Synthesis and Characterization of the New Fluoropolymer Poly(difluorosilylenemethylene); An Analogue of Poly(vinylidene fluoride)

M. Lienhard, I. Rushkin, G. Verdecia, C. Wiegand,
T. Apple,* and L. V. Interrante*

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

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The poly(silylenemethylene)s (PSMs), polycarbosilanes having the general formula [-SiR$_1$R$_2$CH$_2$-]$_n$, are currently under investigation both as precursors to ceramics (SiC and SiO$_x$C$_y$) and as analogs of both the all-carbon backbone polyolefins and such inorganic polymers as the poly(silanes), poly(siloxanes) (PSOs), and poly(phosphazenes) (PPPs).[1] Previous studies of these PSMs have yielded the monosilicon analog of polyethylene, [SiH$_2$CH$_2$-]$_n$ (PSE),[2,3] as well as other PSM analogs of poly(olefins), poly(phosphazenes), and poly(siloxanes).[1] Among the interesting features of these new polymers is a chemical stability analogous to the polyolefins coupled with synthetic flexibility similar to that found for the PSOs and PPPs.

Among the more important polyolefins in terms of both unusual properties and industrial interest is the fluoropolymer, poly(vinylidene fluoride), [-CF$_2$CH$_2$-]$_n$ (PVF$_2$). PVF$_2$ combines, in a way that is unique among existing materials, the ability to form thin, tough, flexible films with unusually high piezoelectric and pyroelectric activity.[4] It has found widespread use in applications that range from protective coatings for metal surfaces to blood flow sensors, underwater hydrophones, and stereo speakers.[5] These interesting dielectric properties result from alignment of the all-trans [-CF$_2$CH$_2$-]$_n$ chains in the β-crystalline form by poling at elevated temperatures to give highly oriented thin films.[5]

The monosilicon analog of PVF$_2$, poly(difluorosilylenemethylene) (PDFSM) has apparently not been reported, although the dimer, 1,1,3,3-tetrafluoro-1,3-disilacyclobutane, TFDSCB, has been previously prepared by using a solid fluorinating agent (AgF) to replace Cl on 1,1,3,3-tetrachlorodisilacyclobutane (ca. 30% yield) and characterized by means of mass spectrometry, IR spectroscopy and X-ray structural determination.[6] Due to the increased polarity of the Si−F bonds relative to C−F bonds, an analogous crystalline form of PDFSM with [-SiF$_2$CH$_2$-]$_n$ chains in the all-trans conformation could potentially have improved piezoelectric properties relative to PVF$_2$. This paper reports the successful synthesis of this monosilicon analog of PVF$_2$ and the characterization of its molecular structure.

The linear, regularly alternating, Si−C backbone of the PSMs is conveniently achieved by the ring opening polymerization (ROP) of disilacyclobutanes.[1,7] Two different approaches which both involve ROP of a disilacyclobutane monomer were employed for the synthesis of PDFSM. In one approach (Scheme 1, method A) the 1,1,3,3-tetraethoxydisilacyclobutane is polymerized directly by ROP using a platinum complex as a catalyst to form the linear polymer poly(diethoxysilylenemeth-

Scheme 1
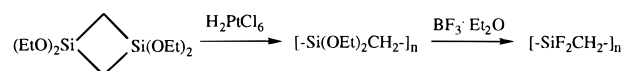
ylene),[8] which was then converted to PDFSM by reaction with an excess of BF$_3$·Et$_2$O.[9]

The alternative approach (method B) simply reverses the order of these fluorination and ROP reactions beginning with the same tetraethoxydisilacyclobutane starting material. This method employs neat BF$_3$·Et$_2$O as the fluorinating agent and solvent for the first reaction, producing TFDSCB in high yield (70%). The pure TFDSCB (purity established by ^{19}F, ^{29}Si, and ^{13}C NMR spectroscopies) was then polymerized at 120 °C by using a platinum complex in a hydrocarbon solvent.

