

## Dramatic Enhancement of Superacid-Catalyzed Polyhydroxyalkylation Reactions

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**ABSTRACT:** Complementary theoretical and experimental studies of the consecutive steps of superacid catalyzed polyhydroxyalkylation reactions have been carried out. Calculations for the superacid catalyzed polyhydroxyalkylation of trifluoroacetone and trifluoroacetophenone with aromatic hydrocarbons explained a number of experimental facts within a single theoretical framework of monoprotection. The principal factors affecting kinetics of superacid mediated hydroxyalkylation were shown to be as follows: (i) the acidity of the superacid affecting protonation energy of carbonyl components; (ii) the electrophilicity of carbonyl components; and (iii) the nucleophilicity of aromatic components. The modification of those factors allows for tuning of the reactivity of carbonyl and aromatic components; thereby, reaction kinetics are controlled. The conclusions were confirmed by the experiments. Theoretically predicted stoichiometrically imbalanced polymerizations of trifluoroacetone, trifluoroacetophenone, octafluoroacetophenone, and isatin with nonactivated, aromatic hydrocarbons gave high-molecular-weight polymers with a very small excess of the carbonyl compound. The main reasons contributing to the polymerization accelerations were found to be an increase of the first, rate-determining step reaction, and a high efficiency of the superacid catalyzed polyhydroxyalkylations. The present work has thus opened a new route to preparations of polymers of linear, hyperbranched, or hybrid (e.g., linear–hyperbranched) architecture by operating on structural parameters and reaction conditions.

### 1. Introduction

The classical theory of step-growth polymerization is based on two concepts.<sup>1–3</sup> The first is an assumption of equal reactivity of both functional groups in a bifunctional reactant. It is also assumed that at any given stage of the polymerization all functional groups are equally reactive regardless of the size of the molecule to which they are attached (and that no intramolecular cyclization occurs). The molecular weight distribution consequently predicted is known as the “most probable” distribution.

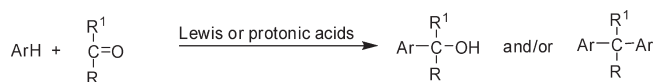
The second concept is that stoichiometric imbalance in monomer feed ratio decreases degree of polymerization. The highest molecular weight of linear polymer is obtained when exactly stoichiometric amount of the monomers are present.

There are many examples of polymerizations involving reactants where the equal reactivity of functional groups assumption is not valid. For example, this occurs with unsymmetrical reactants, such as toluene-2,4-diisocyanate, propane-1,2-diol, and butane-1,3-diol,<sup>4</sup> when the more reactive functional groups react first. Generally, the first reaction rate of a bifunctional monomer is faster than the second one. The opposite situation, when the first reaction enhances the reactivity of the second one, has received very little attention.

In 1999, T. Endo in the course of study of polycondensation of 2,2-dichloro-1,3-benzodioxole and 4,4'-isopropylidenediphenol reported on the rate enhancement of the second reaction by the

first one in the case when two functional groups are present on the same atom.<sup>5</sup> But more important was the finding that the degree of polymerization is enhanced by stoichiometric imbalance if the first condensation of bifunctional monomer enhances the second condensation of the remaining functional group. The highest molecular weight of polyorthocarbonate ( $M_n$  120 000) was obtained when ca. 0.7 equiv. excess of 2,2-dichloro-1,3-benzodioxole was used. A kinetic analysis of the polycondensation was described. It is worth mentioning that a positive effect of the stoichiometric imbalance was also observed in the polycondensation of dichlobenzene with sodium sulfide<sup>6</sup> and in the reactions of methylene bromide with bisphenol salts<sup>7</sup> and 4,4'-thiobis(benzenethiol).<sup>8</sup> In all these cases one of the monomers has the functional groups connected to the same atom.

Another synthesis type with two consecutive reactions is the acid-catalyzed condensation of ketones and aldehydes with aromatic compounds, known as the hydroxyalkylation reaction<sup>9,10</sup>



where R and R<sup>1</sup> are H, alkyl, aryl.

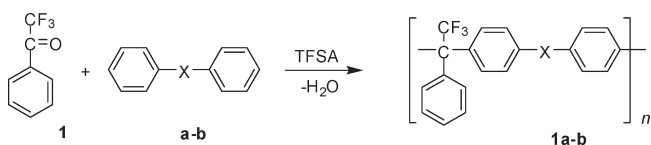
Depending on the monomer structures and reaction conditions, an alcohol, a diaryl-compound or a mixture of these can be obtained. The acid-catalyzed addition reactions of aldehydes and ketones have been known for a long time. For instance, the condensation of chloral with benzene in the presence of sulfuric

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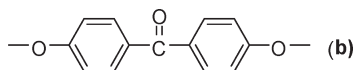
acid was reported by A. Bayer as early as 1872.<sup>11</sup> Nevertheless, these Friedel–Crafts-type reactions have not been studied to the same extent as the corresponding reactions involving alcohols, alkyl halides or aryl halides. Probably, the main reason for such neglect is the generally lower yields and the formation of oligomeric byproducts.

The concept of superelectrophilic activation proposed by Olah and co-workers to explain the high reactivities of electrophilic species in superacidic media<sup>12,13</sup> and its application for hydroxyalkylation reactions turned out to be remarkably successful.<sup>14</sup> Numerous reactions have been carried out using superacids as a reaction medium (mostly trifluoromethanesulfonic acid (TFSA), which has been often acclaimed as one of the strongest of all known monoprotic organic acids.<sup>15,16</sup>

Recently, for the first time, superacid-catalyzed polyhydroxyalkylation reactions of carbonyl compounds with nonactivated aromatic hydrocarbons to produce high-molecular-weight linear<sup>17–24</sup> or hyperbranched<sup>25–28</sup> dendrons and dendrimers<sup>29</sup> were reported. In these reactions, the intermediate alcohol reacts with another aromatic compound to give a diarylation product. Thus, reactions of 2,2,2-trifluoroacetophenone (**1**) with biphenyl and 4,4'-diphenoxybenzophenone in the presence of TFSA gave linear, film-forming polymers with *para*-substitution in the main chain<sup>18</sup>

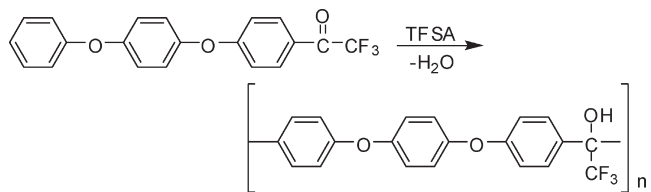


where  $-X-$  is nil (**a**) or



It is worth mentioning that trifluoromethyl groups in carbonyl compounds eventually become substituents in polymer chains, which affords new polymer structures and properties.

