THE QUESTION OF FLEXIBILITY AROUND THE SILICON-NITROGEN BOND IN POLYSILAZANES. A COMPARISON WITH POLYSILOXANES

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(Received August 9th, 1965)

INTRODUCTION

Many of the unique properties of polysiloxanes have been attributed[1–3] to a low barrier of rotation around the silicon–oxygen–silicon bond. In the present work, the effect of replacing oxygen in polysiloxanes with nitrogen was studied. We would like to report the synthesis of essentially linear polysilazanes for comparison with analogous polysiloxanes. Linear polysilazanes were prepared by the polymerization of $Me_2SiCH_2CH_2SiMe_2NH$, 2,2,5,5-tetramethyl-1,2,5-azadisilolidine (I) and $[(Me_2SiO)_2Me_2SiNH]$, 2,2,4,4,6,6-hexamethylperhydro-1,3,5,2,4,6-dioxazatrisiline (II). The rheological properties and broadline NMR spectra of $(Me_2SiO)_x$ (III) were then compared with those of $[(Me_2SiO)_2Me_2SiNH]_x$ (IV) and similarly those of $(Me_2SiCH_2CH_2SiMe_2O)_x$ (V) were compared with those of $(Me_2SiCH_2CH_2SiMe_2NH)_x$ (VI).

EXPERIMENTAL

Preparation of the cyclic monomers

$Me_2SiCH_2CH_2SiMe_2NH$ (I) was prepared by reaction of $ClMe_2SiCH_2CH_2SiMe_2Cl$, 1,2-bis(dimethylchlorosilyl)ethane dissolved in ether with liquid ammonia. After the ammonia had evaporated, ammonium chloride was filtered from the solution and ether was removed through a Friedrich condenser. The product was fractionally distilled to give a yield of 70%; b.p. (uncorrected) 141°; n_D^{25}, 1.4351; d^{25}, 0.8417. (Found: C, 45.95; 46.00; H, 11.23, 11.01; MR_D, 49.16. $C_6H_{17}NSi_2$ calcd.: C, 45.22; H, 10.77%; MR_D, 49.32.)

$[(Me_2SiO)_2Me_2SiNH]$ (II) was prepared by a procedure similar to that reported in the literature[4,5], by reaction of $Cl(Me_2SiO)_2Me_2SiCl$, 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane with liquid ammonia. Boiling point 83.6°C/72 mm; n_D^{25} 1.4055; lit.[4,5] n_D^{20}, 1.4068.

$Me_2SiCH_2CH_2SiMe_2O$, 2,2,5,5-tetramethyl-1,2,5-oxadisilolane (VII) was prepared by the method of Piccoli *et al.*[6].

Polymerization of the cyclic compounds

One per cent of either iodine or anhydrous ferric chloride was an effective catalyst to polymerize the cyclic compounds to linear polymers having viscosities of 3,000 to 10,000 cs. Iodine was removed by warming the polymers under vacuum. Ferric chloride was removed by filtering solutions of the polymers in toluene through calcium oxide. One sample of (VI) had a molecular weight of 2300 measured ebulliometrically. Infrared spectra of liquid films of the polysilazanes revealed only SiNHSi structures with no detectable Si_3N crosslinking structures at 916 cm^{-1} (ref. 7). The absence of significant crosslinking was supported by the presence of only one high resolution NMR peak due to SiMe[8] ($\tau = 9.98$).

The poly(dimethylsiloxamer) was a sample of commercially available Dow Corning® 200 Fluid of about 12,000 cs., uncrosslinked and unfilled.

Measurement of physical properties

The heats of polymerization of (II) and (VII) were measured on a diphenyl ether calorimeter*. Viscosities of the polymers were determined on a Brookfield Synchro-Lectric Viscosimeter (Brookfield Engineering, Inc., Stoughton, Mass.) with the sample at a constant temperature.

