Novel High Molecular Weight Aromatic Fluorinated Polymers from One-Pot, Metal-Free Step Polymerizations

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ABSTRACT: A novel series of linear, high-molecular-weight polymers and copolymers was synthesized by one-pot, metal-free superacid-catalyzed reaction of trifluoromethylalkyl (**1a−1c**) and trifluoromethylaryl (**1d−1h**) ketones with the linear, nonactivated, multiring aromatic hydrocarbons biphenyl (**A**), *p*-terphenyl (**B**), and *p*-quaterphenyl (**C**).

The polymerizations were performed at room temperature in the Brønsted superacid trifluoromethanesulfonic acid (CF_3SO_3H, TFSA) and in a mixture of TFSA with methylene chloride. Polymerizations of trifluoromethyl ketones (**1c**, **1f−1h**) bearing functional groups gave polymers with reactive lateral groups such as bromomethyl, 4-(*N,N*-dimethylamino)phenyl-, 3-sulfophenyl-, and 2,3,4,5,6-pentafluorophenyl. The polymers obtained were soluble in most common organic solvents and flexible transparent films could be cast from the solutions. ^1H and ^{13}C NMR analyses of the polymers synthesized revealed their linear structure with para-substitution in the phenylene fragments of the main chain. The molecular weights (M_w) of the polymers based on trifluoromethylalkyl ketones and aromatic are very high and reach 1 000 000, while the molecular weights of the polymers based on trifluoromethylaryl ketones and aromatic ranged from 30 000 to 300 000 g/mol. The polydispersity of the polymers is generally less than 2. The polymers also possess high thermostability. Mechanistic aspects of polymerization mechanism have been discussed, and a new approach for monomer design has been proposed.
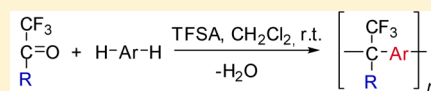
1. INTRODUCTION

Over the past 30 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 fluorine-containing groups) increases polymer solubility, glass transition temperatures, thermal stability and chemical resistance while moisture absorption, dielectric constant and color are decreased.[1−13] In more recent years, such aromatic fluorine-containing polymers have also been explored for applications in gas-separation membranes. Incorporation of trifluoromethyl groups into structures of aromatic polymers is the most efficient way to afford a desired set of properties such as solubility, disruption of the chain packing and increase of the free volume.

Generally, there are two principal methods by which the −CF₃ group is incorporated into polymer matrices. The first is polymerization of monomers containing −CF₃ groups bonded directly to the aromatic ring. The second is polymerization of monomers containing hexafluoroisopropylidene (6F) or 1,1,1-trifluoro-2,2,2-triphenylethane (3F) fragments. A combination of these two methods is also possible. In all cases, however, CF₃-group-containing monomers for polymer preparations are very expensive and few of them are commercially available. It is worth noting that 3F and 6F monomers are obtained by the acid-catalyzed condensations of fluorinated ketones with aromatic compounds. These type of reactions called hydroxyalkylation have been known for a long time.[14] Basically, the hydroxyalkylation is often limited to activated, electron-rich arenes such as phenols and aromatic amines.
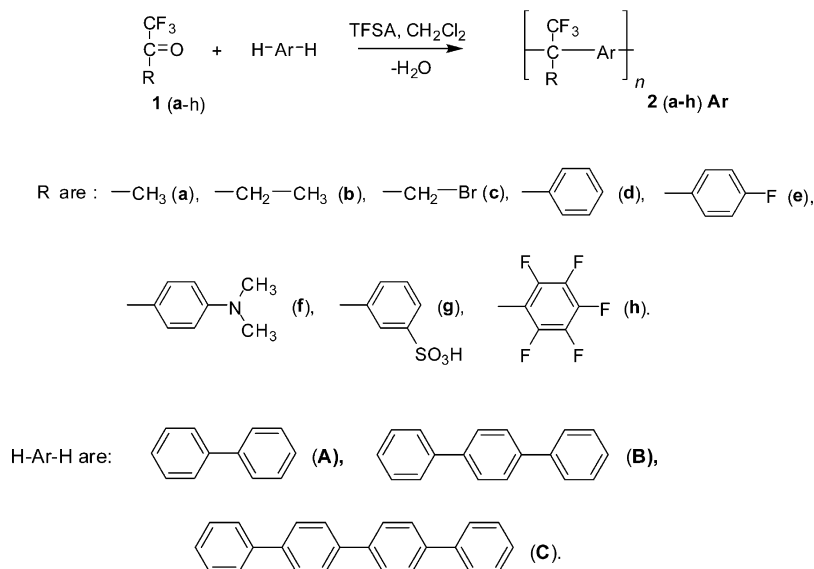
The concept of superelectrophilic activation proposed by G. Olah and its application for hydroxyalkylation reactions using superacidic media to generate highly reactive electrophilic intermediates turned out to be a great success. Numerous

Scheme 1. Step Polymerization of Trifluoromethyl Ketones with Aromatic Hydrocarbons

superacid-catalyzed hydroxyalkylation reactions have been successfully carried out.[15−18]

It was shown that superacid-catalyzed condensation reactions of trifluoromethyl ketones occur with both activated, electron-rich arenes and somewhat deactivated aromatic hydrocarbons to give diaryl derivatives in good yield.[19,20] Subsequent to these findings we have recently developed a simple method for direct preparations of 3F aromatic polymers by step-polymerization of fluoroketones with unactivated aromatic hydrocarbons.[21,22] In such an approach it is important that fluoro-containing groups (particularly, trifluoromethyl groups) eventually become substituents in polymer chains, which will afford new polymer structures and properties. Additionally, in many cases, these reactions are the only route to polymers that are otherwise difficult or impossible to prepare directly.

This straightforward reaction scheme opens up the possibility of synthesizing a large variety of polymers with different structures, and hence diverse physical and chemical properties. The reactions were performed at room temperature in the Brønsted superacid trifluoromethanesulfonic acid (CF₃SO₃H, TFSA) and in a mixture of TFSA with methylene chloride.

In the present study we utilized this strategy to access a variety of novel polymers from the condensations of trifluoromethyl ketones with linear, nonactivated, multiring aromatic hydrocarbons according to Scheme 1.

The effect of the acidity of the reaction medium and reaction conditions are highlighted. The structure of the polymers obtained, the reaction mechanism proposed and general properties are reported.

2. RESULTS AND DISCUSSION

2.1. Monomer Selection. Commercially available trifluoromethyl ketones (**1a−1h**) were used for the polymerizations with linear, nonactivated, multiring aromatic hydrocarbons such as biphenyl, *p*-terphenyl, and *p*-quaterphenyl. These monomers are of particular interest for these reactions because: (i) they are relatively cheap commercial products, (ii) direct involvement of multiring aromatic hydrocarbons in polymer synthesis via an electrophilic substitution reaction presents a new and very promising challenge for Friedel−Crafts polymers, and (iii) incorporation of phenylene fragments in the polymers increases

their glass transition temperatures, chemical inertness and thermostability. More importantly, superacid-catalyzed condensations of trifluoromethyl ketones with aromatic hydrocarbons are the only way to obtain 3F-aromatic polymers without heteroatoms in the main chain which are otherwise very difficult or impossible to prepare. Besides, this route opens up a number of opportunities for the design of 3F copolymers by treating trifluomethyl ketones with mixtures of aromatic hydrocarbons. This monomer selection demonstrates the scope of the reaction and the possibilities for preparation of new polymers.

2.2. Polymer Synthesis and Characterization. Polymer syntheses were carried out as stoichiometric step polymerizations. Very recently, an acceleration of superacid-catalyzed polyhydroxyalkylation in the presence of a small excess of the carbonyl compound (so-called "nonstoichiometric polycondensation" or polymerization with reactive intermediates) was demonstrated.[23] The polymerization of trifluoroacetone with 4,4′-diphenoxybenzophenone was one of the examples. However, this paper is focused on basic features of stoichiometric polymerizations and the properties of the polymers thus obtained. Nonstoichiometric polymerizations involving trifluoromethyl ketones are presently under study and will be reported elsewhere.

