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# Fluoroalkylation of aryl ether perfluorocyclobutyl polymers

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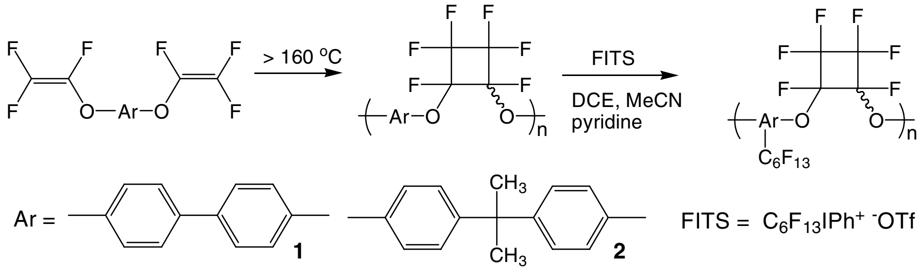
## Summary

Post functionalization of aryl ether perfluorocyclobutyl (PFCB) polymers with fluoroalkyl side chains was accomplished with Umemoto's FITS reagents. The fluoroalkylated PFCB polymers (20 % functionalized) showed increases in both hydrophobicity and oleophobicity. Static contact angle for hexadecane was increased after fluoroalkylation from 0° to greater than 30° for the two PFCB polymers tested. Increased oil repellency makes these materials potential candidates for various coatings applications.

## Introduction

Fluoropolymers find use in a variety of high tech applications due to their generally high thermal, chemical, and oxidative stability [1-3]. More specifically, amorphous fluoropolymers are gaining interest for use as core and cladding in optical fibers since they do not appreciably absorb at telecommunication wavelengths [4,5]. Perfluorocyclobutyl (PFCB) polymers are a class of amorphous fluoropolymers which find use in these optical applications [6,7], in aerospace coatings applications [8], and in battery electrolyte applications [9,10]. Such breadth in applications stems from the ease in processing allowed by PFCB chemistry. PFCB polymers are formed by the thermally induced cycloaddition of aryl trifluorovinyl ethers [11,12]. The aryl trifluorovinyl ether monomers are stable and may be synthesized from a variety of commercially available phenols [13]. Alternatively, a variety of other aryl trifluorovinyl ether monomers have been synthesized by halogen-metal exchange of 4-(trifluorovinyloxy)bromobenzene [14-18]. While this methodology has worked well for incorporating functionality into the monomer, direct post functionalization of the PFCB polymer has only recently been explored. Post functionalizing PFCB polymers with fluoroalkyl tethers [19-21] provides a relatively simple method of increasing fluorine content and provides a novel handle for tailoring polymer properties. Scheme 1 shows the polymerization and conditions for fluoroalkylation.

Perfluoroalkyl groups are incorporated into polymers in a number of ways. Commercially, fluorinated telomers are readily used in the preparation of fluorinated acrylate and methacrylate polymers [2]. These polymers are well known for their very low surface energies making them repellant to both oils and water. This makes the materials useful in a number of coatings applications within the construction and textiles industry [22] and as photoresists for IC fabrication in microelectronics [23]. The breadth and importance of these applications makes the search for new perfluoroalkyl functional polymers pertinent. Two classes of polymers which have received great attention are fluoroalkyl functional polystyrene [24] and styrene/ butadiene copolymers [25,26] and fluoroalkyl functional polythiophene [27]. With this first class of polymers, interest is in low surface energy and liquid crystalline materials, while with the polythiophenes, the fluoroalkyl tether helps segregate conductive polymer chains and improve solubility and device performance. The interesting surface properties of these materials have led us to attempt reactions of perfluorohexyl iodide with aryl trifluorovinyl ether derivatives and with perfluorocyclobutyl polymers.



**Scheme 1.** Cycloaddition of aryl trifluorovinyl ethers to perfluorocyclobutyl polymers and post functionalization with fluoroalkylating agent (FITS)

## Experimental Part

### *Materials*

4,4'-bis(4-trifluovinyloxy) biphenyl (**1**) and 2,2-bis[4-(trifluorovinyloxy)phenyl] propane (**2**) were prepared as previously described[11]. These and many other aryl trifluorovinyl ethers are commercially available from Tetramer Technologies, L.L.C. and distributed by Oakwood Chemicals, Inc. of Columbia, SC. (Perfluorohexyl) Phenyliodonium Sulfonate (**FITS**) was synthesized from *n*-perfluorohexyliodine in two steps by previously published procedures [28].

