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# FLUORO-SUBSTITUTED POLYSILOXANES. I. SYNTHESIS OF POLY(p-FLUOROPHENYLMETHYLSILOXANE)

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## ABSTRACT

The monomer chosen for the synthesis of this polymer, diethoxy-p-fluorophenylmethylsilane, was prepared by the Grignard reaction of methyltriethoxysilane with p-fluorophenyl magnesium bromide. The structure and purity of the monomer were characterized by gas chromatography and mass, infrared, and proton NMR spectroscopy. It was hydrolyzed in aqueous HCl solution and then polymerized by dehydration and ring-chain equilibration. The resulting polymer, poly(p-fluorophenylmethylsiloxane) $[\text{-Si}(p\text{-}C_6H_4F)(CH_3)O\text{-}]_x$ was characterized by infrared spectroscopy, and proton and fluorine NMR spectroscopy. Its number-averagemolecular weight, approximately $7 \times 10^4$ g mol$^{-1}$, may be high enough for evaluation of this material as a gas-separation membrane.

## INTRODUCTION

The polysiloxanes $[\text{Si-RR'-O-}]_x$ generally have exceedingly high permeabilities and have therefore been extensively studied as membrane materials for the separation of gases and liquids.[1-10] Although the most common polymer of this type is poly(dimethylsiloxane), one of the most interesting is a *fluoro*siloxane, poly(3,3,3-trifluoropropylmethylsiloxane) $[\text{-Si}(CH_2)_2CF_3(CH_3)O\text{-}]_x$. This polymer exhibits higher permeability to $CO_2$ than to many other penetrant gases, because of the anomalously high solubility of this gas in it.[4,5] There is speculation that this high solubility might be caused by specific interactions between the O atoms in the $CO_2$ and the F atoms in the side chains of the polymer.[4,5] This raises the interesting question

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of whether fluorine substitution, to various levels, would have a similar effect on other polysiloxanes. Of particular interest would be the much-studied partly-aromatic polysiloxane, poly(phenylmethylsiloxane).[11,12] The investigation of other properties of such fluorine-substituted polysiloxanes, once prepared, would of course also be of interest. Examples are their surface tensions[13,14] and electrical properties.[15]

For the above reasons, a program for synthesizing and characterizing fluorine-substituted polymers of phenylmethylsiloxane was undertaken.[16] The present manuscript describes the first of these polymers, poly(p-fluorophenylmethylsiloxane) (PFPMS) [-Si(p-$C_6H_4F$)($CH_3$)O-]$_x$.

## Experimental Details

### Synthesis of Monomer

All reagents were purchased from the Aldrich Chemical Co., and were used as received.

The starting material, methyltriethoxysilane, was converted into the desired monomer, diethoxy-p-fluorophenylsilane (DEFS), by the Grignard reaction[16,17]

(1)

The desired amount of methyltriethoxysilane was placed in a three-necked flask fitted with a stirrer, dropping funnel and condenser, and an ether solution containing p-fluorophenylmagnesium bromide was added dropwise with stirring at room temperature over a period of one hr.[16,17] The mixture was heated to reflux for three hrs., after which the ether solution was decanted from the insoluble magnesium salts, and the residue washed with $CH_2Cl_2$ three times. The combined solutions were distilled to remove ether and $CH_2Cl_2$, and then purified by using a short column under reduced pressure. A 51 % yield of monomer was thus obtained.

A slight excess of Grignard reagent was used, and it was added as described in an attempt to minimize formation of the disubstituted and trisubstituted products. It was hoped that steric repulsions between the phenyl groups would also be helpful in this regard.

### Characterization of Monomer

Gas chromatograms and mass spectra for the monomer were recorded on a Hewlett Packard 5995 gas chromatograph-mass spectrometer. An IR spectrum was obtained on a Perkin-Elmer 599 spectrophotometer, and a $^1H$-NMR spectrum was recorded on a IBN NR/80 spectrometer operating at 80 MHz with $CDCl_3$ as solvent. Proton chemical shifts were expressed in parts per million (δ) from an internal standard, $(CH_3)_4Si$ (1 wt %).