More recently, M. Ueda reported an interesting case of the TFSA-catalyzed self-polymerization of 2,2,2-trifluoro-1-[4-(4-phenoxyphenoxy)phenyl]ethanone, which led to a linear polyether instead of the expected hyperbranched polymer:<sup>30</sup>



It was also demonstrated<sup>31</sup> that the reactivities of the monomer and the intermediate (the rate constants of the first and the second reactions) can be different and depend on the acidity of the reaction medium.

Taking into account cheaper, more readily available monomers and the promising properties of polymers that might be obtained from possessing large synthetic potential polyhydroxylations, the objectives of this present article deal with (i) a mechanistic analysis of the consecutive electrophilic substitution reactions in superacid-catalyzed polyhydroxylation, and (ii) an increase of the efficiency of polyhydroxyalkylation by means of nonstoichiometric chemistry.

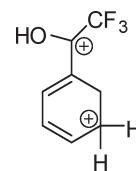
## 2. Results and Discussion

### 2.1. Theoretical Aspects. 2.1.1. Reaction of 2,2,2-Trifluoroacetophenone with Anisole.

It was found that only the

diarylation product, 4,4'-(2,2,2-trifluoro-1-phenylethane-1,1-diyl)bis(methoxybenzene) (**7**), was selectively obtained in methanesulfonic acid (MSA) after the reaction of an equimolar amount of anisole with **1**, whereas a hydroxyalkylation product, 2,2,2-trifluoro-1-(4-methoxyphenyl)-1-phenylethanol (**3**), was formed quantitatively in TFSA (Scheme 1). When two equiv of anisole to **1** were used only diarylation products were isolated in the cases of both MSA and TFSA.<sup>30</sup>

It has been also suggested that in TFSA a very reactive dicationic intermediate is generated.<sup>30</sup>



To verify this hypothesis the reaction of 2,2,2-trifluoroacetophenone (**1**) with anisole has been studied theoretically in both MSA and TFSA media. The inner solvation sphere was represented by two explicit MSA or TFSA molecules (Figure 1).

Figure 1 shows the PBE0/6-311+G(d,p) optimized geometries of **1** in TFSA (**1-TFSA**) and MSA (**1-MSA**), transition state structures for the first reaction step between **1** and anisole in TFSA (**TS1-TSFA**) and MSA (**TS1-MSA**), optimized structures of **2** in TFSA and the corresponding transition state in TFSA (**TS2**).

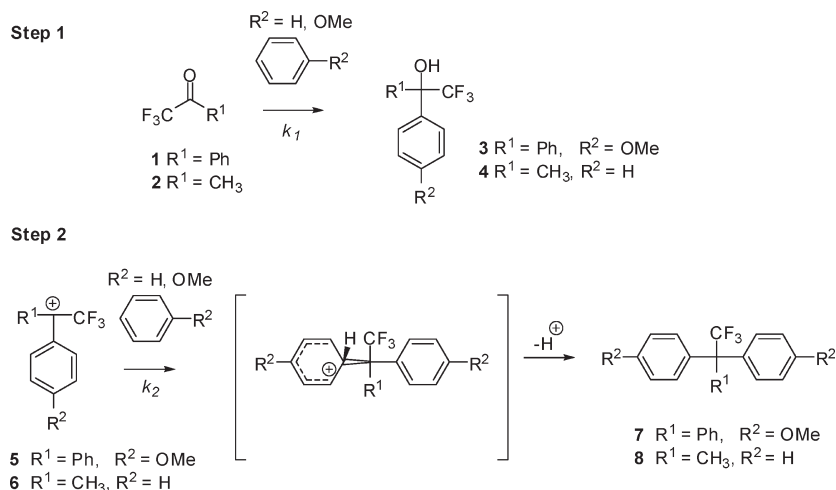
For the outer solvation sphere, the SMD continuous model was used as implemented in Gaussian 09.<sup>32</sup> (Dielectric constant of 77.4 and solvent radius of 2.60 was applied for TFSA. For MSA dielectric constant of 70.0 and solvent radius of 2.34 Å were used (Scheme 1). All geometries were optimized with the PBE0 functional<sup>33</sup> in combination with the /6-311+G-(d,p) basis set. This is the slightly modified computational model described in ref 34, which reproduces  $pK_a$  of selected acids within 1  $pK_a$  unit.

Our model rationalizes different reactivity of **1** in two reaction media without the need to involve the diprotonated carbonyl group. The free Gibbs activation energy of the first step in TFSA (22.51 kcal/mol) is lower than that of the second step (25.98 kcal/mol), in agreement with experimental findings.

However, no diprotonation of the carbonyl group takes place (Figure 1). The proton transfer occurs only during nucleophilic attack of anisole at the carbonyl group and at any given moment only one proton is transferred to the carbonyl oxygen, while the other one forms a hydrogen bond with the carbonyl group at all stages of  $\sigma$ -complex formation. The MSA mediated reaction between anisole and **1** (Figure 1 and Table 1) result in the formation of a monoprotonated transition state (**TS1-MSA**) and a monoprotonated  $\sigma$ -complex similar to that formed in the TFSA catalyzed reaction.

However, the free Gibbs activation energy of the first step increases by 3.5 kcal/mol (Table 1), while the second step has a similar activation energy in both MSA and TFSA. The increase of activation energy in MSA compared to TFSA for the first reaction step is due to more positive protonation energy for MSA (weaker acid), which contributes to the total activation energy for the first reaction step. Therefore, it is possible to change the relative rates of the first and second steps using less a reactive aromatic component to avoid excessive stabilization of the carbocation to decrease the activation energy of the second reactive step. A good model on which to test this hypothesis is the reaction between trifluoroacetone (**2**) and benzene.

