Novel Aromatic Polymers with Pentafluorophenyl Pendent Groups

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ABSTRACT: A novel series of linear, high-molecular-weight polymers was synthesized by one-pot, superacid-catalyzed reaction of pentafluorobenzaldehyde (PFBA) (**1**) with nonactivated aromatic hydrocarbons: biphenyl, diphenyl ether, *p*-terphenyl, 4,4′-diphenoxybenzophenone, and 1,3-bis- and 1,4-bis(4′-phenoxybenzoyl)benzenes. The reactions were performed at room temperature in the Brønsted superacid trifluoromethanesulfonic acid (CF_3SO_3H, TFSA) and in a mixture of TFSA with methylene chloride. The polymer-forming reaction was highly dependent upon the acidity of the reaction medium, as judged from the molecular weights of the polymers obtained. A possible reaction mechanism is suggested. The polymers obtained were soluble in the common organic solvents, and flexible transparent films could be cast from the solutions. ^{1}H and ^{13}C NMR analyses of the polymers synthesized revealed their linear structure. The pendent pentafluorophenyl groups react regioselectively with nucleophiles under basic conditions in polar, aprotic solvents. Side-chain-type sulfonated polymers were obtained from reaction with sodium 4-hydroxybenzenesulfonate.

1. Introduction

The incorporation of fluorine atoms into polymer chains is a very efficient method to increase polymer solubility and chemical resistance, thermal stability and glass transition temperatures (T_g's).

At the same time, fluoropolymers possess low surface energy and refractive index, decreased color, crystallinity, dielectric constants and moisture absorption. Because of these advantages, many types of fluorine-containing aromatic polymers have received ever increasing attention over the past 20 years.[1−9]

However, preparation of fluoro-containing monomers for polymer syntheses still remains a serious problem. Most of the monomers are very expensive, and few of them are commercially available. Simple, reliable syntheses of aromatic fluoro-containing polymers would therefore be of great value.

Recently, we found that condensations of carbonyl compounds containing electron-withdrawing substituents, adjacent or relatively close to the carbonyl group, with nonactivated aromatic hydrocarbons, carried out in a TFSA (or in a mixture of TFSA with methylene chloride) medium at room temperature, afford linear, high-molecular-weight polymers.[10−14]

Taking into account the strong electron-withdrawing effect of the fluorine atom, fluorinated aldehydes and ketones present a promising challenge for the one-pot synthesis of fluorinated aromatic polymers.

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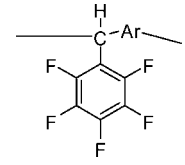
The aim of the present work was to synthesize and characterize new fluorinated aromatic polymers with the following chemical compositions:



where H−Ar−H are biphenyl (**a**), diphenyl ether (**b**), *p*-terphenyl (**c**), 4,4′-diphenoxybenzophenone (**d**), 1,3-bis(4′-phenoxybenzoyl)benzene (**e**), and 1,4-bis(4′-phenoxybenzoyl)-benzene (**f**).

The synthetic approach to these materials involved superacid catalyzed polycondensation of PFBA with aromatic hydrocarbons. Spectral data, solubility, and the thermal properties have been determined and are discussed in relationship to chemical structure.

2. Experimental Part

2.1. Materials. PFBA, biphenyl, *p*-terphenyl, diphenyl ether, TFSA, trifluoroacetic acid (TFA) and methylene chloride were obtained from Aldrich. TFSA was distilled under vacuum prior to use. The aromatic hydrocarbons 4,4′-diphenoxybenzophenone and 1,3- and 1,4-bis(4-phenoxybenzoyl)benzenes were prepared according to published methods[15] and purified by recrystallization from a benzene−ethanol (1:3, v/v) mixture and *N*-methylpyrrolidinone (NMP), respectively.

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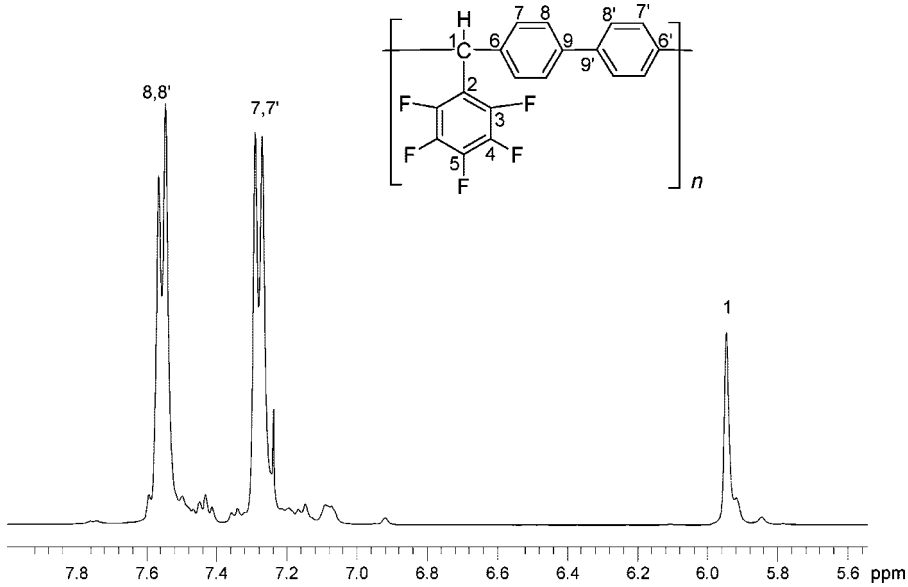


Figure 1. ^{1}H NMR spectrum of polymer **1a** (solution in $CDCl_3$).