A common feature of the polymerizations of trifluoromethyl ketones with multiring aromatic is that reactions proceed as 'precipitation polycondensations'; i.e., 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.[24,25] Depending on monomer structures, solvents, and catalysts, the precipitates formed appear in the form of swollen isolated or aggregated particles or as a colored elastic mass ("reactive gel").

It is worth mentioning that biphenyl is generally considered to be a monomer of low reactivity for Friedel−Crafts polymerizations. Moreover, the first reaction of biphenyl with an electrophilic intermediate (which results in the formation of

Table 1. Polymerization Results for Polymers Based on on Trifluoromethylalkyl Ketones and Aromatics

entry	polymer code	TFSA/ketone, mol/mol	monomer concentration, mol/L	reaction time, h	inherent viscosity η_{inh} dL g^{-1}	molecular weight, $M_n \times 10^{-4}$ g/mol	molecular weight, $M_w \times 10^{-4}$ g/mol	M_w/M_n
1	**2aA**	10	0.68	24	gel	–	–	–
2	**2aA**	8.8	0.68	25	2.57	61.03	107.20	1.7
3	**2aA**	5.2	0.68	29	2.33	50.45	70.81	1.4
4	**2aA**	5.1	0.68	24	2.08	40.65	62.39	1.5
5	**2aA**	4.0	0.68	24	1.28	36.92	57.94	1.6
6	**2aB**	6.5	0.44	24	ins.	–	–	–
7	**2a(A+B)**	7.3	0.63	24	2.58	27.87	50.27	1.8
8	**2bA**	4.5	0.76	10	0.48	3.25	6.83	2.1
9	**2bB**	6.1	0.44	3	1.65	22.45	51.64	2.3
10	**2b(A+B)**	5.3	0.76	4	0.67	14.34	25.81	1.8
11	**2cA**	5.5	0.78	31	0.46	1.23	2.58	2.1
12	**2cB**	6.1	0.45	8	0.80	16.11	25.77	1.6
13	**2c(A+B)**	6.9	0.65	24	0.42	4.86	19.3	3.9

an electron-withdrawing fluorinated alkyl-group) decreases of nucleophilicity (and reactivity) of the second, nonreacted phenyl group.

The first exploratory reactions of trifluoroacetone (**1a**) with biphenyl in mixtures of TFSA with methylene chloride gave polymers of moderate molecular weight, and the ^{1}H NMR revealed the presence of irregular units.

We therefore turned our attention to the optimization of the condensation of trifluoroacetone (**1a**) with biphenyl to try to obtain high-molecular-weight product. The reaction starts at low temperature (0 °C). A colored emulsion is formed when TFSA catalyst is added to the transparent, colorless solution of **1a** and biphenyl in methylene chloride. Thereafter, the reaction temperature is slowly increased and the reaction is continued at room temperature. In the course of polymer synthesis, a coalescence of polymeric droplets produces a voluminous phase of swelling polymer. We have found that both the physical state of the swelling polymer (seemingly density) and polymer viscosity depend on the monomer concentration and proportion of TFSA. The very strong and elastic brown mass formed was shredded, washed thoroughly with methanol and dried overnight in air before reprecipitation from *N*-methylpyrrolidone solution into methanol to get a fibrous material suitable for purification by an extraction with hot methanol and acetone. Maximum viscosity values were obtained for the monomer concentration range 0.60−0.70 mol/L. Another important factor affecting polymer synthesis is the proportion of TFSA. An increase of TFSA relative to **1a** up to 6−9 mol/mol leads to an increase in molecular weight. An ultrahigh-molecular-weight polymer has been obtained (Table 1, entry 2). Such synthetic efficiency could be attributable to the high local concentration of functional groups in the "reactive gel" (precipitated polymer) and to the formation of linear chains at the expense of macrocyclization in the polymerizations involving reactive intermediates.[26] Further increase in the proportion of TFSA results in cross-linking. Although polymerization of **1a** with *p*-terphenyl gave an apparently polymeric but insoluble product, reaction of **1a** with a mixture of biphenyl/*p*-terphenyl produced completely soluble copolymer.

Similar to trifluoromethyl ketone **1a**, trifluoromethylalkyl ketones **1b** and **1c** reacted with biphenyl and *p*-terphenyl to give polymers **2bA, 2bB, 2cA, 2cB** and copolymers **2b(A+B)** and **2c(A+B)**. It is worth noting that molecular weights of these

products were generally lower than that of the polymer from trifluoromethyl ketone **1a**.

Friedel−Crafts electrophilic aromatic substitution reactions are known to be relatively nonselective. Thus, such reactions as alkylation and acylation basically lead to formation of isomer mixtures. It is also difficult to achieve high regioselectivity in acid-catalyzed hydxyalkylation. Surprisingly, NMR analyses of the polymers presented in the Table 1 revealed no structural irregularities (Figure 1, 2). All the NMR spectra are well resolved and the resonances anticipated are all evident.

Interestingly, the polydispersity of the polymers based on **1a** are rather low for step polymerization products. It is worth mentioning the stability of the bromomethyl group in ketone **1c** under reactions conditions. Well-defined polymers **2cA**,
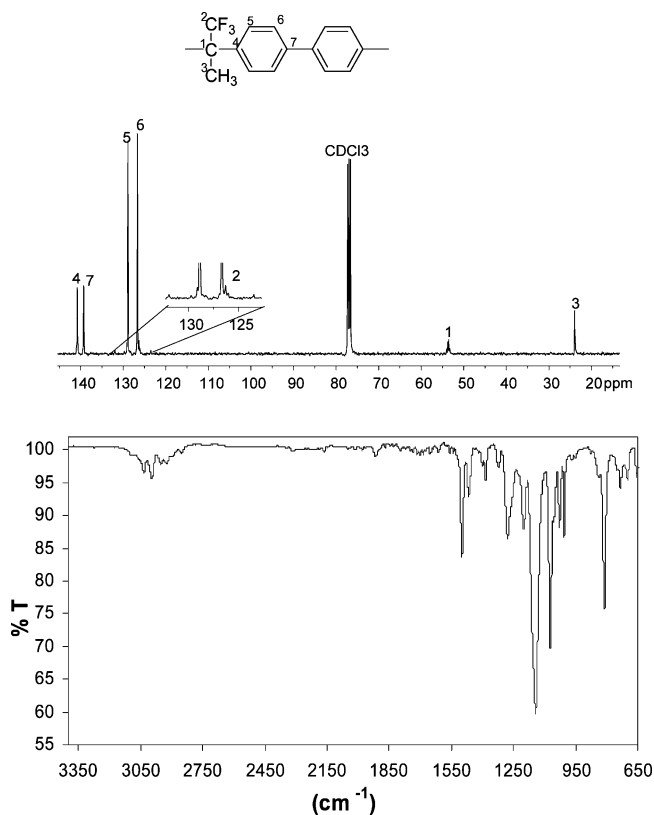
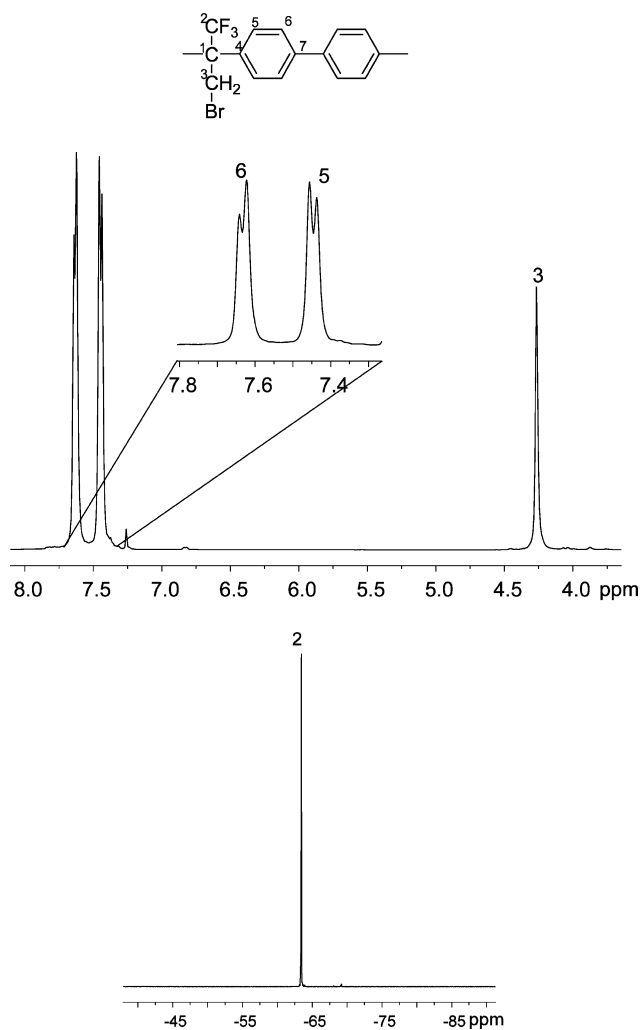**Figure 1.** ^{13}C NMR and IR spectra of polymer **2aA**.