Scheme 1. Reaction between Carbonyl Compounds and Aromatics

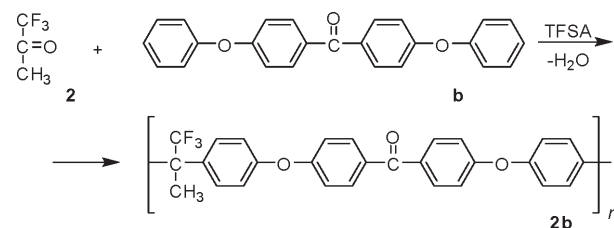


**2.1.2. Reaction of 2,2,2-Trifluoroacetone with Benzene.** Theoretical studies suggested that monoprotonated species are the active electrophiles in this reaction.<sup>34</sup> Calculations demonstrated that the free Gibbs activation energy ( $G_a$ ) of the first reaction step (27.57 kcal/mol) is higher than that of the second (22.09 kcal/mol) (Table 1). The carbonyl group of **2** forms only hydrogen bonds with protons of TFSA (Figure 1). The proton transfer occurs only during the nucleophilic attack of benzene at carbonyl group and at any given moment only one proton is transferred to the carbonyl oxygen, while the other one forms a hydrogen bond with carbonyl group at all stages of  $\sigma$ -complex formation. Therefore, those data suggest the presence of monoprotonated electrophilic species in this reaction. Since  $G_a$  of the first step is higher than that of the second, the first step is slower than the second according to calculations. High and positive protonation energies of the electronically deficient carbonyl group of **2** contribute to the high activation energy of the first step and favor low  $k_1$ .

Since the rate constants ( $k$ ) are related to  $G_a$  through the Eyring equation  $k = (k_b T/h) \exp(-G_a/RT)$ , where  $k_b$ ,  $T$ ,  $h$ , and  $R$  are the Boltzmann constant, absolute temperature, Planck's constant and gas constant, it is possible to calculate  $k_1/k_2$  ratio (Scheme 1). The calculated  $k_1/k_2$  ratio in TFSA for the reaction of **2** with anisole is 350, while for the reaction of **1** with benzene this ratio is only  $10^{-4}$ . The rate constant ratio in MSA for the reaction of **2** with anisole is close to 1. Therefore, high protonation energy of the carbonyl component favors low  $k_1$  ( $k_1 < k_2$ ). Low protonation energy and high reactivity of aromatic component favors high  $k_1$  ( $k_1 > k_2$ ). Generally the  $k_1/k_2$  ratio depends on three factors: the first is the carbonyl group protonation energy. The protonation energy depends on the basicity of a carbonyl group and acid strength. The second one is the electrophilicity of carbonyl component.<sup>35</sup> Those two factors are interconnected since higher electrophilicity implies a lower activation energy of  $\sigma$ -complex formation but higher protonation energy. The third factor is the nucleophilicity of the aromatic component.<sup>36</sup> A less nucleophilic aromatic component decreases  $k_1$  but decreases  $k_2$  with respect to  $k_1$  due to destabilization of carbocation, the reactive intermediate of the second reaction step. The increase of the acidity of the media (all other things being equal) decreases  $k_1$  at the expense of protonation energy but leaves  $k_2$  intact. Therefore, it is possible to adjust the  $k_1/k_2$  value by modifying either the reaction conditions or the monomer structure. As a result, a monoarylated carbinol or diarylated derivative can be obtained selectively in super-

acid-catalyzed hydroxyalkylation. Application of this methodology for the polymer syntheses allows for nonstoichiometric accelerations and for polymers of different topology such as linear, hyperbranched, or linear-hyperbranched hybrids to be obtained.

**2.2. Polymer Syntheses.** **2.2.1. Polycondensation of Trifluoroacetone with 4,4'-Diphenoxybenzophenone.** Calculations demonstrated that in the reactions of trifluoroacetone with non activated aromatic hydrocarbons, Gibbs activation energy ( $G_a$ ) of the first step is higher than that of the second; therefore, the first step is slower than the second one, which should allow for nonstoichiometric polycondensations to occur. To evaluate the effect of the stoichiometric imbalance (excess amount of the carbonyl compound), further experiments were carried out with polycondensations of trifluoroacetone with 4,4'-diphenoxybenzophenone. The polycondensations were carried out according to the following scheme



with variation of molar ratio of comonomers in TFSA medium at room temperature. Figure 2 illustrates the dependence of viscosity  $\eta_{\text{inh}}$  of the polymers on the stoichiometric imbalance.

It is quite remarkable that even a 15% excess of **2** significantly increases polymer viscosity. Further increase of stoichiometric imbalance results in a dramatic increase in molecular weight of the polymers. The viscosity of the reaction mixture very rapidly increased, and the reactions were complete in several minutes. However, a large excess of trifluoroacetone led to extensive cross-linking. The analytical data (IR, <sup>1</sup>H and <sup>13</sup>NMR) of the polymers from the nonstoichiometric syntheses were identical to those from the stoichiometric ones, except for the viscosity. As an example, the NMR spectra of polymer **2b** obtained with 20% excess of trifluoroacetone is given in Figure 3.

Yields of the polymers obtained were close to quantitative (96–97%). Therefore, neither purity nor decomposition of **2**

