A Novel, One-Pot Synthesis of Novel 3F, 5F, and 8F Aromatic Polymers

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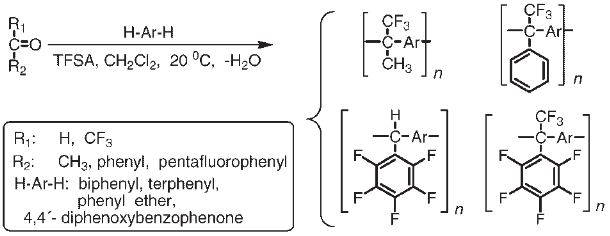
A series of novel, linear, soluble, high-molecular-weight, fluorinated aromatic polymers has been obtained for the first time using a superacid-catalyzed polyhydroxyalkylation reaction of fluorinated carbonyl-containing compounds: 1,1,1,-trifluoroacetone (**1**), 2,2,2-trifluoroacetophenone (**2**), 2,3,4,5,6,-pentafluorobenzaldehyde (**3**), and octafluoroacetophenone (**4**) with aromatic hydrocarbons such as biphenyl (**a**), phenyl ether (**b**), terphenyl (**c**), and 4,4′-diphenoxybenzophenone (**d**). These Friedel-Crafts-type aromatic electrophilic substitution reactions are performed at room temperature in trifluoromethane sulfonic acid or in its mixtures with dichloromethane. The polymers obtained are soluble in common organic solvents, and colorless transparent films could be cast from the solutions. ^1H and ^{13}C NMR analyses of the polymers synthesized reveal their linear, highly regular structure. The polymers also possess high thermostability.



Introduction

Over the past 20 years aromatic fluorine-containing polymers have received ever increasing attention because of their unique properties and high-temperature performance. The incorporation of fluorine atoms (or groups that contain fluorine atoms) into macromolecules leads to polymers with increased solubility, glass transition temperatures, thermal stability, and chemical resistance, while also leading to decreased moisture absorption, dielectric constant, and color.[1] In more recent years such aromatic fluorine-containing polymers have also been explored for applications in gas-separation membranes.[2]

Generally, there are two principal methods by which fluorine is incorporated into polymer matrices. The first one is polymerization of the monomers that contain fluorine or CF_3- groups as substituents in aromatic nuclei. The second one is polymerizations in which monomers contain hexafluoroisopropylidene (6F) or 1,1,1-trifluoro-2, 2,2-triphenylethane (3F) fragments. (A combination of these two methods is also possible.) It is worth noting the recently developed synthesis of polymers that contain perfluorocyclobutane groups by the thermal cyclopolymerization of aryl trifluorovinyl ethers.[3] In all cases,

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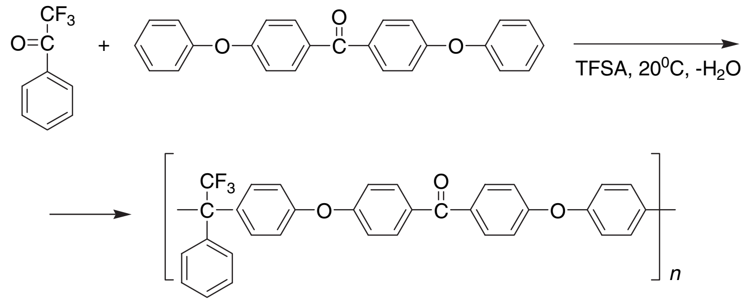
DOI: 10.1002/marc.200600656



Scheme 1.

however, fluoro-containing monomers for polymer preparations are very expensive, and few of them are commercially available.

Clearly, simple, reliable syntheses of aromatic fluorine-containing polymers would be of great importance.