### *Instrumentation and analysis*

300 MHz $^1H$ NMR and 283 MHz $^{19}F$ NMR spectra were obtained using a JEOL ECX-300 Spectrometer. Samples were run in deuterated chloroform using TMS as internal standard for H and $CFCl_3$ for fluorine.

Gel permeation chromatography (GPC) was performed with a Waters 2695 separations module equipped with two consecutive columns (a Polymer Labs PL Gel 5 mm Mixed D and Mixed E) and a 996 UV/vis detector. Sample concentration was

1.2 mg/mL in HPLC grade chloroform. Retention times were calibrated using Polymer Labs EasiCal PS-2 polystyrene standards.

Thermal gravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 using a heating rate of 20°C/ min under nitrogen at a flow rate of 10 mL/ min. Decomposition temperature ($T_d$) is cited as the temperature of loss of 10 wt % of the sample. Differential scanning calorimetry (DSC) was performed with a TA Q1000 under nitrogen with a heating/ cooling rate of 10°C/ min. Glass transition temperatures ($T_g$) are cited as the inflection point measured on the second heating scan.

Static water and oil contact angles were measured with a Rame-Hart NRL CA 100-00 115 Goniometer. Measurements were made on thin polymer films spin cast on to glass slides using deionized water and hexadecane as oil.

### *Fluoroalkylation of* ***poly1 (poly1-(R$_f$))***

2.0 grams of 4,4'-bistrifluorovinyloxy biphenyl (**1**) was heated in a round bottom flask under nitrogen at 170°C for two days. The product was dissolved in THF and precipitated from methanol. The dried solid was dissolved and reprecipitated two more times before drying in vacuum at 120°C for 16 hours. The polymer **poly1** ($M_n$ 18 k) (0.780 g, 2 mmol **1** monomer units) was dissolved with 2.5 mL dichloroethane in a 100 mL round bottom flask. Then, 0.20 g pyridine, 2.0 mL acetonitrile, and 1.49 g **FITS** were added. The mixture was stirred at room temperature under nitrogen then heated to 82°C. Heating was maintained for 24 hours. After this, the reaction was cooled to room temperature and added to methanol to give an off-white precipitate. After precipitating, the polymer was redissolved in THF and precipitated into methanol. This was repeated and the polymer was then dried at 120°C for 24 hours in vacuum before further characterization. $^{19}$F NMR (283 MHz, $CDCl_3$) δ -80.8 (b, 3 F), -103.5 (b, 1 F), -107.8 (b, 1 F), -119.6 (b, 1 F), -120.8 (b, 1 F), -121.6 (b, 2 F), -122.8 (b, 2 F), -126.2 (b, 2 F), -127.5 to -132 (m, 40 F) ppm.

### *Fluoroalkylation of* ***poly2 (poly2-(R$_f$))***

Monomer **2** was polymerized by heating to 160°C neat under a nitrogen atmosphere for 2 days. The resultant polymer **poly2** was dissolved in THF and precipitated from methanol. After repeating this partitioning procedure two more times, the polymer was dried in a vacuum oven at 120°C for 24 hours. This resultant polymer **poly2** was fluoroalkylated with **FITS** using the same procedure as **poly1**. $^{19}$F NMR (283 MHz, $CDCl_3$) δ -80.8 (b, 3 F), -108.1 (b, 2 F), -121.2 (b, 2 F), -121.8 (b, 2 F), -122.7 (b, 2 F), -126.1 (b, 2 F), -127.5 to -132 (m, 36 F) ppm.