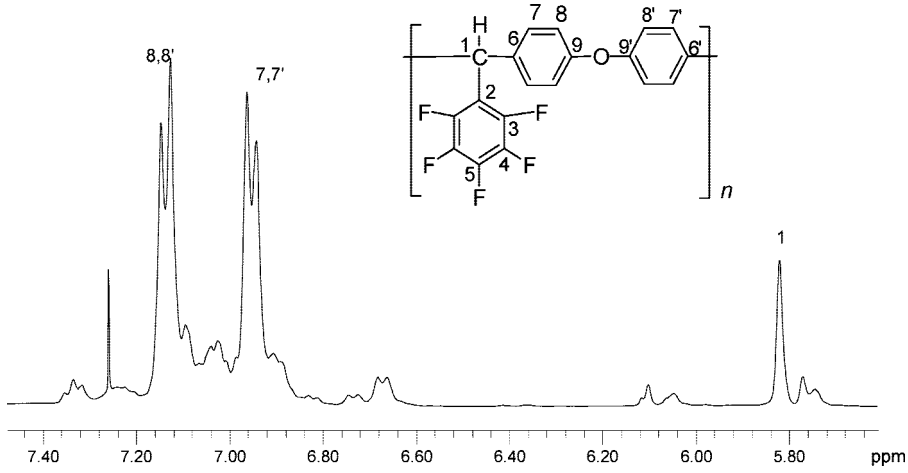


Figure 2. ^{1}H NMR spectrum of polymer **1b.**

2.2. Characterization. NMR spectra were recorded on Bruker Avance 400 Spectrometer, operating at 400.13 and 100 MHz for ^{1}H and ^{13}C respectively. Chloroform-*d* ($CDCl_3$) was used as a solvent. Infrared (IR) spectra were measured on a Perkin-Elmer FT-IR-ATR spectrometrer. The inherent viscosities of 0.2% polymer solutions in 1-methyl-2-pyrrolidinone (NMP) were measured at 25 °C using an Ubbelohde viscometer. Molecular weights were determined by gel permeation chromatography (GPC). The chromatography system was equipped with three Waters styragel columns and measurements were made at 40 °C with THF as the solvent at a flow rate of 1.0 mL/min. The SEC-MALS measurements were performed at 25 °C using a separation system comprising two size-exclusion columns, a Waters HSPgel HR MB-L and a HR MB-B with a range from 5×10^2 to 7×10^5 and from 1×10^3 to 4×10^6 respectively, connected in series. The chromatography system was a Water Alliance 2695, equipped with a 100 μL sample loop and flow rate of the mobile phase was 0.5 mL·min^{-1}; the polymer concentration in tetrahydrofuran solution was 2.5 mL·min^{-1}, the light scattering photometer was a Dawn Eos multiangle light scattering (MALS) instrument (Wyatt Technology, Santa Barbara, CA). Simultaneous concentration detection was performed using an Optilab REX interferometric refractometer (Wyatt Technology, Santa Barbara, CA). Both detectors used a wavelength of 690 nm. The angular dependence of the scattered light was extrapolated to zero angle using the linear Berry fit method. The dn/dc of polymers was determined using a solution with a concentration that ranged from 0.1×10^{-3} to 1.0×10^{-3}. The data acquisition was carried out with ASTRA software version 5.1.7.3 (Wyatt Technologies Corp.). Thermogravimetric analyses (TGA) were carried out in air and under nitrogen at a heating rate of 10 °C/min on a DuPont 951 Thermogravimetric Analyzer. The T_g was evaluated by differential scanning calorimetry (DSC) measured at 10 °C/min on DuPont 910.

2.3. Polymer Synthesis. *Preparation of* **1a**. The polymer synthesis was conducted in a single-necked 10 mL flask equipped with magnetic stirrer. PFBA (0.588 g, 3 mmol), biphenyl (0.462 g, 3 mmol), TFSA (3 mL) and methylene chloride (2.2 mL) were stirred at room temperature for 30 h and the resulting viscous green dispersion was then poured into methanol. The white solid was then filtered off and washed copiously with methanol. The final product was dried at room temperature for 24 h and then dried for 3 h at 90 °C in an oven. The resulting polymer was poured into chloroform (10% w/v), and the insoluble, swelled particles were filtered off. White fibrous polymer **1a** (0.836 g, 79% yield) with an inherent viscosity (η_{inh}) of 0.10 dL g^{-1} (NMP) was obtained after precipitation of soluble fraction in methanol, filtration and drying.

Preparation of **1b**. A 10 mL three-neck flask equipped with a mechanical stirrer and a nitrogen inlet was charged with PFBA (0.529 g, 2.7 mmol), diphenyl ether (0.459 g, 2.7 mmol), methylene chloride (2.4 mL) and TFA (1 mL). The solution was cooled to −20 °C, and TFSA (0.6 mL) was added in one portion to the

