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SUMMARY

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2. BACKGROUND.
Authors: Raymond Campos (UT-Dallas), Aleksander A. Mansur (UTD), Chloe H. Cook (UTD), Benjamin Batchelor (UTD), Scott T. Iacono, and Dennis W. Smith Jr. (UTD)

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1 Tab
Manuscript

AB-Type Monomers for the Preparation of Perfluorocycloalkene (PFCA) Aryl Ether Polymers

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Abstract

A method for the preparation of AB-type monomers with complimentary fluoro-olefin and phenol functionalities is described. The three-step process is amenable to commercial scale up and uses widely-available, commercial reagents including bisphenols and perfluorocycloalkene (PFCA) compounds. Title compounds and intermediates were characterized via multi-nuclear NMR and FT-IR spectroscopy providing structural and mechanistic elucidation of PFCA step-growth polymerizations. The formation of vinyl and allyl substituted products were quantified and shown to be dependent on PFCA ring size and reaction medium. Nearly equal amounts of vinyl- and allyl-substituted products were observed with perfluorocyclohexene (PFCH) while 2-11% allyl-substitution was observed with perfluorocyclopentene (PFCP), depending on reaction medium polarity. Previous PFCA research and characterization of title compounds suggests that fluoride-catalyzed rearrangement is primarily responsible the formation of two substitution products. Polymerization of an AB-type monomer derived from bisphenol A is demonstrated and was shown to reproducibly result in film-forming polymers with higher molecular weights than previously described methods.

Keywords

AB type monomers

perfluorocycloalkene

fluoroolefin monomers

Semi-fluorinated polymers

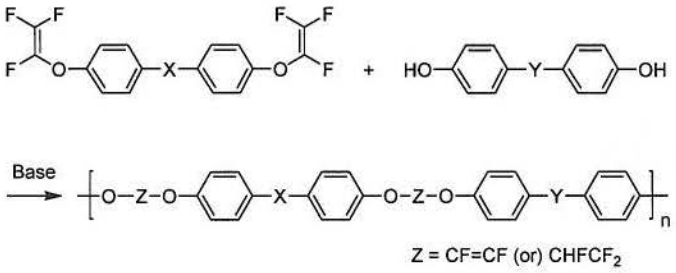
Step-growth polymerization

Nucleophilic vinylic substitution

1. Introduction

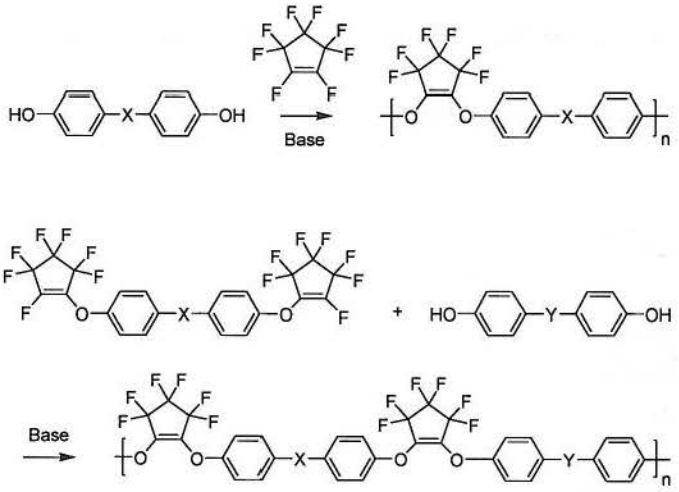
Fluorine-substituted alkenes, or fluoro-olefins, are ubiquitous as monomers in the preparation of commercially available fluoropolymers, such as those derived from tetrafluoroethylene (TFE) and vinylidene fluoride (VDF). These polymers are typically prepared via radical processes involving emulsion polymerization with fluorinated surfactants and water soluble initiators. However, significant advances have been made with the controlled polymerization of VDF homo- and co-polymers.[1] In addition to radical processes, step-growth polymers can be derived from fluoro-olefins via cyclodimerization or nucleophilic substitution. The polycyclodimerization of bis(trifluorovinyl ether) (TFVE) compounds has been widely used for the preparation of perfluorcyclobutyl (PFCB) aryl ether polymers.[2-9] The microstructure and composition of PFCB aryl ether polymers produces highly amorphous materials with ideal properties for optical lenses and electro-optic devices.[10-12] Semi-fluorinated aryl ether polymers with similar properties may also be prepared from TFVE monomers via nucleophilic vinylic substitution with bisphenoxides. A general synthesis of semi-fluorinated arylene vinylene ether (FAVE) telechelic and high molecular weight polymers is shown in **Scheme 1**.[13-15] Although FAVE polymers are more affordable than analogous PFCB polymers commercial viability is still hindered by the relatively high cost of TFVE monomers. For insight into the high cost of TFVE monomers details of their synthesis are

described and discussed herein. The future availability of the TFVE monomer precursor dibromotetrafluoroethane, an antiquated refrigerant, is also questionable.



