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Si-29 NMR SPECTROSCOPY OF POLYSILAZANES AND RELATED SYSTEMS

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INTRODUCTION

Silicon containing compounds/materials are of considerable interest in polymer chemistry, chemistry, geochemistry, ceramics, etc. for various reasons. In the case of ceramics, for example, silicon containing materials have gained tremendous importance as polymer precursors for high technology ceramics. Because of such possible technological applications, the elucidation of the microstructure of the precursors is essential in order to elucidate polymerization mechanisms. Such mechanistic studies should in turn lead to improved synthetic methodology, and ultimately to improved processing technology.

Since ^{29}Si NMR spectroscopy is expected to be very powerful in its ability to differentiate among minor structural changes, we have recently initiated use of this technique for the structural investigations of some Si-N polymer systems and some preliminary results are reported in this communication.

EXPERIMENTAL

The condensation polymerization reactions between $NH_2(CH_2)_2NH_2$ or NH_2NH_2 and $Si(CH_3)_2Cl_2$ or $HSiCH_3Cl_2$ were performed as reported before[1,2] with some minor modifications and the details will be reported elsewhere.[3] Poly(1,2-dimethylsilazane)(PDMS), (1,2-dimethylsilazane)(1-methylsilazane) copolymer(DMS-MS), hexamethylcyclotrisilazanes and bis(monoethylamino)-dimethylsilane were obtained from Petrarch Systems and used as obtained. ^{29}Si NMR spectra were obtained using a Bruker WM-250 NMR spectrometer operating at 49.69 MHz. Samples were run in $CDCl_3$ solutions using TMS as either an internal or external reference. One dimensional ^{29}Si spectra were obtained using either inverse-gated decoupling or INEPT and DEPT with refocussing and decoupling (during acquisition).[4] The delays used for the polarization transfer from proton to silicon via Si-H coupling were 1/20 and 1/40 sec, while the recycle (repetition) period was 4-5 sec.

RESULTS AND DISCUSSION

^{29}Si SPECTRA OF POLYSILAZANES

Spectra of PDMS and DMS-MS. The ^{29}Si spectra of PDMS and DMS-MS are shown in Figure 1. At least seven signals are observed for PDMS(B) with chemical shifts (upfield from TMS) at -5.2, -7.8, -8.8, -10.4, -11, -11.3 and -14.3 ppm. Of these, the peaks at -11.3 to -9 ppm are the most intense. The spectrum covers a range of about 9 ppm. There also appears a very low intensity signal at about -22 ppm which may be due to slight hydrolysis. The spectrum of DMS-MS also shows several resonances, albeit unresolved, at about (upfield from TMS, negative sign left out) 8 to 11, 13.1, 14.5, 16 to 20, 26 to 28, 30 to 32 and 36 to 38 ppm. The whole spectrum covers a range of about 23 ppm with the major resonances between -13 and -22 ppm. From the observed chemical shift dispersion, the spectrum of DMS-MS is obviously relatively much more complex.

Spectra of Hexamethylcyclotrisilazane (HMCTS) and PDMS. Figure 2 shows the spectra of 1,1,3,3,5,5-HMCTS, 1,2,3,4,5,6-HMCTS and PDMS. The former has a single resonance(A) at -4.4 (upfield from TMS) and the PMDS(B) shows resonances at -3.2, -8, -8.7, -12.4, -14.1 ppm and at about -23 ppm. The PDMS samples in Figures 1 and 2 were not obtained at the same time and hence are not probably from the same batch. Although there are gross similarities in the two PDMS spectra, the spectrum in Fig. 2 is fairly well resolved into three main regions (the resonances at about -23 ppm are probably due to hydrolysis, vide infra). The spectrum of 1,2,3,4,5,6-hexamethylcyclotrisilazane is shown in Figure 2,C and gives resonances at -7.8, -8.6 and -9.2 ppm. The spectrum of this sample was run as obtained and is only 90% pure. Nevertheless, there is some similarity between this spectrum and that of PDMS in the -8 to -10 ppm region as seen in Figure 2. Since silazane polymers/oligomers are expected to be comprised of ring, linear and branched structures, one may be inclined to assign the PDMS signal at about -8 to -9 ppm to ring structures by comparison to that of 1, 2, 3, 4, 5, 6-HMCTS. The monomers for this polymer are not trifunctional and hence branched structures can be ruled out. For the same reason, cyclic structures within a polymer chain can be ruled out since such structures can not be formed without formation of branches. This would suggest that PDMS should exist either as a macrocycle or a linear polymer thus leading possibly to two main regions of ^{29}Si resonances. Specific assignments of the resonances of PDMS in Figures 1 and 2 have to, however, await further studies. Unlike PDMS, the NH_3 monomer for DMS-MS is capable of branching reactions that might lead to cyclic structures and cross-linking reactions. The unresolved characteristics of the spectrum of DMS-MS may indeed be due to such branching/cyclization and crosslinking reactions. Both materials were at best viscous liquids and restricted segmental motion akin to that expected in polycyclic and cage-like molecules should not be operative.[5] Nevertheless, the preliminary results seem to suggest that ^{29}Si NMR can potentially be used to follow polymerization reactions for which the monomers are not trifunctional (or higher) thus avoiding branching and cross-linking.

