

SYNTHESES AND STRUCTURES OF POLYPHENYLSILSESQUIOXANES

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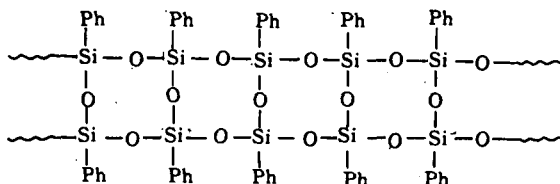
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ABSTRACT

Phenyltrichlorosilane was hydrolyzed both in toluene and in ether from which two kinds of prepolymers were obtained with different structures, molecular weights, and molecular weight distributions. Polymers were prepared from the prepolymers in various polymerization conditions. The ladderlike, branched, and crosslinked structures formed under different polymerization conditions were characterized by means of FTIR, ^1H and ^{29}Si -NMR, and elemental analysis. Azeotropic distillation of solvents and H_2O formed during polymerization was found useful in removing H_2O from the system and high molecular weight products with perfect ladderlike structure were obtained.

INTRODUCTION

Polyphenylsilsesquioxanes (PPS) are ladderlike polymers with structure as follows:



Its intriguing structure and excellent solubility in common organic solvents made it be an attractive object both in a series of theoretical studies and in a variety of applications. Since the first report of synthesis of PPS in 1960 by Brown^[1], most of the published papers and patents were concentrated on the solution properties, solid state structures, and its applications^[2-11]. It was anticipated that the structures of PPS depend significantly on the preparative methods, yet the real relationship between them is still ambiguous. In the present work, the structures of prepolymers and PPS prepared under different conditions were characterized with infrared spectroscopy, ^1H and ^{29}Si NMR, elemental analysis, and gel permeation chromatography (GPC). Experimental results indicate that the molecular configurations and molecular weights of both the prepolymers and PPS were closely related to the preparative conditions. We succeeded in obtaining higher molecular weight PPS with perfect ladderlike structure by applying azeotropic polycondensation.

EXPERIMENTAL

Preparation of Prepolymers

Prepolymer A: Monomer phenyltrichlorosilane ($\text{C}_6\text{H}_5\text{SiCl}_3$) was distilled 3 times before use. In order to determine the purity of $\text{C}_6\text{H}_5\text{SiCl}_3$, about 0.3 ml accurately weighed $\text{C}_6\text{H}_5\text{SiCl}_3$ was

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charged into a specially made flask containing 10 ml n-butanol and 20 ml ion-free water. After the completion of hydrolyzation, the amount of HCl formed was determined by titration with standardized NaOH solution. The purity of $C_6H_5SiCl_3$ was calculated according to:

$$C_6H_5SiCl_3 \% = \frac{N_{NaOH} \times V_{NaOH} \times M_{C_6H_5SiCl_3} \times 100}{3 \times 1000 \times W_{sample}}$$

where N_{NaOH} is the normality of NaOH, V_{NaOH} , the volume of NaOH solution used, $M_{C_6H_5SiCl_3}$, the molecular weight of $C_6H_5SiCl_3$, and W_{sample} , the weight of the sample. The resultant purity of $C_6H_5SiCl_3$ is $\geq 99\%$.

A mixture of 300 ml ether (A. R.) and 200 ml $C_6H_5SiCl_3$ was dropped slowly into a 3000 ml flask containing a mixture of 2000 ml ion-free water and 100 ml ether at 15–18°C with rotation. After the reaction, the ether solution was separated from water, and washed 10 times with ion-free water, distilled, and then dried under vacuum for 48 hrs. The yield was 99% on the basis of $C_6H_5SiCl_3$.

Prepolymer B: In preparing prepolymer B, the same procedure stated above was adopted except the solvent ether was replaced by toluene. Since toluene has higher boiling point, reduced pressure distillation (at 50°C) was employed to remove the solvent from the product. The yield was 81%.

The Preparation of Polymers

The preparative recipes are shown in Table 1. 10g of prepolymer A was employed in all of

Table 1 Preparative methods of polyphenylsilsesquioxanes

No	Cat. (g)		Solvents (ml)				Temp. (°C)	Time (h)
	DCC*	KOH	Benzene	Toluene	Xylene	Diphenylether		
1	10		12.5**	12.5			110	13
2	10						207	13
3	1				12.5		130	13
4	1			12.5			110	13
5		1		12.5			110	13
6		0.1		12.5			110	13
7		1		12.5		1	110	13
8		0.1		12.5		0.1	110	13
9	1			12.5		1	110	13
10	1	0.1		12.5			110	13
11	1	0.1		12.5		1	110	13
12		0.1		5		1	260	13
14		0.001		5		5	230	5***
15		4×10^{-4}	10	5	5	10	260	7

* Dicyclohexylcarbodiimide.