Figure 2. ^{1}H and ^{19}F spectra of polymer **2cA** (solution in CDCl$_3$).

2cB, and **2c(A+B)** bearing bromomethyl functionalities are promising materials for various chemical modifications including controlled cross-linking and polymer grafting by means of the atom transfer polymerization methods (ATRP).

The results of polymerizations based on trifluoromethylaryl ketones (**1d**) are given in Table 2.

As can be seen from the table, trifluoromethylaryl ketones are less reactive than trifluoromethylalkyl ketones and preparation of high-molecular-weight products takes longer times and larger amounts of TFSA. It was reported that the TFSA-catalyzed condensation of 2,2,2′,4′-tetrafluoroacetophenone (**1h**) with benzene is accompanied by the formation of ca. 5% impurity identified as 1,1,1-trifluoro-2,2,2-triphenylethane.[20] In contrast, polymerizations of **1h** with aromatic hydrocarbons proceed highly selectively to give only para-substituted polymers (Figure 3, 4). Reactions involving trifluoromethylaryl ketones bearing 4-(N, N-dimethylamino) (**1f**) and 3-sulfo (**1g**) groups also gave high-molecular-weight polymers. A polymer based on **1g** and p-terphenyl swells in methanol whereas the copolymer **2(d + g)B** does not. The trifluoromethylaryl ketone **1h** had low reactivity and the polymerization of **1h** with p-terphenyl took almost one month. Yields of the polymers obtained were close to quantitative (95−98%). All polymers obtained were completely soluble in organic solvents.

Because of limited solubility, p-quaterphenyl is seldom if ever used for direct Friedel−Crafts polymerizations. To the best of our knowledge, superacid-catalyzed copolymerization of p-quaterphenyl and isatin with 4,4′-diphenoxybenzophenone is the only known example.[27] Polymerization of trifluoromethyl ketone (**1d**) with p-quaterphenyl gave apparently polymeric but insoluble product in particle form. Thermogravimetric analysis of the particles both in air and in nitrogen atmosphere revealed no significant weight loss below 500 °C which confirms the polymeric nature of the product. It is known that copolymerization is an efficient way to improve solubility of polymers. We therefore turned our attention to the copolymerizations of **1d** with a mixture of p-quaterphenyl with biphenyl and terphenyl.

Polymerizations of **1d** with biphenyl/p-quaterphenyl [75/25, 50/50, 25/75)] gave two polymers (Table 3, entries 1 and 2) that were soluble in a wide range of solvents, including chloroform, methylene chloride, NMP and N, N-dimethylformamide (DMFA).

All the polymers from the reactions involving p-quaterphenyl were reprecipitated and washed with refluxing methanol and acetone to exclude the presence of unreacted p-quaterphenyl. It should be noted that yields of the polymers were quite high (90−95%). The high solubility of the polymers allowed us to perform reliable spectral studies to delineate their structure.

Table 2. Polymerization Results for Polymers Based on on Trifluoromethylaryl Ketones and Aromatics

entry	polymer code	TFSA/ketone, mol/mol	monomer concentration, mol/L	reaction time, h	inherent viscosity η_{inh} dL g^{-1}	molecular weight, $M_n \times 10^{-4}$ g/mol	molecular weight, $M_w \times 10^{-4}$ g/mol	M_w/M_n
1	**2dA**	8.7	0.69	24	0.28	1.08	2.18	2.0
2	**2dA**	8.7	0.69	48	0.33	1.85	3.33	1.8
3	**2dA**	8.7	0.68	72	0.47	2.12	5.66	2.7
4	**2dA**	9.7	0.64	96	0.58	6.04	8.75	1.4
5	**2dB**	6.2	0.45	24	0.89	10.40	13.52	1.3
6	**2dB**	6.5	0.42	46	1.10	15.20	20.70	1.4
7	**2d(A+B)**	10.1	0.61	48	0.80	6.43	10.70	1.7
8	**2eA**	10.6	0.50	48	0.89	2.43	5.08	2.1
9	**2eB**	6.8	0.42	48	1.01	5.86	11.16	1.9
10	**2e(A+B)**	10.2	0.61	72	0.46	3.98	6.96	1.7
11	**2hB**	11.1	0.54	24 d	0.56	22.76	29.60	1.3
12	**2h(A+B)**	11.1	0.55	24 d	0.47	6.65	24.60	3.7
13	**2fA**	14.9	0.65	79	0.38	1.10	3.14	2.9
14	**2(d+g)B**	9.9	0.56	9	0.67	–	–	–

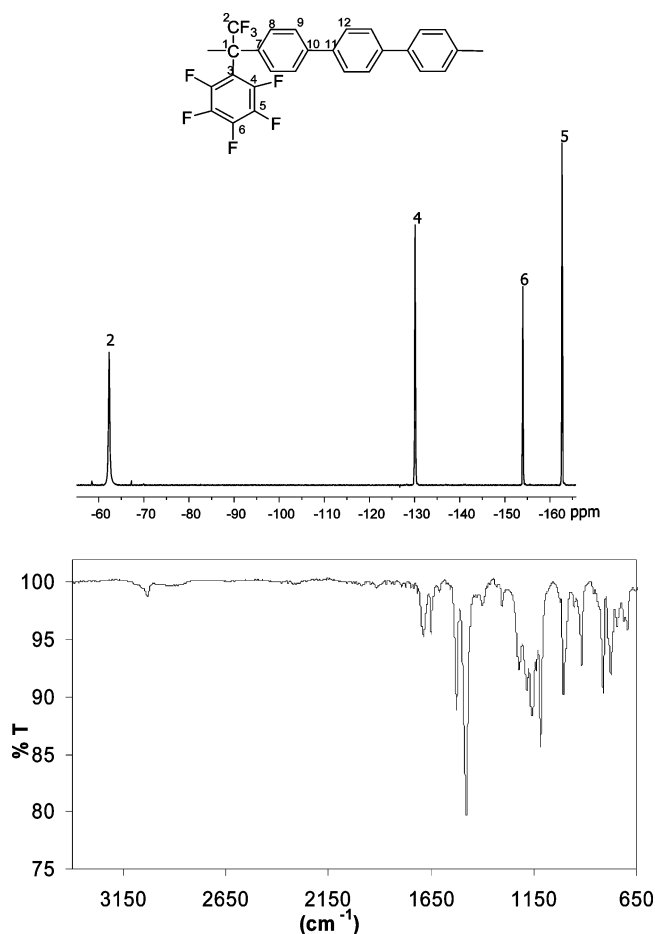**Figure 3.** ^{19}F NMR and IR spectra of polymer **2hB**.

Figure 4. ^{13}C NMR and IR spectra of polymer **2eA**.