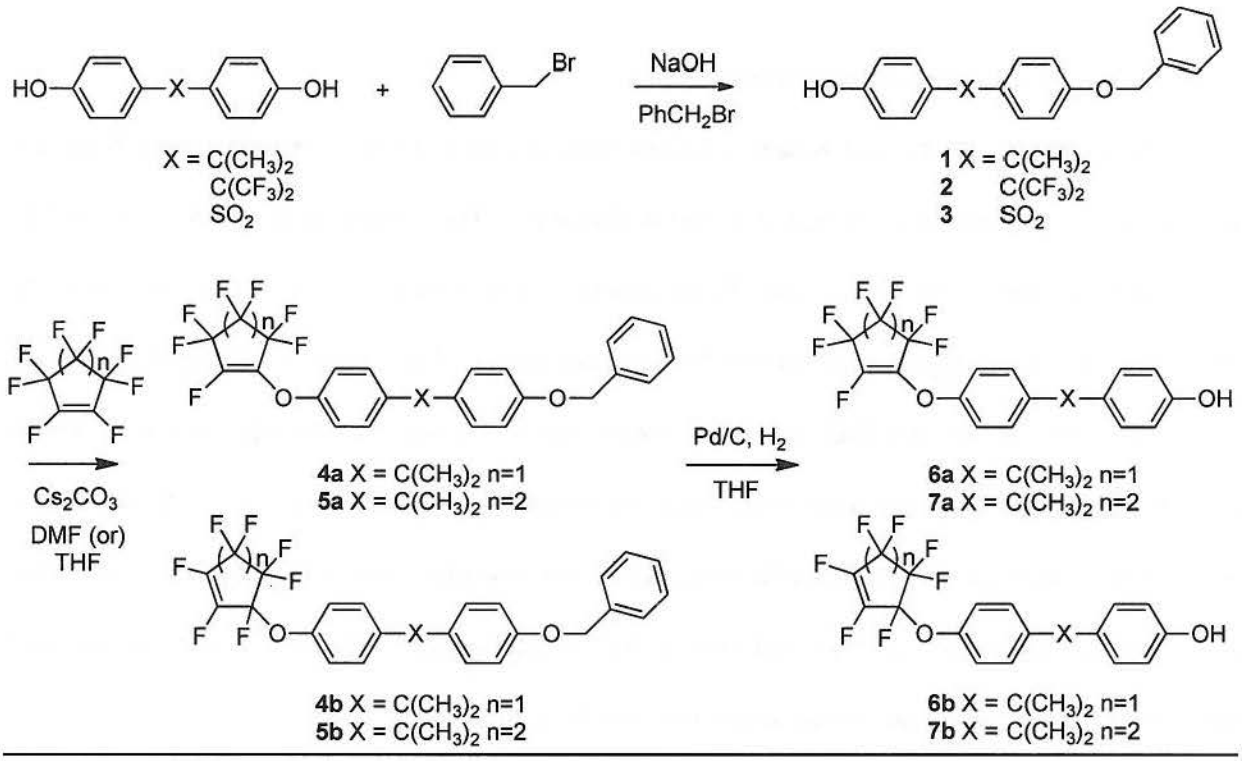
Scheme 1. Previously reported nucleophilic vinylic substitution of trifluorovinyl ether (TFVE) monomers with bisphenoxides to produce fluorinated arylene vinylene ether (FAVE) polymers.[15]

Perfluorocycloalkene (PFCA) compounds and derivatives are an alternative to TFVE-based monomers for the synthesis of semi-fluorinated aryl ether polymers. Commercially available PFCA compounds, most commonly perfluorocyclopentene (PFCP), have been used directly in polymer synthesis. PFCP does not undergo radical-mediated homopolymerization, but can be copolymerized with various aliphatic olefins with number-average molecular weights and yields as high as 12000 g mol^{-1} and 51%, respectively.[16-18] Cracowski and co-workers prepared aryl ether polymers via step-growth nucleophilic substitution of PFCP with bis(phenoxide) with maximum reported M_w/M_n and yields of 22900/9100 g mol^{-1} and 90%, respectively (**Scheme 2**, top).[19] However, molecular weight and yields reported have been difficult to reproduce, with recovered materials typically being powders comprised of cyclics and oligomers (< 5000 g mol^{-1}), or insoluble solids when increasing reaction time and temperature. A similar strategy using bis(trimethysilyl ethers) with a fluoride catalyst rather than deprotonated phenols has been reported with similar results.[20] The low boiling point, high volatility, and high toxicity[21] of PFCA compounds causes difficulty in handling and controlling stoichiometry. These factors have been attributed to challenges in reproducibly preparing high molecular weight polymers derived directly from PFCA compounds.



Scheme 2. Previously reported nucleophilic vinylic substitution of perfluorocycloalkene (PFCP) monomers with bisphenols to produce PFCP aryl ether polymers[19]

PFCA derivatives that are solids at room temperature have been prepared (**Scheme 2**, bottom) to address issues handling volatile PFCA compounds. The PFCP-derived AA-type monomer was reported to produce a similar degree of polymerization as the first method that used PFCP directly.[19] A recent report[22] that included ^{19}F NMR spectra and gas chromatograms for the monomers prepared via the route shown in **Scheme 2** (bottom) suggested that allylic substitution may be occurring, but was not quantified nor were the consequences of allylic substitution on polymerization discussed. The synthetic protocol developed and described herein provides an opportunity to quantify the vinylic and allylic substitution of PFCA compounds with phenoxides. The present research expands on emerging PFCA-derived polymeric materials through the synthesis of AB-type monomers with complementary phenol (Ar-OH) and fluoro-olefin (C_{sp2}-F) functionalities contained in a single molecule. This approach is aimed at studying new mechanistic pathways by structure elucidation in order to improve the molecular weight and reproducibility of PFCA-derived polymers.



Scheme 3. The general synthesis of AB-type monomers with complimentary perfluorocycloakene (C_{olefin}-F) and phenol functional groups.

2. Results and Discussion

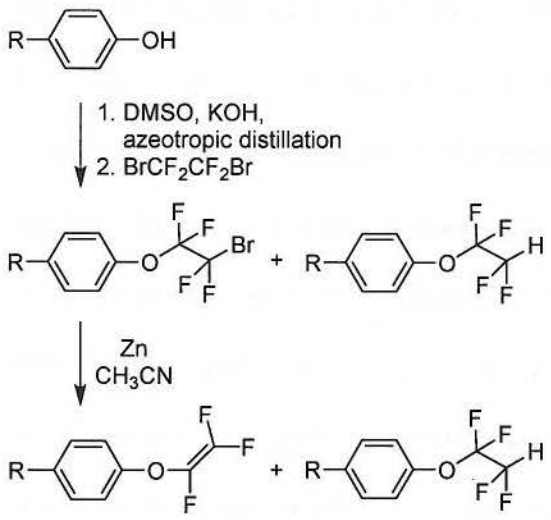
2.1 General Comments

The original aim of the current study was to improve the reproducibility and achievable molecular weight of perfluorocycloalkene-derived aryl ether polymers through the synthesis of AB-type monomers with complementary fluoro-olefin (C_{sp2}-F) and phenol moieties. The presence of these functionalities in one compound ensures the 1:1 stoichiometry needed for high conversion in a step-growth polymerization to achieve film-forming properties. The successful utilization of these AB-type monomers also enables sequential monomer addition for gradient copolymer synthesis, expanding the utility of this relatively new class of semi-fluorinated aryl ether polymer. During the work reported herein we have also gained understanding into the substitution pathways of PFCA-phenoxide step-growth polymerizations and the structure/properties of resulting polymeric materials.

