

SYNTHESIS AND CHARACTERIZATION OF NOVEL REACTIVE POLYORGANOSILOXANE CONTAINING NITRO GROUPS*

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Abstract A novel reactive polyorganosiloxane containing nitro groups was first prepared by acid-catalyzed equilibration polymerization. The monomer, 3-(4-nitrophenoxy)propylmethyldichlorosilane (NPPMS), was synthesized by hydrosilylation reaction with dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2) catalyst in high yield. The synthesized polynitro-organosiloxane, which has potential application as a precursor for synthesizing advanced functional polymers, was characterized by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{29}\text{Si-NMR}$, vapor pressure osmometry (VPO) and gel permeation chromatography (GPC).

Keywords Polyorganosiloxane, Equilibration polymerization, Hydrosilylation, Characterization

INTRODUCTION

Polyorganosiloxane (POS) has flexible and hydrophobic main chains. POS having functional groups such as nitro, amino, imidazole, pyridine or carboxy groups is an excellent functional polymer and its synthesis has recently attracted much attention^[1-8]. However, reports on POS containing nitro groups are relatively few. We previously tried to synthesize POS containing side-chain nitro groups via hydrosilylation reaction of polymethylhydrosiloxane with vinyl-terminated molecules containing nitro groups. Unfortunately, we could not obtain the target product because of the relatively low grafting ratio and the difficulty of separating the unreacted vinyl-terminated molecules.

In this paper, a novel reactive POS containing nitro groups was prepared by acid-catalyzed equilibration polymerization from the dichlorosilane monomer with nitro groups, synthesized via hydrosilylation. The yield of the monomer is very high and there is no difficulty in purifying the crude polymer product.

EXPERIMENTAL

Materials

All solvents were commercially available and of analytically pure grade. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Methyldichlorosilane, 4-nitrophenol, allyl bromide, acetone, K_2CO_3 , trimethylchlorosilane, toluene and anhydrous Na_2SO_4 were purchased from Beijing Chemical Factory and were of analytically pure grade. Cp_2PtCl_2 catalyst was prepared according to a literature method^[9].

* The authors gratefully thank the National Natural Science Foundation of China (No. 29874034) and Dow Corning Corporation for their financial support.

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Received February 29, 2000

Characterization

FTIR spectroscopy was performed on a PE-80 FTIR spectrometer. ^1H -NMR and ^{13}C -NMR spectra were obtained from a JNH-FX100 (JBOX) 300 MHz NMR spectrometer. ^{29}Si -NMR measurement was performed on a Varian Unity 200 MHz NMR instrument. Molecular weight was measured with a Knauer vapor pressure osmometer using THF as solvent, and simultaneously on a Shimadzu LC-4A gel permeation chromatograph (GPC) relative to polystyrene standards in THF using a differential refractive index detector.

Preparation of Monomer: 3-(4-Nitrophenoxy)propylmethyldichlorosilane (NPPMS)

Synthesis of 1-allyloxy-4-nitrobenzene 1

To a 500 mL three-necked flask equipped with a refluxing condenser and a magnetic stirrer were added 41.7 g (0.3 mol) 4-nitrophenol, 69 g (0.5 mol) K_2CO_3 , 200 mL acetone, and 48.4 g (0.4 mol) allyl bromide. The mixture was refluxed for 7 h, then cooled, filtered, and washed with diethyl ether for three times. The filtrate was collected and the solvents and residual allyl bromide were removed with a rotatory evaporator. The product was purified by adsorption chromatography with a flash silica gel column and using chloroform/hexane (2:1) as eluent to give 49.4 g of light yellow oil. The yield is 92%. ^1H -NMR (CDCl_3 , δ): 8.2, 6.9 ($-\text{C}_6\text{H}_4-$, *dd*, 4H); 6.0 ($-\text{CH}=\text{C}-$, *m*, 1H); 5.4 ($\text{CH}_2=\text{C}-$, *m*, 2H); 4.6 ($-\text{OCH}_2-$, *d*, 2H). Elemental analysis (%): Calcd. (for $\text{C}_9\text{H}_9\text{NO}_3$): C 60.34, H 5.03, N 7.82. Found: C 60.42, H 4.96, N 7.89.

Synthesis of 3-(4-Nitrophenoxy)propylmethyldichlorosilane (NPPMS)

A 250 mL round-bottomed flask equipped with a refluxing condenser, a magnetic stirrer and a two-way stopcock was evacuated, flushed with dry argon, and charged with 17.9 g (0.1 mol) of 1, 3 mL of THF solution of Cp_2PtCl_2 (1 mg/mL) and 50 mL of THF. The mixture was stirred at room temperature for 30 min, then 15.0 mL (0.15 mol) of trichlorosilane was added. This mixture was again stirred and subsequently warmed to 40°C for 36 h. Then the volatile components were removed under reduced pressure below 40°C , and product NPPMS was obtained as a clear light yellow liquid in 96% yield. The characterization results are shown in Table 1.