** Tetrahydronaphthalene.

***With reduced pressure.

the experiments (with prepolymer B, the similar resultant polymers were obtained). The preparation procedures are as follows: prepolymer, catalysts, and solvents were added into a flask at a proportion given in Table 1. For recipe No.1 to No.12, heat the mixture quickly to refluxing temperature, and keep the reaction proceeding for 13 hrs. with rotation. For No. 14 and No.15, heat the mixture stepwisely with a distillation of solvents so that H_2O produced during the reaction was removed by azeotropic distillation. This process is in favor of obtaining higher molecular weight PPS. The designed temperature was reached in 3 hrs.

After the reactions, an adequate amount of solvent was added into the solution which was then washed with ion-free water to neutral. The gel (if formed) was separated by filtering in a G-3 sintered glass funnel. The final products were purified by precipitations with methanol, and dried in vacuum oven at 50°C for 48 hrs.

NMR Spectra

Spectra were obtained on a EM-360L equipment (for ^1H NMR spectra) and a JNM-FX100 (for ^{29}Si NMR spectra). The measuring conditions are as follows: solvents: CDCl_3 (for ^1H) and $o\text{-Cl}_2\text{C}_6\text{D}_4$ (for ^{29}Si NMR spectra); temperature: 20°C ; references: TMS (for ^1H) and HMDS (for ^{29}Si). For ^{29}Si NMR spectra, NNE technique specified by the manufacturer of the equipment was employed to overcome Overhauser Effect, and a small amount of $(\text{CH}_3\text{COCHCOCH}_3)_3\text{Cr}$ was added to shorten T_1 .

IR Spectra

FTIR spectra were obtained on a Brüker-113V instrument. Samples were prepared by pressed pellet technique.

GPC Chromatograms

Measurements were made on a Waters 244 instrument at 25°C with tetrahydrofuran (THF) as eluent. Three columns J 101, 103, and 105 connected in series were made by Jiling University. The flow rate of THF was 1.0 ml/min. A UV detector with $\lambda = 254\text{nm}$ was used.

Number average molecular weight ($\bar{M}_n$)

$\bar{M}_n$ was obtained on a KNAUER VPO instrument which was calibrated with benzil and phenanthrene. Benzene was used as the solvent.

Intrinsic viscosity ($[\eta]$)

Measurements were committed with a Ubbelodhe viscometer in toluene at 25°C

RESULTS AND DISCUSSIONS

1. Structures of prepolymers

Prepolymer A has a $\bar{M}_n$ of 2820, corresponding to about 22 $\text{C}_6\text{H}_5\text{SiO}_{1.5}$ units. ^1H NMR spectrum gives two peaks, a and b (Fig. 1). After exchanged with D_2O , peak b disappeared. This

indicates that a and b peaks represent resonance absorptions of ^1H on phenyl and on hydroxyl, respectively. From the area ratio A_b/A_a of the two peaks, we can get the ratio of number of groups, $\text{OH}/\text{C}_6\text{H}_5 = \text{OH}/\text{Si} = A_b/(A_a/5)$ which gives 50/100. ^{29}Si NMR spectrum (Fig. 2a) of prepolymer A also has two peaks, α and β . When the molecular weight was increased by the condensation of $\equiv\text{Si}-\text{OH}$ groups, α peak decreased and β peak increased. This means that α and β peaks are related to the resonance absorptions of Si atoms in $\text{C}_6\text{H}_5\text{Si}(\text{O}_{1/2})_2\text{OH}$ and $\text{C}_6\text{H}_5\text{Si}(\text{O}_{1/2})_3$ respectively. Detailed data will be published elsewhere^[12]. From the area ratio, a group ratio of $\text{OH}/\text{Si} = 50.5/100$ was obtained which well matched the result from ^1H NMR spectrum. The combination of ^1H and ^{29}Si NMR results shows us the distribution of OH groups on Si atoms. That is, the number of OH groups on each Si atom will not be more than one. In other words, such

configuration as $\text{C}_6\text{H}_5\text{Si}(\text{OH})_2\text{O}-$ does not exist in prepolymer A molecules. GPC curve

(Fig. 3a) of prepolymer A illustrates that it is polydispersed in molecular weight in contradiction to a monodispersed value in the case of cage-like structures of T_8 , T_{10} , or T_{12} .