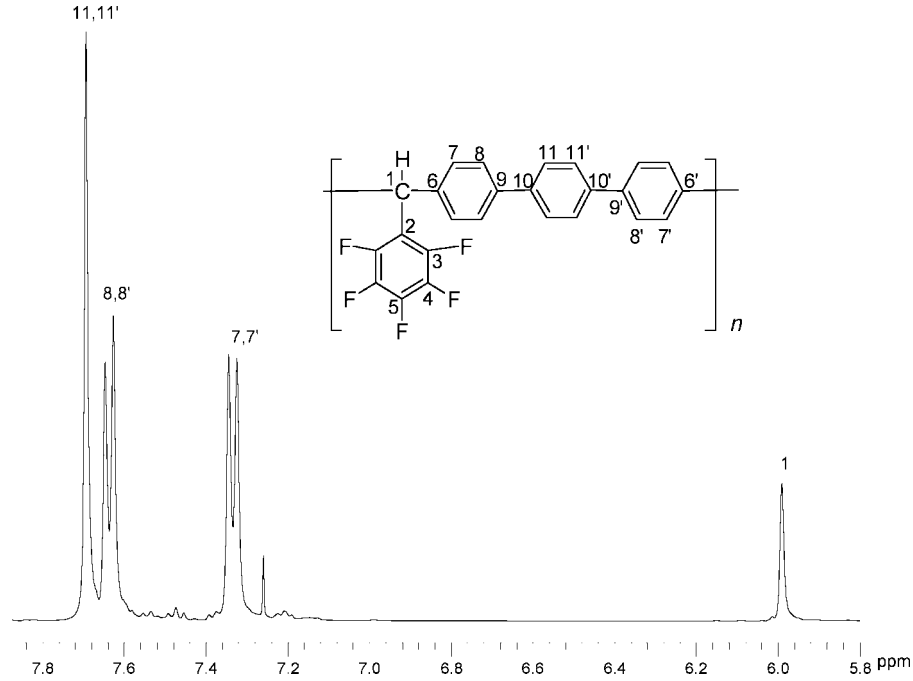


Figure 3. [1]H NMR spectrum of polymer **1c.**

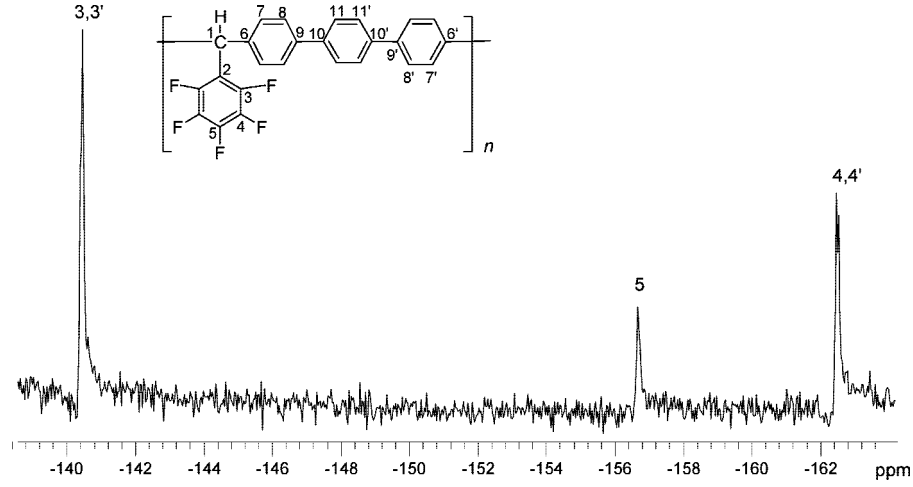


Figure 4. [19]F NMR spectrum of polymer **1c.**

solution and the reaction mixture was stirred for 30 min. Thereafter, the temperature was raised to 20 °C over 2 h and reaction was continued at this temperature for 6 h. The resulting dark-red viscous solution was then poured slowly into methanol. The precipitated, white solid was filtered, extracted with refluxing methanol and dried in air overnight. After separation of gel-fraction and reprecipitation, the final product was dried at room temperature for 24 h. The air-dried product was heated at 100 °C overnight under vacuum to give polymer **1b** (0.578 g, 58% yield). The inherent viscosity of the polymer, measured in NMP at 25 °C., was 0.23 dL g^{-1}.

Preparation of **1c**. PFBA (0.529 g, 2.7 mmol), *p*-terphenyl (0.621 g, 2.7 mmol), TFSA (0.3 mL) and methylene chloride (3.7 mL) were stirred for 23 h at room temperature. The resulting green solution was then poured slowly into methanol. The precipitated, pale white solid was filtered off and extracted with refluxing methanol for 12 h. The final product was dried at room temperature for 24 h and then oven-dried for 3 h. The resulting pure white fibrous polymer **1c** (1.082 g, 94% yield) had an inherent viscosity (η_{inh}) of 0.43 dL g^{-1} (NMP).

Preparation of **1d**. PFBA (0.529 g, 2.7 mmol), 4,4′-diphenoxybenzophenone (0.988 g, 2.7 mmol), TFSA (2.4 mL) and methylene chloride (1.6 mL) were stirred at room temperature for 35 min.

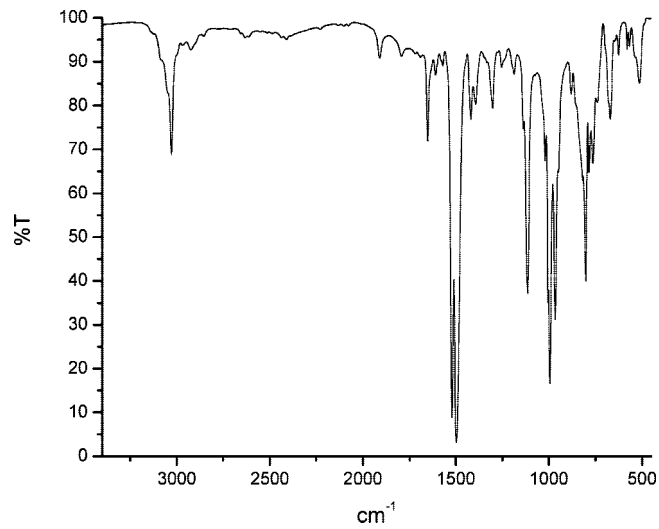


Figure 5. IR spectra of polymer **1c** (film).

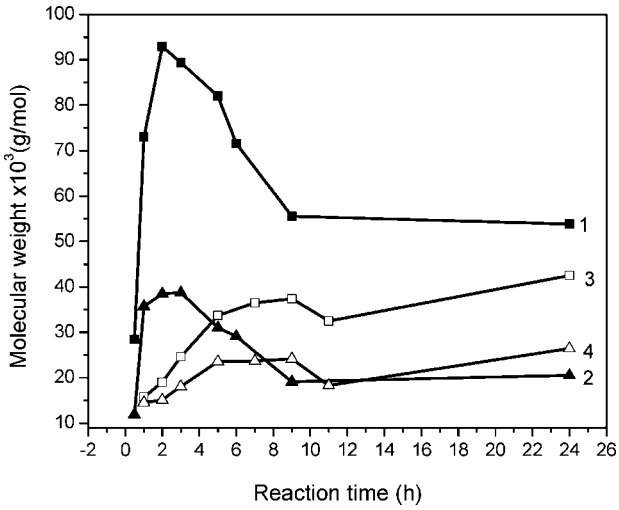


Figure 6. Dependence of the polymer molecular weights on reaction time. (1, 2) Molecular weights (M_w and M_n) of polymer **1c** obtained at a ratio TFSA/PFBA = 2.09 (mol/mol). (3, 4) Molecular weights (M_w and M_n) of the polymer **1c** obtained at a ratio TFSA/PFBA = 1.24 (mol/mol).

The resulting viscous orange solution was then poured into methanol. The precipitated, pale white solid was filtered off and extracted with refluxing methanol for 12 h. The final product was dried at room temperature for 24 h and then in an oven. The resulting pure white polymer **1d** (1.485 g, 98% yield) had an inherent viscosity (η_{inh}) of 0.62 dL g^{-1} (NMP).