2.2 AB-type Monomer Synthesis and Characterization

AB-type monomers **6a**, **6b**, **7a**, and **7b** with complimentary phenol and fluoro-olefin functionalities were prepared using the three-step process depicted in **Scheme 3**. The developed synthetic route utilizes commercially available monomers and facile reaction and purification protocols amenable to commercial scale-up. Using this scheme the AB monomer derived from bisphenol A and PFCP (**6**) was produced in a 49% overall yield. Each step of the preparation of PFCA-phenol, AB-type monomers will be subsequently described in detail with contrasting comparisons to previously developed TFVE monomers. First, it is important to note that the limiting step in the reaction scheme (step 1; 60% yield after purification for compound **1**) does not involve fluoroalkyl incorporation, which from a financial standpoint is advantageous over previously synthesized TFVE monomers.

The synthesis of TFVE compounds (**Scheme 4**) involves fluoroalkyl incorporation in the first step, with reported yields for this first step ranging from 22-98%: 22%, 85.4%, 77.9%, 98;[2] 41%, 42%;[23] 95%;[24] 50%;[4] 72%;[3] 70%;[8] 40.9%;[25]. The overall yield of TFVE monomers derived from bisphenols are reported to range from 27-55%: 54.5%;[2] 32.8%, 42.8%;[23] 60%, 81%;[7] 27%;[4] 23%[25]. The efficient preparation of TFVE monomers requires complete de-protonation and removal of produced water in the first step of synthesis (**Scheme 4**). Residual phenol and/or water results in the formation of a 2-hydrotetrafluoroethoxy phenyl compound that does not undergo Zn reduction to afford the desired TFVE moiety. The formation of this saturated side product is a manifestation of a somewhat unusual ionic chain mechanism.[26] Such compounds do not polymerize and can act as chain-terminating species when only one side of a bis(TFVE) monomer possesses a 2-hydrotetrafluoroethoxy phenyl moiety. The relatively low overall yield of TFVE monomers is attributed to the need to remove this byproduct via distillation or column chromatography and is operationally complex in comparison to the new sequence described in **Scheme 3**.



Scheme 4. General synthesis of trifluorovinyl ether (TFVE) compounds.

Mono-benzyl protection of bisphenol A (**Scheme 3**; compound **1**) was accomplished using a commonly practiced literature procedure.[27, 28] The purified yield of compound **1** was very close to that reported by Gibson *et al.*,[28] 67% and 65%, respectively. Further attempts to optimize this reaction were unsuccessful unless an excess of bisphenol A was used. The relatively low amount of the di-benzyl protected bisphenol A byproduct when using equal amounts of bisphenol A and benzyl bromide is due to the low solubility of compound **1** in water. Once formed, compound **1** precipitates and does not undergo a second substitution. This method was adopted to mono-protect two additional commercially-available bisphenol compounds: bisphenol S and bisphenol AF. The reduced nucleophilicity of bisphenoxides derived from bisphenol S and bisphenol AF required longer reaction times for complete conversion and produced lower yields for compounds **2** and **3** relative to compound **1** (See Experimental Section for details). The hydrophilic sulfone group of bisphenol S enhanced the solubility of compound **3** in water resulting in higher di-benzyl substitution, requiring purification by column chromatography and reducing the purified yield to 16%. ^{1}H and ^{13}C DEPTQ135 NMR spectra for compounds **1**-**3** are provided in the supporting information.

Mono-protected bisphenol compounds **1-3** were then used in the vinylic substitution of two PFCA compounds, perfluorocyclopentene (PFCP) and perfluorocyclohexene (PFCH). The reagents and reaction conditions are shown in the second step of **Scheme 3**. Mono-substitution was reproducibly accomplished when ≥2.5 equivalents of PFCA was reacted with one equivalent of protected bisphenol compound in the presence of 0.5 equivalents of cesium carbonate. A mixture of mono- and di-substituted products is observed if a 1:1 stoichiometry is used.[19] The low boiling point of PFCA compounds allows for facile recovery of unreacted starting material via distillation and would be amenable to a commercial process. These reactions were performed at 0° C and quenched with water after 1 h. A kinetic study of model compounds derived from phenols and PFCP suggested that complete consumption of starting materials occurred after 15 min. The complete consumption of benzyl-protected bisphenol intermediates was observed after 1 h for all reactions by thin-layer chromatography, even when using the weak nucleophiles **2** and **3**. Unfortunately, PCFA products derived from compounds **2** and **3** rapidly degraded when attempting to dry products in a vacuum oven at 40 °C. GC-MS and multi-nuclear NMR spectroscopy revealed the presence of the parent bisphenols, hydrofluoric acid, and a variety of fluoroalkanes, including the parent PFCA compounds, in the dark brown/black products that were recovered. Due to the low stability of intermediates derived from bisphenol S and bisphenol AF, and the toxic nature of their degradation products, subsequent work was focused on the synthesis and polymerization of AB-type monomers derived from bisphenol A (**4a**, **4b**, **5a**, **5b**).

The electrophilic nature of fluoro-olefins has been previously elucidated using hybridization theory using bond angles and bond lengths of $\angle$R-C_{olefin}-F and C_{olefin}-F, respectively.[29] This type of analysis reveals a significantly higher p-character for fluoro-olefin C-F groups (e.g. $sp^{2.92}$ for TFE and $sp^{3.03}$ for *cis*-difluoroethylene) compared to their sp^2 hydrocarbon analogues. Although PFCA compounds were not included in the aforementioned study, structural data for PFCP is available with a reported C_{olefin}-F

bond length of 1.311 Å and ∠R-C_{olefin}-F of 118.2°, compared to 1.098 Å and 127.2° for cyclopentene.[30] The angle strain of fluoro-olefins are typically relieved upon fluoride substitution accompanied by an increase in stabilizing s-character. Crystal structures of PFCA-phenol compounds and precursors have not been solved, but the AA-type of PFCA monomers shown in **Scheme** 2 (bottom) have been previously reported.[22] From these crystal structures we can see that upon mono-substitution of PFCP with one equivalent of phenoxide the remaining C_{olefin}-F bond extends to 1.338 Å with no change in ∠R-C_{olefin}-F. The longer C_{olefin}-F bond is attributed to substitution of the the first C_{olefin}-F with an electron-donatiing ether bond (C_{olefin}-O-Ar) alpha to the remaining C_{olefin}-F. The lack of angle strain relief after the first substitution suggests that the remaining C_{olefin}-F remains highly electrophilic. We can assume that the first substitution is faster than the second due to reduced C_{olefin}-F polarity, but further kinetic studies are needed to elucidate and are beyond the scope of the current study. Mono-substituted PFCH displays a C_{olefin}-F bond length and ∠R-C_{olefin}-F of 1.330 Å and 113.3°, respectively. The increased angle strain of PFCH relative to PFCP implies greater electrophilicity and is consistent with the following discussion of vinyl and allyl product distribution.