NMR measurements were taken on a Schlumberger Model 104 Analyzer having a permanent magnet with a magnetic field intensity of 1717 gauss, pole face diameter of ten inches and a two-inch gap between pole faces. The magnet poles are equipped with sweep coils permitting a stepwise variable sweep amplitude from 0.1 to 50 gauss. A crystal-controlled oscillator of 7.313 megacycles in conjunction with the 1717 gauss field strength met the requirements for resonance. An audio modulator supplied a square wave modulating current to the modulation coils allowing the modulation amplitude to be varied stepwise from 0.005 to 5 gauss.

The spectrometer was equipped to allow measurements to be taken from about 140°K to 296°K and also at 77°K[10]. Samples were immersed in liquid nitrogen in the probe to cool them to 77°K. From 140 to 296°K, the samples were cooled by a metered stream of cold gaseous nitrogen[10]. The samples were held at each temperature at least ten minutes to reach equilibrium. To check against hystersis effects, measurements were taken on both warming and cooling cycles. Line widths were defined, for convenience, as the separation measured in gauss between points of maximum and minimum slope on the recorded derivative curve.

The infrared spectra were run on liquid films with a Beckman IR 8 double beam recording spectrophotometer. The high-resolution NMR spectrum of (VI) was run on a Varian A-60.

RESULTS AND DISCUSSION

The infrared spectrum of (I) revealed bands at 1094 cm^{-1} and 860 cm^{-1} which are apparently the NH bending and SiNSi asymmetric stretching modes respectively. In the polymer, these shift to 1180 cm^{-1} and 930 cm^{-1}**. A similar shift in the SiOSi stretching frequency on polymerization of (VII) was ascribed to relief of strain in the five-membered cyclics[6]. The large frequency shift would apparently indicate a fair

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* Measured in this laboratory by O. FLANNINGHAM by a modified technique of Giguere *et al.*[9]. Details will be described in a forthcoming publication.

** The normal frequencies for NH bending and SiNSi asymmetric stretching modes in silazanes are 1150–1180 and 910–950 cm^{-1} respectively[11].

amount of strain in the five-membered silazane. Similar but smaller shifts were also observed for (II)[4,5]. The heat released on polymerization, primarily the strain energy in the cyclic, was found to be 4.2 ± 0.5 kcal for (I) and 5.8 ± 0.5 kcal for (VII). The latter value compares with an estimate of 8 to 12 kcal previously reported[6]. The lower value obtained for the silazane compared with the siloxane value would be expected from the smaller SiNSi angle than the SiOSi angle, recently reported[12], thus partially relieving the strain. The higher SiOSi asymmetric stretching frequency in (II) relative to hexamethylcyclotrisiloxane[4,5], would suggest lower strain in the former.

TABLE 1

THE ENERGY OF ACTIVATION OF VISCOUS FLOW FOR THE POLYSILAZANES (IV) AND (VI) AND FOR THEIR SILOXANE ANALOGUES

Polymer	E_{vis} *(kcal)*	*Ref.*
$(C_6H_5CH_3SiO)_x$	11.9	13
$(CF_3CH_2CH_2CH_3SiO)_x$	7.9	13
$[(CH_3)_2SiCH_2CH_2Si(CH_3)_2NH]_x$	5.5	
$\{[(CH_3)_2SiO]_2(CH_3)_2SiNH\}_x$	4.6	
$[(CH_3)_2SiCH_2CH_2Si(CH_3)_2O]_x$	4.3	
$(CH_3CH_2CH_2CH_3SiO)_x$	4.3	13
$[(CH_3)_2SiO]_x$	3.4	13
$[(CH_3)_2SiCH_2]_x$	~ 6[a]	

[a] Estimated from extrapolation of E_{vis} for lower members in the series $Me(Me_2SiCH_2)_xSiMe_3$[14].

Table 1 contains the E_{vis}, the energy of activation of viscous flow, of (IV), (VI), and for their siloxane analogues. Values for other silicon-containing polymers are included for comparison.