## Results and discussion

### *Synthesis and characterization of fluoroalkylated polymers*

Umemoto's FITS reagents provide a highly versatile method for attaching fluoroalkyl tethers to organic molecules [20]. While FITS reagents react with anionic nucleophiles with very high regioselectivity, they react with neutral aromatics by both ionic and radical pathways [29,30]. This leads to loss of regioselectivity and both

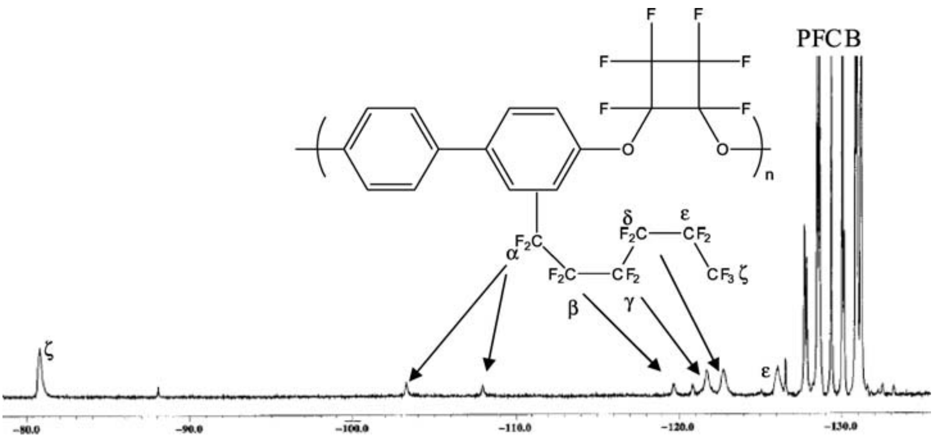


**Figure 1.** $^{19}$F NMR spectrum of fluoroalkylated **poly1 (poly-($R_f$))**

*ortho* and *meta* substitution. This may be seen by $^{19}$F NMR of **poly1-($R_f$)** (Figure 1) where the alkyl fluorines closest to the ring give different chemical shifts. Signals at -103 and -108 ppm are assigned to the fluorines alpha to the ring and the peaks at -120 and -121 ppm are assigned to the fluorines beta to the ring. The remaining signals (-122, -123, and -126 ppm) are assigned to the fluorines further from the aromatic ring. It is predicted based on inductive effects that the peak at -103 ppm is from the alpha fluorines *ortho* to the perfluorocyclobutyl oxy group indicating that *ortho* substitution is more favorable (65:35). This would be expected if the perfluorocyclobutyl oxy group is ring deactivating inductively and acts as a weak *ortho*/ *para* director by pi donation.

FITS reagent was also used to fluoroalkylate **poly2**. The $^{19}$F NMR spectrum of this product (Figure 2) shows six peaks indicating that the tether attaches exclusively to one carbon on the aromatic ring. This is likely the carbon *ortho* to the isopropylidene group since this group is a very strong *ortho*/ *para* director while the oxy PFCB group is only a weak director. The multiplets at -120 ppm, at -126 ppm (beneath the ε peak), and at -134 ppm are from the trifluorovinyl ether end groups indicating that **poly2** is much lower in molecular weight than **poly1**.

NMR may also be used to determine extent of fluoroalkylation by peak integration of the PFCB region from -127 ppm to -132 ppm and comparing with that of the fluorinated tether. This tells that only 15 % of the biphenyls of **poly1** are fluoroalkylated and that 16.7 % of the rings of **poly2** are fluoroalkylated. Although these low yields were obtained using equal molar amounts of FITS reagent and monomer repeat, this is expected due to low reactivity of fluorinated aromatics in electrophilic substitution. Higher substitution yields may be possible by running the reaction at a slightly higher temperature for a longer time. However, one likely side reaction would be the reaction of the FITS reagent either with itself or with the iodobenzene side product to give fluoroalkylated iobobenzene.

GPC of the unfunctionalized and fluoroalkylated polymers shows a slight shift in retention time. Based on polystyrene standards, this indicates an increase in molecular weight ($M_n$) from 12,300 to 14,700 for **poly1** and from 6,300 to 8,500 for **poly2** (Table 1). An increase in polydisperisity for the fluoroalkylated polymers is also detected. The decrease in retention time and the lack of any additional peaks indicate