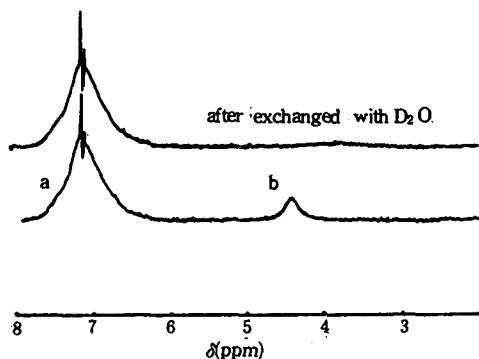


Fig. 1 ^1H NMR spectrum of prepolymer A.

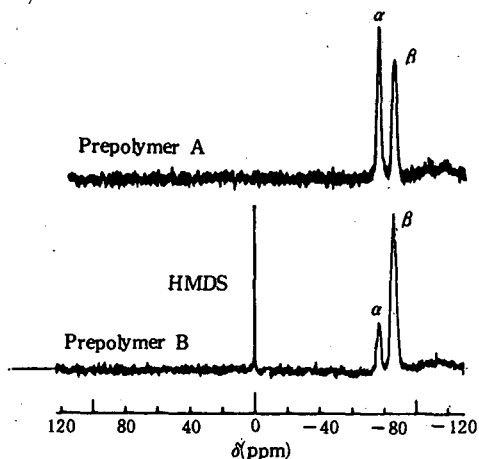
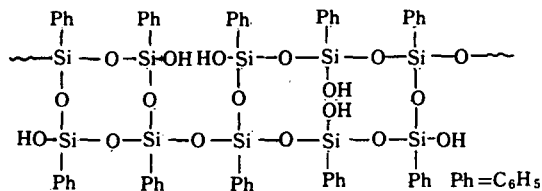


Fig. 2 ^{29}Si NMR spectra of prepolymers

Infrared spectrum (Fig. 4) gives vibrational absorption bands of $\text{Si}-\text{OH}$ (3427 cm^{-1}), $\text{C}_6\text{H}_5-\text{Si}$ (3074 , 3051 , 1431 , 1134 , 741 , 698 cm^{-1}). The feature of regular ladderlike structure represented by the splitting of 1134 cm^{-1} peak into two peaks^[12] was not observed for prepolymer A. All of the stated results suggest a structure of prepolymer A as follows:



Analysis: Calculated for prepolymer A: C, 53.90; H, 4.11; Si, 21.03; O, 20.87. Found: C, 53.84, 53.80; H, 4.26, 4.10.

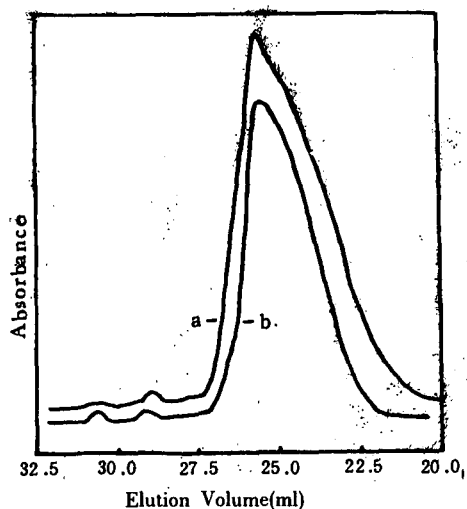


Fig. 3 GPC spectra of prepolymers
a prepolymer A; b prepolymer B.

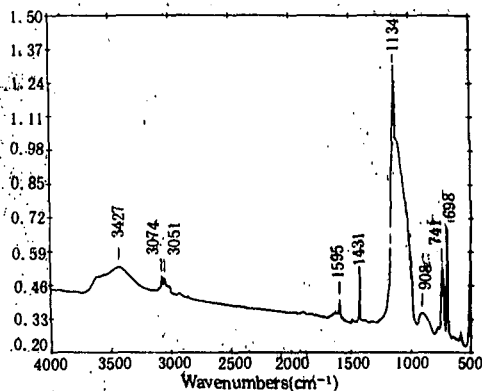


Fig. 4 IR spectrum of prepolymer A

Prepolymer B has a $\bar{M}_n$ of 1080 corresponding to about 8 $C_6H_5SiO_{1.5}$ units. ^1H NMR spectrum (Fig. 5) gives $OH/C_6H_5 = OH/Si = 18.1/100$.