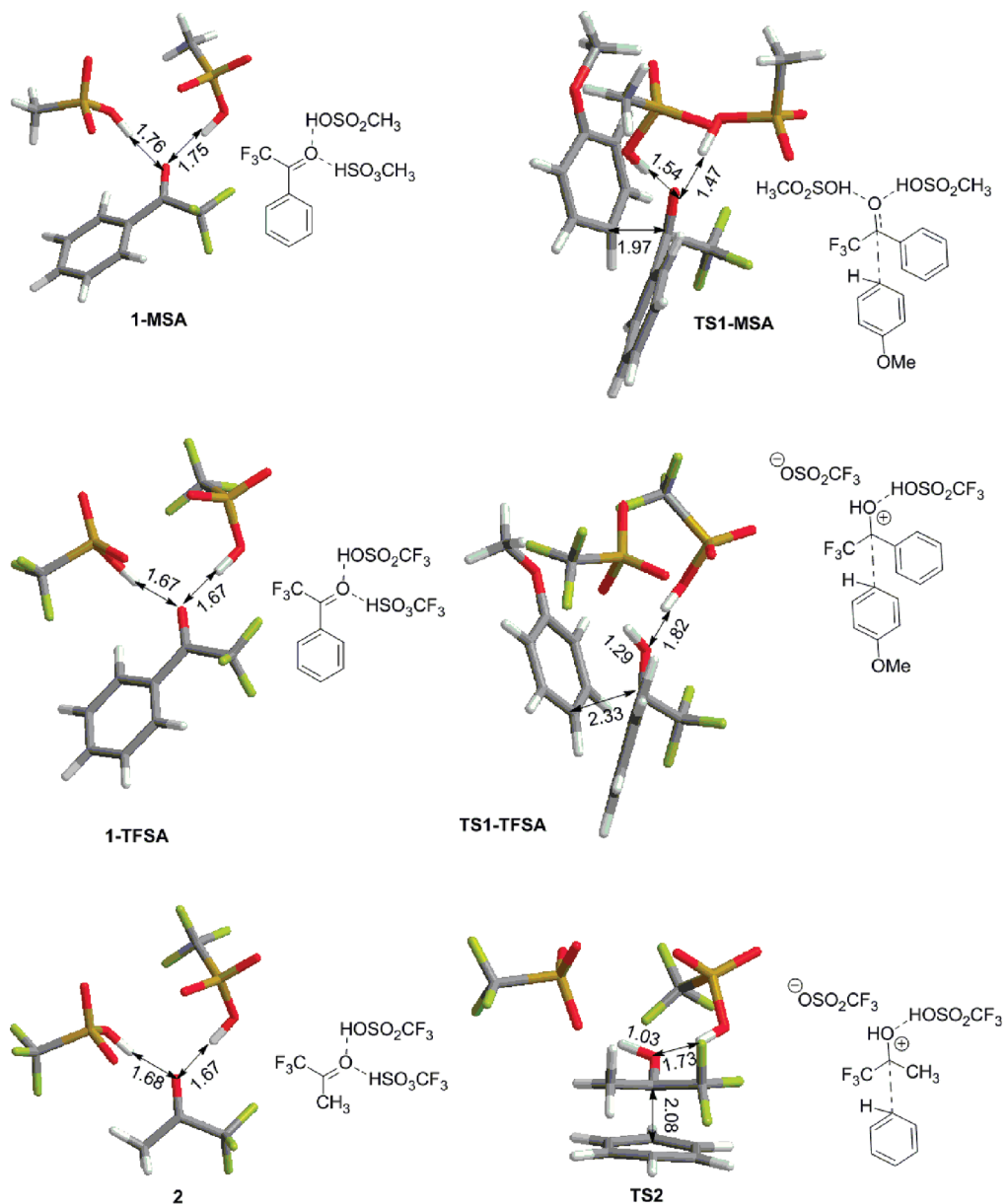


Figure 1. Optimized geometries of the reaction intermediates.

Table 1. Free Gibbs Activation Energies  $G_a$  (kcal/mol) of Studied Reaction, Calculated at the PBE0/6-311+Gd,p Level in TFSA and MSA, Respectively

| reaction                    | $G_a$ (kcal/mol) |
|-----------------------------|------------------|
| TFSA                        |                  |
| 1 + anisole $\rightarrow$ 3 | 22.51            |
| 5 + anisole $\rightarrow$ 7 | 25.98            |
| 2 + benzene $\rightarrow$ 4 | 27.57            |
| 6 + benzene $\rightarrow$ 8 | 22.09            |
| MSA                         |                  |
| 1 + anisole $\rightarrow$ 3 | 26.00            |
| 5 + anisole $\rightarrow$ 7 | 25.89            |

could be the reason for the most effective polycondensation. Table 2 shows the effect of stoichiometric imbalance on the viscosity and weight- and number-averaged molecular weights and polydispersity of 3.

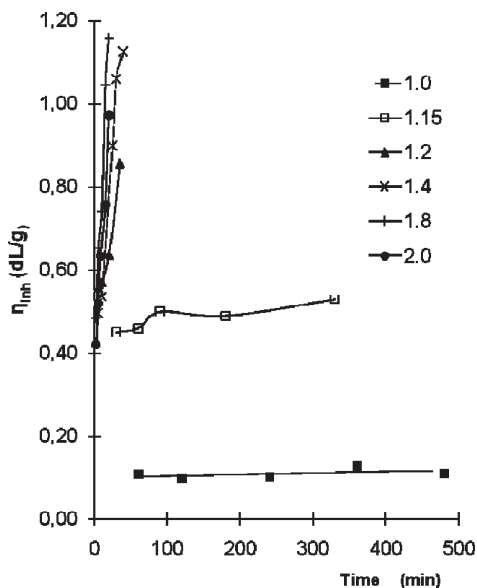
The results clearly indicate that the polymers with higher molecular weight are obtained under nonstoichiometric

conditions. As can be seen from the table, the molecular weight and polydispersity of the resulting polymer increased with the increase in stoichiometric imbalance.

The high polydispersity of the polymers obtained with a large excess of trifluoroacetone points to the occurrence of side reactions. Structural studies of the polymers by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy revealed *para*-substituted phenylene fragments in the main chain of the polymers. There are, however, small broad multiplets around the main signals. It is very likely that the signals are due to products of some reactions of diphenyl ether fragments.<sup>37</sup>

During the past 10 years, H. Kricheldorf and co-workers have shown that in kinetically controlled stoichiometric polycondensation of linear monomers ring closure competes with propagation at any concentration and at any stage of the polycondensations.<sup>38</sup> Besides, any optimization of the reaction conditions toward high molecular weights also raises the fraction of cyclic molecules at the expense of all linear chains. As a result, all reaction products are necessarily macrocycles at 100% conversion when side reactions are absent. Obviously, suppression of macrocycle formation would

give result in very high molecular weight linear polymers. One may assume that the decrease in the macrocyclic content could