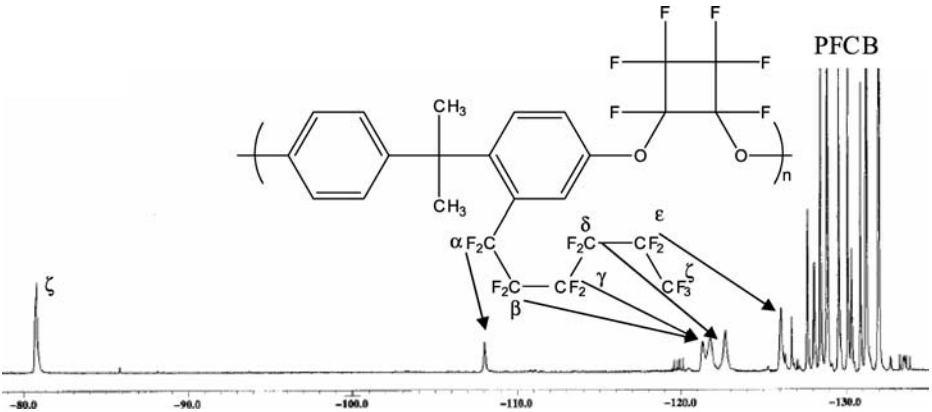


**Figure 2.** $^{19}$F NMR of fluoroalkylated **poly2 (poly-(R$_f$))**

that the fluoroalkylated tether is attached to the polymer. Assuming this, degree of functionalization may then be calculated from the increase in relative molecular weight.

$$\% \text{ functionalization} = [M_n(\textbf{poly1-(R}_\textbf{f}\textbf{)}) - M_n(\textbf{poly1})] / (\text{MW(Rf)} * \text{DP}) \qquad (\textbf{1})$$

This gives a degree of functionalization of 21.2 % for **poly1** and a % functionalization of 42.4% for **poly2**. Both of these values are higher than those calculated by NMR. This indicates that the fluoroalkyl tethers may have a greater effect on the retention time of the polymers than extension of the main chain.

**Table 1.** Polymer properties before and after fluoroalkylation

| polymer | $M_n$ | $M_w$ | PDI | % func[a] | $T_g$ (°C) | $T_d$ (°C) | θ ($H_2O$) | θ (oil) |
|---|---|---|---|---|---|---|---|---|
| poly1 | 12,300 | 36,400 | 2.97 | 0 | 150 | 500 | 83 | wets |
| poly1-($R_f$) | 14,700 | 48,300 | 3.30 | 15 | 145 | 500 | 106 | 33 |
| poly2 | 6,300 | 11,900 | 1.90 | 0 | 87 | 500 | 88 | wets |
| poly2-($R_f$ ) | 8,500 | 17,300 | 2.05 | 17 | 82 | 470 | 96 | 38 |

[a] As determined by NMR.

Thermal properties of the functionalized and unfunctionalized polymers were also measured. While thermal stability was unchanged for **poly1**, the fluoroalkylated **poly2-(R$_f$)** has a lower $T_d$. This could be from formation of HF with readily available aliphatic protons beta to the aromatic ring. Differential scanning calorimetry of the polymers was also performed. A slight decrease in $T_g$ is measured for both of the fluoroalkylated polymers. These small changes in the glass transition would be expected for the functionalized polymers if the fluoroalkyl tethers are contributing to chain mobility. These phenomena are likely to be highly dependent on degree of functionality and on heating rate.

Hydrophobicity and oleophobicity of the polymers were also tested by measuring static contact angles with both oil (hexadecane) and water (Table 1). Hydrophobicity of **poly1** and **poly2** were both increased. The static contact angle of water on **poly1** increased from 83° to 106° after fluoroalkylation. This value increased much less for **poly2** (from 88° to 96°). Oleophobicity increased dramatically after fluoroalkylation. Both of the unfunctionalized polymers were completely wetted by hexadecane. After fluoroalkylation, however, both polymers have static contact angles above 30°. These increases in oleophobicity indicate that these polymers may find use in new coatings applications.

## Conclusions

Aryl ether PFCB polymers have been fluoroalkylated with Umemoto's FITS reagents. Degree of functionaliztion for two different PFCB polymers was between 15 and 20 % molar. The low degree of functionality has a minor effect on thermal properties of the polymers. However, hydrophobicity and oleophobity are both significantly improved. The more general use of electrophilic substitutions on these aryl ether polymers is currently being explored.

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