The ^{1}H NMR and ^{13}C NMR spectra (Figure 5) clearly indicate resonances of biphenyl and *p*-quaterphenyl fragments adjacent to trifluoroacetophenone moiety. Pattern of signals centered at 139.90 point to the presence of the triads characteristic for a random copolymer. Surprisingly, polymerizations of **1d** with *p*-terphenyl/*p*-quaterphenyl proceed similarly to the polymerizations of **1d** with biphenyl/*p*-quaterphenyl. Despite generally limited solubility of the polymers with *p*-terphenyl moieties in the main chain, two copolymers of **1d** with *p*-terphenyl/*p*-quaterphenyl (Table 3, entries 4 and 5) were completely soluble. NMR studies have shown the existence of high regioselectivity in polymer-forming reactions that lead to polymers with para-substitution in the aromatic fragments (Figure 6). The experimental results thus demonstrate a high efficiency of the polymerizations of trifluoromethylketones with aromatic hydrocarbons.

A novel series of linear, high-molecular-weight polymers and copolymers was synthesized by one-pot, metal-free superacid-catalyzed step polymerizations.

To gain further insights into the polymerization mechanism we have estimated the free Gibbs activation energies for the rate-limiting steps of representative hydroxylakylation reactions. To obtain a complete picture, the extreme cases of ketones possessing only donor (acetone, **6H**) and only acceptor groups (hexafluoroacetone, **HFA**) have been taken as model compounds for the calculations.

2.3. Mechanistic Aspects. Acid-catalyzed reactions between carbonyl compounds and aromatic hydrocarbons (hydroxyalkylation) proceed as electrophilic aromatic sub-
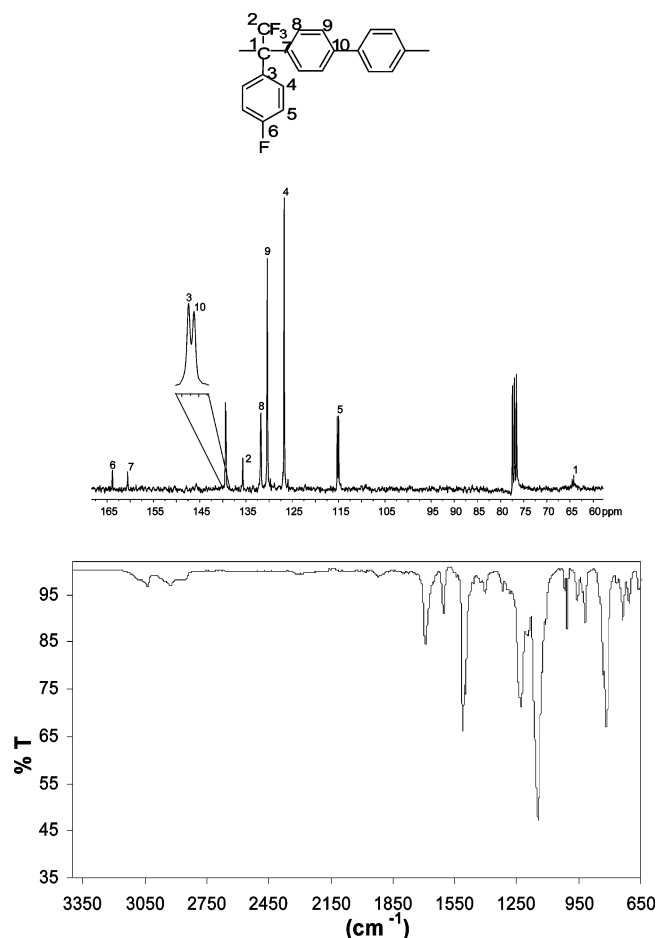
Table 3. Polymerization Results for Polymers Containing Quaterphenyl

entry	polymer code	TFSA/ketone, mol/mol	monomer concentration, mol/L	reaction time, h	inherent viscosity, η_{inh} dL g^{-1}
1	**2d**(0.75A +0.25 C)	11.3	0.25	24	0.74
2	**2d**(0.50A +0.50 C)	6.6	0.42	24	1.18
3	**2d**(0.25A +0.75 C)	6.8	0.42	24	ins.
4	**2d**(0.75B +0.25 C)	11.3	0.25	8	2.01
5	**2d**(0.50B +0.50 C)	11.3	0.25	24	1.27
6	**2d**(0.25B +0.75 C)	11.3	0.25	24	ins.

stitutions. The process can be catalyzed by protic or Lewis acids. Depending on the monomer structures and reaction conditions, an alcohol, a diaryl-compound or a mixture of these can be obtained. According to recent studies,[28] the reaction mechanism of the superacid-catalyzed hydroxyalkylation can be postulated as shown in Scheme 2.

The computational model used for the reaction mechanism calculations is described as follows.

A flexible cluster-continuum solvation model has been used for the solvent modeling, where the inner solvation sphere contains explicit solvent molecules whereas the outer sphere is modeled using SMD modification of polarizable continuum
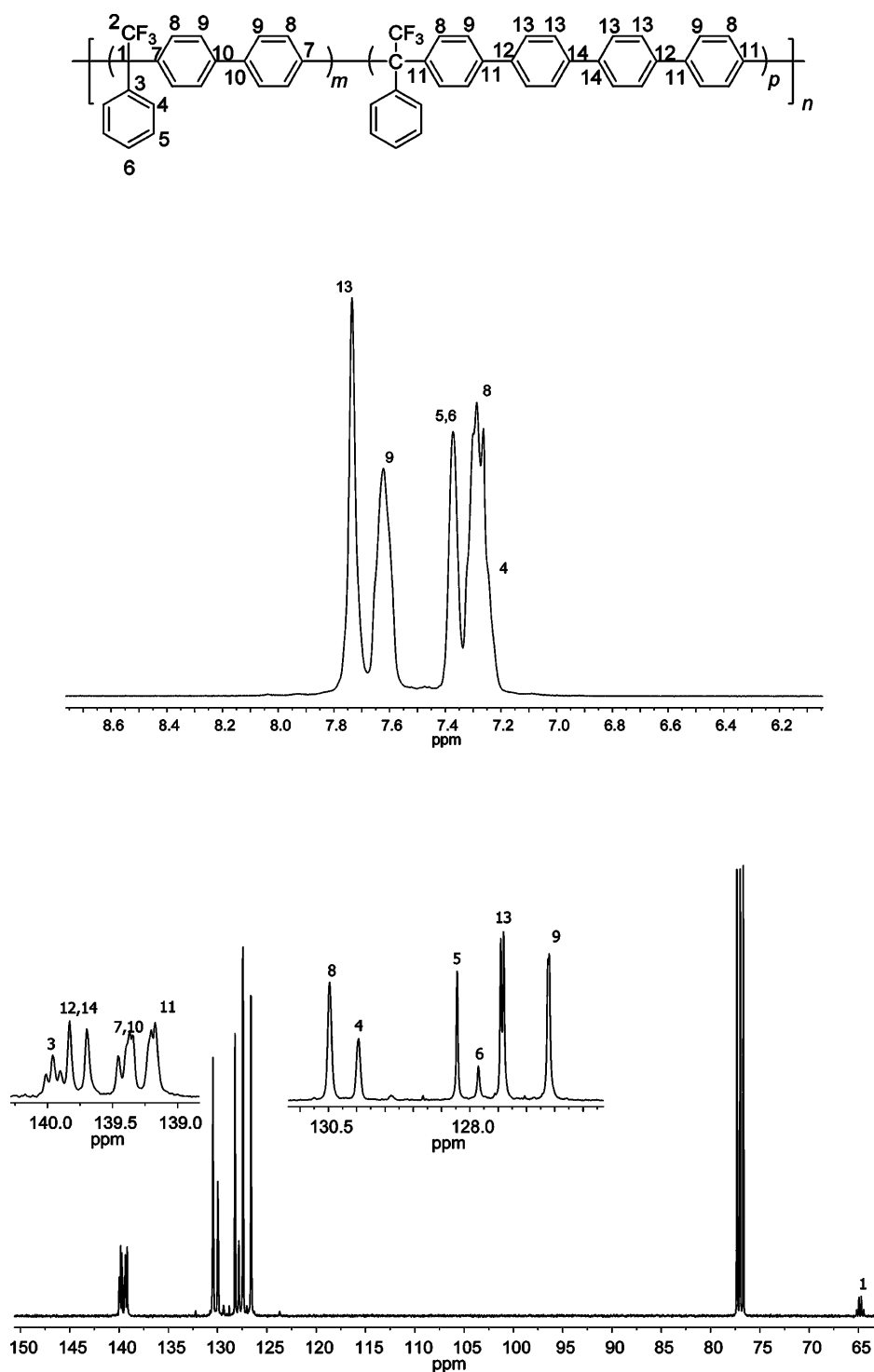
Figure 5. ^{1}H and ^{13}C NMR spectra of polymer **2d**(0.50A+0.50 C).

