

STUDIES ON REGULARITY OF POLY PHENYLSILSESQUIOXANE CHAINS

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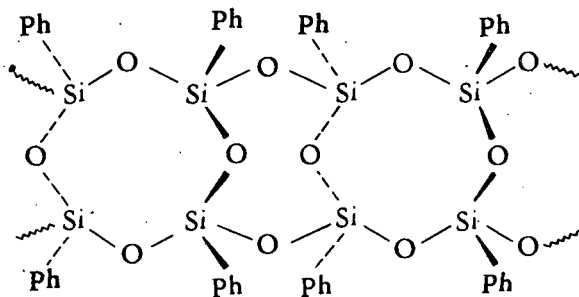
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ABSTRACT

IR and ^{29}Si NMR were used to determine the structures of ladderlike polymer polyphenylsilsesquioxanes (PPS). It was found that PPS with lots of defects had a wide and strong absorption band in $1000\text{--}1400\text{ cm}^{-1}$ with only one sharp peak at 1137 cm^{-1} while two peaks (1130 and 1045 cm^{-1}) were observed for PPS with perfect ladderlike structure. Branching and crosslinking of PPS lead to the reduction of 1045 cm^{-1} peak. ^{29}Si NMR spectra, however, showed two peaks ($\delta = -78\text{ ppm}$ and -87 ppm when $\delta_{\text{HMDS}} = 0\text{ ppm}$) for defective or branched PPS. The -87 ppm peak is related to the ladderlike constructed Si atoms and -78 ppm corresponds to defective Si atoms. PPS with defects less than 0.1% chain units was obtained by azeotropic polycondensations.

INTRODUCTION

Poly phenylsilsesquioxanes (PPS) are considered as ladderlike polymers whose structure^{*} as shown in the following:



was first suggested by Brown and coworkers^[1,2] on the results of X-ray diffraction patterns, ultraviolet spectroscopy, and bond length and bond angle calculations to give least stress. Frye and Klosowski^[3], however, reported that the equilibration of $\text{PhSiO}_{3/2}$ produced random structures instead of highly ordered ladder structure. Elias^[4] also considered that ladderlike polymers were hardly of regular construction since it is improbable for two bonds lying opposite to each other in cage structures to break simultaneously during polymerization. Kovar et al.^[5,6] studied the correlation between intrinsic viscosity, radius of gyration, second virial coefficient, and molecular weight of PPS. Their experimental results indicated the presence of branching in PPS molecules. It seems that the structure of PPS is quite complicated and is still open.

Our previous work shows that the molecular structures of PPS depend rather on the method of preparation. Each of the samples mentioned above represents only the behavior of a particularly made polymer which may have a special structure. In other words data from any one polymer

prepared by certain method is usually not enough in describing the structures of PPS as a whole.

Since the constructions of PPS vary with preparation conditions, it is important to use proper methods for characterizing the polymers. It is also important to have a PPS sample with perfect ladderlike structure to be used as a basis for comparison.

The results given here show that IR and ^{29}Si NMR techniques can be effectively used in studying the configurations of PPS qualitatively or quantitatively, and that high molecular weight PPS with perfect ladderlike structure can be obtained by azeotropic polycondensation during which H_2O will be eliminated as soon as it is formed. New data on the structures of PPS prepared by different methods were given and discussed.

EXPERIMENTAL

Samples

PPS samples were prepared through the polycondensation of the hydrolyzates of PhSiCl_3 . Detailed description of the preparation methods will be published elsewhere.

IR Spectra

Perkin-Elmer 180 Infrared Spectrometer was used for samples pressed in KBr disk at 25°C .