Preparation of **1e**. To a 10 mL flask were added PFBA (0.529 g, 2.7 mmol), 1,3-bis(4-phenoxybenzoyl)benzene (1.26 g, 2.7 mmol), TFSA (3 mL), and methylene chloride (1 mL); the mixture was stirred for 3 h. The resulting orange solution was then poured into methanol. The precipitated, pale white solid was filtered off and extracted with refluxing methanol. The final product was dried at room temperature for 24 h and then in an oven. The resulting pure white polymer **1e** (1.711 g, 96% yield) had an inherent viscosity (η_{inh}) of 0.16 dL g^{-1} (NMP).

Preparation of **1f**. PFBA (0.529 g, 2.7 mmol), 1,4-bis(4-phenoxybenzoyl)benzene (1.247 g, 2.7 mmol), TFSA (0.6 mL), TFA (2.9 mL), and methylene chloride (1.1 mL) were stirred for 1.5 h. The resulting orange mixture was then poured into methanol. The precipitated, white solid was filtered off and extracted with refluxing methanol. The final product was dried at room temperature and then in an oven. The resulting pure white polymer **1f** (1.708 g, 96% yield) had an inherent viscosity (η_{inh}) of 0.31 dL g^{-1} (NMP).

Preparation of **1c-2**. Polymer preparation was carried out in a three-necked flask of 25 mL equipped with a Dean−Stark trap. In a typical synthesis, a mixture of polymer **1c** (0.200 g, 0.49 mmol), phenol (0.046 g, 0.49 mmol), potassium carbonate (0.085 g, 0.612 mmol), *N*,*N*′-dimethylacetamide (4 mL), and toluene (2 mL) was stirred at 120 °C for 2 h 30 min. The resulting yellow solution was precipitated in methanol. The white fibrous product was filtered off, washed with methanol and dried to give an overall yield of 0.216 g (90%). The polymer had an inherent viscosity (η_{inh}) of 0.32 dL g^{-1} (NMP).

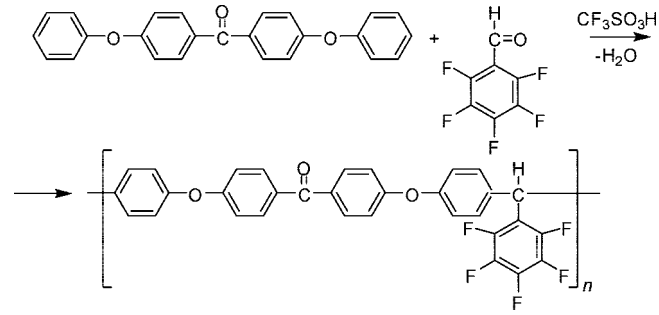
Preparation of **1c-3**. Polymer preparation was carried out in a three-necked flask of 25 mL equipped with a Dean−Stark trap. In a typical synthesis, a mixture of polymer **1c** (0.3 g, 0.733 mmol), sodium 4-hydroxybenzenesulfonate dihydrate (0.0425 g, 0.183 mmol), potassium carbonate (0.032 g, 0.229 mmol), N,N′-dimethylacetamide (6 mL) and toluene (3 mL) was stirred at 120 °C for 3 h. The resulting yellow solution was precipitated in water. The polymer formed was filtered off, washed with water and dried to give an overall yield of 0.302 g (91%). The polymer had an inherent viscosity (η_{inh}) of 0.48 dL g^{-1} (NMP).

3. Results and Discussion

3.1. Polymer Synthesis. The acid-catalyzed reaction of benzaldehyde with benzene has been known since 1886.[16] Under highly acidic conditions (for example, 2 equiv of $AlCl_3$, at 60 °C) benzaldehyde reacts with benzene to give a complex mixture of triphenylmethane, diphenylmethane, triphenylmethanol and anthracene with generally low yields.[17] Recent studies of the reaction have revealed that under superacid conditions (in TFSA) benzaldehyde reacts with benzene at room temperature. The reaction was completed in 30 h to give a 90% yield.[18] A reaction temperature of 50 °C gave a mixture of diphenylmethane and triphenylmethanol from decomposition of the initially formed triphenylmethane.[19]

Benzaldehydes bearing electron-withdrawing groups were shown to react smoothly with benzene in the presence of a superacid to give substituted triphenylmethanes in high yields.[20]

Our preliminary results have shown that the stirring of an equimolar mixture of PFBA with 4,4′-diphenoxybenzophenone in a TFSA medium at room temperature affords a soluble, linear, polymer:[14]



In the present study, we utilized this finding to access a variety of novel polymers derived from PFBA and various bi- and polynuclei aromatic hydrocarbons, such as biphenyl, diphenyl ether, *p*-terphenyl, 4,4′-diphenoxybenzophenone and bis(4′-phenoxybenzoyl)benzenes. This monomer selection allows for the estimation of the scope of the reaction and preparation of new polymers.

Generally, biphenyl is considered to be a monomer of low reactivity for Friedel−Crafts polymerizations. However, recently we have found that in superacid-catalyzed polyhydroxyalkylation biphenyl reacts with such compounds as acenaphthequinone to give high-molecular-weight products.[11]

Condensation of biphenyl with PFBA performed in a mixture of methylene chloride with TFSA proceeds as a precipitation polycondensation, i.e., the polymer formed precipitates from the initially homogeneous solution. It is well-known that, depending on the physical state of the precipitate (i.e., if it is a swelling gel or a compact mass), a polymer-forming reaction may or may not produce a precipitate).

The precipitates formed during the course of polycondensation that involve PFBA and biphenyl appears as a colored elastic particles. After completion of the reactions, the precipitates formed are isolated from the reaction medium, shredded, washed thoroughly with methanol, and air-dried overnight. The polymer thus obtained was partially soluble in chloroform. After filtration through cotton filter, the sol-fraction was poured into methanol. Yield of the dried polymer was 79%.

Surprisingly, the ^{1}H and ^{13}C NMR spectra of the polymer (Figure 1) shows mostly para-substituted phenylene fragments in the main chain. (There are, however, side structures giving rise to multiplets at 7.44, 7.16 and 7.08 ppm, and broadening of the singlet at 5.92 ppm.)