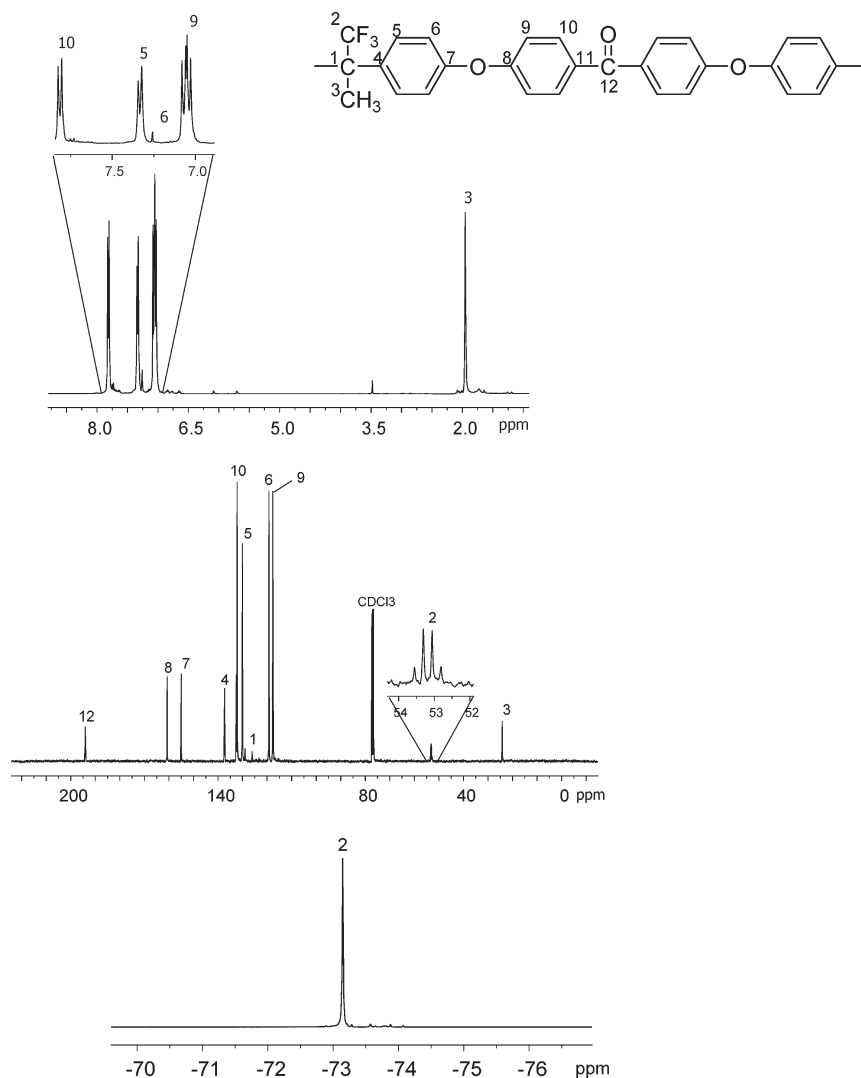
**Figure 2.** Relationship between the monomer feed ratio and the inherent viscosity of the polymers.

contribute to the efficiency of nonstoichiometric polyhydroxyalkylations.

In this connection, two polymer samples obtained from stoichiometric (**2bs**,  $M_w = 15\,400$ ,  $M_n = 9860$ ) and nonstoichiometric (**2bns**,  $M_w = 299\,000$ ,  $M_n = 108\,000$ ) syntheses were characterized. The MALDI-TOF mass spectra (Figure 4) revealed the existence of macrocycles in both samples.

An interesting and important result is the observation that the sample from stoichiometric synthesis contains also linear chains having diphenoxybenzophenone end groups. This is additional evidence that the second reaction is faster than the first one. Although only mass peaks of cycles (**M2–M5**), were detectable in the sample **2bns**, it is obvious that high molecular weight cycles and linear structures are also present in these samples. It is well-known that high molar mass polymers are discriminated in MALDI-TOF measurements, and the low signal-to-noise ratio of **M2–M5** in the B-spectrum indicates that only a small fraction of cyclic oligomers appears in this mass spectrum. See Figure 5 for structures of **M** and **L**.

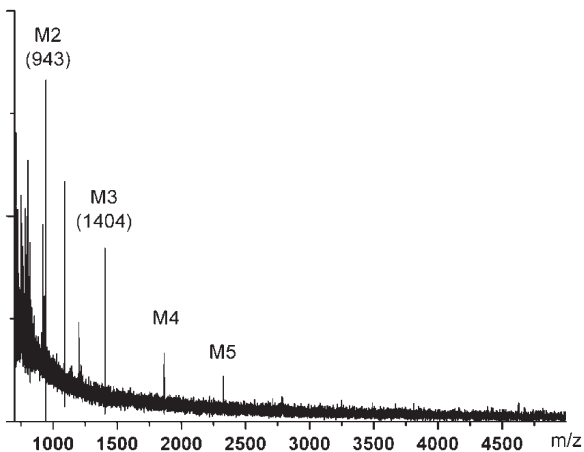
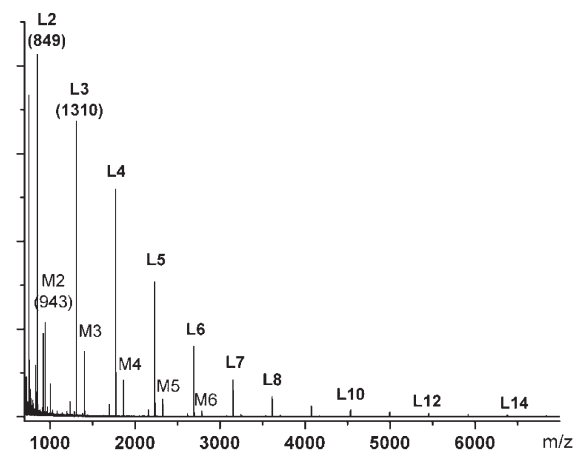
On the whole, one may conclude that in the structural aspect the nonstoichiometric polyhydroxyalkylation is in line with modern theory of step-growth polymerizations.<sup>38,39</sup> If so, the main reason for the nonstoichiometric acceleration should be increase of the first reaction as the concentration of **2** and  $k_2/k_1$  value are increased.<sup>40</sup> Since the rate-determining



**Figure 3.** The  $^1\text{H}$  (top),  $^{13}\text{C}$  (middle), and  $^{19}\text{F}$  (bottom) spectra of polymer **2b** (solution in  $\text{CDCl}_3$ ).