The product distribution obtained from the nucleophilic substitution of PFCP or PFCH with benzyl-protected bisphenol A (**1**) was determined via ^{19}F NMR spectroscopy, shown in **Figure 1** and **Figure 2**, respectively. Since the vinyl and allyl-substituted products differ in symmetry, the number of resonant signals and their integration values allowed for simplistic assignment of chemical shifts. Although every fluorine on vinyl-substituted PFCP and PFCH rings are technically chemically non-equivalent, ring puckering/chair flipping is faster than the NMR experiment time-scale[31] and results in equivalent signals for geminal fluorines. The $^3J_{FF}$ coupling of PFCA vicinal fluorines varied between 0-12 Hz as expected.[32] In contrast, the decreased symmetry of ally-substituted products caused every fluorine to be non-equivalent, displaying geminal fluorine values of $^2J_{FF}$ = 250-290 Hz, within the expected range of 220-290 Hz. From these two spectra, a clear increase in ally substitution is observed

when using PFCH compared to PFCP, 56% and 11%, respectively. Similar trends have been observed for the synthesis of small molecules derived from PFCA compounds and has been included in reviews of vinylic substitution.[33, 34] The formation of the ally product (**5b** and **6b**) produces two electrophilic sites for subsequent substitution. This analysis is consistent with previous reports[19, 35] and our observations when reacting PFCA compounds directly with bisphenoxides. When reacting PFCP directly with bisphenoxides in a 1:1 ratio fluoro-olefin end-groups are not observed and low molecular weight species (< 5000 g mol^{-1}) are typically isolated. This observation is consistent with a stoichiometric imbalance between phenoxide (Ph-O^-) and fluoro-olefin (C_{olefin}-F) moieties that results when allyl species are formed. The formation of allyl species when polymerizing also allows for crosslinking of polymer chains. When additional PFCP is added with extended reaction times and increased temperatures an insoluble solid is typically obtained, consistent with a highly branched/cross-linked material. For PFCH, increased electrophilicity and the tendency to form ally species results in mainly insoluble material. These trends reveal the need to elucidate the underlying mechanism of PFCA nucleophilic substitution and to suppress allyl product formation to promote linear polymer synthesis.

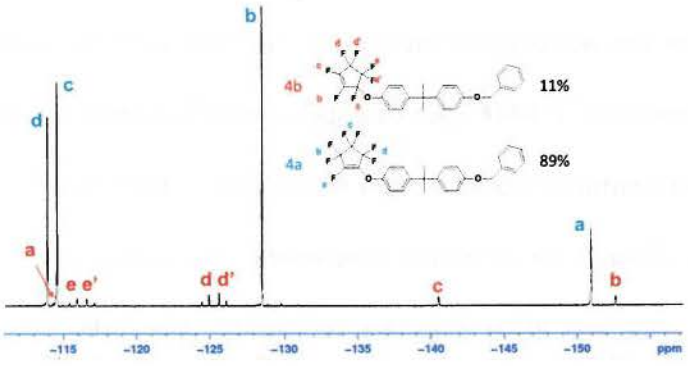


Figure 1. ^{19}F NMR spectrum of product mixture **4** in displaying the product distribution resulting from the nucleophilic substitution of PFCP with compound **1** in the presence of 0.5 equivalents of Cs_2CO_3 partially dissolved in THF.

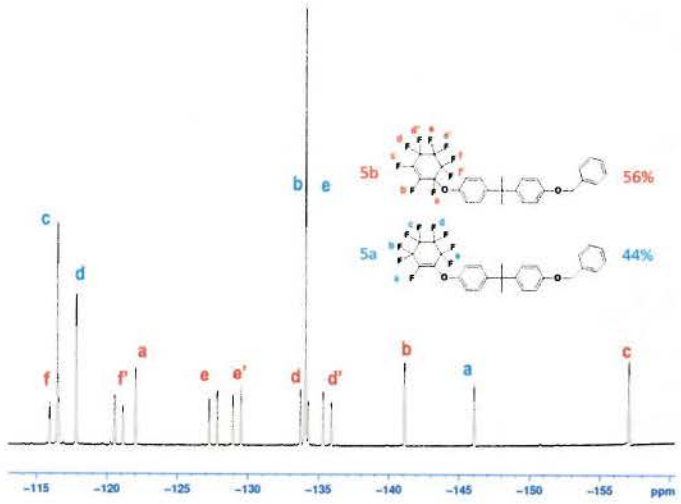


Figure 2. ^{19}F NMR spectrum of product mixture **5** displaying the product distribution resulting from the nucleophilic substitution of PFCH with compound **1** in the presence of 0.5 equivalents of Cs_2CO_3 partially dissolved in THF.

The product distribution observed from the nucleophilic vinylic substitution of TFVE compounds and other fluoro-olefins suggests the formation of a short-lived fluorocarbanion intermediate.[36] A general mechanism for the nucleophilic vinylic substitution of TFVE compounds is shown in **Figure 3** (top). An analogous mechanism for PFCA compounds is shown in **Figure 3** (bottom). Although this mechanism is widely accepted for fluoro-olefins the lack of addition products for PFCA compounds implies that the carbanion intermediate mechanism may be inadequate to fully describe the nucleophilic substitution of PFCA compounds. If assuming a carbanion intermediate, there is no clear reason why PFCH substitution would favor allylic substitution compared to PFCP. Further observations made when using different solvents points to rearrangement, rather than two different substitution pathways.