Table 1. Characterization results of monomer NPPMS

	NPPMS
Appearance	Light yellow liquid
Solubility	Soluble in THF, chloroform, acetone etc.
FTIR (in cm^{-1})	3087, 1593, 846 ($-\text{C}_6\text{H}_4-$); 1263 ($-\text{SiCH}_3$); 1512, 1342 ($-\text{NO}_2$)
^1H -NMR (δ)	8.11, 6.90 (<i>dd</i> , 4H, $-\text{C}_6\text{H}_4-$); 4.08 (<i>t</i> , 2H, $-\text{O}-\text{CH}_2-$); 2.01 (<i>m</i> , 2H, $-\text{CH}_2\text{CH}_2-\text{Si}-$); 1.30 (<i>t</i> , 2H, $-\text{CH}_2\text{CH}_2-\text{Si}-$); 0.79 (<i>s</i> , 3H, $\text{CH}_3\text{Si}-$)
^{13}C -NMR (δ)	163.63, 141.14, 125.6, 114.18 (4H, $-\text{C}_6\text{H}_4-$); 69.44 (2H, $-\text{O}-\text{CH}_2-$); 22.11 (2H, $-\text{SiCH}_2\text{CH}_2-$); 17.62 (2H, $-\text{SiCH}_2\text{CH}_2-$); 4.88 ($\text{CH}_3-\text{Si}-$)
^{29}Si -NMR (δ)	33.49
Elemental analysis (cal. (%) / found (%))	C (40.82/40.93); H (4.42/4.35); N (4.76/4.89)

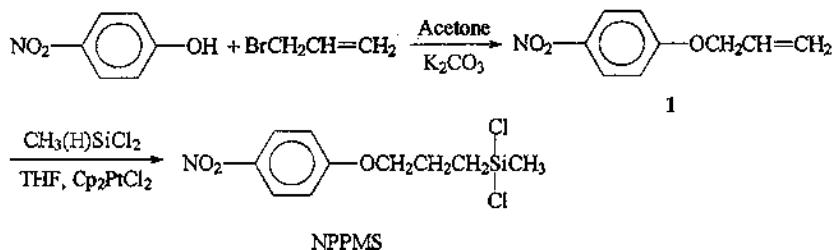
Preparation of Polymer: Poly((4-nitro phenoxy)propylmethylsiloxane) (PNPPMS)

A mixture of 17.9 g (0.06 mol) NPPMS, 0.6 g (5.5 mmol) trimethylchlorosilane and 10 mL toluene was added dropwise to a mixture of 74 mL distilled water and 10 mL toluene cooled in an ice bath, with vigorous stirring for 2 h. Then the mixture was stirred for another 2 h. 30 mL chloroform was then added to the mixture. The oil layer was separated and washed several times with distilled water till neutral and dried with anhydrous Na_2SO_4 . After the removal of the solvents an oily liquid containing cyclic compounds 2 was obtained. The cyclosiloxane mixture was polymerized by 4 wt% concentrated H_2SO_4 , which is a catalyst for ring-opening polymerization. The mixture was stirred at room temperature for 8 h. Then 2 wt% concentrated H_2SO_4 was added to the reaction mixture and then stirred at room temperature for 4 h before 50 mL chloroform was added. The product was washed with distilled water to remove the catalyst and then dried in vacuum. The molecular weight of the viscous PNPPMS was determined by GPC and VPO, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomer NPPMS

Monomer NPPMS was synthesized via the hydrosilylation reaction of 1-allyloxy 4-nitrobenzene with methylchlorosilane using Cp₂PtCl₂ as the catalyst (Scheme 1). The characterization data of NPPMS are listed in Table I.



Scheme 1 Synthetic route to monomer NPPMS

In order to avoid possible side reactions during the hydrosilylation reaction process, THF was dried with anhydrous Na₂SO₄ and distilled from sodium-benzophenone prior to use, and the reaction system was protected with dry argon. The monomer obtained was stored under dry argon as the monomer's Si—Cl bond can be easily hydrolyzed. With careful control of reaction conditions, the yield of the monomer is very high (96%). It is also worthwhile mentioning that the hydrosilylation reaction led to the selective formation of the β -adduct as shown in Scheme 1, and no α -adduct was formed possibly due to the higher steric hindrance for the formation of α -adduct than that of β -adduct.