Replacement of some of the oxygen atoms in $(Me_2SiO)_x$ or all in $(Me_2SiCH_2CH_2SiMe_2O)_x$ with nitrogen atoms does not greatly alter the energy of activation of viscous flow. This lack of significant difference in E_{vis} would tend to indicate that chain segment mobility is not greatly altered. The low energy of activation of viscous flow has been explained in terms of high mobility of chain segments arising from low barriers of rotation around SiOSi bonds and their low intermolecular interaction[1,2]. The presence of a CH_2 group or a CH_2CH_2 group in the backbone structure also apparently stiffens the chain in comparison to poly(dimethyl)siloxamer.

There have been several studies of broadline NMR on polysiloxanes[2,15-19]. There is some disagreement whether this narrowing is a result of chain motion within a crystal phase[16,17] or within the amorphous phase[15]. The rapid line narrowing is not a crystal phase change since it occurs more than 50° below the generally accepted melting point of the polymer[18,19], but is due to chain segment motion either translational or rotational[2,15-19]. The line widths *versus* temperature for the broadline NMR data* on the $(Me_2SiCH_2CH_2SiMe_2Z)_x$ ($Z = O$ or NH) systems are shown on Fig. 1 and for (Me_2SiZ) systems ($Z = O$ or NH) on Fig. 2 and ($Z = CH_2$) on Fig. 3. It is apparent that in both systems the abrupt freezing of chain motions occurs about 30–40° higher for the silazanes than for the siloxanes. Recently Barrante and Rochow[20]

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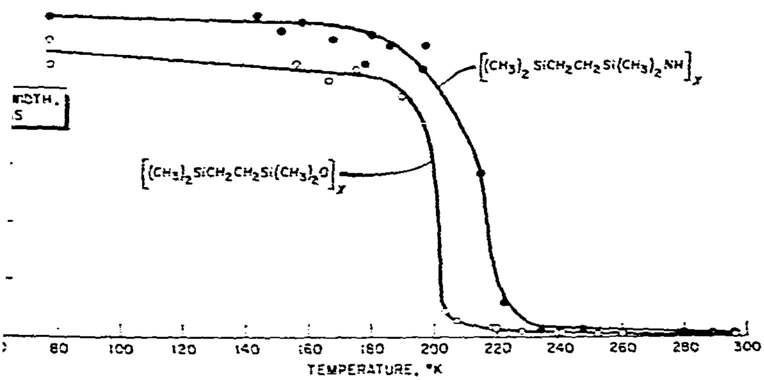
* Second moment data are not included since the qualitative observations discussed are the same as for the peak width data.



1. Broadline ^{1}H NMR line widths in gauss *versus* the absolute temperature for $[(CH_3)_2SiCH_2$-$Si(CH_3)_2O]_x$, open circles, and for $[(CH_3)_2SiCH_2CH_2Si(CH_3)_2NH]_x$, closed circles.

orted that a broadline NMR study on highly cross-linked silicon–nitrogen polymers ained from the reaction of dichlorodimethylsilane with ethylenediamine or with monia. They found significant stiffening of the polymer structures in these polymer tems. In contrast to the observations on the highly cross-linked silicon–nitrogen ymer systems[20], no gradual freezing out of the MeSi motion is observed. The nperature of abrupt change in polymer motion is raised about 30–40° with the ertion of a CH_2CH_2 unit in the backbone, emphasizing the stiffer structure of a CSi backbone unit over that of a SiOSi or SiNHSi backbone. Similarly, the nperature of abrupt change is higher for $(Me_2SiCH_2)_x$ than the analogous siloxane siloxazane.