^{29}Si SPECTRA OF POLYCARBOSILYLAMINES

Spectra of Polydimethysilylethylenediamine(PDMSED) and Polymethylsilylethylenediamine(PMSED). The ^{29}Si spectra of PDMSED and PMSED are shown in Figure 3. PDMSED has three major resonances at 11.6, -8.4 and -10.1 ppm. From detailed two-dimensional heteronuclear shift correlated spectroscopy experiments, the signal at 11.6 has been assigned to a azasilacyclopentane moiety while the other two are due to dimethysilyl groups in linear/branched segments.[6] The residual type resonances at about -6, -13 and -22 ppm are due to apparently inadvertent hydrolysis. By contrast, the spectrum of PMSED has four major resonances (-2, -8, -24, -30(31) ppm) and broad featureless signals in the -1 to -6 and -14 to -22 ppm ranges. Detailed analysis of this spectrum has not been completed yet. It is conceivable that the signal at -23 ppm is due to hydrolysis. Both polymer systems have a ring to linear/branched ratio of about 3.1. It is evident from these spectra that one can obtain reasonably resolved signals in organosilylamines system even in cases where cyclization and branching/cross-linking occur.

Spectra of polydimethylsilylhydrazine (PDMSH) and polymethylsilylhydrazine (PMSH). The ^{29}Si spectra for PDMSH and PMSH are shown in Figure 4. Details of the reaction conditions for these systems will be reported elsewhere. PDMSH is only a viscous liquid while PMSH is a solid. It is clear that the spectrum of PMSH is featureless but covers a range of about 30 ppm. This broad spectrum is probably due to structural heterogeneity as a result of extensive cyclization and cross-linking.

Although further studies of such systems is required, the preliminary results presented here, overall, appear to indicate that systems with Si-H functionality are apt to result in more structural heterogeneity.

In an attempt to see if the ^{29}Si technique might be useful to follow polymerization reactions under different conditions, we have looked at the condensation polymerization of hydrazine and dimethyldichlorosilane under four solvent-base systems:

a. Xylene (XY) with pyridine(PY) or triethylamine (TEA) as bases (XY/PY or XY/TEA)
b. Dioxane (DX) with PY or TEA as bases (DX/PY or DX/TEA)

After work-up, the reactions gave viscous liquids in all four cases. This suggested that the molecular weights of the polymers were fairly low. Comparison of the IR spectra of the polymers/oligomers indicated only some salient features which were different. The solution ^{29}Si NMR (all determined inverse-gated decoupling conditions) of the polymers however showed remarkable differences. Although the XY/TEA and DX/TEA systems gave oligomers of conceivably similar structure, the DX/PY system apparently results in a cleaner reaction as judged by the observation of primarily one ^{29}Si resonance at approximately -22 ppm. In contrast, the XY/PY system primarily gave resonances in the 0-5 ppm range and a signal at about 11.5. A signal at -22 ppm was also observed for this system but was relatively of minor intensity.

Summary/Conclusions. The results presented here, although very preliminary, seem to strongly suggest that ^{29}Si NMR might be a powerful tool for the elucidation of polymerization mechanisms in the preparation of Si-N containing ceramic precursors. Work pertaining to this aspect is currently in progress in our laboratories.

ACKNOWLEDGEMENTS

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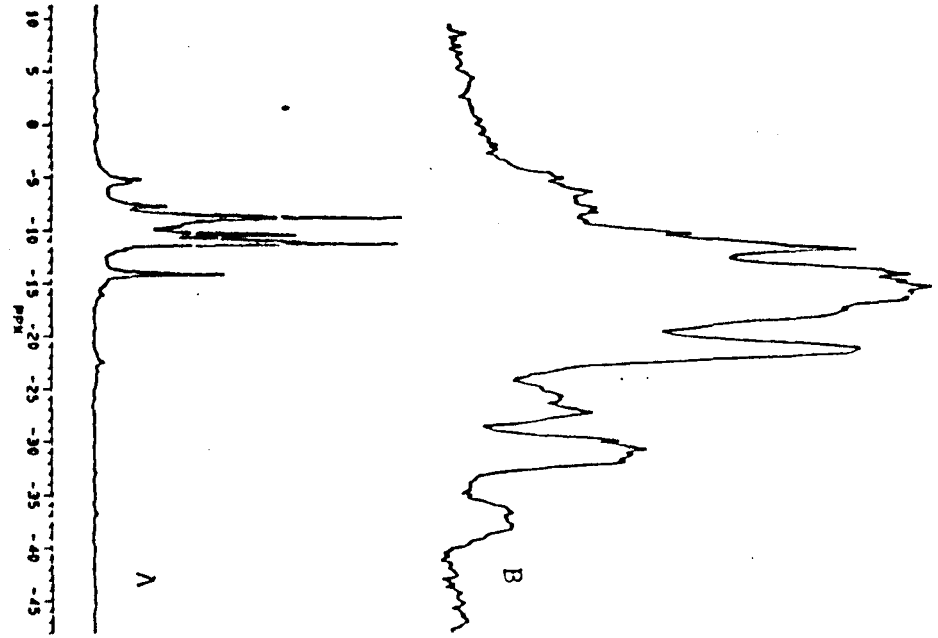