Table I
Effects of the Amounts of $(CH_3)_4NOH$ and HCl on the Number-Average Molecular Weight and Yield of Polymer

| Exp. No. | DEFS (g) | 0.2 N HCl (g) | $(CH_3)_4OH$ (g) | $M_n$ of PFPMS ($g\ mol^{-1}$) | Yield (%) |
|---|---|---|---|---|---|
| 1 | 10 | 20 | 0.0759 | 68,000 | 78 |
| 2 | 10 | 20 | 0.1198 | 58,000 | 71 |
| 3 | 10 | 20 | 0.1518 | 46,250 | 65 |
| 4 | 5 | 7 | 0.0377 | 43,500 | 68 |
| 5 | 5 | 10 | 0.0377 | 74,000 | 77 |
| 6 | 5 | 13 | 0.0377 | 72,000 | 74 |
| 7 | 5 | 16 | 0.0377 | 61,000 | 77 |

### Hydrolysis of Monomer

The monomer and 0.2 N HCl were added to a three-necked flask and the mixture was heated to 78 °C, with stirring.[16] The ethanol formed was continuously and completely removed by distillation, and the water concentration continuously adjusted. The hydrolysis product was extracted twice with benzene in a separatory funnel. The organic phase was then washed twice with water, and the benzene removed under vacuum. The final product was a flocculent, white material.

### Condensation Polymerization

The compound $(CH_3)_4NOH$ was added to the hydrolysis product and the mixture dehydrated under vacuum at 125 °C for two hrs.[16] A ring-chain equilibration reaction was then carried out under these same conditions for an additional six hrs. The $(CH_3)_4NOH$ was then decomposed at 180 °C under atmospheric pressure for two hrs., and volatiles removed at 210 °C under vacuum for three hrs. Some of the details of the polymerizations are given in Table I. In the first three experiments, a constant amount of HCl was used, and the amount of $(CH_3)_4NOH$ was varied. In experiments 4 through 7, th amount of HCl was varied while the amount of $(CH_3)_4NOH$ was kept constant. The polymer thus prepared was a clear, highly viscous fluid.

### Characterization of Polymer

The IR spectrum of the polymer was recorded on a Perkin-Elmer 599 spectrophotometer. The $^1H$-NMR spectrum was obtained in $CDCl_3$ solution with $(CH_3)_4Si$ as internal standard ($\delta = 0$) on an NR 80 spectrometer. Similarly, the $^{19}F$-NMR spectrum was run in a $C_6D_6$ solution on a Nicolet NT-300 Broad Band spectrometer, with chemical shifts reported in parts per million relative to $C_6F_6$. The GPC molecular weight analyses were carried out using a Waters 599 high pressure

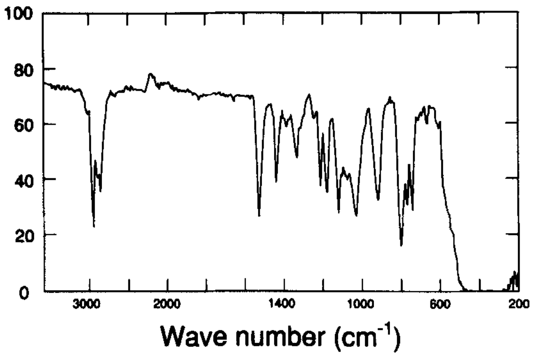
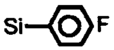


**Figure 1.** Infrared spectrum of the monomer.

**Table II**
**Spectral Data for the Polymer**

| Group | IR spectrum (in cm$^{-1}$) | $^{1}$H - NMR (δ ppm) | $^{19}$F-NMR (δ ppm) |
|---|---|---|---|
| Si-CH3 | 1255, 955 | 0.20 | - |
|  | 1395 | 6.70, 7.30 | 53.63, 53.27 |
| Si-O-Si | 1000-1130 | - | - |
| $Si\text{-}OC_2H_5$ | Disappearance at 1065 | Disappearance at 1.25, 3.80 | - |