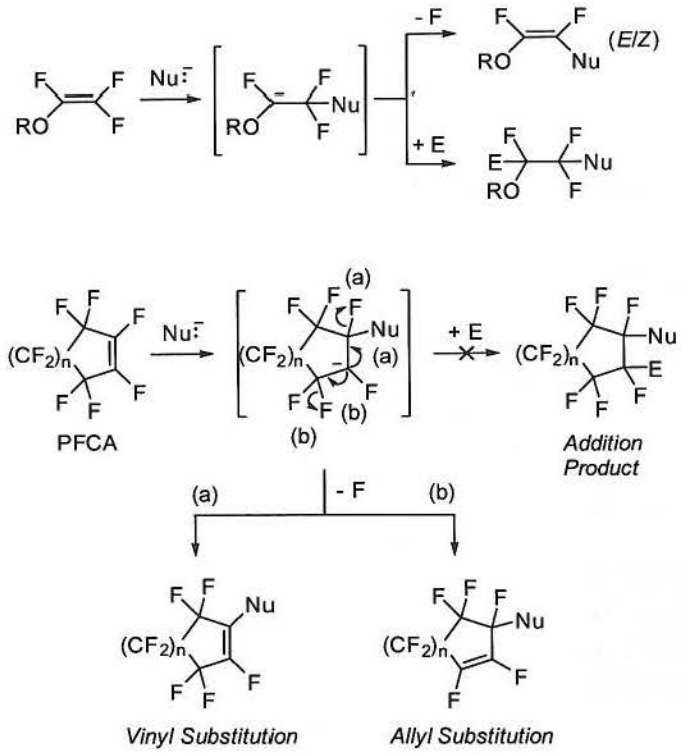


Figure 3. Previously described nucleophilic substitution pathways for (top) TFVE and (bottom) PFCA compounds.

Solvent was shown to play a role in the product distribution for the nucleophilic vinylic substitution of PFCA compounds. The ^{19}F NMR spectrum of product **4** when using THF is shown in **Figure 1** while the product when using DMF is shown in **Figure 4**. The amount of allyl product observed when using DMF ranged from 2-5 mol%, down from 11% when using THF.

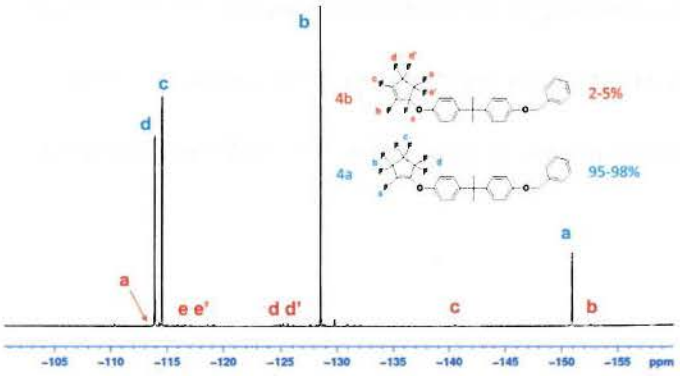


Figure 4. ^{19}F NMR spectrum of **4** displaying the product distribution resulting from the nucleophilic substitution

of PFCP with compound **1** in the presence of 0.5 equivalents of Cs_2CO_3 dissolved in DMF.

The increase in allyl substitution when using DMF instead of THF as a solvent, and using PFCH instead of PFCP, is attributed to fluoride-catalyzed rearrangement (**Figure 5**). Cesium carbonate has higher solubility in DMF than THF, increasing the availability of the fluoride scavenging Cs^{2+} ion. The more electrophilic PFCH fluoro-olefin undergoes nucleophilic rearrangement with fluoride anion faster than with PFCP. Previous reports of multiple nucleophilic substitutions (ranging 4-6) of PFCP provides additional evidence of fluoride-catalyzed rearrangement, which would not be possible with the mechanism shown in **Figure 4**.[37]

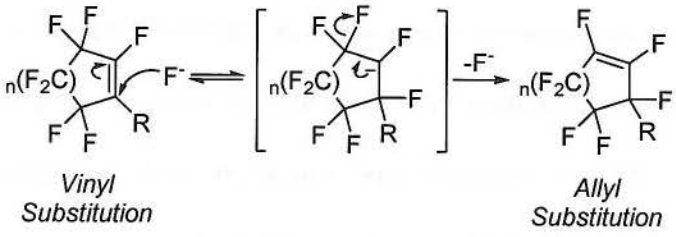


Figure 5. Proposed fluoride-catalyzed rearrangement from vinyl- to allyl-substituted product.

Palladium-catalyzed hydrogenolysis of benzyl-protected AB-type monomers was achieved in 1-2 h when using UHP-grade hydrogen at 15 psi. There was no evidence that the fluoro-olefin moiety was being reduced in these conditions. ^{1}H, ^{13}C, and ^{19}F spectra for all successfully prepared AB-type monomers and their precursors are provided in the supporting information.

2.3 Polymerization of AB-type Monomers

Step-growth polycondensation of the AB-type monomer derived from bisphenol A and PFCP (**6a**) was successful, resulting in a film-forming, fibrous solid when using ideal conditions. The reaction conditions were augmented several times before a successful polymerization was achieved (**Figure 6**). Because monomer **6a** is a viscous liquid at room temperature solvent-free conditions using DBU as a base was initially attempted. A solvent-free system is attractive for an industrial process and reduces the

formation of cyclic species. Unfortunately, the reaction system rapidly darkened and resulted in an insoluble, black solid. Based on the discussion in the previous section we attribute this to inadequate fluoride scavenging resulting in rearrangement and crosslinking, along with the formation of hydrofluoric acid. Future work using solid-supported fluoride scavengers may enable the solvent free polymerization of PFCA-phenol AB-type monomers. Polymerizations were successful when using a minimal amount (*ca.* 0.5-1 mL for 0.5 g monomer) of either THF or DMF in the presence of 0.5 equivalents of cesium carbonate. ^{1}H and ^{19}F spectra for these successful polymerizations are provided in the supplemental section. Decreased yields were observed with increasing reaction times due to branching and crosslinking after fluoride-catalyzed rearrangement. Attempts to polymerize monomer 7 under various conditions, including the same conditions used for monomer **6**, resulted in mainly sticky, yellow solids that could not be re-dissolved after precipitation in either water or methanol. These observations when using the PFCH-derived AB-type monomer are consistent with a highly branched/crosslinked material due to the tendency for allyl substitution when using PFCH.

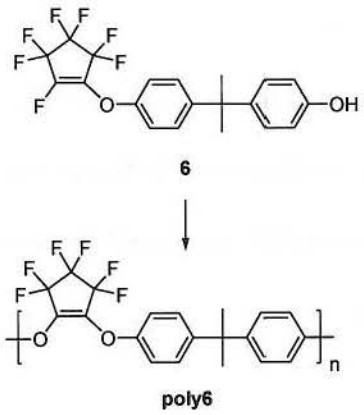


Figure 6. Polymerization of PFCP-BPA AB-type monomer (**6**) to afford PFCP aryl ether polymer (**poly6**).

The most successful reaction conditions and resultant properties are shown in **Table 1**. Decreased yields were observed with increasing reaction times due to branching and crosslinking after fluoride-catalyzed rearrangement. Optically transparent films were successfully produced in only 2

hours when using DMF as a solvent in the presence of 0.5 equivalents of Cs_2CO_3. Thermal properties were greater than or equal to previous reports using AA + BB step-growth polymerizations.