Figure 1. 49.69 MHz ^{29}Si spectra of PDMS(A) and DMS-MS(B).

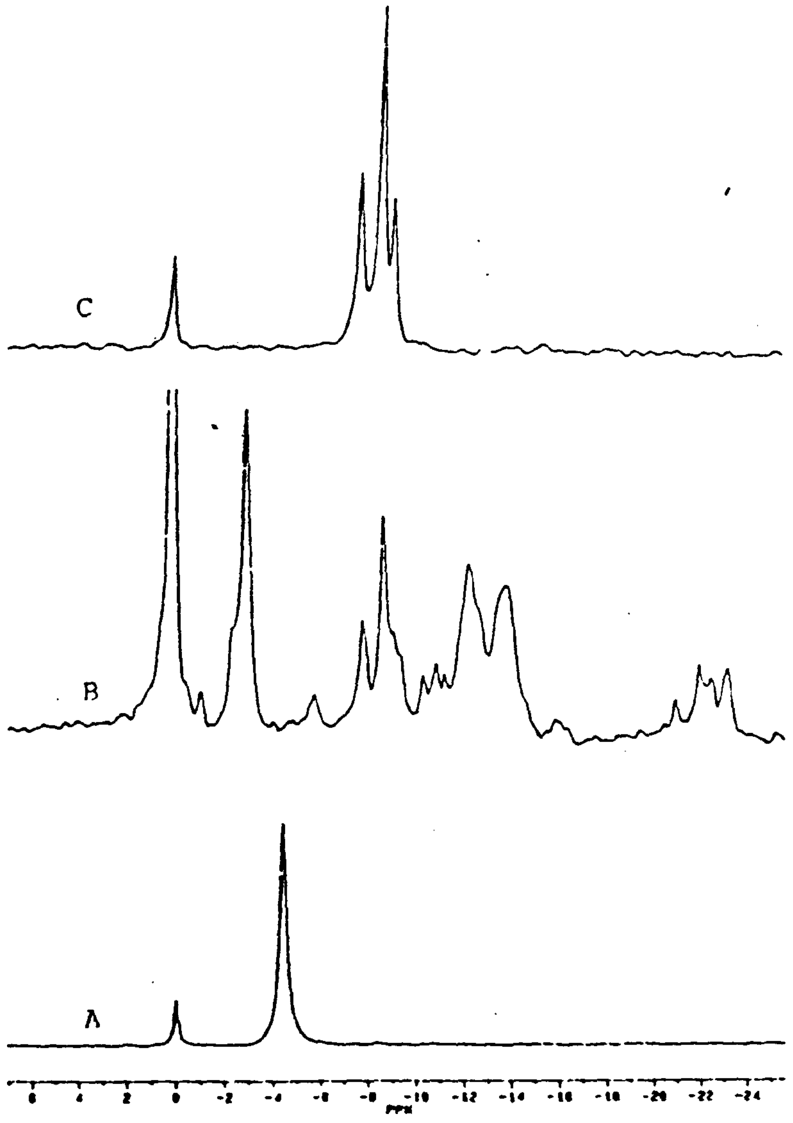

Figure 2. ^{29}Si NMR spectra of 1,1,3,3,5,5-HMCTS(A), PDMS(B), 1,2,3,4,5,6-HMCTS(C).