Recently, we found that acetophenone does not react with 4,4′-diphenoxybenzophenone in the presence of trifluoromethane sulfonic acid (TFSA), while 2,2,2-trifluoroacetophenone does so.[4] Stirring of an equimolar mixture of 2,2,2-trifluoroacetophenone with 4, 4-diphenoxybenzophenone in a TFSA medium at room temperature for 10 h gives a linear, soluble, film-forming polymer of inherent viscosity 0.28 dL · g^{-1} (0.2% solution in N-methylpyrrolidone (NMP), 25 °C) (Scheme 1).

The aim of the present work is to utilize this finding and devise a flexible, one-step preparation of a family of novel aromatic fluoro-containing polymers. The synthetic approach to these materials involves a superacid-catalyzed polyhydroxyalkylation reaction of fluorinated aldehydes and ketones (compounds **1**–**4**, Figure 1) with non-activated aromatic hydrocarbons, such as biphenyl (**a**), phenyl ether (**b**), fluorene (**c**), terphenyl (**d**), and 4,4′-diphenoxybenzophenone (**e**) according to Scheme 2. The structures of the polymers obtained, their synthesis, and their general properties are reported.

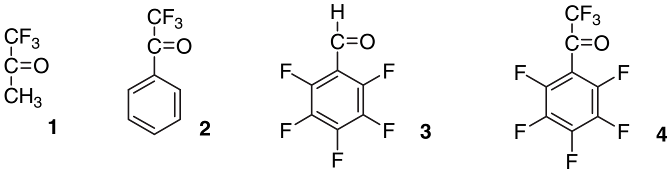
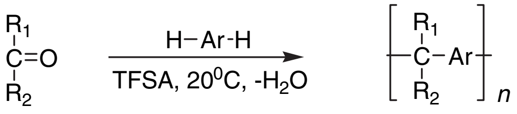


Figure 1. Structure of compounds **1**–**4**.



R_1: H, CF_3
R_2: CH_3, phenyl, perfluorophenyl
H–Ar–H: aromatic hydrocarbons.

Scheme 2.

Results and Discussion

The acid-catalyzed condensation (or hydroxyalkylation) of ketones and aldehydes with benzenes has been known since 1872.[5] Interestingly, despite a long history and intensive research of the hydroxymethylation of phenols with formaldehyde, the hydroxyalkylation reactions involving non-activated aromatics have not been used for the preparation of linear polymers. It is believed that this Friedel-Crafts-type reaction proceeds by formation of carboxonium intermediates. In studies of superacid systems, Olah et al. found that the electrophilic solvation (or protosolvation) of electrophiles such as onium, carboxonium, and related ions involves their further interaction with Lewis or Brønsted acids to give extremely reactive species.[6] Apart from that, the reactivity (electrophilicity) of the carboxonium ion can also be increased by the presence of electron-withdrawing substituent, adjacent or relatively close to a carbocation center.[7]

Taking into account the strong electron-withdrawing effect of the fluorine atom, one can expect that fluorinated aldehydes and ketones would react with non-activated aromatic hydrocarbons under superacid conditions to yield high-molecular-weight polymers.

Exploratory reactions were first carried out by treating aromatic hydrocarbons with equimolar quantities of fluorinated compounds in TFSA at room temperature. However, satisfactory results were obtained only from the reactions involving diphenoxybenzophenone. It is likely that the protonation of polynuclear aromatics (such as biphenyl, terphenyl and fluorene) in strong TFSA decreases their nucleophilicity and prohibits an electrophilic substitution reaction.[8] Attention was, therefore, turned to the syntheses in mixtures of TFSA with dichloromethane. Interestingly, reactions in that mixture proceeded as ‘precipitation polycondensations’, when the polymer formed precipitates from the initially homogeneous solution. It is generally accepted that premature polymer formation in polycondensation syntheses prevents further macromolecular chain growth reactions. However, it has been found that under certain conditions polymer-forming reactions can occur in the precipitate, i.e., after phase separation, to yield high-molecular-weight polymers.[9–11] The precipitates formed during the course of polymerizations that involve fluorinated carbonyl compounds and biphenyl, terphenyl, and fluorene appear as a colored elastic mass (‘reactive gel’). After completion of the reaction, the precipitates formed are isolated from the reaction medium, shredded, and washed thoroughly with methanol and dried overnight in air. After reprecipitation from chloroform into methanol followed by filtration and washing, white fibrous polymers are extracted with

DOI: 10.1002/marc.200600656

refluxing methanol before drying at 100 °C under vacuum. Yields of the polymers obtained are close to quantitative. (It should be noted that all the polymerizations were carried out under non-optimized conditions.)