model.[29] For all calculations, the Gaussian 09 suit of programs has been used.[30] The M06-2X functional 6-311+G(d,p) basis set have been used with the calculations. To test the performance of M06-2X/6-311+G(d,p) model we estimated gas phase proton affinities for acetone and trifluoroacetone and compared them with available experimental data.[31] The calculated and experimentally determinate proton affinities were found to be 193.6 and 194.2 kcal/mol respectively, for acetone and 170.0 and 173.0 kcal/mol for trifluoroacetone, respectively. For the inner solvation sphere the number of

explicit molecules was equal to the number of the lone pairs at oxygen atoms; two for ketones and three for carbinols. For the outer solvation sphere SMD continuous model was used as implemented in Gaussian 09 (dielectric constant of 77.4 and solvent radius of 2.60 Å were used for TFSA)

All of the geometries were fully optimized without imposing any symmetry restrictions and frequency calculations were ran to ensure that a ground state (0 imaginary frequencies) or a transition state (1 imaginary frequency) is found. The
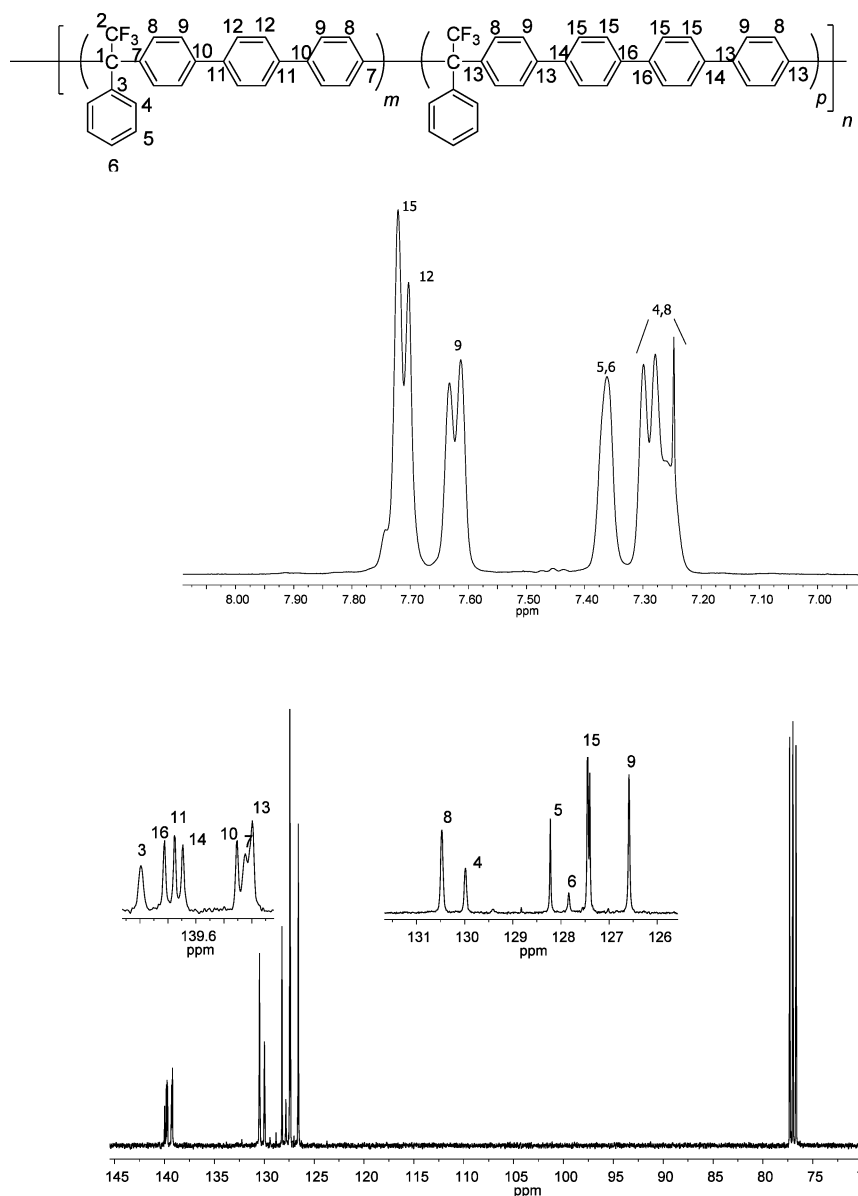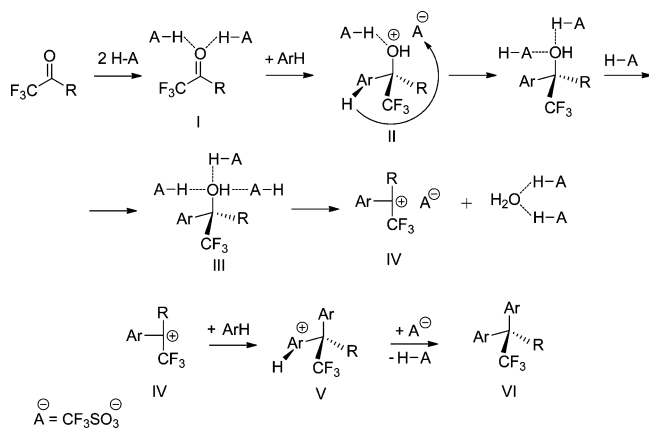
Figure 6. ^{1}H and ^{13}C NMR spectra of polymer **2d**(0.50**B**+0.50 **C**).

Scheme 2. Mechanism of Superacid-Catalyzed Hydroxyalkylation Reaction

frequency calculations data were used for calculations of the reaction thermochemisty.

The initial reactive intermediate is the solvated ketone (**I**) that forms when the ketone dissolves in TFSA. Calculations using explicit solvation models for inner solvation spheres demonstrated that at least in the case of acetone (**6H**) and ketones **1a** and **HFA** incomplete protonation of ketone occurs but only strong hydrogen bonds are formed.[28] It is noteworthy that protonated trifluoroacetone (**1a**) was detected experimentally.[32] In this case, a very strong "magic acid" (SbF$_5$–HSO$_3$F) which is 11 orders of magnitude stronger than TFSA was used for the protonation. The reaction of the solvated ketone with aromatic hydrocarbons (ArH) produces the σ-complex (**II**) where one proton is totally transferred to the carbonyl oxygen while the second one forms a hydrogen bond. After aromatization of intermediate **II** carbinol **III** is formed. The inner solvation sphere of carbinol **III** involves 3 explicit acid molecules. The dissociation of the C–O bond of **III** produces a water molecule and carbocation **IV**, which reacts with a second aromatic molecule to produce diarylmethane derivative (**VI**).