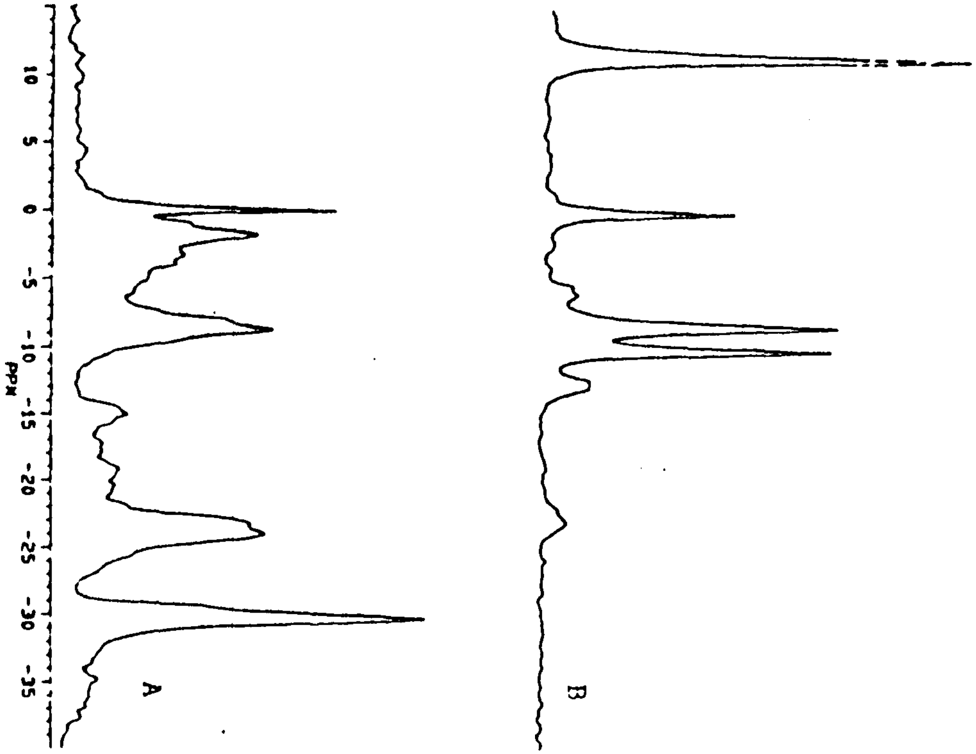

Figure 3. ^{29}Si NMR spectra of polycarbosilylamines: PMSED(A); PDMSED(B).

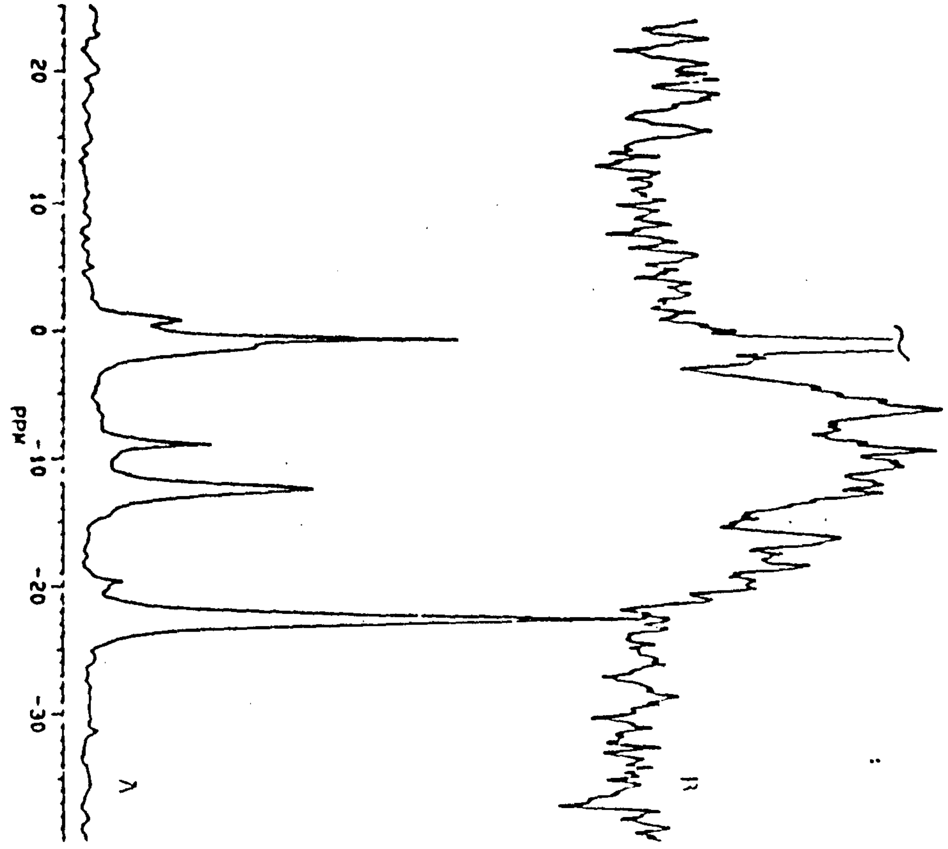

Figure 4. ^{29}Si NMR spectra of polydimethylsilylhydrazines: PDMSH(A); PMSH(B).