The high solubility of the polymers allowed reliable spectroscopic studies to delineate their structure. Analysis of the ^{1}H and ^{13}C NMR spectra of polymers in $CDCl_3$ solution has confirmed the anticipated structure of the polymers obtained. The ^{1}H NMR spectrum of polymers **1a** and **4d** are given in Figure 2. The spectra are well resolved, and the aromatic resonances anticipated for methyl and biphenylene (top) and diphenoxybenzophenone (bottom) are all evident. It is worth mentioning that all the polymerizations were carried out using aldehydes and ketones 'as received', without any purification.

In a further exploration of the scope of the polymer-forming reactions of fluorinated carbonyl compounds with aromatic hydrocarbons catalyzed by superacids, calculations have been carried out of the mechanism of the elemental steps of the C–C forming reaction in superelectrophilic polycondensation.

Although polymerizations of carbonyl compounds have been carried out only with hydrocarbons **a**–**d**, it is obvious that a variety of aromatic compounds can be used in these reactions. Remarkably, high-molecular-weight products are obtained even from the reactions that involve biphenyl, which is unusual for the Friedel-Crafts polymerizations.

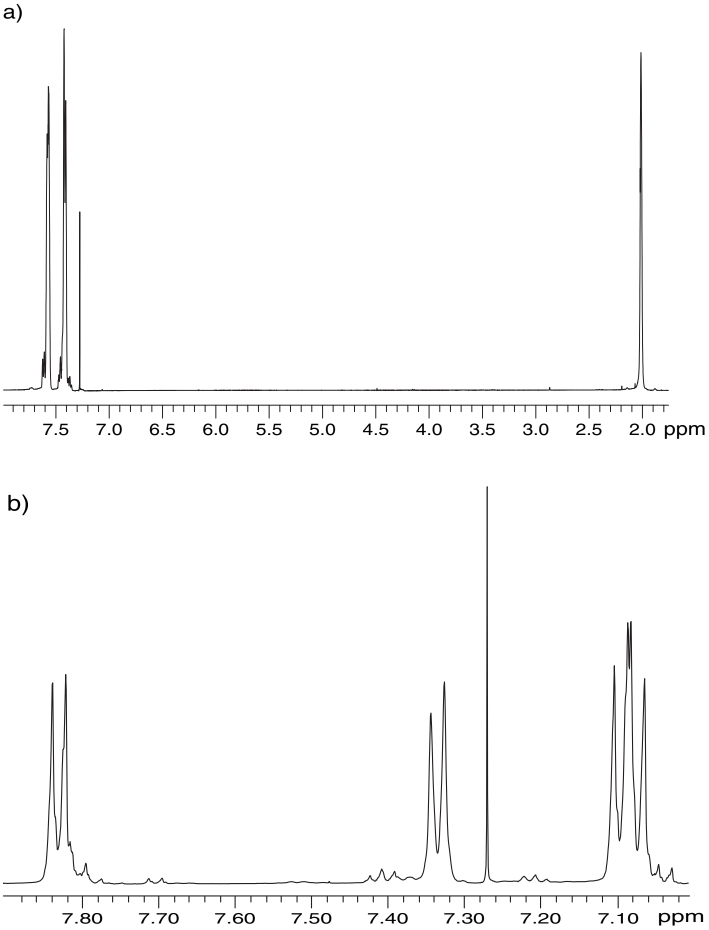


Figure 2. ^{1}H NMR spectra of polymers **1a** (a) and **4d** (b) in $CDCl_3$. Singlets at 7.27 ppm come from residual $CHCl_3$.