Nuclear magnetic resonance

NMR spectra were carried out on a JEOL JNM-F $\times 100$ equipment. $o\text{-C}_6\text{D}_4\text{Cl}_2$ was used as solvent. Other experimental conditions are as follows: range of concentration, 0.15–0.20g/ml; observation frequency, 19.73MHz; temperature, 120°C ; irradiation Mode, NNE; pulse repetition, 2 sec.; Small amount of $(\text{CH}_3\text{COCHCOCH}_3)_3\text{Cr}$ was used in order to shorten relaxation time. When quantitative measurements were taken, octamethyl cyclotetrasiloxane (D_4) was employed as internal standard. D_4 has only one peak under the test conditions (Fig.1), and it was anticipated that the area ratio $A_{\text{D}_4}/A_{\text{PPS}}$ of D_4 and PPS was equal to the Si atom ratio $\text{Si}_{\text{D}_4}/\text{Si}_{\text{PPS}}$. Hexamethyl disiloxane was used as the internal reference whose chemical shift was considered to be 0 ppm.

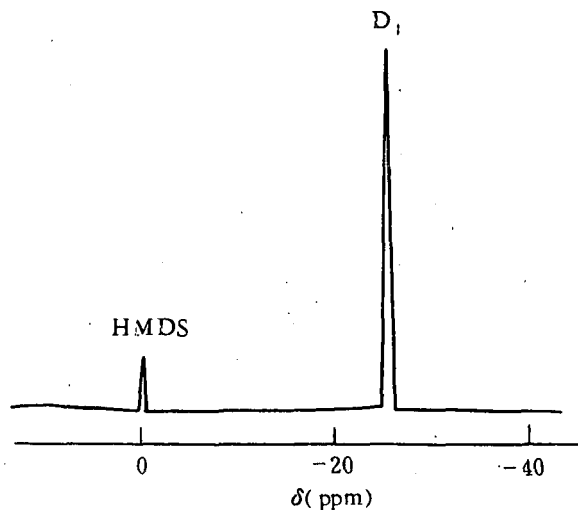
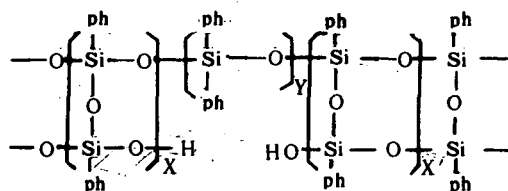


Fig.1 ^{29}Si NMR spectrum of D_4 with the peak at -26ppm .

RESULTS AND DISCUSSIONS

1, IR spectra of PPS with different structures

The investigations of PPS's structure regularity with IR is not available in literature. The difference in structure of various PPS (defective, branched, crosslinked, and ordered ladderlike) are mainly reflected in the range of $1000\text{--}1400\text{ cm}^{-1}$. The IR spectrum of PPS with lots of defects (determined by ^1H NMR and other methods) has a strong absorption band in $1000\text{--}1400\text{ cm}^{-1}$ with one peak at 1137 cm^{-1} due to the combined absorption of Si-*Ar* ($1137\text{ cm}^{-1(7)}$) and Si-O(1045 cm^{-1}) stretching vibrations(Fig.2,a). One peak in $1000\text{--}1400\text{ cm}^{-1}$ is the character of highly defective PPS. For instance, the spectrum of the following copolymer:



also has one peak in $1000\text{--}1400\text{ cm}^{-1}$ (Fig. 3) since it also has lots of "defects" when the ladderlike structure was concerned (this polymer was obtained by cohydrolysis of two monomers, PhSiCl_3 and Ph_2SiCl_2 and then polymerized).

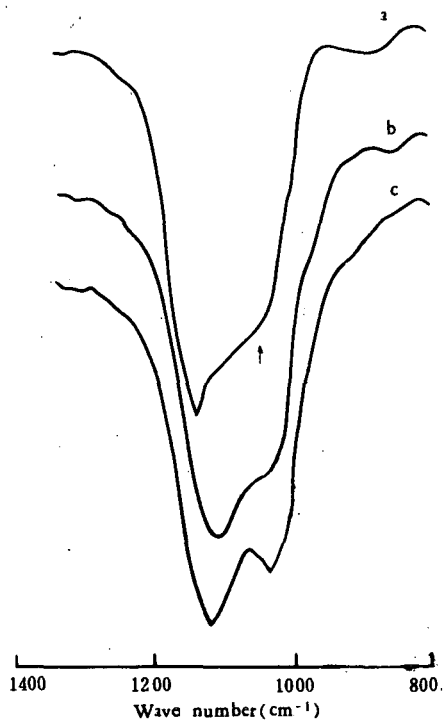


Fig. 2 IR spectra of PPS with different defective degrees

(a) PPS with 50% (chain unit) defects; (b) PPS with less defects; (c) PPS with perfect ladderlike structure