It is common knowledge that the reactivity of electrophilic species can be quantified using electrophilicity which is defined as a kinetic quantity. The more electrophilic the species are the faster they react. Therefore, in this particular case the electrophilicity and the reactivity are synonymous. It is noteworthy that there is no correlation whatsoever between total electron density at a site (charge) and the corresponding electrophilicity since the aromatic electrophilic substitution consists of the reaction between soft acids and soft bases, which are known to show orbital but not charge control. Thus, it has been demonstrated that there is good correlation between the LUMO of a carbonyl component and the reactivity (activation energy) of hydroxyalkylation.[33]

The reactivity of monomers studied in polyhydroxyalkylation reactions depends notably on their nature. Thus, the reactivity decreases in the order **6H**, **1a**, **1d**, **1h**, and **HFA**. Actually **HFA** does not react at all. In the case of the first three monomers, there is a correlation between the energy of LUMO and their reactivity. **1h** and **HFA** monomers, however, do not follow this trend. Organic chemistry textbooks state that the rate-limiting step for the hydroxyalkylation reaction is the formation of the σ-complex (**II**).[34] However, the calculation demonstrated that this is the case only for "conventional" carbonyl compounds.[28]

When very strong and multiple electron-withdrawing groups are attached directly to the carbonyl group, the cleavage of the C−O bond in carbinol (**III**) becomes the rate-determining step. (For the first time D. Klumpp observed this effect in the superacid-promoted reaction of 2-(trifluoroacetyl)pyridine with benzene.[35]) Thus, the corresponding calculated activation energies of two steps for the reaction of ketones **6H**, **1a**, **1d**, **1h**, and **HFA** with benzene are shown in Table 4.

Table 4. Free Gibbs Activation Energies of σ-Complex Formation (G_{a1}) and C−O Bond Cleavage (G_{a2}) for the Reaction of Selected Carbonyl Components with Benzene in TFSA (kcal/mol)

monomer	G_{a1}	G_{a2}
acetone (**6H**)	27.3	3.9
1d	25.1	13.0
1a	23.2	15.4
1h	22.9	25.9
HFA	19.2	31.0

On the one hand, electron-withdrawing groups reduce the free Gibbs activation energy of the σ-complex (**II**) formation due to increasing of the electrophilicity of carbonyl carbon. On the other hand, the electron-withdrawing group reduces the stability of the carbocation formed upon C−O link cleavage, which increases the free Gibbs activation energy of this step. Therefore, the reactivity of the carbonyl component can be rationalized in terms of those two steps. When the carbonyl component has no electron-withdrawing groups, the rate-determining step is the σ-complex formation and the introduction of electron-withdrawing groups increases the reactivity of carbonyl molecule. When the rate-determining step is the C−O bond cleavage, additional electron-with-drawing substituents at the carbonyl group increases the activation energy and therefore reduces the reactivity of the carbonyl component. This behavior is illustrated in Figure 7.

Thus, in extreme cases of the comparatively unreactive monomers **6H** and **HFA**, their low reactivity is related to high G_{a1} and high G_{a2}, respectively. Therefore, the introduction of
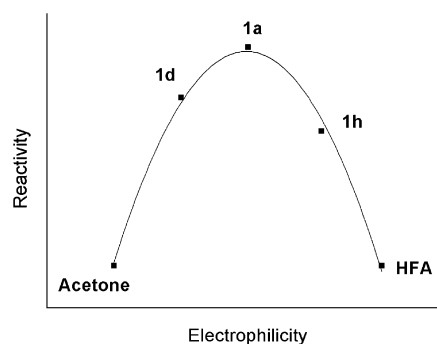

Figure 7. Relative reactivities of carbonyl compounds in the reaction of TFSA-catalyzed hydroxyalkylation.

electron-withdrawing substituents in ketones increases their reactivity in the reaction of polyhydroxyalkylation only to a certain extent. When G_{a1} and G_{a2} become equal, further increase of carbonyl-group electrophilicity reduces the mono-mer reactivity. This finding allows for tuning of the reactivity of the carbonyl component in hydroxyalkylation reactions by changing the electron-withdrawing ability of substituents adjacent or relatively close to a carbocation center.

2.4. Polymer Properties. The polymers obtained after being isolated from the reaction medium, washed, and dried have the appearance of white fiber-like fibrous powders with a λ_{max} value of 254.8 nm in methylene chloride solutions, and no absorption occurs above 340 nm. The qualitative solubility properties of the polymers are reported in Table 5. As can be seen from Table 5, the majority of the polymers obtained possess good solubility in chlorinated and aprotic solvents. Transparent, strong, flexible films could be cast from the polymer solutions. The polymers are insoluble in sulfuric acid, alcohols, and aromatic hydrocarbons.

Some properties of the polymers are presented in Table 6. DSC analyses of the polymers revealed glass transitions temperature ranging from 187 to 330 °C and the absence of heat transitions for polymers **2bB**, **2b(A+B)**, **2cA**, **2c(A+B)**, **2dB**, **2eA**, **2eB**, **2hB** and **2h(A+B)** up to 400 °C. The wide angle X-ray diffraction (WAXD) patterns of the polymers show amorphous haloes.

The polymers obtained also possess high thermostability. No significant weight loss below 480 °C (air) was observed for fully aromatic 3F polymers. The amount of carbonized residue (char yield) of these polymers depends on the chemical composition of the polymers. It is in the range of 70−75% for fully aromatic 3F polymers. Decomposition temperatures of polymer **2aA** were surprisingly high: 528 and 492 °C in nitrogen and air, respectively (Figure 8).

Intrigued by those results we decided to estimate the energy of dissociation of weakest chemical bonds for polymer model compounds (Figure 9). It is well-known that the energies of C−C bonds decrease in the following order sp²−sp², sp²−sp³ and sp³−sp³. Therefore, the gas phase bond dissociation energies of C−C bonds formed by sp^3 carbon atoms have been estimated. All calculations were carried out using the Gaussian 09 suit of programs.[30] B3LYP functional in combination with 6-311G(d,p) basis set was used for calculations. As seen from the Figure 9, there is a very notable correlation between C−C bond dissociation energy and polymer thermostability. Those data suggest that the first step in the thermal decomposition of the polymers involves the cleavage of the corresponding C−C bond. It is worth noting that Tg and 5% weight loss of polymer

Table 5. Solubility[a,b] of Polymers

solvent	2aA	2aB	2a(A+B)	2bA	2bB	2b(A+B)	2cA	2cB	2c(A+B)	2dA	2 dB	2d(A+B)	2eA	2eB	2e(A+B)	2hB	2h(A+B)	2fB
CH₂Cl₂	+	±↑	+	+	±	+	+	±↑	+	+	+	+	±↑	+	+	+	+	±
CHCl₃	+	±↑	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
CCl₄	+	±↑	+	+	−	+	+	+	+	+	+	+	+	+	+	+	+	+
H₂SO₄	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
DMFA	+	−	±↑	+	−	+↑↓	+	+	+	+	±↑	±↑	±	+	+	+	+	±↑
NMP	+	±↑	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DMAA	−	−	−	±↑	−	±↑	+	±↑	+	±↑	±	−	±↑	+↑	+↑	↑↓	+↑↓	±↑
DMSO	+	−	+	+	±↑	+	+	+	+	+	+	+	+	+	+	+	+	+
dioxane	+	−	+	+	±↑	+	+	+	+	+	+	+	+	+	+	+	+	+
THF	+	−	+	+	±↑	+	+	+	+	+	+	+	+	+	+	+	+	+
cyclohexanone	+	−	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

[a] + Soluble, +↑ Soluble heating, +↑↓ Soluble on heating and precipitate on cooling, ± swell, ± ↑ swell heating, − insoluble. [b] Solubility was determined for the polymer concentrations 50 mg/mL.