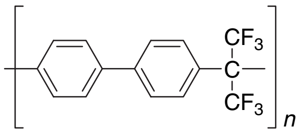


Figure 3. A 6F-analog of polymer **1a**.

The polymers obtained present the appearance, after separation from the reaction media followed by washing and drying, of white fibrous powders that are fully soluble in chlorinated and aprotic solvents. The polymers are not soluble in alcohols, aromatic hydrocarbons, or ethers. Transparent, flexible colorless films could be cast from the polymer solutions. Some properties of the polymers are presented in Table 1.

The polymers synthesized possess high values of molecular weight. Differential scanning calorimetry (DSC) analysis of the polymers reveals glass transition temperatures (T_gs) that range from 155 to 326 °C, and the absence of heat transitions for polymer **2c** up to 400 °C. The thermogravimetic analysis (TGA) onset is in the range of 440 to 530 °C.

Surprisingly, the polymers based on 1,1,1,-trifluoroacetone and aromatic hydrocarbons posses a very high thermostability. It should be noted that TGA of a 6F-analog of polymer **1a** (Figure 3) showed 5% weight loss values at 515 °C for both nitrogen and air.[12]

One may expect that the polymers also have exceptional light and chemical resistance in addition to low surface energy and low water absorption. Obviously, the combination of these properties is of great interest for potential use of the polymers in the area of membrane separation processes, microelectronics, and high-performance functional polymer-based materials.

It is also important that, according to characterization data, some of the polymers (in particular those based on 1,1,1,-trifluoroacetone and 2,2,2-trifluoroacetophenone) are promising candidates for high T_g amorphous engineering plastics.

Conclusion

The application of a superacid-catalyzed polyhydroxyalkylation reaction for the preparation of 3F, 5F, and 8F

Table 1. Characterization of the polymers.

Polymer code	$\overline{M}_{\mathrm{w}}$	$\overline{M}_{\mathrm{n}}$	T_{g}	Dec. temp in N_2 (TGA onset)
	$g \cdot mol^{-1}$	$g \cdot mol^{-1}$	°C	°C
1a	38 200	17 400	280	527
1e	45 290	15 550	155	517
2a	128 600	47 360	326	503
2b	63 900	31 040	216	498
2c	249 500	107 900	>400	472
3a	65 550	12 890	230	480
4d	22 630	15 850	180	444

aromatic polymers is demonstrated for the first time. These Friedel-Crafts-type aromatic electrophilic substitution reactions of fluorinated aldehydes and ketones with non-activated aromatic hydrocarbons proceed selectively at room temperature in TFSA and its mixtures with dichloromethane to give linear, high-molecular-weight polymers.

All the polymers exhibit excellent solubility and high thermal stability. The strong, flexible, and colorless films are easily obtained by solution casting.

The simple, practical, metal-free, one-pot reactions of fluorinated aldehydes and ketones with non-activated aromatic hydrocarbons open up wide possibilities for constructing new fluorinated aromatic polymers using commercially available monomers.

Experimental Part

Materials

1,1,1,-Trifluoroacetone (**1**), 2,2,2-trifluoroacetophenone (**2**), 2,3,4,5,6,-pentafluorobenzaldehyde (**3**), octafluoroacetophenone (**4**), 2,2,2-trifluoroacetophenone, biphenyl, diphenyl ether, and terphenyl were used as received from Aldrich. 1,4-Diphenoxybenzophenone was prepared according to published methods[10,13] and purified by recrystallization from a benzene/ethanol 20/80 (v/v) mixture. TFSA was obtained from Aldrich and distilled prior to use.