Synthesis of Functional Polymer PNPPMS

As previously reported in the literature, POS containing functional groups can be prepared by two known approaches. One is the hydrosilylation of polymethylhydrosiloxane containing Si—H groups with either vinyl- or alkynyl-terminated molecules with functional groups^[5, 7], another is the direct synthesis via acid- or base-catalyzed equilibration polymerization from the hydrolysis product of dichlorosilane monomers possessing organo-functional groups synthesized via hydrosilylation^[3]. We tried to synthesize the functional polymer PNPPMS by the first method, *i.e.*, hydrosilylation reaction of polymethylhydrosiloxane with 1-allyloxy-4-nitrobenzene in the presence of Cp₂PtCl₂ catalyst. This method is a very simple one-step synthesis method because polymethylhydrosiloxanes are readily available. Unfortunately, however, we could not obtain pure PNPPMS because of the relatively low grafting efficiency and the difficulty in removing the remaining 1-allyloxy-4-nitrobenzene from the product. Therefore, we conducted our preparation of PNPPMS by the second method, *i.e.* by hydrosilylation reaction for synthesizing the monomer and acid-catalyzed equilibration polymerization for synthesizing PNPPMS (Scheme 2).

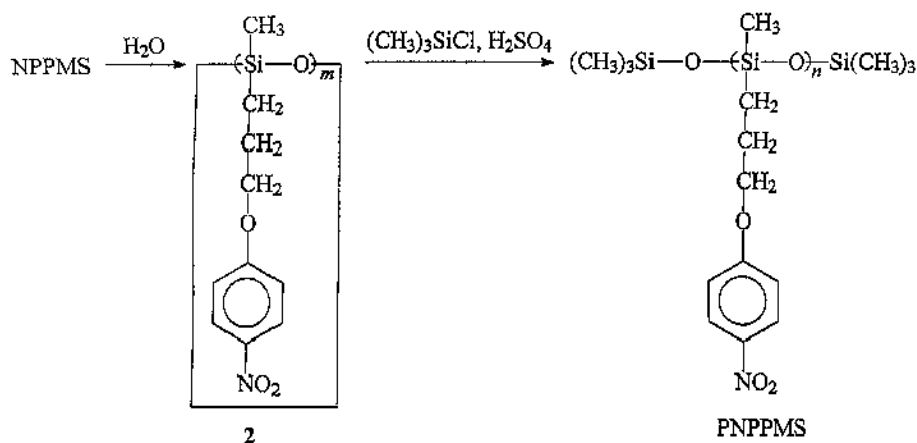
It is noted that the grafting ratio of the hydrosilylation reaction for preparing NPPMS monomer is much higher than that of the hydrosilylation reaction for preparing polymeric PNPPMS. This is due to the greater steric hindrance of polymethylhydrosiloxane chain. It is worth mentioning that the purification procedure for the final product is quite easy because there is no need to remove the unreacted nitro-containing molecules from the final polymer.

The synthesized PNPPMS can be dissolved readily in polar solvents such as THF, acetone, chloroform, but not in nonpolar solvents such as benzene and toluene due to the existence of polar nitro groups in PNPPMS.

Characterization of Functional PNPPMS

FTIR spectrum

The FTIR spectrum of PNPPMS is shown in Fig. 1. The band at 1261 cm⁻¹ is assigned to the vibration mode of Si—Me. The strong band at 1010–1109 cm⁻¹ belongs to the stretching vibration of Si—O—Si. The bands at 3087, 1594 cm⁻¹ are attributed to C₆H₄ vibration and the strong bands at 1513 and 1341 cm⁻¹ are assigned to the stretching vibration of NO₂.



