were reacted with additional EDA or NH_3, the above proton signals and ^{29}Si signals D and E disappeared, indicating that they were associated with a Si–Cl reactive group.
(17) Feng, K.; Mariam, Y. H. Manuscript in preparation.
(18) We have also carried out experiments in which an oligomer with $R = 1$ has been reacted with ODS and EDA in a stepwise and an alternate fashion (data not shown here), and ^{29}Si NMR spectra very similar to those in Figure 1b were obtained, i.e., oligomers with various structures as in Figure 1b, depending on the monomer used in the stepwise reaction. Other preliminary experiments, also not shown here, included reactions of the reactive multifunctional oligomers with conventional di- and trifunctional monomers such as NH_3, $AlCl_3$, BBr_3, etc., and condensation copolymerization of preformed oligomers.

Ke Feng and Yitbarek H. Mariam*
Department of Chemistry, Clark Atlanta University
Atlanta, Georgia 30314

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