Even more surprisingly, the M_w and M_n of the polymer were found to be 95150 and 26490 g/mol, respectively. However,

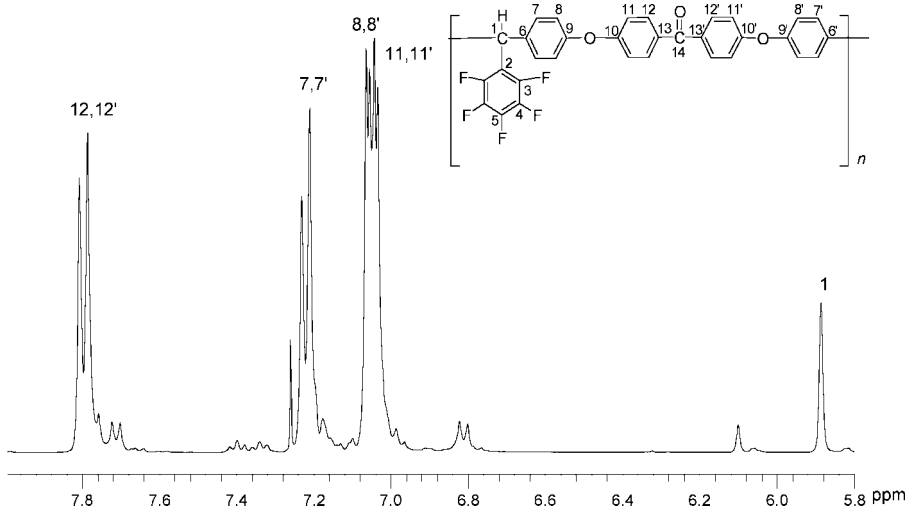


Figure 7. [1]H NMR spectrum of polymer **1d.**

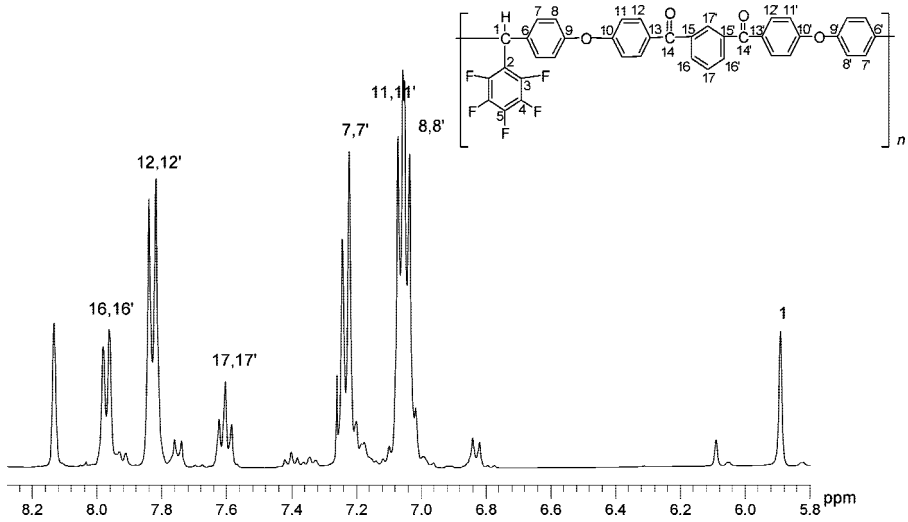


Figure 8. [1]H NMR spectrum of polymer **1e.**

broad polydispersity of 3.592 reveals nonhomogeneity of the reaction products.

Although reproducibility of the preparation of polymer **1a** was not good, one may expect that optimization of the reaction conditions would allow for more selective polymer-forming reaction.

Diphenyl ether is known to be a highly reactive nucleophile in the reaction of electrophilic aromatic substitution to give diacyl derivatives. It is very likely that, because of high reactivity, condensations of diphenyl ether with PFBA in the presence of TFSA were uncontrolled and gave mostly cross-linked products.

The [1]H NMR spectrum of the soluble fraction of polymer **1b** shows broad multiplets resulting from defect structures.

Molecular weights of the sol-fraction (M_w and M_n) are 65300 and 16700 g/mol.

Condensations of PFBA with *p*-terphenyl were much more successful. Completely soluble, high-molecular-weight polymers were obtained after several hours of reaction.(Figure 2)(Figure 3)

The [1]H NMR spectrum of the polymer (Figure 3) is well resolved and all the signals relating to *p*-terphenylene fragment are evident. The spectra [13]C NMR and [19]F NMR of the polymer (Figure 4) are also confirm linear structure with para-substituted terphenylene fragments and pentafluorophenyl side groups.

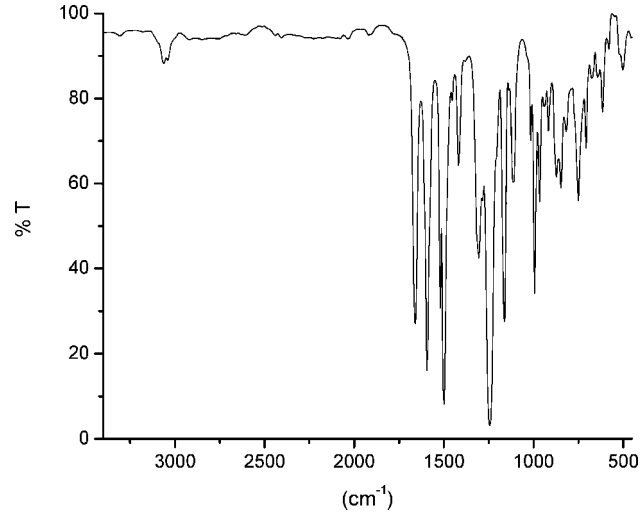


Figure 9. IR spectra of polymer **1c** (film).

The high-resolution IR spectra of polymer **1c** revealed the expected presence of the set of bands typical for aromatic hydrocarbons (Figure 5).

