

Note

SYNTHESIS AND CHARACTERIZATION OF A NOVEL ALCOHOL-SOLUBLE POLYORGANOSILOXANE CONTAINING AMINO SIDE GROUPS*

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Abstract A novel alcohol-soluble polyorganosiloxane containing amino side groups, poly[3-(4-aminophenoxy)propylmethylsiloxane] (2), was first prepared by the reduction of nitro groups on 4-nitrophenoxypropyl side chains of poly[3-(4-nitrophenoxy)propylmethylsiloxane] (1). The reaction proceeded easily with nearly 100% conversion. The synthesized alcohol-soluble polymer 2, which has potential application as a precursor for preparing advanced functional polymers, was characterized by FTIR, ¹H-NMR, ¹³C-NMR, ²⁹Si-NMR, VPO and GPC, respectively.

Keywords Alcohol-soluble polyorganosiloxane, Reduction, Characterization

INTRODUCTION

It is well known that polyorganosiloxane (POS) has flexible and hydrophobic chains. Incorporation of POS chains into polymer materials is expected to afford some specific characteristics inherent in the POSs such as heat resistance, surface properties, water repellency, gas permeability, etc. If a POS has functional groups such as nitro, amino, amide, imide, imidazole, pyridine, hydroxyl or carboxy groups, it would be an excellent functional polymer or be used as a precursor for further preparing advanced functional polymers. Based on this viewpoint, POSs with various functional groups have been synthesized and a number of investigations have been made to apply these polymers to various functional materials^[1]. Recently, a series of POSs having amino groups have been reported^[2-13]. For example, Herczynska *et al.*^[2] reported the preparation of polysiloxanes containing pyridyl groups through the free-radical addition of pyridylthiols to the vinyl groups of the polymer. Zeldin *et al.*^[3, 4] reported a series of polysiloxanes by incorporating 4-(dialkylamino)pyridyl group into the polymer backbone or as side-chain substituents. Takamiya *et al.*^[10] reported the application of POSs containing dialkylaminopyridine in their side chains. Boutevin *et al.*^[13] first reported the successful preparation of telechelic aromatic diamines containing an oligo- or polysiloxane chain, but the aromatic amino groups were introduced to both ends of the oligo- or polydimethylsiloxane as terminal groups instead of side groups. Up to now, preparation of polyorganosiloxane containing aromatic amino groups on the side chains has not been reported.

In the present study, the reduction of nitro groups attached to 4-nitrophenoxypropyl side chains of poly[3-(4-nitrophenoxy)propylmethylsiloxane] (1) to amino groups is described. The conversion of this reduction reaction is very high and there is no difficulty in purifying the crude polymer product.

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EXPERIMENTAL

Materials

All solvents were commercially available and of analytically pure grade. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Methylchlorosilane, 4-nitrophenol, allyl bromide, acetone, K_2CO_3 , trimethylchlorosilane, HCl, H_2SO_4 , $SnCl_2 \cdot 2H_2O$, NaOH, toluene and anhydrous Na_2SO_4 were of analytically pure grade. Dicyclopentadienylplatinum (II) chloride (Cp_2PtCl_2) catalyst was prepared according to a literature method^[14].

Characterization

FTIR spectra were obtained from 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 spectrometer. Molecular weight was measured using a Knauer vapor pressure osmometer using THF as solvent, and simultaneously on a Shimadzu LC-4A gel permeation chromatography relative to polystyrene standards in THF using a differential refractive index detector.

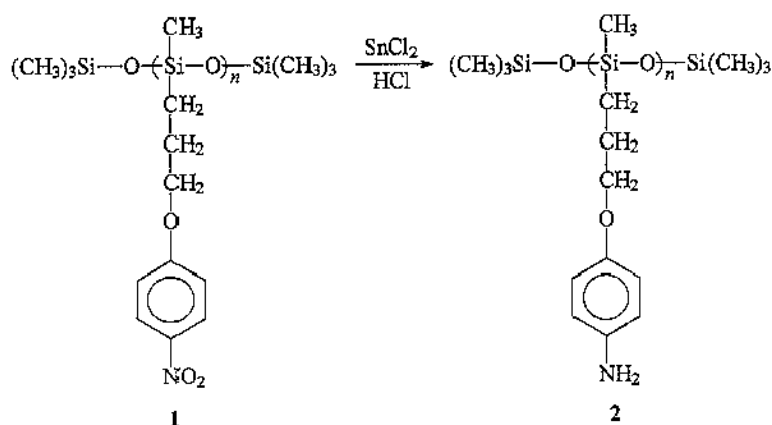
Preparation of Poly[3-(4-aminophenoxy)propylmethylsiloxane] 2

Synthesis of poly[3-(4-nitrophenoxy)propylmethylsiloxane] 1

Polymer 1 used for preparing poly[3-(4-aminophenoxy)propylmethylsiloxane] 2 bearing aromatic amino groups on side chains was synthesized by acid-catalyzed equilibration polymerization from the dichlorosilane monomer 3-(4-nitrophenoxy)propylmethylchlorosilane according to the literature^[15].