Both synthetic approaches produced a light brown powder which precipitated out of solution during polymerization. This solid has thus far resisted efforts to dissolve it in various organic solvents, including perfluoromethyldecalin; however, it was observed to melt at ca. 150 °C, yielding a clear, dark melt. Thermal gravimetric analysis (TGA) under N$_2$ showed a decomposition onset at around 320 °C, with a 20% char yield by 700 °C. The insolubility of the PDFSM prevented further purification as well as characterization by solution NMR methods and GPC.

Method A affords control and characterization of the chain length and molecular weight of the intermediate ethoxy-substituted polymer because it is soluble. Due to its hydrolytic sensitivity, the actual molecular weight distribution of this diethoxy-substituted PSM was not directly determined; however, on reduction with LiAlH$_4$ in diethyl ether, the PSE so obtained was found to have a (GPC) molecular weight of 22000/5800 (M_w/M_n), corresponding to ca. 130 monomer units.[8] A potential drawback of this approach is the possibility of incomplete fluorine substitution. In contrast method B is expected to produce a totally fluorinated polymer, but because an insoluble product is formed, the molecular weight is likely to be lower.

A completely fluorinated polymer was obtained by using method A, when exposure to atmospheric moisture was rigorously excluded during both the polymer synthesis and subsequent handling. In a N$_2$-filled glovebox, 10 mL of BF$_3$·Et$_2$O was added to 2 g of the [Si(OEt)$_2$CH$_2$]$_n$ polymer, which was dissolved in 50 mL of hexane, and the mixture was stirred and heated at reflux overnight. The liquids were decanted, and the solid polymer was dried under vacuum, initially at 80 °C for 1 h and then at 200 °C for 1 h. The ^{1}H-decoupled ^{29}Si non-spinning spectrum of this sample, obtained at 180 °C (above the melting transition) consisted of three lines having a 1:2:1 intensity ratio (J_{Si-F} = 284 Hz) centered at −6.2 ppm (Figure 1). A single peak was observed in the ^{13}C NMR spectrum under the same conditions at 0.9 ppm. These observations, and reference to previously reported chemical shift data,[10] are consistent with a [-SiF$_2$CH$_2$-]$_n$ chain structure. A sample run at room temperature under magic angle spinning (MAS) conditions showed the same 1:2:1 triplet centered at −4.2 ppm.

When the synthesis was carried out under less-stringent conditions,[11] the ^{29}Si MAS NMR spectrum of the product at room temperature showed two distinct resonances, one at −4.2 ppm and a minor resonance (ca. 9% relative intensity) at −13 ppm. The peak at −4.2 ppm is again assigned to the C-SiF$_2$-C

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(11) The herein reported reaction procedures were carried out using standard Schlenk line techniques without rigorous exclusion of air and moisture during reaction workup and subsequent handling of the product.
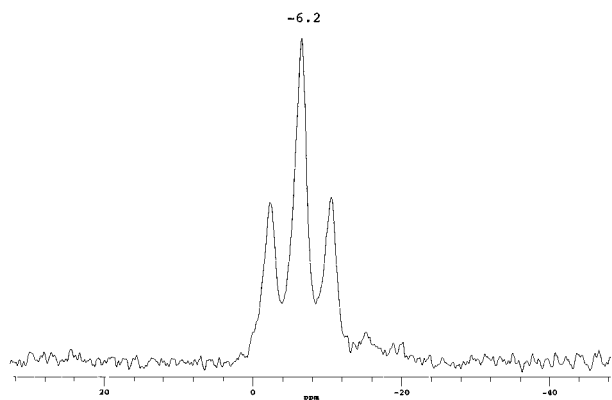
Figure 1.

moiety. The minor peak at -13 ppm is assigned to C-SiO$_2$-C species. This assignment is based upon comparison to shifts for oxycarbosilanes,[12] its failure to cross-polarize from ^{19}F with short contact times, and analysis of a sample of poly(diethoxysilylenemethylene), which was fluorinated to 70% substitution.