**Table 2.** Effect of feed ratio on the polycondensation of trifluoroacetone (**2**) with 4,4'-diphenoxybenzophenone (**b**)

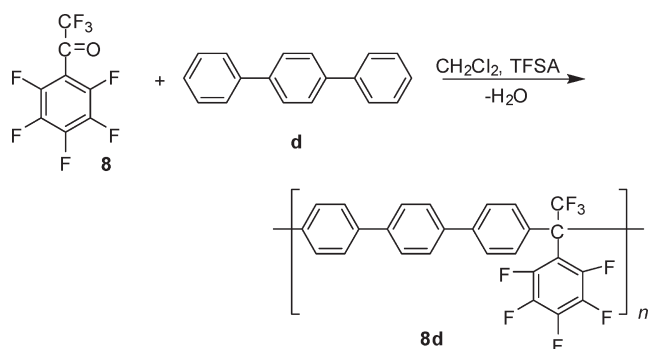
| <b>2:b</b> (mol/mol) | reaction time, min | inherent viscosity $\eta_{inh.}$ , dL g <sup>-1</sup> (NMP) | molecular weight, (g/mol), $M_w \times 10^4$ | molecular weight, (g/mol), $M_n \times 10^4$ | $M_w/M_n$ |
|----------------------|--------------------|-------------------------------------------------------------|----------------------------------------------|----------------------------------------------|-----------|
| 1                    | 60                 | 0.22                                                        | 1.843                                        | 1.112                                        | 1.66      |
|                      | 360                | 0.27                                                        | 15.82                                        | 8.040                                        | 1.96      |
| 1:2                  | 5                  | 0.56                                                        | 25.09                                        | 12.63                                        | 1.98      |
|                      | 35                 | 0.86                                                        | 36.26                                        | 12.77                                        | 2.84      |
| 1:4                  | 5                  | 0.49                                                        | 17.79                                        | 8.04                                         | 2.21      |
|                      | 30                 | 1.06                                                        | 61.70                                        | 16.27                                        | 3.79      |
| 1:8                  | 5                  | 0.65                                                        | 18.15                                        | 5.71                                         | 3.17      |
|                      | 20                 | 1.16                                                        | 117.50                                       | 25.32                                        | 4.65      |

**Figure 4.** MALDI-TOF spectra of polymer **2bs** (top) and **2bns** (bottom).

step  $k_1$  governs the net rate of the polymerization, the net rate of the polymerization also increases, and a high molecular weight polymer would be obtained.

**2.2.2. Polycondensations of Trifluoroacetophenone, Octafluoroacetophenone, and Isatin with Aromatic Hydrocarbons.** According to calculations, in TFSA catalyzed hydroxyalkylations involving 2,2,2-trifluoroacetophenone (**1**) and an aromatic hydrocarbon less reactive than anisole, the rate of the second reaction can be faster than that of the first one. Therefore, one can expect that polycondensation of **1** with diphenyl ether (**c**) would be enhanced by stoichiometric imbalance. Indeed, the high molecular weight polymer was obtained in 3 h when 0.4 equiv excess of **1** was used (Table 3). Biphenyl (**a**), an aromatic hydrocarbon less nucleophilic than diphenyl ether in aromatic electrophilic substitution reactions, still reacts with **1** to give a polymer with an inherent viscosity 0.59 dL/g. Remarkably, nonstoichiometric polycondensation of biphenyl with an excess of **1** gave in 7.5 h a polymer **1a** with  $\eta_{inh.} = 1.19$  dL/g.

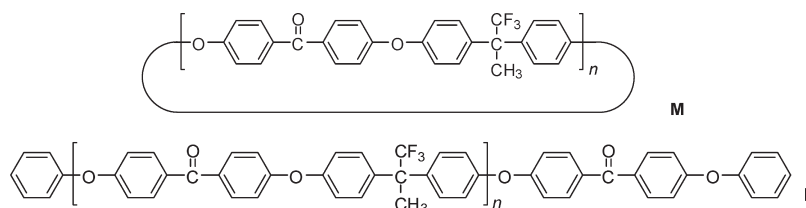
Octafluoroacetophenone (**8**) is significantly less reactive (electrophilic) than **1**. Polycondensation of octafluoroacetophenone with terphenyl proceeds very slowly to give in 24 days a film-forming polymer with an inherent viscosity 0.47 dL/g



It is very likely that the low basicity (which means high protonation energy) of octafluoroacetophenone (which favors low rate constant of the first reaction) is the main reason for its low reactivity. Therefore, it seems plausible that the degree of polymerization can be elevated by a stoichiometric imbalance. Polycondensation of terphenyl (**d**) with 0.4 equiv excess of octafluoroacetophenone (**8**) gave in 2 days a polymer **8d** with an inherent viscosity 0.71 dL/g (Table 3, entry 5 and 6).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the polymer **8d** (Figure 6) are well resolved, and all signals related to the *para*-substituted terphenylene and pentafluorophenyl fragments are evident. Detail analysis of these spectra revealed no essential indications of structural irregularities

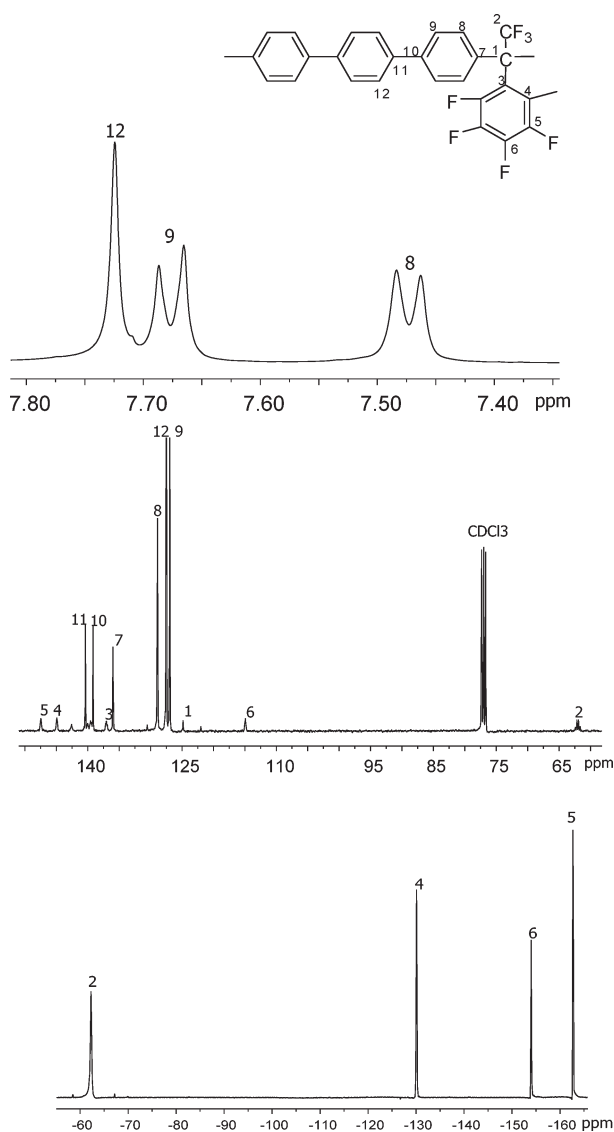
It is worthy of mention that the reaction medium in the course of the polycondensation of phenyl ether with **1** was homogeneous, whereas the reactions involving biphenyl and terphenyl proceeded as 'precipitation polycondensations', when the polymer formed precipitated from the initially homogeneous 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.<sup>41,42</sup> The precipitate formed during the course of polymerizations that involve fluorinated carbonyl compounds and biphenyl or terphenyl, appear as a colored elastic mass ("reactive gel"). After completion of the reaction, the precipitates formed are isolated from the reaction medium, shredded, washed thoroughly with methanol, and dried overnight in air. After reprecipitation from chloroform into methanol, followed by filtration and extraction with refluxing methanol before drying at 100 °C under vacuum, white fibrous polymers were obtained.