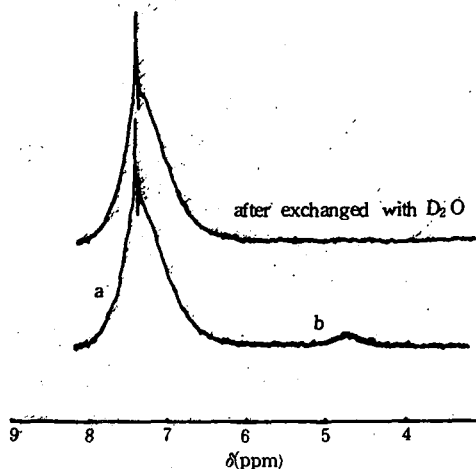


Fig. 5 ^1H NMR spectrum of prepolymer B. a and b peaks represent resonance absorptions of ^1H in C_6H_5- and $OH-$, respectively.

^{29}Si NMR spectrum (Fig. 2b) gives $OH/Si = 20/100$, which is agreeable with the value from ^1H NMR spectrum. The results also prove that there is no Si atom connected with two OH groups. In addition, two resonance lines were identified in $-74 \sim -77$ ppm. Further investigation about this phenomenon is in progress. GPC experiment of prepolymer B shows us a narrower molecular weight distribution than that of prepolymer A (Fig. 3b). Infrared spectrum (Fig. 6) is almost the same as that of prepolymer A except for the stronger absorption of $1030cm^{-1}$ band ($\nu_{Si-O-Si}$). The following structure is suggested for prepolymer B:

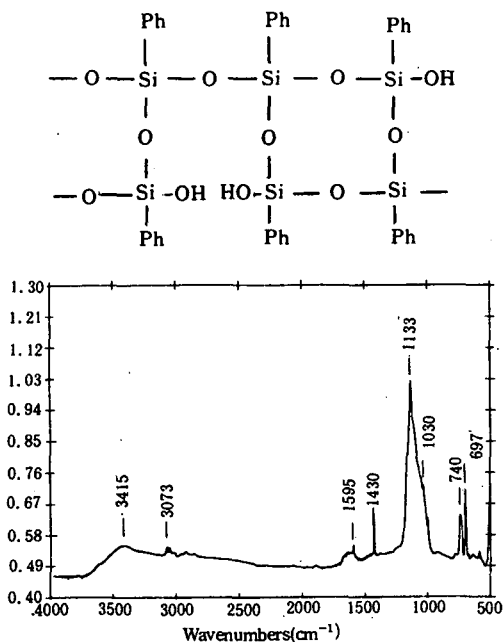


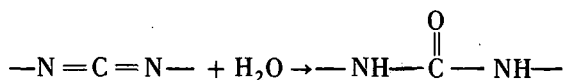
Fig. 6 FTIR spectrum of prepolymer B

Analysis: Calculated for prepolymer B: C, 55.06; H, 4.00; Si, 21.45; O, 19.49. Found: C, 54.35; 54.04, H, 3.77, 3.89.

2. Structures and molecular weights of PPS polymers

A. In the case of using DCC as a catalyst

DCC does not contain metal ions, so the polymers prepared should have very good insulating properties, and should be useful in electronic industry. DCC can react with H_2O which was produced in the process of condensation^[13]:



The molecular weights are usually in the range of 3,000 ~ 12,000 (Table 2). When tetralin was used as a solvent (No. 2), and reaction temperature was 207°C, polymer with low molecular weight was obtained. If xylene was the solvent (No.3), FTIR (Fig. 7, compare with Fig. 8) gives a weaker 1045 cm^{-2} peak and ^{29}Si NMR spectrum shows a small resonance peak at -78ppm. These are the

Table 2 Molecular weight, solubility and intrinsic viscosity of PPS prepared by different methods