When the preparation procedure involved room temperature treatment with BF$_3$·Et$_2$O or washing the product with methanol, an increased intensity for the C-SiO$_2$-C resonance was observed in the ^{29}Si solid-state NMR spectrum, presumably due to incomplete substitution of OEt and/or hydrolysis of the Si−F bond. Samples of PDFSM that are stored in humid environments show an increased intensity for the resonance assigned to C-SiO$_2$-C, indicating that hydrolysis of the Si−F bonds does indeed occur on exposure of the polymer to atmospheric moisture.

Solid-state ^{29}Si NMR spectra of polymer samples made by method B[13] show similar resonances to those made by method A. The ratio of the intensity of the C-SiF$_2$-C resonance to the C-SiO$_2$-C peak is a strong function of time when the sample is stored in a capped vial, changing from 2:1 to 1:1 over the course of 6 months. One interesting difference between samples made by method B from those of method A is the presence of a weak resonance at -65 ppm, which is not attributable to spinning side bands. This peak may arise from end groups of the type C-SiX$_3$ (X = any combination of O or F).[10] The detection of end groups for samples made by method B would be consistent with the expected lower molecular weights of these polymers compared to those made by method A.

The FTIR spectra of the polymers produced by methods A and B were essentially the same. Three weak bands were observed between 2960 and 2910 cm^{-1} which correlate well with the three peaks assigned to CH$_2$ stretching in PSE, as well as an additional strong band at 1350 cm^{-1} which correlates with

the CH$_2$ scissoring vibrational mode assigned to PSE.[3a] A strong sharp band at 780 cm^{-1} is assigned to the Si−C asymmetric stretch of the polymer backbone, also in good agreement with that of PSE. The two strongest, broadest bands in the spectrum at around 1070 and 890 cm^{-1} resemble absorptions previously assigned to the SiF$_2$ units in TFDSCB.[6] The remaining medium to strong bands in the IR spectrum at 1270 and 680 cm^{-1} are currently unassigned.

The crystallinity of the samples was examined by powder XRD measurements ($2\theta = 15-75°$). The polymers obtained from the two procedures exhibit identical multipeak diffraction patterns indicating that both samples are at least semicrystalline with the same crystal structure. DSC measurements[13] of a sample prepared by method A showed a broad, endothermic peak with a maximum at ca. 160 °C, presumably corresponding to the observed melting transition. Repeated temperature cycling between room temperature and 250 °C indicated that this transition was reversible in terms of T_m and ΔH_m. The reversibility of the melting transition was also evidenced by the observation of the original XRD pattern after repeated heating and cooling cycles from room temperature to 250 °C.

Analysis of the ^{29}Si NMR chemical shifts as a function of temperature from room temperature to just below the melting transition reveals two-component behavior for all resonances consisting of a broader, readily cross-polarized component which is slightly downfield of a narrow component that does not cross-polarize. This suggests the peaks are from crystalline and amorphous regions, respectively. At high temperatures, the amorphous mobile regions, which sample both trans and gauche conformations, resonate at -6.2 ppm for the C-SiF$_2$-C unit and -17.1 ppm for those polymers having the C-SiO$_2$-C unit. This places the broad crystalline region $2-4$ ppm downfield of the amorphous region, indicating that the crystalline region is in a predominantly all-trans conformation,[15] analogous to the β-form of PVF$_2$.

Thus, the characterization data obtained for PDFSM obtained by two different methods are entirely consistent with expectations for a linear polymer comprised mainly of a regularly alternating -SiF$_2$CH$_2$- chain structure, analogous to that observed for PVF$_2$. This polymer is at least partially crystalline and appears to melt reversibly at around $140-170$ °C, again resembling PVF$_2$. The characterization and analysis of the XRD pattern for this polymer, as well as efforts to obtain a poled sample for dielectric measurements, are currently in progress.

Supporting Information Available: ^{29}Si SSNMR, ^{13}C NMR, FTIR spectra, DSC trace, TGA plot, and powder XRD pattern for **PDFSM** (7 pages). See any current masthead page for ordering and Internet access instructions.

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