Table 6. Thermal Properties of the Polymers

acronym	T_g (°C)	T_d (onset,°C) N₂	T_d (onset,°C) air	char yield, 800 °C (wt %) in N₂
2aA	296	528	492	37
2a(A+B)	>400	523	519	51
2bA	250	454	432	60
2bB	>400	452	434	65
2b(A+B)	>400	453	428	64
2cA	>400	300	299	55
2cB	276	269	259	60
2c(A+B)	>400	282	274	56
2dA	330	505	501	72
2 dB	>400	498	495	75
2d(A+B)	364	485	483	71
2eA	>400	479	480	67
2eB	>400	492	487	71
2e(A+B)	187	483	477	70
2hB	>400	432	428	65
2h(A+B)	>400	419	416	61
2d(0.50A+0.50 C)	>400	499	496	60
2d(0.50B+0.50 C)	>400	495	494	62

of repeating structure **4** were reported to be 255 and 515 °C, respectively.[36] The dissociation energies of the corresponding C−C bond can be rationalized in the following manner:

The weakest bond calculated for compound **6** is due to the formation of stable trityl radical followed by **3** where the bond dissociation produces less stable diphenylmethyl radicals. The stronger C−C bond of **4** is related to the lower stability of the diphenyltrifluoromethyl radical compared to the diphenylmethyl one due to the strong electron-withdrawing character of the trifluoromethyl group. The strongest C−C bond is estimated for **5**. In this case formation of unstable diphenyltrifluoromethyl and methyl radicals favors the bond stability. It is worth mentioning that prediction of thermostability based on bond dissociation energy can be applied only to the case of purely thermal and not to oxidative decomposition.

The dielectric constants and surface properties for some polymers are presented in Table 7.

It is well-known that the presence of small amounts of water in polymers both increases ε and causes other problems. The highly hydrophobic nature of these new 3F polymers ensures that the dielectric constants will not be significantly influenced
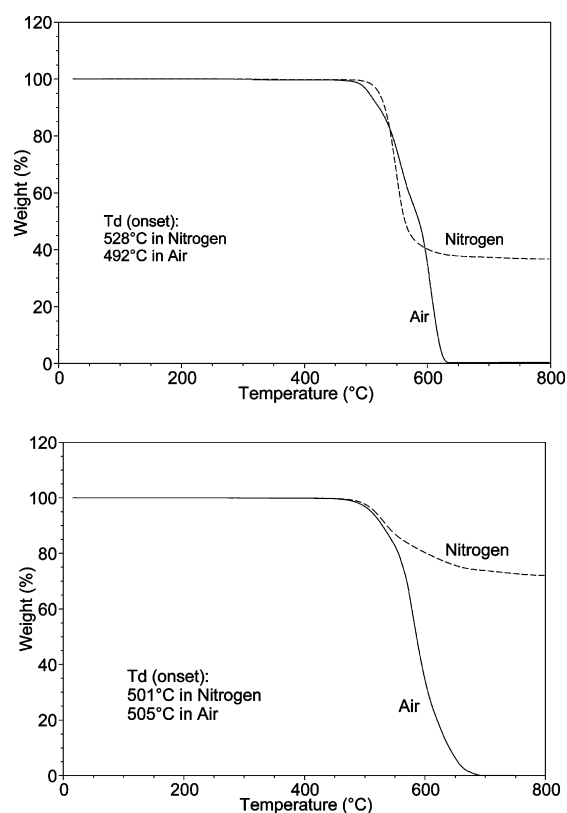
Td (onset):
528°C in Nitrogen
492°C in Air

Nitrogen

Air

Td (onset):
501°C in Nitrogen
505°C in Air

Nitrogen

Air

Figure 8. TGA thermograms of polymer **2aA** (top) and **2dA** (bottom).

3 — 69.9

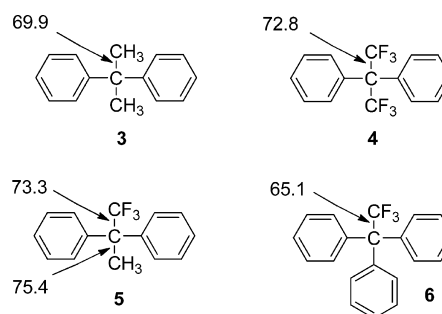**4** — 72.8

5 — 73.3, 75.4

6 — 65.1

Figure 9. Selected bond dissociation energies calculated at B3LYP/6-311G(d, p) level of theory (kcal/mol).

Table 7. Dielectric Constants, Contact Angle, and Superficial Tension of Polymers 2aA, 2dA, 2d(A+B) and 2hB

polymer code	dielectric constant ε (f = 1 kHz)	contact angle θ (deg)	superficial tension γ (mN/m)
2aA	3.08	85	15.3
2dA	3.13	90	24.4
2d(A+B)	2.74	94	14.9
2hB	2.82	93	20.9

by humidity. On the whole, these fluoropolymers demonstrate good processability combined with high thermal stability and excellent chemical inertness while containing pendent functional groups.

3. CONCLUSIONS

A novel series of linear, high-molecular-weight polymers and copolymers was synthesized by one-pot, metal-free superacid-catalyzed reaction of trifluoromethylalkyl (**1a−1c**) and trifluoromethylalkylaryl (**1d−1h**) ketones with linear, non-activated, multiring aromatic hydrocarbons biphenyl (**A**), *p*-terphenyl (**B**), and *p*-quaterphenyl (**C**). Aromatic 3F copolymers were obtained by both polymerization of trifluoromethyl ketones with a mixture of aromatic hydrocarbons and polymerization of aromatic hydrocarbons with a mixture of trifluoromethyl ketones. Polymerizations of trifluoromethyl ketones (**1c, 1f−1h**) bearing functional groups gave polymers with reactive lateral groups, such as bromomethyl, 4-(*N,N*-dimethylamino)phenyl, 3-sulfophenyl, and pentafluorophenyl. It seemed plausible that trifluoromethyl ketones would also react with variety of aromatic hydrocarbons capable of the formation of disubstituted derivatives in the Friedel−Crafts reactions. The polymerizations performed at room temperature in the Brønsted superacid CF$_3$SO$_3$H and in a mixture of TFSA with methylene chloride or TFA tolerant of bromomethyl, pentafluorophenyl and 3-sulfophenyl groups demonstrate wide applicability and include simple reaction conditions, readily available starting materials and reagents, and generation of an inoffensive byproduct (water).

The polymers obtained were soluble in most common organic solvents, and flexible transparent, colorless films could be cast from the solutions. ^{1}H and ^{13}C NMR analyses of the polymers synthesized revealed high region-selectivity of the polymerizations yielding linear structures with para-substitution in the phenylene fragments of the main chains.

The polymerizations of trifluoromethylalkyl ketones with aromatic hydrocarbons afford polymers with molecular weights (M_w) up to 1 000 000, while the molecular weights of the polymers based on trifluoromethylaryl ketones and aromatic ranged from 30 000 to 300 000 g/mol. The polydispersity of the polymers is generally well below 2.

Complementary theoretical and experimental studies of superacid-catalyzed polymerization of trifluoromethyl ketones with aromatic hydrocarbons revealed that electron-withdrawing substituents at the carbonyl initially increases the carbonyl reactivity by reducing the activation energy of σ complex formation, the rate-limiting step of the hydroxyalkylation reaction. On the other hand, the electron-withdrawing effect destabilizes the carbocation, which thereby increases both the activation and reaction energies of its formation. This dual effect of electron-acceptor substituents leads to a maximum in the reactivity profile of the carbonyl component when one trifluoromethyl group activates the carbonyl group toward the

hydroxyalkylation reaction, whereas two electron-acceptor groups inhibits it. Therefore, the highest reactivity of the carbonyl component is achieved when only one strong acceptor group is present in the molecule.

These are the principal factors governing reaction of superacid-mediated hydroxyalkylation of trifluoromethyl ketones with aromatic hydrocarbons, which should be taken into account for the design of new polymerizations to gain ready access to macromolecular architectures with desired properties.

These new fluoropolymers obtained demonstrate good processability, excellent chemical inertness and thermal stability. 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.

The results obtained can also be considered to be the basis for the design of nonstochiometric step polymerizations that can afford high-molecular-weight polymers in shorter reaction times. The efficient reactions of trifluoromethylalkyl- and trifluoromethylarylketones with macromonomers and oligomers bearing terminal aromatic hydrocarbons can be also used as a coupling step in the formation of various polymer families (polyamides, polyketones, polyesters, etc.).