The presence of a nitrogen–hydrogen linkage giving rise to a small amount of drogen bonding could account for the slight stiffening in linear silazane polymers. rrante and Rochow[20] have suggested as an alternate explanation to stiffening by osslinking, that enhanced $d\pi$–$p\pi$ bonding between nitrogen and silicon giving rise

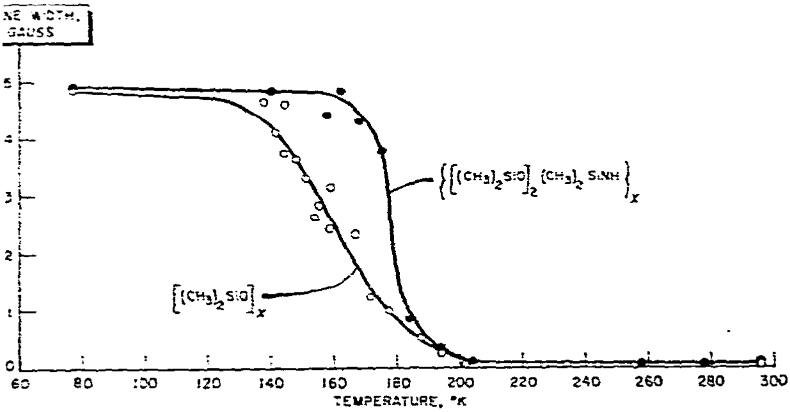


Fig. 2. Broadline ^{1}H NMR line widths in gauss *versus* the absolute temperature for $[(CH_3)_2SiO]_x$, open circles, and for $\{[(CH_3)_2SiO]_2(CH_3)_2SiNH\}_x$, closed circles.

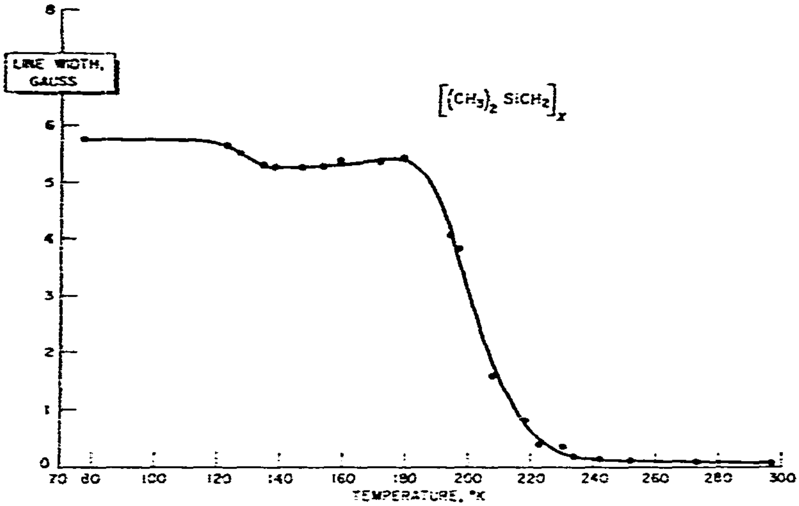


Fig. 3. Broadline ¹H NMR line width in gauss *versus* the absolute temperature for $[(CH_3)_2SiCH_2]_x$.

to restricted motion in a SiNHSi structure might explain their broadline NMR data. This explanation of chain stiffening can apparently be ruled out in view of the lack of apparent extensive chain stiffening observed both by E_{vis} and by broadline NMR in our non-crosslinked systems.

ACKNOWLEDGEMENTS

We are grateful to Dr. Donald Weyenberg of Dow Corning Corporation for the sample of $(Me_2SiCH_2)_x$ and to Mr. Ronald Krager for preparing the polysilazanes and polysiloxazanes.

SUMMARY

A novel polymer system containing SiNSi backbone structures, $(Me_2SiCH_2CH_2SiMe_2NH)_x$, has been synthesized. Comparison of this polymer system with its siloxane analogue along with related siloxane and silazane polymer systems by broadline NMR studies and studies of temperature dependence of viscosities revealed no extensive stiffening of the SiNSi chains.

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