Synthesis of poly[3-(4-aminophenoxy)propylmethylsiloxane] 2

Polymer 2 was synthesized according to Scheme 1. A mixture of 4.8 g 1 (0.02 mol) and 20 mL THF was added dropwise to a mixture of 22.5 g $SnCl_2 \cdot 2H_2O$ (0.1 mol), and 22 mL concentrated HCl with vigorous stirring at room temperature over 1 h. Then the mixture was stirred at reflux temperature for another 6 h. The mixture was added slowly to 100 mL 40 wt% sodium hydroxide solution with stirring and cooled with ice. Then the THF and water solvents in the mixture were removed by filtration and the viscous solid product was obtained. The obtained product was washed with distilled water several times, and dried under vacuum. After that, the dried viscous gum was dissolved in 120 mL dry THF. The insoluble solid was removed by filtration. THF in the filtrate was removed by evaporation to give a viscous gum and after it was dried under vacuum for 48 h polymer 2 was obtained.



Scheme 1 Synthetic route to polymer 2

RESULTS AND DISCUSSION

Synthesis of Alcohol-soluble Polymer 2

As reported in 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^[16], 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^[6]. In this note, we report the preparation of polymer 2 by the second method, *i.e.*, the acid-catalyzed equilibration polymerization followed by reduction reaction. It can be seen from Scheme 1 that polymer 2 was prepared from polymer 1 containing nitro-terminated side chains.

Characterization of Polymer 2

FTIR spectra

The FTIR spectrum of polymer 1 is shown in Fig. 1(a), and that of polymer 2 is shown in Fig. 1(b). The band at 1260 cm^{-1} is assigned to the vibration mode of Si—Me. The strong band at about $1000\sim 1100\text{ cm}^{-1}$ belongs to the stretching vibration of Si—O—Si. The bands at 3087 , 1594 and 1513 cm^{-1} (Fig. 1a) or 3011 and 1512 cm^{-1} (Fig. 1b) are attributed to C—H, C=C stretching and/or bending vibrations of phenylene groups. The 1340 cm^{-1} band in the spectrum of 1 which is assigned to the stretching vibration of NO_2 is absent in the spectrum of 2 (Fig. 1b), while the band at 1626 cm^{-1} which is attributed to the scissors vibration of N—H and the bands at 3417 cm^{-1} and 3357 cm^{-1} which are due to the stretching vibrations of N—H appear in the spectrum of 2 (Fig. 1b).

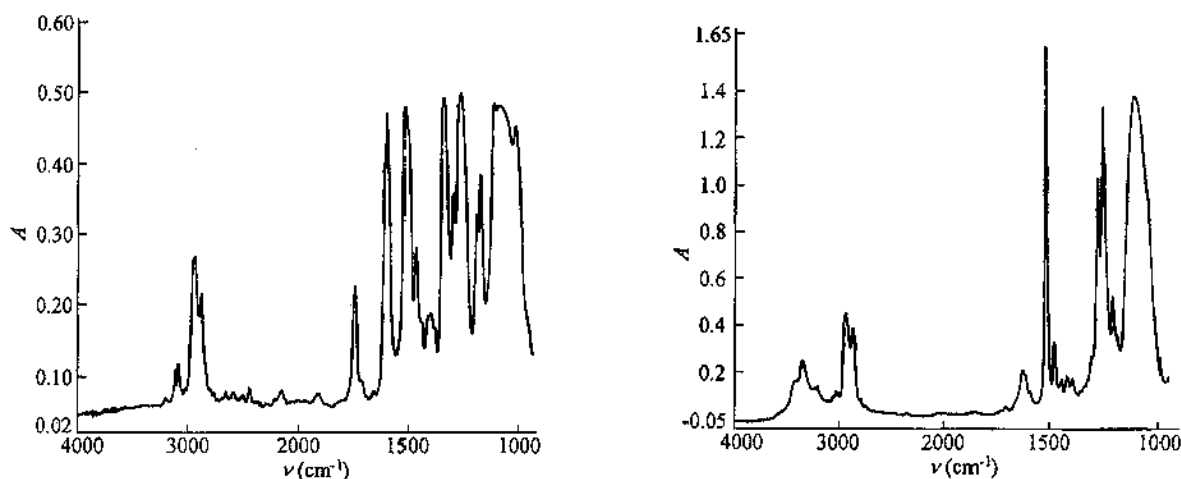


Fig. 1 FTIR spectra of polymer 1, (a) and 2, (b)

