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FLUORO-SUBSTITUTED POLYSILOXANES. II. SYNTHESIS OF POLY(PENTAFLUOROPHENYLMETHYLSILOXANE)

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ABSTRACT

Pentafluorophenylmethyldiethoxysilane is an interesting new monomer for preparing fluoropolysiloxanes because of its unusually high fluorine content. It was synthesized using either a bromo- or iodo-Grignard reagent, and its structure was characterized by GC-MS, IR, and ^{1}H-NMR. It was polymerized by hydrolysis and condensation reactions to yield poly(pentafluorophenylmethylsiloxane) $[\text{-Si}(C_6F_5)(CH_3)O\text{-}]_x$, which was characterized by FTIR and ^{1}H-NMR. Its relatively high number-molecular weight, 6.5×10^4 g mol^{-1}, should encourage further characterization studies with regard to unusual properties such as permeability and surface activity.

INTRODUCTION

The properties of the polysiloxanes $[\text{Si-RR'-O-}]_x$ can be modified to a considerable extent by variation of the nature of the alkyl or aryl R and R' side chains. One of the most interesting ways of doing this is to introduce fluorine atoms into them, because of the interesting properties of these fluorosiloxanes.[1-5] The most common polymer of this type is poly(3,3,3-trifluoropropylmethylsiloxane) $[\text{-Si}(CH_2)_2CF_3(CH_3)O\text{-}]_x$ which is, in fact, commercially available. This polymer exhibits high permeability to many penetrant gases, possibly because of specific interactions between the penetrant molecules and the F atoms in the side chains of the polymer.[4-6] It is therefore of considerable interest to study a variety of fluorosiloxane polymers varying in the nature and amount of their fluorine substitution. One recent preparative study of this type[7] involved the much-studied partly-aromatic polysiloxane, poly(phenylmethylsiloxane) $[\text{-Si}(C_6H_5)(CH_3)O\text{-}]_x$.[8,9] In this cause a single fluorine atom was substituted into the <u>para</u> position of the phenyl groups. The monomer having two F atoms attached to the phenyl group has also been synthesized.[10]

The purpose of the present report is to describe the preparation of poly(phenylmethylsiloxane) in which the entire phenyl group is fluorinated, i. e.,

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poly(pentafluorophenylmethylsiloxane) [-Si(C_6F_5)(CH_3)O-]$_x$. This polymer will contain an unusually large amount of fluorine, 42 wt %, which should make it an extremely interesting member of the fluorosiloxane polymer series for structure-property investigations.

Experimental Details

Materials

For the monomer synthesis, bromopentafluorobenzene and iodopentafluorobenzene were purchased from Pfaltz and Bauer, Inc., methyltriethoxysilane from the Aldrich Chem. Co., and magnesium turnings from the Mallinckrodt Chem. Co. For the polymerization, HCl (37 % in water) was purchased from the Fisher Co., and $(CH_3)_4NOH$ (10 % in water) from the Eastman Kodak Co.

Synthesis of Monomer

Pentafluorophenylmagnesium bromide or iodide was prepared using a suspension of magnesium in 40 ml of ether which was cooled to 0 °C under N_2.[11-13] A solution of bromo(or iodo)pentafluorobenzene in ether was added dropwise to the stirred suspension for a period of approximately about 1 hr. The completion of the reaction was indicated by the nearly complete disappearance of the magnesium turnings.[6]

The monomer, pentafluorophenylmethyldiethoxysilane, was then prepared, under N_2 and at 0 °C. The methyltriethoxysilane was added dropwise to the above solution of the Grignard reagent. The mixture was then heated to reflux with stirring for 10 hrs. The residue obtained by filtration was washed with ether three times. The combined ether solutions thus obtained were distilled to remove the ether, under atmospheric pressure, followed by fractional distillation under reduced pressure. The monomer was obtained as a colourless liquid in the range 56 - 58 °C at approximately 1 mm Hg.

Characterization of Monomer

The monomer was characterized by gas chromatography and mass spectroscopy (GC-MS), infrared (IR), and proton nuclear magnetic resonance spectoscopy (^{1}H-NMR) as described elsewhere.[7] Elemental analyses were carried out by the M-H-W Laboratories.