4. EXPERIMENTAL PART

4.1. 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$_3$) and dimethyl sulfoxide-*d$_6$* were used as solvents. Infrared (IR) spectra were measured on a Nicolet FT-IR-ATR spectrometer. The inherent viscosities of 0.2% polymer solutions in 1-methyl-2-pyrrolidone (NMP) were measured at 25 °C using an Ubbelohde viscometer. Molecular weights were determined by gel permeation chromatography (GPC −MALLS) according to the published method.[26]

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.

4.2. Materials. All starting materials were obtained from Aldrich. Biphenyl, *p*-terphenyl, and *p*-quaterphenyl were used as received. Methylene chloride, 1,1,1-trifluoroacetone, 1,1,1-trifluoro-2-butanone, 1-bromo-3,3,3-trifluoroacetone 2,2,2-trifluoroacetophenone, and octafluoroacetophenone were distilled. TFSA was distilled prior to use.

4.3. Polymer Synthesis. Polymer syntheses were carried at room temperature conditions. In a typical synthesis to produce **2aA**, a 10 mL three-neck flask equipped with a mechanical stirrer was charged with trifluoroacetone (0.504 g, 4.498 mmol), biphenyl (0.694 g, 4.500 mmol), and dichloromethane (3.3 mL). The solution was cooled to 5 °C, TFSA (3.3 mL) was added in one portion to the solution, and the reaction mixture was stirred for 30 min. The temperature was then raised to 20 °C over 1 h, and the reaction mixture was stirred at this temperature for 25 h. The resulting dark-brown, gel-like mass was then shredded and poured slowly into methanol. The precipitated white solid was filtered, washed with hot methanol and dried in air overnight and at 100 °C under vacuum. The resulting pure white fibrous polymer **2aA** (0.971 g, 87% yield) had an inherent viscosity of 2.57 dL/g when a 0.2% polymer solution in NMP was measured at 25 °C in an Ubbelohde viscometer.

Copolymer **2a(A+B)**. A mixture of trifluoroacetone (**1a**) (0.732g, 6.532 mmol), biphenyl and *p*-terphenyl (0.504 g, 3.270 mmol and 0.752 g 3.265 mmol respectively), methylene chloride (6.2 mL) and TFSA (4.2 mL) was stirred at room temperature for 24 h and then poured into methanol. The white fiber formed was filtered off and washed with hot methanol. After drying 0.758g, (94%) of white fiber like polymer was obtained. The inherent viscosity (η_{inh}) was 2.58 dL/g (NMP).

Polymer 2bA. TFSA (2.9 mL) was added to a mixture of 1,1,1-trifluoro-2-butanone (**1b**) (0.792g, 6.28 mmol), biphenyl (0.969 g, 6.28 mmol) and dichloromethane (5.3 mL). The reaction mixture was stirred at room temperature for 10 h and then poured into methanol. The resulting pure white fibrous polymer (1.582g, 96%) had an inherent viscosity (η_{inh}) of 0.48 dL/g.

Polymer 2bB. 1,1,1-Trifluoro-2-butanone (**1b**) (0.204g, 1.61 mmol), *p*-terphenyl (0.371 g, 1.61 mmol), dichloromethane (3.8 mL) and TFSA (1.2 mL) were stirred at room temperature for 3 h and then poured into methanol. White fibrous polymer **2bB** (0.535g, 98%) with an inherent viscosity (η_{inh}) of 1.65 dL/g was obtained.

Copolymer 2b(A+B) was obtained by analogous procedure. 1,1,1-Trifluoro-2-butanone (0.213g, 1.69 mmol), biphenyl and *p*-terphenyl (0.130 g, 0.84 mmol and 0.195 g 0.84 mmol, respectively), dichloromethane (1.4 mL) and TFSA acid (0.8 mL) were stirred at room temperature for 4 h and then poured into methanol. The resulting pure white fibrous polymer (0.492g, 97%) had an inherent viscosity (η_{inh}) of 0.67 dLg^{-1}.

Polymer 2cA. 1-Bromo-3,3,3-trifluoroacetone (**1c**) (0.739g, 3.90 mmol), biphenyl (0.597 g, 3.90 mmol), dichloromethane (3.1 mL) and TFSA (1.9 mL) were stirred at room temperature for 31 h and then poured into methanol. White fibrous polymer (1.139g, 90%) had an inherent viscosity (η_{inh}) of 0.46 dL/g.

Polymer 2cB. 1-Bromo-3,3,3-trifluoroacetone (1.312g, 6.88 mmol), *p*-terphenyl (1.587 g, 6.88 mmol), dichloromethane (11.5 mL) and TFSA (3.8 mL) were stirred at room temperature for 8 h and then poured into methanol. The resulting pure white fibrous polymer (2.469g, 89%) had an inherent viscosity (η_{inh}) of 0.90 dL/g.

Copolymer 2c(A+B) was obtained by analogous procedure. 1-Bromo-3,3,3-trifluoroacetone (0.627g, 3.28 mmol), biphenyl and *p*-terphenyl (0.253 g, 1.64 mmol and 0.378 g, 1.64 mmol respectively) were dissolved in dichloromethane (3.0 mL); TFSA (2.0 mL) was added and the reaction mixture was stirred at room temperature for 24 h. After precipitation, washing and drying the resulting pure white fibrous polymer (1.079g, 90%) had an inherent viscosity (η_{inh}) of 0.42 dL/g.

Polymer 2dA. 2,2,2-Trifluoroacetophenone (**1d**) (8.41 g, 45.45 mmol), biphenyl (7.0 g, 45.45 mmol), dichloromethane (33.7 mL) and TFSA (41.3 mL) were stirred at room temperature for 96 h. The resulting green, two-phase system was then poured slowly into methanol. The precipitated, pale white solid was filtered off, extracted with refluxing methanol and dried at 100 °C under vacuum. After drying, 14.300g, (98%) of white polymer had an inherent viscosity (η_{inh}) of 0.66 dL/g.

Polymer 2 dB. 2,2,2-Trifluoroacetophenone (**1d**) (5.52 g, 31.24 mmol), *p*-terphenyl (7.19 g, 31.24 mmol), dichloromethane (56.3 mL), and TFSA (18.7 mL) were stirred at room temperature for 45 h. The resulting green viscous solution was poured into methanol and the precipitated white powder was filtered off, extracted with refluxing methanol and dried at 80 °C in an oven. The resulting pure white fibrous polymer (11.905g, 98%) had an inherent viscosity (η_{inh}) of 1.10 dL/g.

Copolymer 2d(A+B) was obtained by analogous procedure. 1,1,1-Trifluoroacetophenone (7.42 g, 42.70 mmol), biphenyl and *p*-terphenyl (3.292 g, 21.35 mmol and 4.917 g, 21.35 mmol, respectively), dichloromethane (32 mL) and TFSA (38 mL) were stirred at room temperature for 48 h and then poured into methanol. The resulting pure white fibrous polymer (14.414g, 97%) had an inherent viscosity (η_{inh}) of 0.80 dL/g.

Polymer 2d(A+C). TFSA (1 mL) was added to a mixture of 2,2,2-trifluoroacetophenone (0.170g, 0.976 mmol), biphenyl (0.075g, 0.487 mmol), *p*-quaterphenyl (0.150g, 0.489 mmol) and dichloromethane (3 mL). The reaction mixture was stirred at room temperature for 20h and then poured into methanol. After drying, a white fiber-like polymer (0.353g, 93%) was obtained. The inherent viscosity (η_{inh}) was 1.43 dL/g.

Polymer 2d(B+C). A mixture of 2,2,2-trifluoroacetophenone (0.171g, 0.982 mmol), *p*-terphenyl (0.113g, 0.490 mmol), *p*-quaterphenyl (0.150g, 0.492), dichloromethane (3 mL) and TFSA (1 mL) was stirred at room temperature for 24h and precipitated into

methanol. The white fiber formed was washed with hot methanol. After drying, a white fiber-like polymer (0.409g 98%) was obtained. The inherent viscosity (η_{inh}) was 1.27 dL/g.

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Notes
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