No	1	2	3	4	5	6	7	8	9	10	11	12	14	15
$\bar{M}_n \times 10^{-3}$	8.6	3.9	11.5	8.2	gel	11.6	13.9	18.0	9.4	13.0	9.0	26.0	550 ^a	340 ^a
Solubility ^b	E	E	L	E	I	E	E	E	E	E	E	E	G	E
$[\eta]$ (ml/g) ^c	6.49	4.02	6.05	5.90		7.10	9.70	9.80	6.51	8.40	6.76	27.6		80.2

a. $\bar{M}_w$ by SALLS; b. in benzene, toluene and THF; E. excellent; L. low; I. insoluble; G. good; g. in toluene.

features of branching structure^[12]. The branched structure of sample No. 3 was also proved by the measurements of solubility and intrinsic viscosity which is lower for branched polymer (Table 2). Regularly constructed ladderlike polymer which has a strong and sharp 1042 cm⁻¹ peak can be obtained with toluene as a solvent (Fig. 8, ref. [12]).

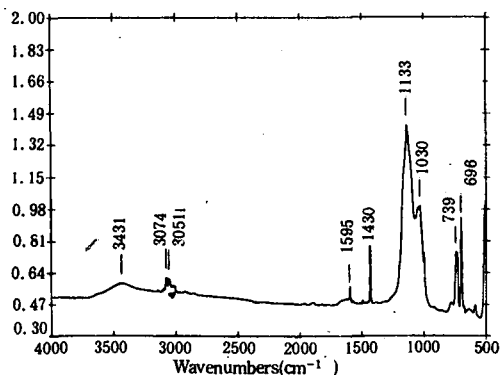


Fig. 7 FTIR spectrum of branched PPS

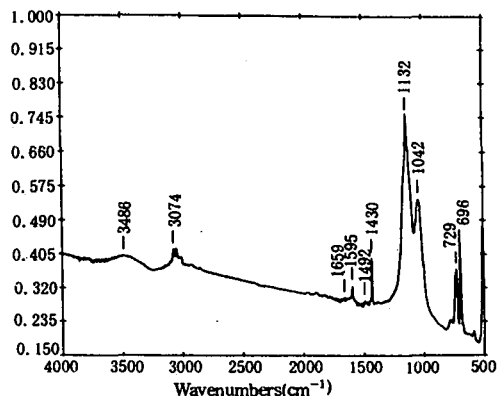
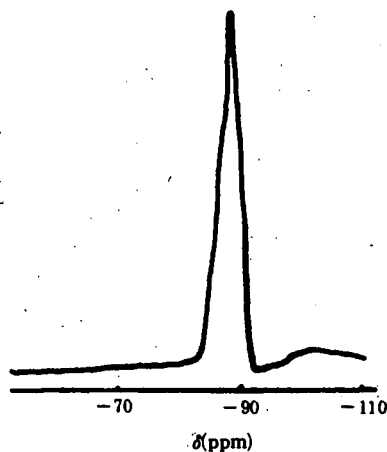
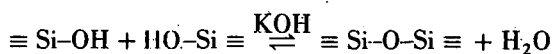


Fig. 8 FTIR spectrum of ladderlike PPS

B. In the case of using KOH as a catalyst

The molecular weight of PPS was remarkably increased by KOH catalyzed polymerization. However, we found that the addition of diphenyl ether as a co-solvent led to a more regular structure of PPS. If the concentration of KOH was fairly high, and there was no diphenyl ether in the system (compare No.5 and No.7), insoluble, crosslinked product was usually obtained. Crosslinked PPS has one peak ($\sim 1134\text{cm}^{-1}$) in $1,000 \sim 1,200\text{cm}^{-1}$ on FTIR spectrum^[12].

As the polycondensation process is an equilibrium-controlled process

Fig. 9 ²⁹Si NMR spectrum of regularly structured PPS

the removal of byproduct H_2O is very important in order to get high molecular weight polymer. In the present work, solvents with different boiling points were added to the system so that the azeotropic distillation of solvents and H_2O helps to remove H_2O away. High reaction temperatures ($> 200^\circ C$) is also necessary for high molecular weight products. Polycondensations in the way of azeotropic distillation (No. 14, 15) produced regularly structured polymers (no gel) whose ^{29}Si NMR spectrum is shown in Fig. 9, and FTIR spectrum is very similar to Fig. 8. The molecular weights can be controlled with ease.

Keywords:

Polyphenylsilsesquioxanes; Prepolymers; Synthesis; Characterization

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