Hydrolysis of Monomer

Some of the monomer was mixed with 0.2N HCl and C_2H_5OH in a 50 mL three-necked flask fitted with a stirrer and reflux condenser. The mixture was heated to reflux with stirring for 10 hrs. After the hydrolysis, the C_2H_5OH was removed by distillation. The hydrolysis products were poured into a separatory funnel and washed with water until a pH of neutrality was obtained. Most of the water phase was thus separated, with the little remaining removed by distillation with benzene.[7] The hydrolysis product was a flocculent white mass.

Polymerization

A trace amount of $(CH_3)_4NOH$ was added to the hydrolysis product, and the mixture dehydrated at 130 °C at 5 mm Hg for 2 hrs. A ring-chain equilibration reaction was then carried out at the above temperature and under vacuum for 6 hrs. The $(CH_3)_4NOH$ was then decomposed at 180 °C for 2 hrs and the low-boiling components removed at 210 °C at 3 mm Hg for 3 hrs. The polymer thus obtained was a colorless, viscous fluid.

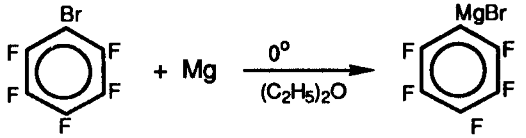
Characterization of Polymer

Fourier-transform infrared (FTIR) spectra were obtained on a Perkin-Elmer Model 1600 spectrophotometer. The ^{1}H-NMR spectrum was obtained in a $CDCl_3$ solution on an NR-80 spectrometer, with $(CH_3)_4Si$ (TMS) as internal standard (δ=0). The number-average molecular weight M_n was measured by gel permeation chromatography, as described elsewhere.[6,7]

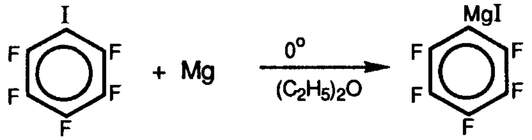
RESULTS AND DISCUSSION

Synthesis of Monomer

The preparation of the Grignard reagents described above can be summarized by the equations

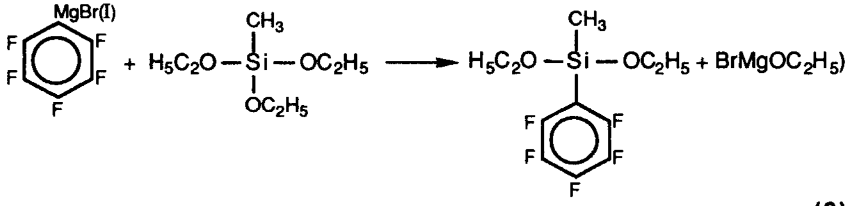


(1)



(2)

In the case of the iodopentafluorobenzene, the color of reaction mixture gradually changed from colorless to light yellow, and finally to brown or dark brown. The reaction giving the monomer is given by the equation



(3)

The yields of monomer thus obtained are given in column two of Table I. The yield of monomer which had been prepared using the bromopentafluorobenzene is seen to be higher than that obtained using the iodopentafluorobenzene. The gas chromatograms and mass spectra of both samples of monomer were found to be consistent with the expected structure.[6] The results of the elemental analyses are given in the final column of Table I. There is good agreement between the values of the % F calculated from the assumed structure and the values found experimentally. This also supports the proposed structure.

Table I

Yields of Monomer and Its Fluorine Content

Formula	Yield (%)	F (%)	
		Calc.	Found
$CH_3C_6F_5Si(OC_2H_5)_2$	30[a]	31.66	30.88
$CH_3C_6F_5Si(OC_2H_5)_2$	25[b]	31.66	31.81

[a] Obtained using bromopentafluorobenzene.

[b] Obtained using iodopentafluorobenzene.

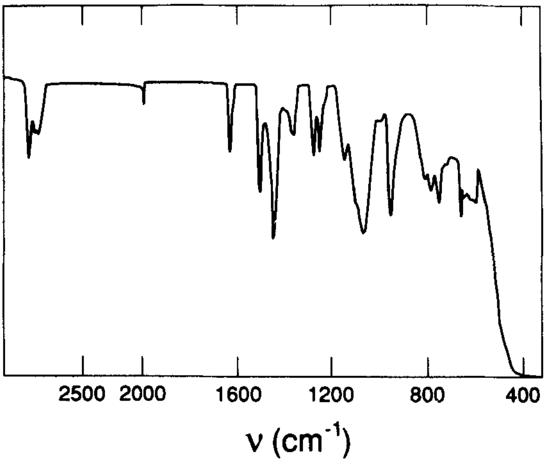


Figure 1. Infrared spectrum of the monomer.