Scheme 1. Formation of Transition States for the Reaction of Benzaldehyde and PFBA with Benzene (Reactions 1 and 2, Respectively) and Corresponding Retro-Electrophilic Substitution Reactions for *ipso* Protonated Models (Reactions 3 and 4)

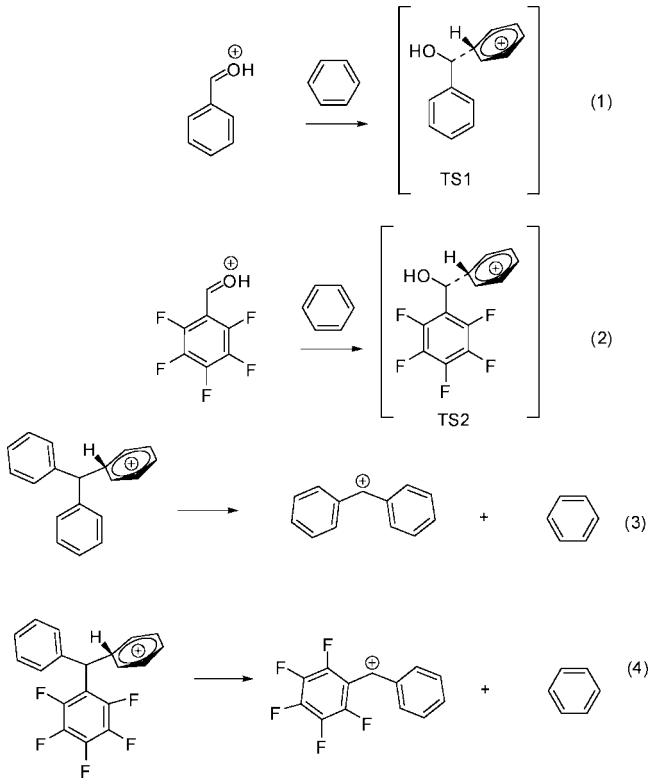


Table 1. Solubility of the Polymers[a]

solvent[b]	polymer **1a**−**1f**					
	a	**b**	**c**	**d**	**e**	**f**
methylene chloride	+	+	+	+	+	+
dichloroethane	+	+	+	+	+	+
chloroform	+	+	+	+	+	+
H_2SO_4	−	−	−	+	+	+
DMFA	+	+	+↑↓	+	+	+
NMP	+	+	+	+	+	+
DMSO	−	+↑↓	±	±	±	
DMAA	+	+	+	+	+	+
THF	+	+	+	+	+	+
dioxane	+	+	+	+	+	+

[a] Key: (+) soluble at room temperature; (±) swells; (+↑↓) soluble on heating and precipitate on cooling; (−) insoluble. [b] DMFA = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide, DMAA = *N*,*N*-dimethylacetamide, THF = tetrahydrofuran.

Bands at 1492 and 1516 cm^{-1} correspond to conjugated C═C bonds of phenylene fragments and band at 3027 cm^{-1} correspond to valence vibration of C−H groups.

The polymer-forming reaction was found to be greatly dependent upon the acidity of the reaction medium, as judged from the molecular weights of the polymers obtained. Increase of the amount of TFSA causes rapid molecular-weight growth. However, significant decomposition of the polymer chains can be observed in 3−4 h of the reaction. Thus, dependence of the molecular weights on the amounts of TFSA (Figure 6) clearly indicates the presence of side reactions leading to the decomposition of the main chain.

It is well-known that triphenylmethane in the presence of TFSA may produce various products as a result of disproportionation.[21] It is very likely that a similar process takes place in the synthesis of polymer **1c** (see Mechanistic Aspects, below).

Despite these side reactions it is obvious that synthesis of polymer **1c** performed during 3−5 h allows for the preparation of high-molecular-weight linear polymers with polydispersity ca. 2.

Exploratory reactions of PFBA with monomers **1d**−**1f** were carried out in pure TFSA. However, a mixture of methylene chloride with TFSA was found to be a more convenient (and cheaper) reaction medium. Thus, stirring PFBA with 4,4′-diphenoxybenzophenone in mixture of TFSA with methylene chloride (60:40, v/v) gave in 30 min a polymer of very high molecular weight (M_w = 391400 g/mol, M_n = 187300 g/mol).

Analysis of the ^1H and ^{13}C NMR spectra of polymer in $CDCl_3$ solution confirmed the anticipated structure of polymer **1d**. There are, however, small signals: doublets at 7.72 and 7.68 ppm, multiplet at 7.36 and singlet at 6.08 ppm, which possibly relate to ortho-substituted isomer structures (Figure 7).

1,3-Bis(4′-phenoxybenzoyl)benzene (**e**) and 1,4-bis(4′-phenoxybenzoyl)benzene (**f**) are known to be less reactive than 4,4′-diphenoxybenzophenone in electrophilic substitution reactions. Therefore, condensations of PFBA with these monomers were performed under more acidic conditions in a mixture of TFSA with methylene chloride (75: 25, v/v). Completely soluble, film-forming polymers **1e** and **1f** were obtained. Molecular weights M_w and M_n were found to be 75740 and 20430 g/mol and 109300 and 20200 g/mol, respectively. Somewhat surprisingly, polydispersities of the polymers are broad. (Figure 7).

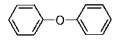
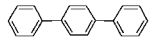
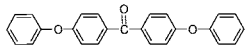
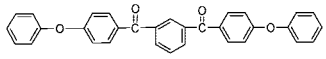
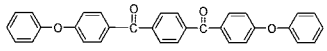
Similar to polymer **1d**, the NMR spectra of the polymers **1e** and **1f** shows the signals corresponding to defect structures (Figure 8). One can estimate that the amount of the defect structures is ca. 5−8%.

In the IR spectrum (Figure 9), the characteristic peaks of the aryl ether ketone fragment were observed at 1657 cm^{-1} (carbonyl), two peaks at 1590 and 1497 cm^{-1} (−C═C−); and the peak of ether bond was also observed at 1240 cm^{-1}.

3.2. Mechanistic Aspects. The formation of high-molecular-weight polymers from PFBA is related to the increase of reactivity of the ketone component by the introduction of electron withdrawing groups. It has been shown earlier[22] that the introduction of the electron withdrawing substituents reduces the activation energy of σ-complex formation due to lowering of LUMO energy. The calculation of the free Gibbs activation energy of σ-complex formation (transition states TS1 and TS2) for the model reactions between protonated PFBA and benzene versus benzaldehyde and benzene, using a theoretical model[23] that allows a mean error of 1−2 kcal/mol, gave 25.1 and 31.4 kcal/mol, respectively (Scheme 1). The formation of σ-complex is the rate-determining step in the aromatic electrophilic substitution reaction, and therefore the reduction of the free activation energy for the σ-complex formation in case of PFBA compared to benzaldehyde can explain the formation of high-molecular-weight polymer.