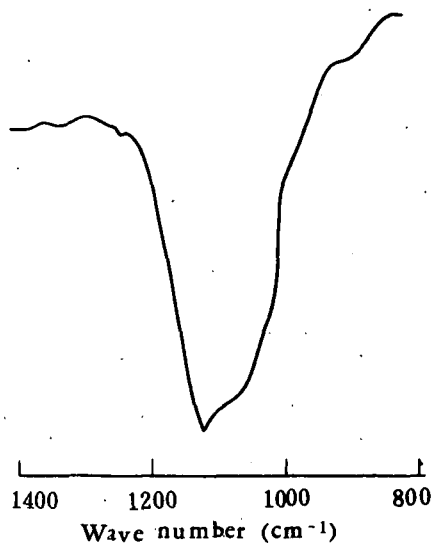
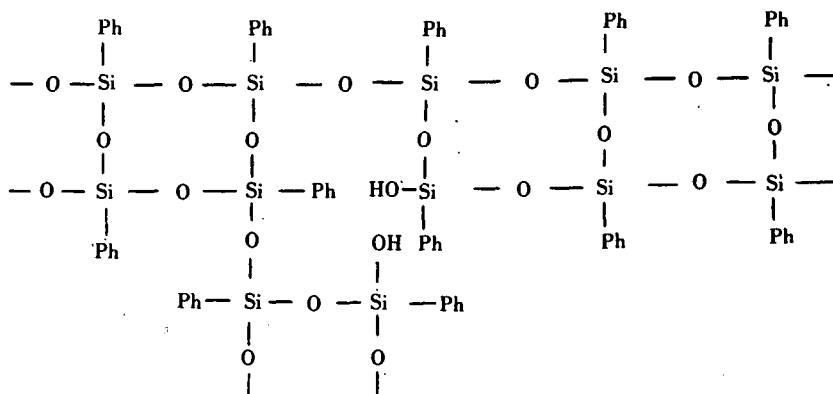


Fig. 3 IR spectrum of copolymer $\text{-(C}_6\text{H}_5\text{SiO}_{1.5})_x \text{-(C}_{12}\text{H}_{10}\text{SiO)}_y$

Defective PPS can react gradually under certain conditions to form ladderlike structures which give another peak (1045 cm^{-1}) in IR spectrum (Fig. 2,b).

Highly ordered ladderlike PPS has two sharp peaks (1130 cm^{-1} , Vs Si—Ar and 1045 cm^{-1} , Vs Si—O—Si) (Fig. 2,c) in the range of $1000\text{--}1400\text{ cm}^{-1}$. The sharpness and intensity of 1045 cm^{-1} peak depend on the regularity of ladderlike configurations. The more regular the structure (this can be checked by ^{29}Si NMR, solubility, the relationship between intrinsic viscosity and molecular weight, and molecular weight distribution), the sharper the peak.

Branching configuration of PPS resulted from defects:



so branched PPS has a similar IR spectrum (Fig. 4, a,b) as that of defective PPS whose 1045 cm^{-1} band is weaker than that of perfect ladderlike PPS.

Increasing degree of branching eventually leads to the formation of crosslinking configuration in which the ordered structure is disrupted, so 1045 cm^{-1} peak disappears (Fig. 4, c).