Table 1. Successful reaction conditions and properties for the polymerization of AB-type monomer **6**

Entry	Solvent	Base	Time (h)	Yield (wt%)[a]	$M_w \times 10^{-3}$ (g mol^{-1})[b]	$M_n \times 10^{-3}$ (g mol^{-1})[b]	$T_{d,10\%}$[c] (°C)	T_g[d] (°C)
Poly6	DMF	Cs_2CO_3	2	70-85	n. d.[e]	11.4[e]	375	90
Poly6	THF	Cs_2CO_3	24	20-50	50.0	20.0	435	93

[a]remained soluble after precipitation
[b]SEC in THF
[c]TGA at 10 °C/min in N_2
[d]DSC at 10 °C/min in N_2, second scan
[e]end-group analysis via ^{1}H NMR

3. Conclusions

A three-step method for preparing AB-type monomers with complimentary fluoro-olefin and phenol functional groups was described and found to be viable for the synthesis of film-forming PFCA aryl ether polymers. The synthesis of PFCA-containing AB monomers was found to be more amenable to commercial scale-up than previously described TFVE monomers. Through the synthesis of these AB-type monomers the formation of observed vinyl- and allyl-substituted products were quantified and found to be related to fluoride-catalyzed rearrangement. Allyl substitution during polymerization was attributed to polymer branching and crosslinking. Based on the research described herein guidelines for the optimization of PFCA-derived polymers via the polycondensation of fluoro-olefins and phenoxides were as follows: Suppression of fluoride-catalyzed rearrangement through efficient fluoride scavenging; short reaction times and low temperatures to reduce/prevent fluoride-catalyzed rearrangement; and the use of PFCP over PFCH for linear polymer synthesis.

4. Experimental Section

4.1 Materials

Perfluorocyclopentene (PFCP) and perfluorocyclohexene (PFCH) were purchased from Synquest Laboratories and distilled before use. 2,2-Bis(4-hydroxyphenyl)propane (bisphenol A; BPA), 4,4'-(hexafluoroisopropylidene)diphenol (bisphenol AF; BPAF), and 4,4'-sulfonyldiphenol (bisphenol S; BPS) were purchased from Alfa Aesar and recrystallized before use. Benzyl bromide was purchased from Alfa Aesar and used as received. Sodium hydroxide (NaOH), HPLC-grade tetrahydrofuran (THF), HPLC-grade ethanol (EtOH), and anhydrous methanol (MeOH) were purchased from Fisher Scientific and used as received. Dimethylformamide (DMF) purchased from Fisher Scientific was distilled and then stored over 3Å molecular sieves in a moisture-free glovebox before use. Palladium 10 wt% supported on carbon (Pd/C) was purchased from Acros Organics and used as received. Cesium carbonate purchased from Acros Organics was dried under vacuum (ca. 200 mTorr) at 120 °C and then stored in a moisture-free glove box before use. Ultra high pure (UHP-grade) hydrogen was purchased from Airgas and used as received. Deuterated solvents were purchased from Cambridge Isotopes Laboratories and used as received. $CFCl_3$ was purchased from Sigma-Aldrich and used as received.

4.2 Instrumentation and Methods

All NMR experiments were conducted on a Bruker Advance III 500 NMR spectrometer at 25 °C and referenced internally. ^{1}H and ^{13}C NMR spectra were referenced to $CHCl_3$ or DMSO, and ^{19}F spectra were referenced to $CFCl_3$. Size-exclusion chromatography (SEC) was performed using a Viscotek VE 3580 system equipped with ViscoGEL™ columns (GMHHR-M), connected to a refractive index (RI) detector. SEC calibration was relative to polystyrene standards using THF as an eluent using the following parameters: flow rate = 1.0 mL/min, injector volume = 100 µL, detector temperature = 30 °C, column temperature = 35 °C. Gas-chromatograpy tandem mass spectrometry (GC-MS) was performed using a Shimadzu QP 2010 GCMS. Melting points of intermediates and monomers were determined using a TA

Q2000 dynamic scanning calorimeter (DSC). The glass transition temperature (T_g) of polymers was also determined using the same DSC from the second heating scan, which were found not to be significantly different from a third scan. Degradation temperatures (T_d) were determined using a TA SDT Q600 thermogravimetric analysis (TGA) instrument. Attenuated total reflectance, Fourier-transform Infrared (ATR-FTIR) spectra were collected on a Shimadzu IR-Affinity 1 spectrometer.

*4.3 Synthesis of benzyl-protected bisphenol A (**1**)[27, 28]*

Bisphenol A (20 mmol, 4.566g) was added to a 250 mL round bottom flask containing NaOH aqueous solution (40 mmol, 150 mL, 1.599 g). The reactor was then equipped with a reflux condenser and brought to 80 °C in a nitrogen environment with vigorous stirring via a Teflon-coated magnetic stir bar. Once completely dissolved, benzyl bromide (20 mmol, 0.342 g) was added via syringe. The mixture was allowed to stir for 2 h at 80 °C in a nitrogen environment. After stirring was ceased, a beige precipitate settled out in a clear solution. While still hot, the supernatant was decanted and the crude product washed with water (ca. 80°C). The crude product was then dissolved in chloroform, transferred to a separatory funnel, washed w/ 10% HCl (v/v), and then washed twice with DI H_2O. The organic layer was then dried over magnesium sulfate, filtered into a tared receiver flask, and isolated under vacuum as an off-white solid. The compound was then recrystallized twice from hexanes/ethyl acetate to afford a white, crystalline solid (3.80 g, 59.7% yield, mp (DSC) = 109 °C). ATR-FTIR (neat, cm^{-1}): 3170, 3080, 3030, 2960, 2910, 2860, 1610, 1600, 1580, 1510, 1450, 1380, 1300, 1230, 1180, 1010, 827, 742, 696, 553. ^{1}H NMR (δ, ppm, 500 MHz, acetone-d_6): 1.60 (s, C(**CH_3**)$_2$, 6H), 5.08 (s, -**CH_2**Ph, 2H), 6.74 (d, 2H, $^3J_{HH}$ = 8.7 Hz), 6.91 (d, 2H, $^3J_{HH}$ = 8.8 Hz), 7.06 (d, 2H, $^3J_{HH}$ = 8.7 Hz), 7.16 (d, 2H, $^3J_{HH}$ = 8.8 Hz), 7.3-7.5 (m, 5H), 8.08 (s, OH, 1H). ^{13}C (δ, ppm, 125 MHz, DMSO-d_6): 31.3, 41.5, 69.6, 114.5, 115.1, 127.8, 127.9, 128.1, 128.2, 128.9, 137.7, 141.2, 143.6, 155.4, 155.5.