On the other hand, it is known that triphenylmethane decomposes in the presence of TFSA with C−C bond cleavage.[21] This process could be responsible for the destruction of the polymer chain after the polymerization has been completed. We estimated the free Gibbs activation energies of the retro electrophilic substitution reaction for *ipso*-protonated model compounds (Scheme 1) triphenylmethane and (pentafluorphenyl)diphenylmethane. The calculation show that the free Gibbs activation energy for this type of dissociation for triphenylmethane is only 0.8 kcal/mol, whereas for (pentafluorophenyl)-diphenylmethane it is 5.5 kcal/mol. These results reveal that PFBA not only shows higher polymerization rates due to lower activation energy of the rate-determining step compared to benzaldehyde, but polymers based on PFBA are more stable to the superacid degradation, which facilitates formation of higher-molecular-weight polymers.

Table 2. Inherent Viscosity, Molecular Weights, Glass Transition Temperature, and Decomposition Temperature in Air and Nitrogen Determined for the Polymers Reported in This Work

Polymer code	H-Ar-H	η^a (dL/g)	M_n (g/mol)	M_w (g/mol)	T_g (°C)	$T_d{}^b$ (°C)	
						Air	Nitrogen
1a		0.10	26490	95150	253	502	459
1b		0.23	18700	56340	166	460	440
1c		0.43	16190	50760	321	477	470
1d		0.62	187300	391400	171	534	450
1e		0.16	20430	75740	161	556	462
1f		0.31	20200	109300	172	537	453

[a] Inherent viscosity measured in 1-methyl-2-pyrrolidone (NMP) at 25 °C. [b] Decomposition temperature in air and nitrogen, TGA onset of mass loss.

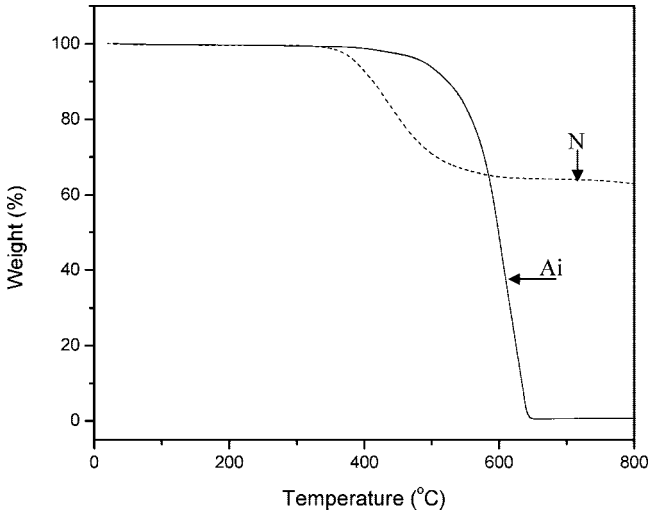


Figure 10. TGA traces (10 °C/min in N_2 and air) of polymer **1f**.

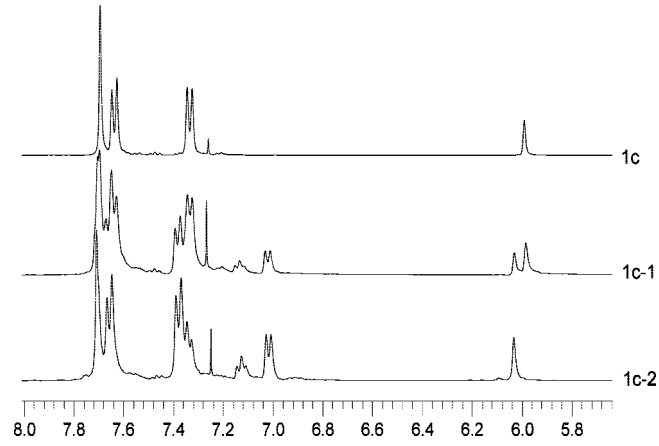
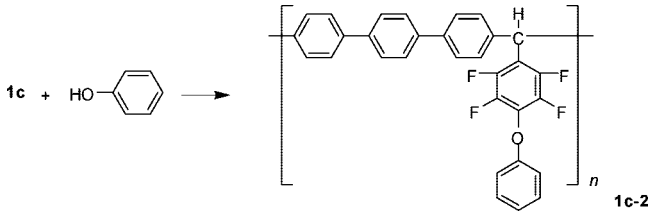


Figure 11. ^{1}H NMR spectra of polymer **1c** and its phenoxy derivatives. Polymer **1c-1** was obtained from the reaction with 40% mol phenol. Polymer **1c-2** was obtained from the reaction with 100% mol phenol.

Scheme 2. Reaction of Polymer 1c with Phenol



3.3. Polymer Properties. It was stated above that the polymers obtained present the appearance of white fiber-like powders after separation from the reaction media followed by washing and drying. All polymers obtained were completely soluble in selected organic solvents (Table 1). As can be seen from Table 1, the majority of the polymers obtained possess good solubility in chlorinated and aprotic solvents and cyclic ethers. Interestingly, polymers with high aromatic content (**1a** and **1c**) are insoluble in sulfuric acid. Polymers are insoluble in alcohols, aromatic hydrocarbons, or ethers. Transparent, strong, flexible films could be cast from the polymer solutions.

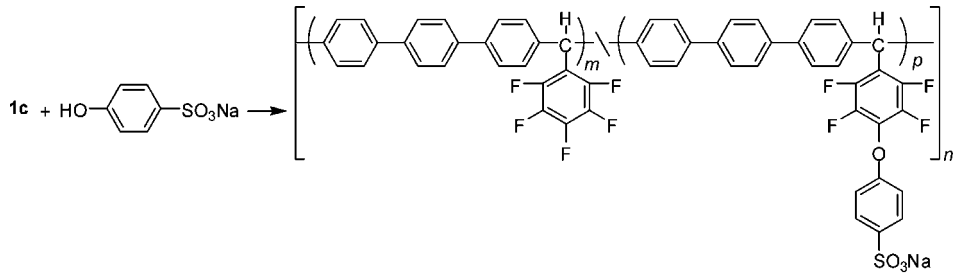
Some properties of the polymers are presented in Table 2. Most of the polymers synthesized possess high values of molecular weight DSC analysis of the polymers revealed glass transitions ranging from 166 to 321 °C. Interestingly, T_g values for polymers **1d-1f** containing etherketone fragments are generally very similar to those of aromatic polyketones without side groups.