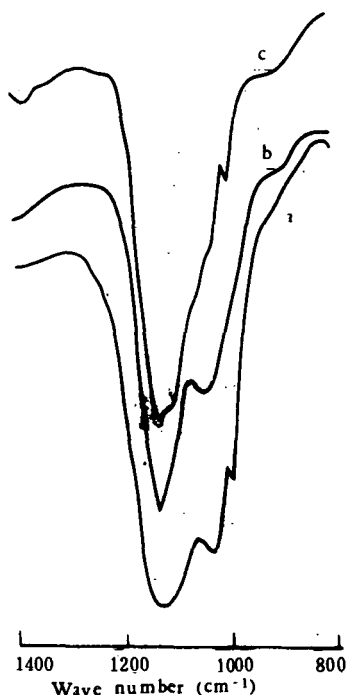
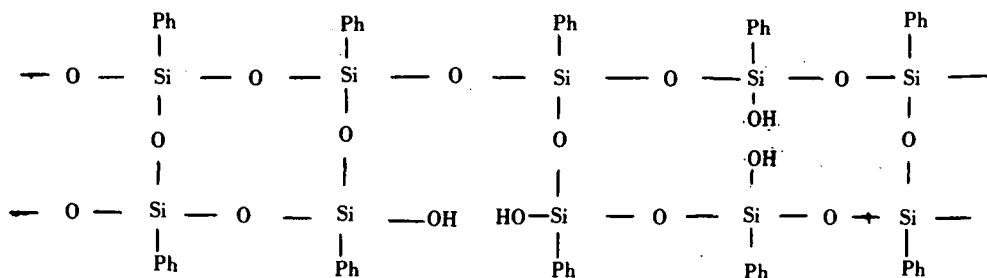


Fig. 4 IR spectrum of branched and crosslinked PPS
(a) slightly branched; (b) seriously branched; (c) crosslinked

2. ^{29}Si NMR spectra of PPS

Our previous work showed that ^1H NMR spectra of highly defective PPS have a strong resonance absorption at 4.4 ppm (when $\delta_{\text{TMS}} = 0$ ppm) due to the existence of OH groups. The



number of papers reporting ^{29}Si NMR results on polymeric or oligomeric siloxanes has been quite significant^[8], but no literature was found about the work on regularity of ladderlike structures. The ^{29}Si isotope is a very difficult nucleus to observe because of its low natural abundance, negative nuclear Overhauser effect (NOE), and long spin-lattice relaxation time (T_1). Fortunately, the use of NNE technique and a relaxation reagent can eliminate NOE and significantly shorten T_1 .

Herein the effects of PPS structures on ^{29}Si NMR spectra are the main subject to be discussed. PPS prepolymer which possesses lots of defects gives two peaks (α, β) on ^{29}Si NMR spectrum (Fig. 5,a). α peak ($\delta = -78\text{ppm}$) is related to the defective Si atoms (shown in the following which have one hydroxyl group attached to each of them). β peak ($\delta = -87\text{ppm}$) is the

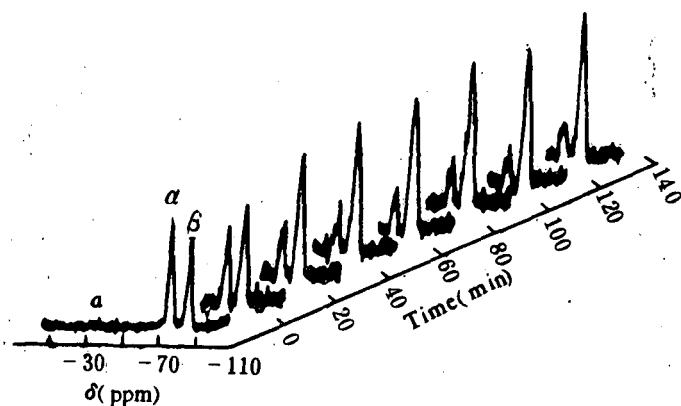


Fig. 5 ^{29}Si NMR spectra of PPS prepolymer (a) with 50% (chain unit) defects, and the prepolymer reacted for different time at 120°C to eliminate the defects

resonance absorption due to ladderlike constructed Si atoms. The integral intensity ratio is 1/1. The elimination of hydroxyl groups by heating at 120°C gives a more ordered structure, thus α peak is weakened and β peak is enhanced (Fig. 6).