Characterization

The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 spectrometer, operating at 400.13 and 100 MHz for ^{1}H and ^{13}C, respectively. TGA was carried out in air and under nitrogen at a heating rate of 10 °C · min^{-1} on a TGA 2950 thermogravimetric analyzer, TA Instruments. DSC measurements were performed at 20 °C · min^{-1} on a DSC 2910 TA Instruments. The SEC-MALS measurements were performed at 25 °C using a separation system that consisted of 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 Waters Alliance 2695, equipped with a 100 μL sample loop, and the flow rate of the mobile phase was 0.5 mL · min^{-1}. The polymer concentration in tetrahydrofuran solution was 2.5 mg · mL^{-1}. The light scattering photometer was a DAWN EOS multi-angle light scattering (MALS) instrument (Wyatt Technology, Santa Barbara, CA, USA). Simultaneous concentration detection was performed using an Optilab REX interferometric refractometer (Wyatt Technology, Santa Barbara, CA, USA). 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 six solutions with a concentration that ranged from 0.5×10^{-3} to 8×10^{-3}. The data acquisition was carried out with ASTRA software version 5.1.7.3 (Wyatt Technologies Corp.).

Polymer Synthesis

Preparation of **1a**

A typical polymer synthesis was conducted in a single-necked 10 mL flask equipped with a magnetic stirrer. TFSA (1.4 mL) was added to an ice-cooled mixture of 1,1,1,-trifluoroacetone (0.188 g, 1.67 mmol), biphenyl (0.258 g 1.67 mmol), and dichloromethane (1 mL), with vigorous stirring. After the addition of the reagents, the cooling bath was removed. The reaction mixture was stirred at room temperature for 10 h. The dark grey, elastic precipitate was washed copiously with methanol, and then extracted with refluxing methanol for 12 h before drying at 100 °C under vacuum. The resulting white polymer **1a** (0.409 g, 98% yield) had molecular weights, $\overline{M}_{\mathrm{w}}$ and $\overline{M}_{\mathrm{n}}$, of 38 200 and 17 200, respectively. The ^{1}H NMR spectrum of the polymer is presented in Figure 1.

Preparation of **2a**

TFSA (8.0 mL) was added to an ice-cooled mixture of 2,2,2,-trifluoroacetophenone (1.537 g, 8.82 mmol), biphenyl (1.360 g 8.82 mmol), and dichloromethane (7.0 mL), with vigorous stirring. After the addition of the reagents, the cooling bath was removed. The reaction mixture was stirred at room temperature for three days. The dark blue, elastic precipitate was shredded and washed copiously with methanol, and then extracted with refluxing methanol for 12 h before drying at 100 °C under vacuum. The resulting white polymer **2a** (2.62 g, 96% yield) had molecular weights, $\overline{M}_w$ and $\overline{M}_n$, of 128 600 and 47 360, respectively.

Preparation of **4d**

Octafluoroacetophenone (0.396 g, 15.0 mmol), diphenoxybenzophenone (0.549 g, 15.0 mmol), and TFSA (2.1 mL) were stirred at room temperature for 16 h, and the resulting clear, viscous, orange solution was then poured slowly into water (200 mL). The white fiber formed was filtered off, washed with water, and extracted with hot methanol. After drying, 0.87 g (95%) of white fiber-like polymer **4d** was obtained. The polymer had molecular weights, $\overline{M}_w$ and $\overline{M}_n$, of 22 630 and 15 850, respectively. The ^{1}H NMR spectrum of the polymer is presented in Figure 1.

Acknowledgements: *M. A. Canseco* is thanked for his assistance with thermal and spectroscopic analysis. The authors also thank *Atilano Gutierrez* from Universidad Autonoma Metropolitana (campus Iztapalapa) for his help with NMR measurements. Financial support from *DGAPA* (projects PAPIIT IN101405-3 and IN100806/17) is appreciated.

Received: September 23, 2006; Accepted: October 27, 2006; DOI: 10.1002/marc.200600656

Keywords: films; fluoropolymers; synthesis; thermal properties

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