The thermal properties of the polymers were investigated by TGA analysis. The results are given in Table 2 and Figure 10.

All of the polymers synthesized exhibited a similar TGA pattern with no significant weight loss below 400 °C both in air and in nitrogen atmosphere. Decomposition temperatures in air are generally higher than those in nitrogen. Possibly, the reason for this seemingly higher thermostability is oxidation of triphenylmethane moieties.

3.4. Polymer Substitution. Nucleophilic aromatic substitution reactions of aryl fluorides, widely used in polymer chemistry, are known to be nearly quantitative, as evidenced by the synthesis of aromatic polyethers.[24] Basically, strong electron-

Scheme 3. Reaction of Polymer 1c with Sodium 4-Hydroxybenzenesulfonate



1c-3

withdrawing groups such as carbonyl-, trifluoromethyl-, sulfonyl- or nitrogen-containing heterocycles connected to aryl fluoride are necessary to facilitate the reaction. Perfluorinated aromatic hydrocarbons (for example, hexafluorobenzene or decafluoro-1,1′-biphenyl) also react with bisphenols under basic conditions in polar, aprotic solvents.[25−30]

Therefore, we have tested the polymers obtained in nucleophilic aromatic substitution reactions. The model study was conducted to determine reactivity of polymer **1c** in reaction with phenol. The substitution reaction (DMAA, toluene, 120 °C, 3 h) was found to be quantitative, which demonstrates the high reactivity of the pentafluorophenyl group (Scheme 2)(Figure 11).

It is important that the degree of substitution can be easily controlled by the amount of phenol.

The substitution reaction was monitored by ^{1}H NMR spectroscopy. The spectra (Figure 11) clearly indicate disappearance of resonances of initial polymer **1c** and appearance of resonances of the modified polymers (**1c**-**1** and **1c**-**2**). These spectra also show that the nucleophilic aromatic substitution occurred only at the C^5 carbon.

Similar to the reaction of polymer **1c**, phenoxy-derivatives were also obtained from the reactions of polymers **1d-1e** with phenol. In general, the properties of modified polymers are similar to initial ones. Phenoxy-substituted polymers possess good solubility and flexible films can be prepared by casting. Polymer substitution does not affect thermal stability of the polymers. However, T_g of phenoxy-substituted polymers is decreased. Thus, decrease of T_g for polymer **1c** from 321 to 291 °C (50% substitution) and to 264 °C (100% substitution) was observed. For the polymers with etherketones fragments changes in T_g with the extent of chemical modifications are less pronounced. For example, for polymer **1e** T_g of the initial polymer and its phenoxy-derivatives (50 and 100%) are 161, 156 and 154 °C, respectively.

Having obtained successfully a phenoxy-derivative, we reacted polymer **1c** with sodium 4-hydroxybenzenesulfonate. It seemed plausible that this reaction would lead to a side-chain sulfonated polymer where the hydrophilic sulfonic group is separated from the hydrophobic main chain. It is believed that the existence of hydrophobic chain between the sulfonic acid groups and polymer main chain favors the nanophase separation in sulfonate polymer, which will suppress the effect of water sorption on the hydrophobic polymer main chain and thereby improve hydrolytic stability of the ionomer. This is important for the application of sulfonated polymers as a proton exchange membranes in a proton exchange membrane fuel cell (PEMFC).

The reaction of polymer **1c** with sodium 4-hydroxybenzenesulfonate proceeded very smoothly to give the expected sulfonated polymer **1c-3**. (Scheme 3).

The degree of sulfonation was controlled by the amount of sodium 4-hydroxybenzenesulfonate used. The polymer recovery was nearly quantitative. No swelling in water was observed in modified polymers with degrees of sulfonation (p) up to 70 mol %.

The viscosity values and T_g of the resulting sulfonated polymers are increased. Thus, viscosity of polymer **1c** with 25 and 50% substitution were found to be (η_{inh}) = 0.48 and 56 dL g^{-1} (NMP), respectively. Polymer **1c** with 50% substitution exhibited T_g of 368 °CC.

Although polymer substitution reactions were carried out only with phenol and sodium 4-hydroxybenzenesulfonate, one can predict that polymers **1a**−**1f** would also react with other nucleophiles, such as amines (e.g., butylamine, octylamine, diethylamine, piperidine), or substituted phenols and alcohols.

4. Conclusions

A series of novel wholly aromatic high-molecular-weight polymers with pendent pentafluorophenyl groups was readily obtained for the first time by superacid catalyzed condensation of PFBA with nonactivated aromatic hydrocarbons. The reactions were performed at room temperature in the Brønsted superacid CF_3SO_3H and in a mixture of TFSA with methylene chloride. Most of the polymers thus obtained were *para*-connected linear structures, as confirmed by NMR spectroscopy. The weight-average and number-average molar masses of the polymers determined by gel permeation chromatography and multiangle laser light scattering ranged from 50760 to 391400, and from 26490 to 187300 g/mol, respectively.

The polymers obtained were reacted quantitatively with phenol and sodium 4-hydroxybenzenesulfonate to give side-chain-type sulfonated ionomers. The sulfonate content of the copolymers can be readily controlled by adjusting the reaction ratio of polymer to nucleophilic agent. Remarkably, that these highly reactive polymers (**1a**−**f**) are obtained in one step using commercially available monomers.

It is to be noted that although the superacid catalyzed reactions were carried out only with several hydrocarbons, it is evident that a large variety of aromatics can react with PFBA to give polymers. PFBA can be also used as a coupling agent for different aromatic blocks. Cheaper, more readily available monomers and the promising properties of polymers that might be obtained from them would stimulate interest in that field.

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