**Figure 5.** Chemical compositions of cyclic (**M**) and linear (**L**) products.

**Table 3.** Effect of Feed Ratio on the Inherent Viscosities

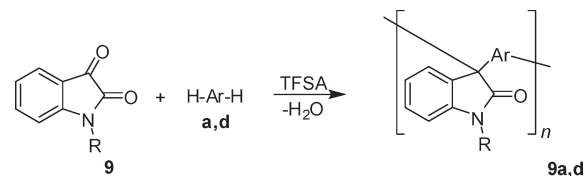
| entry | carbonyl compound                  | aromatic hydrocarbon        | ketone/aromatic (mol/mol) | reaction time | inherent viscosity $\eta_{inh}$ , dL/g, (NMP) |
|-------|------------------------------------|-----------------------------|---------------------------|---------------|-----------------------------------------------|
| 1     | trifluoroacetophenone ( <b>1</b> ) | diphenyl ether ( <b>c</b> ) | 1.0                       | 3 h           | 0.14                                          |
| 2     |                                    |                             | 1.4                       | 3 h           | 0.60                                          |
| 3     |                                    | biphenyl ( <b>a</b> )       | 1.0                       | 24 h          | 0.59                                          |
| 4     |                                    |                             | 1.4                       | 7.5 h         | 1.20                                          |
| 5     | octafluoroacetophenone( <b>8</b> ) | terphenyl ( <b>d</b> )      | 1.0                       | 24 days       | 0.47                                          |
| 6     |                                    |                             | 1.4                       | 2 days        | 0.71                                          |
| 7     | isatin ( <b>9</b> )                | biphenyl ( <b>a</b> )       | 1.0                       | 6 h           | 0.39                                          |
|       |                                    |                             | 1.1                       | 6 h           | 2.37                                          |
| 8     |                                    | terphenyl ( <b>d</b> )      | 1.0                       | 6 h           | 0.45                                          |
|       |                                    |                             | 1.3                       | 3 h           | 2.29                                          |
|       |                                    |                             | 1.5                       | 2 h 50 m      | 4.40                                          |



**Figure 6.** The  $^1\text{H}$  (top),  $^{13}\text{C}$  (middle), and  $^{19}\text{F}$  (bottom) spectra of polymer **8d** (solution in  $\text{CDCl}_3$ ).

As seen in Table 3, despite the heterogeneous reaction medium the stoichiometric imbalance enhances above-mentioned polycondensations.

Finally, stoichiometric and nonstoichiometric polymerizations of isatin with aromatic hydrocarbons were carried out according to the following scheme:



To decrease reactivity of isatin the reactions were performed in a mixture of TFSA with trifluoroacetic acid (TFA). Nevertheless, the effect of stoichiometric imbalance in these reactions is even more pronounced (Table 3, entries 7, 8). Remarkably, all the polymers obtained are completely soluble. Recently, we reported on highly efficient reactions of isatin with linear, nonactivated, multiring aromatic hydrocarbons.<sup>24</sup> We found that isatin based polymerizations meet the criteria needed for “click” polymer chemistry. Therefore, another factor contributing to the nonstoichiometric acceleration could be efficiency of the polymerization.

### 3. Conclusions

The calculations for the consecutive superacid catalyzed electrophilic aromatic substitution reactions of trifluoroacetone and trifluoroacetophenone with aromatic hydrocarbons explained a number of experimental facts within one theoretical framework of monoprotection. They also revealed principal factors affecting kinetics of superacid mediated hydroxyalkylation, such as (i) the acidity of superacid affecting protonation energy of carbonyl component, (ii) electrophilicity, and (iii) nucleophilicity of carbonyl and aromatic components, respectively. The modification of those factors allows for tuning of the reactivity of carbonyl and aromatic components; thereby, reaction kinetics are controlled. Thus, an increase of acid strength and electrophilicity of the carbonyl component increase  $k_1$ , while the decrease of nucleophilicity of aromatic monomer increases  $k_2$  with respect to  $k_1$ .

A proper relationship between the electrophilicity of the carbonyl group, the nucleophilicity of the aromatic hydrocarbon, and the acidity of the reaction medium allows for the selection of favorable conditions for the nonstoichiometric polymerizations.

The conclusions were confirmed by the experiments. Theoretically predicted stoichiometrically imbalanced polymerizations of trifluoroacetone, trifluoroacetophenone, octafluoroacetophenone and isatin with nonactivated, aromatic hydrocarbons gave high molecular weight polymers with a very small excess of the carbonyl compound. The acceleration of nonstoichiometric polymerizations does not depend on the phase state (heterogeneity) of the reaction medium.

The main reasons contributing to the polymerization accelerations were found to be an increase of the first reaction, the rate-determining step reaction, and a high efficiency of the superacid catalyzed polyhydroxyalkylations.

The present work has thus opened a new route to preparations of polymers of linear, hyperbranched or hybrid (e.g., linear-hyperbranched) architecture by operating on structural parameters and reactions conditions. Cheaper, commercially available monomers and the promising properties of polymers that might be obtained from them would stimulate interest in that field.