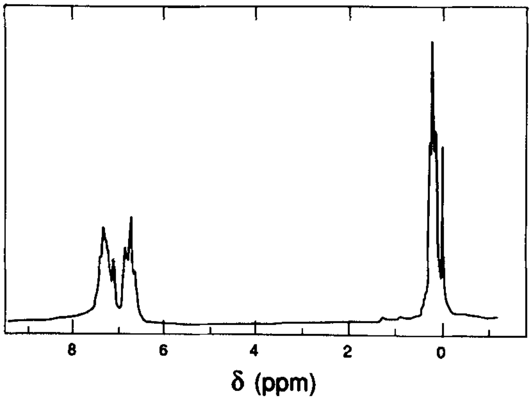


**Figure 2.** Proton NMR spectrum of the polymer.

liquid chromatograph with THF as the eluent, and with polystyrene samples as standards. The detection system consisted of a Waters Model 481 LC spectrophotometer set at 260 nm and a Waters 410 differential refractometer. Samples of each polymer solution were filtered through a 0.5 μm Milipore filter. The flow rate was 1 ml $min^{-1}$.

## RESULTS AND DISCUSSION

### Monomer

The gas chromatogram of the reaction product before purification consisted of three peaks, the largest of which corresponded to 84 wt % of the mixture.[16] Its mass spectrum gave an m/e of 228, the expected value for the desired monomer. The purified product gave an identical mass spectrum.

The monomer was further characterized by IR and $^1H$-NMR spectra. In the IR spectrum, shown in Figure 1, absorptions at 1065, 1385 and 1255 $cm^{-1}$ indicate $Si\text{-}OC_2H_5$, Si-⌬F and $Si\text{-}CH_3$ groups, respectively. In the latter, chemical shifts of the protons of the phenyl group appeared at 7.70 and 7.06 ppm. The proton peaks at 0.36, 1.25 and 3.80 ppm indicate $CH_3$ and $OCH_2CH_3$ groups. Additional evidence comes from the peaks due to the $H_a$ and $H_b$ atoms in the phenyl rings, the $H_c$ atoms in the methyl groups in $OC_2H_5$, the $H_d$ atoms in the methylene groups in $OC_2H_5$, and the $H_e$ atoms in the methyl groups directly attached to the Si atoms. The ratio of the number of $H_a$, $H_b$, $H_c$, $H_d$, and $H_e$ atoms obtained from the integral of the peaks is 2:2:4:6:3. These ratios are consistent with the structure expected for the monomer. The splitting of the proton peak of the phenyl group is caused by the fluorine atom, and shows that the substitution was indeed *para*.

### Polymer

The structure of the polymer was first characterized by IR, $^1H$-NMR and $^{19}F$-NMR.[16] Some of these results are summarized in Table II. IR peaks at 1395, 1255 and 955 $cm^{-1}$ proved the existence of Si⌬F and $SiCH_3$ groups. The $^1H$-NMR spectrum, shown in Figure 2, showed no signal for $OC_2H_5$ groups at the expected locations of 1.25 and 3.80 ppm. The $^{19}F$-NMR spectrum showed signals at 53.63 and 53.27 ppm, relative to $C_6F_6$, for F atoms in F⌬ groups. All of the spectroscopic data were thus in agreement with the expected structure.

As can be seen from the last two columns of Table I, all of the experiments yielded high molecular weight polymer in good yield. The molecular weights ranged from 44,000 to 74,000 g $mol^{-1}$. The highest values were obtained when the weight ratio of 0.2 N HCl to monomer was in the range 2.0:1 to 2.6:1, and the weight ratio of $(CH_3)_4NOH$ to monomer was approximately 0.007:1.[16]

These molecular weights may well be high enough for evaluation of this polymer as a gas-separation membrane.

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