*4.4 Synthesis of benzyl-protected bisphenol AF (**2**)*

Synthesis was analogous to compound **1** with an extended reaction time of 17 h. The compound was purified by column chromatography (silica/dichloromethane, R_f = 0.4) to afford a white, crystalline solid (470 mg, 32% yield). ^{1}H NMR (δ, ppm, 500 MHz, acetone-d_6): 5.61 (s, -**CH$_2$**Ph, 2H), 7.35 (d, 2H, $^3J_{HH}$ = 8.9 Hz), 7.54 (d, 2H, $^3J_{HH}$ = 9.0 Hz), 7.67 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 7.78 (m, 3H), 7.94 (d, 2H, $^3J_{HH}$ = 7.5 Hz), 9.25 (s, OH, 1H). ^{13}C (δ, ppm, 125 MHz, acetone-d_6): 70.6, 115.3, 115.4, 116.0, 124.4, 124.6, 126.1, 126.7, 128.6, 128.8, 129.3, 132.2, 137.9, 158.9, 160.2. ^{19}F (δ, ppm, 471 MHz, acetone-d_6): -64.7.

*4.5 Synthesis of benzyl-protected bisphenol S (**3**)*

Synthesis was analogous to compound **1** with an extended reaction time of 24 h. Significant amounts of di-benzyl protected side product was produced, requiring purification by column chromatography (silica/90:10 DCM:MeOH, R_f =0.67) to afford a white, crystalline solid (215 mg, 16% yield, mp (DSC) = 92.3 °C). ATR-FTIR (neat, cm^{-1}): 3570, 3380, 3100, 3070, 3040, 2950, 2900, 2860, 2830, 1590, 1500, 1460, 1420, 1380, 1290, 1250, 1150, 1110, 1080, 1030, 1010, 845, 829, 744, 727, 702, 665, 600, 553. ^{1}H NMR (δ, ppm, 500 MHz, acetone-d_6): 5.27 (s, -**CH$_2$**Ph, 2H), 7.09 (d, 2H, $^3J_{HH}$ = 8.7 Hz), 7.25 (d, 2H, $^3J_{HH}$ = 8.9 Hz), 7.40-7.55 (m, 5H), 7.91 (d, 2H, $^3J_{HH}$ = 8.7 Hz), 7.97 (d, 2H, $^3J_{HH}$ = 8.9 Hz), 9.45 (s, OH, 1H). ^{13}C (δ, ppm, 125 MHz, acetone-d_6): 70.9, 116.2, 116.7, 128.5, 128.9, 129.3, 130.2, 130.6, 134.2, 135.8, 137.4, 162.3, 163.1.

*4.6 Synthesis of benzyl-protected bisphenol A/perfluorocyclopentene (PFCP) A-B type monomer (**4a, 4b**)*

In a 25-mL round bottom flask was added a Teflon-coated magnetic stir bar, cesium carbonate (3.14 mmol, 1.023g) and compound **1** (3.14 mmol, 1 g) dissolved in THF (ca. 3 mL). The round bottom flask was then allowed to cool in an ice bath under a dry nitrogen purge. The adapter to the nitrogen source was temporarily removed under a nitrogen blanket to introduce ≥2.5 equivalents of perfluorocyclopentene (at 0 °C) via syringe. The reaction mixture was allowed to stir at 0 °C for 1 h. After 1 h, the reaction flask was quenched with water (ca. 1 mL) and then allowed to warm to room temperature. After outgassing of excess PFCP had ceased and was allowed to dissipate in a fume hood,

the reaction mixture transferred to a seperatory funnel using aliquots of $CHCl_3$ to facilitate transfer. The reaction mixture was then washed with 10 wt% HCl and twice with DI H_2O , dried over magnesium sulfate, and isolated on a rotary evaporator/schlenk vacuum manifold to afford a white, crystalline solid (1.17 g, 89% yield, mp (DSC) = 71.6 °C (2 additional endothermic transitions centered at 38.9 °C and 56.5 °C). ATR-FTIR (neat, cm^{-1}): 3036, 2974, 2930, 2876, 1734, 1609, 1508, 1375, 1327, 1287, 1242, 1203, 1171, 1148, 1119, 1009, 980, 837, 748, 700. ^{1}H NMR (δ, ppm, 500 MHz, acetone-d_6): 1.68 (s, -C(**CH_3**)$_2$, 6H), 5.09 (s, -**CH_2**Ph, 2H), 6.95 (d, Ar-**H**, 2H, $^3J_{HH}$ = 8.8 Hz), 7.18 (d, Ar-**H**, 2H, $^3J_{HH}$ = 8.8 Hz), 7.3-7.4 (m, Ar-**H**, 7H), 7.38 (d, Ar-**H**, 2H, $^3J_{HH}$ = 8.7 Hz). ^{13}C (δ, ppm, 125 MHz, DMSO-d_6): 31.4, 42.6, 70.0, 115.2, 119.4, 128.4, 128.6, 128.7, 129.1, 129.4, 138.2, 142.9, 150.4, 151.9, 157.3. ^{19}F (δ, ppm, 471 MHz, $CDCl_3$): **4a**, -150.29 (m, C_{olefin}-**F**, 1F), -130.06 (m, **CF_2**, 2F), -116.10 (m, **CF_2**, 2F), -115.91 (m, **CF_2**, 2F); **4b**, -154.83 (m, C_{olefin}-**F**, 1F), -142.74 (m, C_{olefin}-**F**, 1F), -126.28 (dm, **CF_2**, 1F, $^2J_{FF}$ = 243 Hz), -125.42 (dm, **CF_2**, 1F, $^2J_{FF}$ = 243 Hz), -118.53 (dm, **CF_2**, 1F, $^2J_{FF}$ = 265 Hz), -116.39 (dm, **CF_2**, 1F, $^2J_{FF}$ = 265 Hz), -115.9 (CFO, 1F). GC-MS (m/z, **4a/4b** = 98.06%/1.94%): Theoretical M, M+1, M+2 = 510.14, 511.15 (29.5%), 512.15 (4.6%); Measured M, M+1, M+2 = 510.20, 511.20 (31.1%), 512.20 (5.2%)