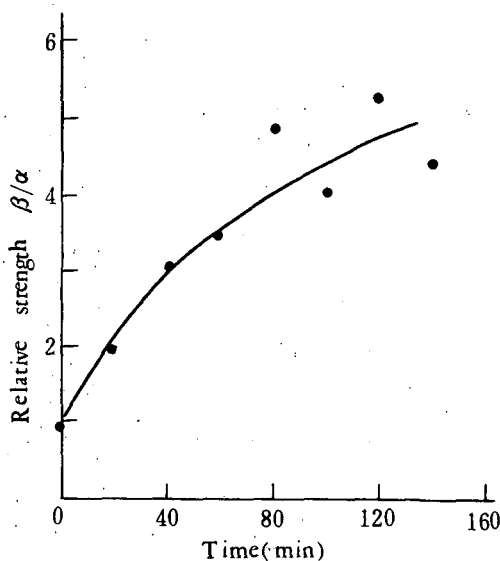
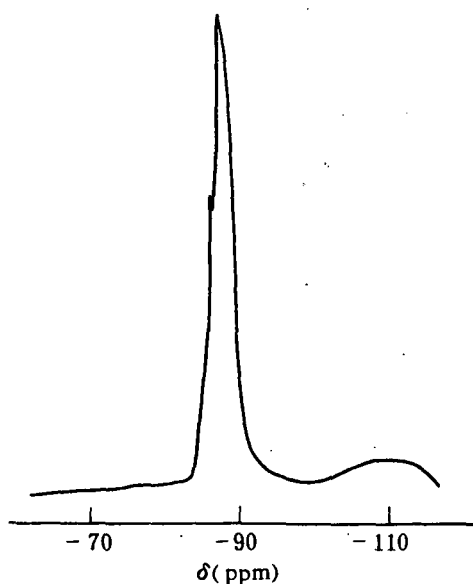
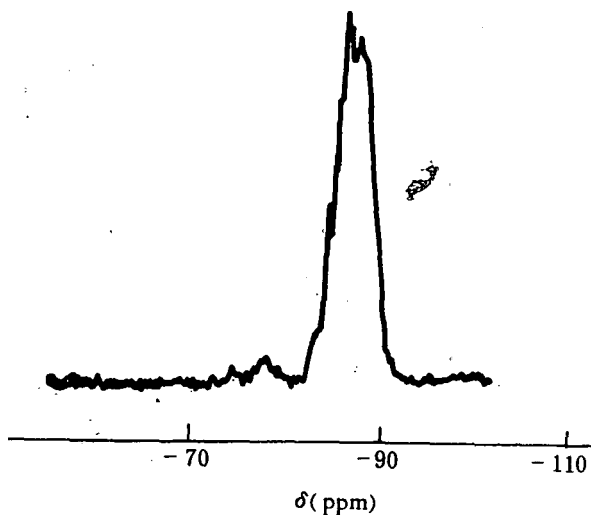


Fig. 6 The relationship between the integral intensity ratio of α and β and reaction time

High molecular weight PPS can be obtained in 7 hrs. by azeotropic polycondensation. Its ^{29}Si NMR is shown in Fig. 7, D_4 was used as an internal standard in quantitative determination of PPS configuration regularity. Thus, 0.1% ($\text{SiD}_4/\text{SiPPS}$) of D_4 was added into the solution and NMR intensity was accumulated to 10,000 times so that the resonance absorption peak of D_4 can be seen. Still PPS made from azeotropic method had one peak. This means that the defect concentration in PPS must be less than 0.1% (chain unit), in other words, the prepared PPS is very regular.

Fig. 7 ^{29}Si NMR spectrum of ladderlike PPSFig. 8 ^{29}Si NMR spectrum of branched PPS

The ^{29}Si NMR spectrum of branched PPS can be seen in Fig. 8. Two peaks have the chemical shifts in keeping with those of defective PPS. This matches the results from IR spectra. The defect content calculated from the ^{29}Si NMR spectra is 5.8% (chain unit).

Keywords:

Ladderlike polymer; Regularity; Characterization

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