The structure of the monomer was further investigated by IR and ^{1}H-NMR. The IR spectrum of the sample of monomer prepared from the bromopentafluorobenzene is shown in Figure 1. The absorptions at 1085, 1265, and 1465 cm^{-1} indicate Si-OCH$_2$CH$_3$, Si-CH$_3$ and Si -  bonds, respectively. Figure 2 shows the NMR results, specifically the chemical shifts of the protons in the same sample of monomer. They are 0.50 ppm (CH$_3$, 3H), 1.25 ppm (OCH$_2$CH$_3$, 3H) and 3.90 ppm (OCH$_2$CH$_3$, 2H). Equivalent results were obtained using the sample of monomer prepared from the iodopentafluorobenzene.[6]

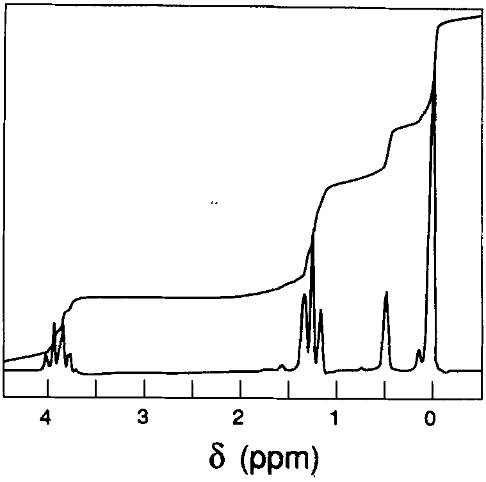


Figure 2. Proton NMR spectrum of the monomer.

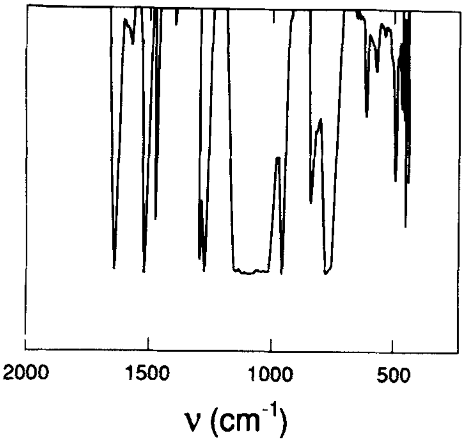


Figure 3. Fourier-transform infrared spectrum of the polymer.

Synthesis of Polymer

It was found that the hydrolysis rate of the present monomer, $C_6F_5(CH_3)(OC_2H_5)_2Si$, was slower than that of mono-substituted monomer,[7] $C_6H_4F(CH_3)(OC_2H_5)_2Si$, because of larger steric hindrances involving the C_6F_5 group. Similarly, higher temperatures and longer reaction times were found to be required to obtain polymer of relatively high molecular weight.[6]

The absorption band of the Si-O-Si group in linear small-chain siloxanes is narrow and located at about 1050 cm^{-1}. With increase in molecular weight, this band gradually broadens to occupy the region 1130-1000 cm^{-1}. The FTIR spectrum of the hydrolysis products of the monomer did have an absorption band for Si-O-Si that was narrow and sharp. This means that the initial products consisted primarily of low molecular weight cyclic and linear molecules. After ring-chain equilibration, the absorption band became somewhat broader.[6] Removal of low-boiling components by distillation yielded the spectrum shown in Figure 3. The broadness of this band indicates the material to be polymer of relatively high molecular weight. This was confirmed by the gel permeation chromatography results,[6] which indicated a number-average molecular weight of approximately 65,000 g mol^{-1}. The peaks at 1271 and 970.5 cm^{-1} are from the Si-CH_3 group, and the absorption band at 1479.5 cm^{-1} is from the Si -  entity.

The structure of the polymer was also characterized by ^1H NMR.[6] The chemical shift of the proton in the CH_3 groups was at 0.45 ppm (3H). In addition, there are very weak peaks at 3.60 and1.15 ppm. They are possibly due to a small number of unhydrolyzed OC_2H_5 groups remaining in the polymer.

The preparation of this polymer and its monosubstituted analogue[6] to relatively high molecular weights should encourage further characterization studies with regard to unusual properties such as permeability and surface activity.[4,5,14]

ACKNOWLEDGEMENTS

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