*4.7 Synthesis of benzyl-protected bisphenol A/perfluorocyclohexene (PFCH) A-B type monomer (**5a, 5b**)*

Synthesis analogous to **6a**, **6b**. Beige, crystalline solid: 1.1 g, 83% yield. ^{1}H NMR (δ, ppm, 500 MHz, acetone-d_6): 1.62 (s, -C(**CH_3**)$_2$, 6H), 5.06 (s, -**CH_2**Ph, 2H), 6.93 (d, 2H, 8.7 Hz), 7.12 (d, 2H, 8.6 Hz), 7.2-7.5 (9H). ^{19}F (δ, ppm, 471 MHz, DMSO-d_6): **5a**, -146.10 (m, C_{olefin}-**F**, 1F), -134.12 (m, **CF_2**, 4F), -117.84 (m, **CF_2**, 2F), -116.59 (m, **CF_2**, 2F); **5b**, -157.06 (m, C_{olefin}-**F**, 1F), -141.13 (m, C_{olefin}-**F**, 1F), -135.38 (dm, **CF_2**, 1F, $^2J_{FF}$ = 288 Hz), -133.75 (dm, **CF_2**, 1F, $^2J_{FF}$ = 285 Hz), -128.98 (dm, **CF_2**, 1F, $^2J_{FF}$ = 288 Hz), -127.28 (dm, **CF_2**, 1F, $^2J_{FF}$ = 285 Hz), -122.07 (m, CFO, 1F), -120.59 (dm, **CF_2**, 1F, $^2J_{FF}$ = 298 Hz), -115.95 (dm, **CF_2**, 1F, $^2J_{FF}$ = 298 Hz).

*4.8 Synthesis of PFCP-Bisphenol A, AB-type monomer (**6a**) via hydrogenolysis of (**4a**)*

Compound **4 (0.50 g, 0.98 mmol)** was dissolved in methanol or THF (ca. 0.5 g in 5 mL) and placed in a 20 mL scintillation vial with a PTFE-coated magnetic stir bar and 10 wt% Pd/C (20 wt% Pd). The vial was

placed in a stainless steel Parr reactor and charged with 15 psi H_2. The reaction was allowed to stir in the Parr reactor for two hours at room temperature. The content was then passed through a plug of celite and isolated under vacuum to afford a viscous, yellow liquid (0.46 g, 91% yield). ^{1}H NMR (δ, ppm, 500 MHz, DMSO-d_6): 1.63 (s, -C(**CH$_3$**)$_2$, 6H), 6.71 (d, Ar-**H**, 2H, $^3J_{HH}$ = 8.6 Hz), 7.04 (d, Ar-**H**, 2H, $^3J_{HH}$ = 8.6 Hz), 7.32(d, Ar-**H**, 2H, $^3J_{HH}$ = 9.0 Hz), 7.39 (d, Ar-**H**, 2H, $^3J_{HH}$ = 9.0 Hz), 9.26 (s, **OH**, 1H). ^{13}C (δ, ppm, 125 MHz, DMSO-d_6): 31.5. 42.5, 115.7, 119.3, 128.3, 129.1, 140.9, 150.7, 151.8, 156.1. ^{19}F (δ, ppm, 471 MHz, DMSO-d_6): **6a**, -150.9 (m, C_{olefin}-**F**, 1F), -128.4 (m, **CF$_2$**, 2F), -114.5 (m, **CF$_2$**, 2F), -113.8 (m, **CF$_2$**, 2F).

*4.9 Synthesis of PFCH-Bisphenol A, AB-type monomer mixture (**7a, 7b**) via hydrogenolysis of (**5a, 5b**)*

Analogous to compound **6**. ^{1}H NMR (δ, ppm, 500 MHz, DMSO-d_6): 1.98 (s, -C(**CH$_3$**)$_2$, 6H), 7.08 (d, Ar-**H**, 2H, $^3J_{HH}$ = 10 Hz), 7.40 (m, Ar-**H**, 2H), 7.54 (m, Ar-**H**, 1H), 7.59 (m, Ar-**H**, 1H), 7.69 (m, Ar-**H**, 1H), 9.61 (s, Ph-**OH**, 1H). ^{19}F (δ, ppm, 471 MHz, DMSO-d_6): **7a**, -146.10 (m, C_{olefin}-**F**, 1F), -134.12 (m, **CF$_2$**, 4F), -117.84 (m, **CF$_2$**, 2F), -116.59 (m, **CF$_2$**, 2F); **7b**, -157.06 (m, C_{olefin}-**F**, 1F), -141.13 (m, C_{olefin}-**F**, 1F), -135.38 (dm, **CF$_2$**, 1F, $^2J_{FF}$ = 288 Hz), -133.75 (dm, **CF$_2$**, 1F, $^2J_{FF}$ = 285 Hz), -128.98 (dm, **CF$_2$**, 1F, $^2J_{FF}$ = 288 Hz), -127.28 (dm, **CF$_2$**, 1F, $^2J_{FF}$ = 285 Hz), -122.07 (m, **CF**O, 1F), -120.59 (dm, **CF$_2$**, 1F, $^2J_{FF}$ = 298 Hz), -115.95 (dm, **CF$_2$**, 1F, $^2J_{FF}$ = 298 Hz).

4.10 Polymerization of AB-type monomers

Compounds PFCP-BPA (**6**) and PFCH-BPA (**7**) were polymerized in the same manner. For example, compound **6** (0.5 g, 1.2 mmol) was dissolved in a minimal amount of dimethylformamide (0.25-0.5 mL) and placed in a 15 mL scintillation vial. A Teflon-coated magnetic stir bar and cesium carbonate (194 mg, 0.6 mmol) was then added and the mixture was allowed to stir at room temperature for 2-24 h. The polymer was precipitated in cold methanol to afford a fibrous, white solid. **Poly6**: ^{1}H NMR (δ, ppm, 500 MHz, DMSO-d_6); 1.5-1.7 (-C(**CH$_3$**)$_2$, 6H), 6.6-6.8 (Ar-**H**, 2H), 6.9-7.1 (d, Ar-**H**, 2H), 7.95-8.05 (**OH**). ^{19}F (δ, ppm, 471 MHz, DMSO-d_6); -156- -158 (C_{olefin}-**F**), -130.5- -131.0 (**CF$_2$** 2F), -115- -116 (**CF$_2$**, 4F).

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