Scheme 2 Synthetic route to polymer PNPPMS

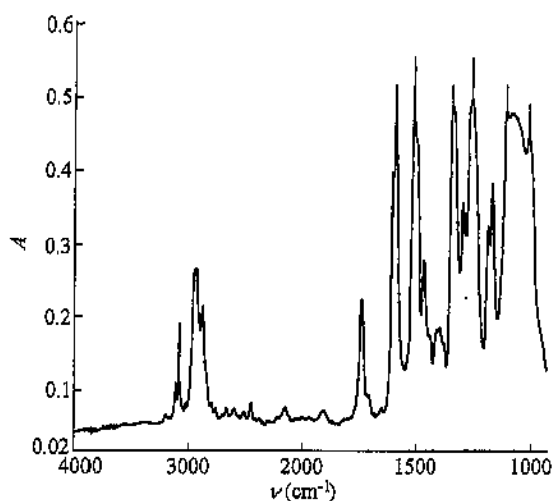


Fig. 1 FTIR spectrum of polymer PNPPMS

¹H-NMR and ¹³C-NMR spectra

¹H-NMR and ¹³C-NMR spectra of PNPPMS are shown in Fig. 2 and 3, respectively. In Fig. 2, $\delta = 0.1, 0.2, 0.7, 1.8, 4.0, 6.9$ and 8.1 signals are assigned to the a, b, c, d, e, f and g resonances, respectively. It can also be seen from Fig. 2 that the peaks are all broad peaks compared with those sharp peaks in the ¹H-NMR spectrum of NPPMS monomer indicating the formation of polymer. In the ¹³C-NMR spectrum of PNPPMS as shown in Fig. 3, $\delta = -0.6, -0.3, 13.2, 22.8, 70.8, 114.4, 125.9, 137.9$ and 164.1 signals are assigned to the a, b, c, d, e, f, g, h, and i resonances, respectively.

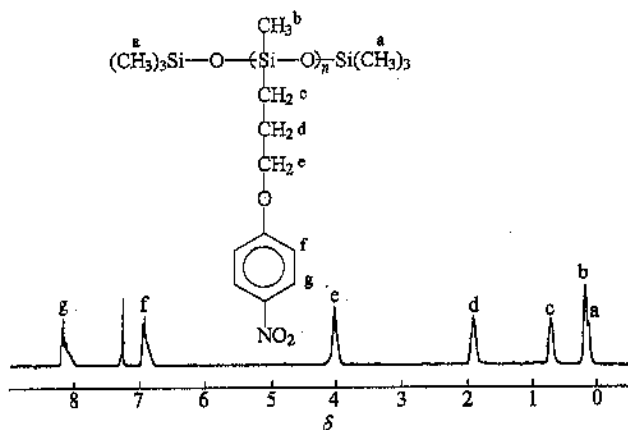
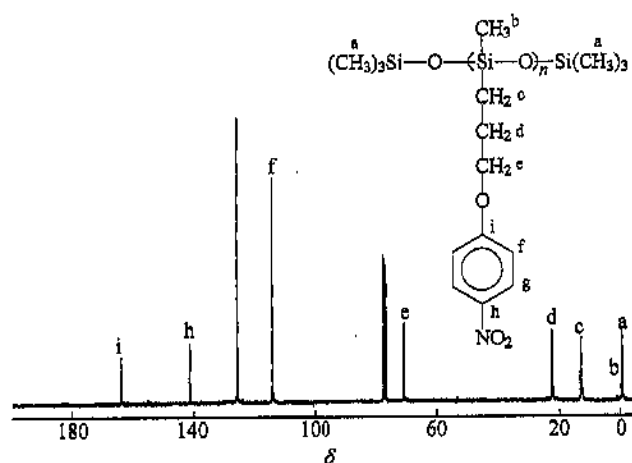
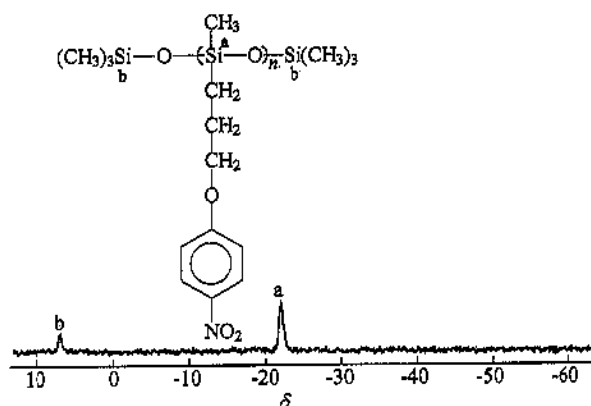
²⁹Si-NMR spectrum

In the ²⁹Si-NMR spectrum of PNPPMS (Fig. 4), two sharp peaks at $\delta = -21.9$ and 6.9 are ascribed to a and b signals, respectively.

The results obtained from FTIR, ¹H-NMR, ¹³C-NMR and ²⁹Si-NMR spectral analysis of the final product verify the structure of PNPPMS.

GPC and VPO Results

The molecular weight of PNPPMS was determined by GPC and VPO in THF, respectively. It is indicated that the molecular weight of PNPPMS is about 8900 dalton (M_w) determined by GPC, and about 7120 dalton (M_n) determined by VPO.

Fig. 2 ¹H-NMR spectrum of polymer PNPPMSFig. 3 ¹³C-NMR spectrum of polymer PNPPMSFig. 4 ²⁹Si-NMR spectrum of polymer PNPPMS

CONCLUSIONS

A new polyorganosiloxane containing side-chain nitro groups, which has potential applications as a precursor for preparing advanced functional polymers, has been synthesized successfully.

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