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra

$^1\text{H-NMR}$ spectra of 1 and 2 are shown in Fig. 2(a) and 2(b), respectively. In Fig. 2(a), the signals at $\delta = 0.1$, 0.2 , 0.7 , 1.8 , 4.0 , 6.9 and 8.1 are assigned to the a, b, c, d, e, f and g resonances, respectively. When 1 was reduced to 2, the signal at $\delta = 8.1$ (Fig. 2a) which belongs to g resonance disappears completely and moves to $\delta = 6.6$ in the spectrum of 2 (Fig. 2b). Additionally, in the $^{13}\text{C-NMR}$ spectrum of 1 as shown in Fig. 3(a), the signals at $\delta = -0.6$, -0.3 , 13.2 , 22.8 , 70.8 , 114.4 , 125.9 , 137.9 and 164.1 are assigned to the a, b, c, d, e, f, g, h, and i resonances, respectively. However, the signals at 114.4 , 125.9 , 137.9 and 164.1 which are assigned to phenyl group of 1 move to $\delta = 115.4$, 116.4 , 139.5 and 152.1 respectively in the spectrum of 2 (Fig. 3b). These results indicate that nearly all the nitro groups on the side chains of 1 are reduced to amino groups on the side chains of 2, and the conversion nearly approaches to 100%.

$^{29}\text{Si-NMR}$ spectra

In the $^{29}\text{Si-NMR}$ spectrum of 1 (Fig. 4a), two peaks at $\delta = 21.9$ and 6.9 are ascribed to a and b signals, respectively. In the $^{29}\text{Si-NMR}$ spectrum of 2 (Fig. 4b), the peaks ascribed to a and b signals appear at $\delta = 21.4$ and $\delta = 6.9$, respectively. These results indicate that the reduction of nitro groups to amino groups does not affect

the ^{29}Si -NMR of **1** and **2** significantly, and FTIR, ^1H -NMR, ^{13}C -NMR and ^{29}Si -NMR spectral analysis of **1** and **2** verify the formation of **2** containing amino groups on the side chains.

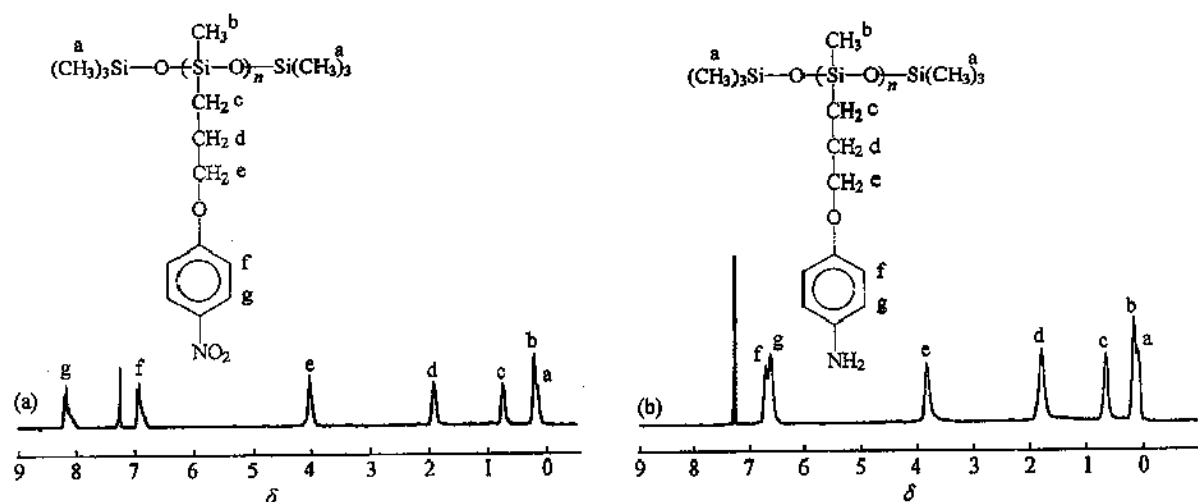


Fig. 2 ^1H -NMR spectra of polymer **1**, (a) and **2**, (b)

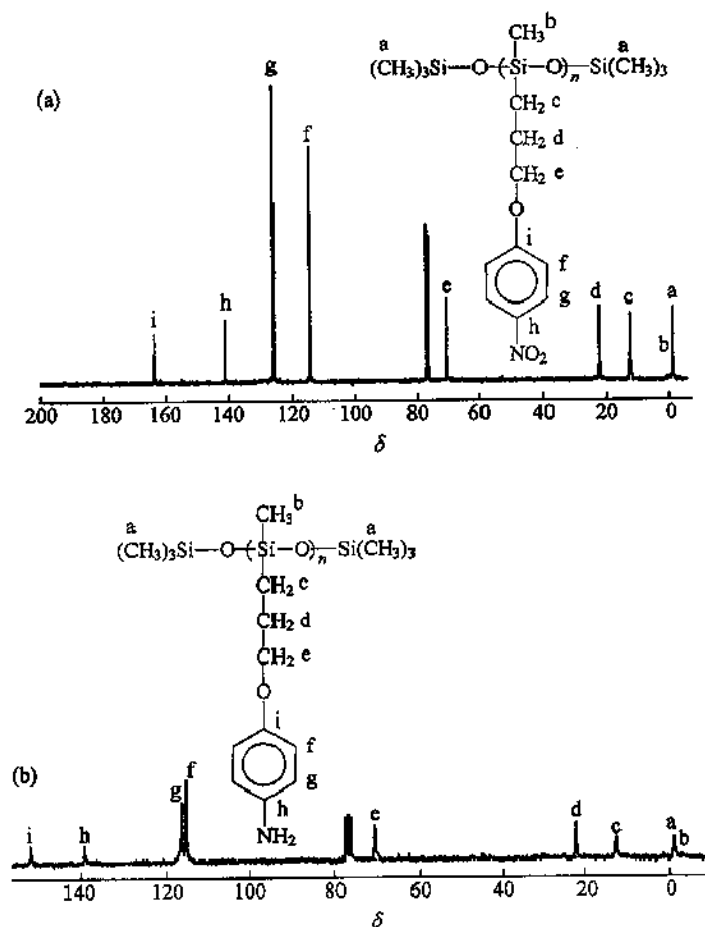


Fig. 3 ^{13}C -NMR spectra of polymer **1**, (a) and **2**, (b)

GPC and VPO results

The molecular weight of polymer 1 was found to be about 8900 dalton (M_w) from GPC, and about 7120 dalton (M_n) from VPO in THF. The molecular weight of polymer 2 is about 7810 dalton (M_w) by GPC and about 5920 dalton (M_n) by VPO. The GPC and VPO results indicate that the molecular weight (M_w and M_n) obtained for the final product 2 from the reduction reaction of the nitro siloxane polymer 1 are not very high.

The introduction of amino groups to the side chains of polymer 2 is one of the main reasons for the good solubility of polymer 2 in alcohol. Furthermore, it may allow polymer 2 to coordinate with metal ions intra- and intermolecularly in alcohol solution to form polymer metal complexes, which are expected to show interesting catalytic activity and will be a subject of further investigations.

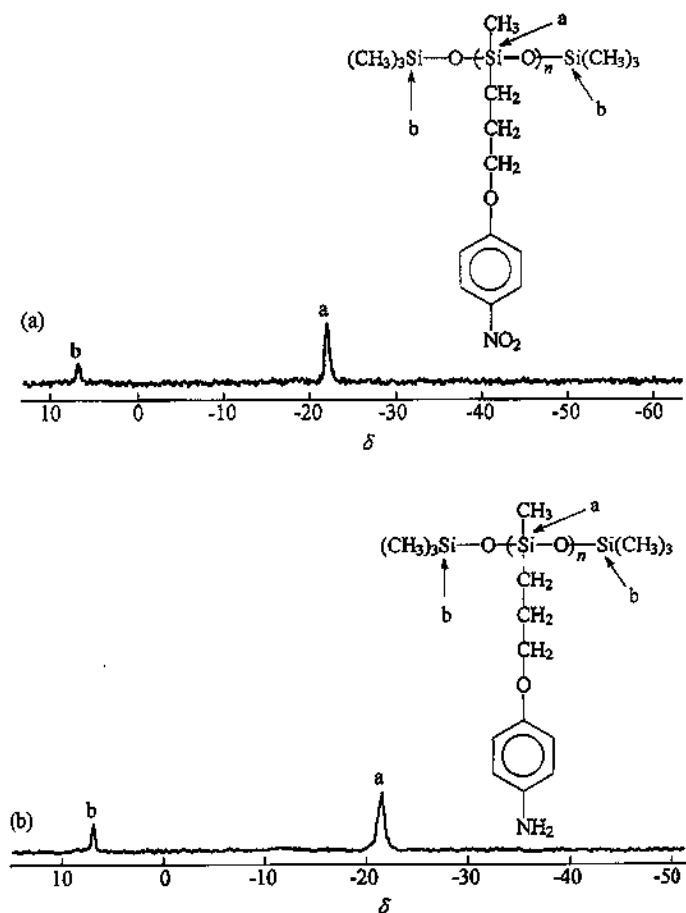


Fig. 4 ^{29}Si -NMR spectra of polymer 1, (a) and 2, (b)

CONCLUSIONS

A new alcohol-soluble polyorganosiloxane 2 containing amino groups on the side chains has been prepared by the reduction of nitro groups on the side chains of polyorganosiloxane 1. The synthesized alcohol-soluble polymer 2 containing amino groups on the side chains can be further applied to synthesize novel functional polymers.

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