## 4. Experimental Part

**4.1. Characterization.** NMR spectra were recorded on Bruker Avance 400 Spectrometer, operating at 400.13 and 100 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  respectively. Chloroform-*d* ( $\text{CDCl}_3$ ) was used as solvent. Infrared (IR) spectra were measured on a Nicolet FT-IR-ATR spectrometer. 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–MALLS) according to the published method.<sup>40</sup> 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. An Autoflex III MALDI–TOF mass spectrometer (Bruker Daltonik, Germany) was used. The system is equipped with a “Smartbeam” laser working at 355 nm. Samples were dissolved in chloroform (1–2 mg/mL) and mixed with (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitril) (DCTB) matrix solution (10 mg/mL in tetrahydrofuran) and sodium trifluoroacetate (NaTFA, 2 mg/mL in tetrahydrofuran) in a ratio of 20/50/2 (v/v/v). A 1  $\mu\text{L}$  sample of this solution was dropped on the target and inserted in the mass spectrometer after evaporation of the solvent. A total of 2000 single laser shots were accumulated for one spectrum.

**4.2. Materials.** All starting materials were obtained from Aldrich. Biphenyl, phenyl ether, and *p*-terphenyl were used as received. Methylene chloride, TFSA, trifluoroacetone, trifluoroacetophenone, and octafluoroacetophenone were distilled before use. Isatin was purified by recrystallization with charcoal from ethanol.

**4.3. Polymer Syntheses.** *Preparation of Poly[oxy-1,4-phenylene-carbonyl-1,4-phenyleneoxy-1,4-phenylene(2,2,2-trifluoro-1-methylethylidene)-1,4-phenylene] (2b).* 1,1,1-Trifluoroacetone (0.313 g 2.8 mmol), diphenoxybenzophenone (1.027 g 2.8 mmol) and TFSA (5 mL) were stirred at room temperature for 8 h and the resulting clear, viscous red solution was then poured slowly into methanol (100 mL). The white fiber formed was filtered off and extracted with hot methanol. After drying 1.333 g (99% yield) of white fiber polymer was obtained. The polymer had an inherent viscosity ( $\eta_{\text{inh}}$ ) of 0.27 dL g<sup>-1</sup> in NMP.

*Nonstoichiometric Synthesis of Poly[oxy-1,4-phenylene-carbonyl-1,4-phenyleneoxy-1,4-phenylene(2,2,2-trifluoro-1-methylethylidene)-1,4-phenylene] (2b).* 1,1,1-Trifluoroacetone (0.375 g 3.36 mmol), diphenoxybenzophenone (1.027 g 2.8 mmol) and TFSA (5 mL) were stirred at room temperature for 5 min and the

resulting viscous red solution was then poured slowly into methanol (100 mL). The white fiber formed was filtered off and extracted with hot methanol. After drying 1.303 g (97% yield) of white fiber polymer was obtained. The polymer had an inherent viscosity ( $\eta_{\text{inh}}$ ) of 0.42 dL g<sup>-1</sup> in NMP.

*Poly[[1,1'-biphenyl]-4,4'-diyl(2,2,2-trifluoro-1-phenylethylidene)] (1a).* TFSA (41.3 mL) was added to a mixture of 2,2,2-trifluoroacetophenone (8.42 g 48.3 mmol), biphenyl (7 g 48.3 mmol), and  $\text{CH}_2\text{Cl}_2$  (33.7 mL). The reaction mixture was stirred with magnetic stirrer at room temperature for 4 days and the resulting viscous, green solution was then poured slowly into methanol (500 mL). The white fiber polymer was filtered off and extracted with refluxing methanol for 12 h. The resulting polymer (15 g 98%) had an inherent viscosity ( $\eta_{\text{inh}}$ ) of 0.59 dL g<sup>-1</sup> in NMP.

*Poly[oxy-1,4-phenylene(2,2,2-trifluoromethyl-1-phenylethylidene)-1,4-phenylene] (1c).* Polymer synthesis was conducted in single necked 15 mL flask equipped with magnetic stirrer. 2,2,2-Trifluoroacetophenone (0.992 g 5.7 mmol), diphenyl ether (0.9705 g 5.7 mmol),  $\text{CH}_2\text{Cl}_2$  (3.2 mL) and TFSA (0.8 mL) were stirred at room temperature for 3 h and the resulting clear, viscous orange solution was then poured slowly into methanol (200 mL). The white fiber formed was filtered off and extracted with hot methanol. After drying, 1.769 g (95% yield) of white fiber polymer was obtained. The polymer had an inherent viscosity  $\eta_{\text{inh}}$  of 0.14 dL g<sup>-1</sup> in NMP.

*Poly[1,1':4',1''-terphenyl-4,4''-diyl(2,2,2-trifluoro-1-(2,3,4,5,6-pentafluorophenyl)ethylidene)] (8d).* TFSA (4.5 mL) was added to a mixture of octafluoroacetophenone (1.264 g 4.8 mmol), terphenyl (1.102 g 4.8 mmol), and  $\text{CH}_2\text{Cl}_2$  (3.9 mL). The reaction mixture was stirred at room temperature for 30 days and the resulting viscous green solution was then poured slowly into methanol (400 mL). The white fiber formed was filtered off and extracted with hot methanol. After drying, 2.2 g (96% yield) of white fiber polymer was obtained. The polymer had an inherent viscosity  $\eta_{\text{inh}}$  of 0.46 dL g<sup>-1</sup> in NMP.

*Preparation of Poly[(2,3-dihydro-2-oxo-1*H*-indole-3,3-diyl)-[1,1':4',1''-terphenyl]-4,4''-diyl] (9a).* A typical example of polymer preparation is as follows. TFA acid (1.2 mL) and TFSA (1.8 mL) were added to a mixture of isatin (0.066 g, 0.45 mmol) and biphenyl (0.069 g, 0.45 mmol). The reaction mixture was stirred at room temperature for 6 h and precipitated into methanol. The slightly yellow fiber formed was filtered off and washed with hot methanol. After drying, 0.1234 g (97%) of white fiber like polymer (9a) was obtained. The inherent viscosity  $\eta_{\text{inh}}$  of the 0.2% solution of the polymer in NMP was found to be 0.39 dL g<sup>-1</sup>.

*Synthesis of poly[(2,3-dihydro-2-oxo-1*H*-indole-3,3-diyl)-[1,1':4',1''-terphenyl]-4,4''-diyl] (9d).* Isatin (0.066 g, 0.45 mmol), *p*-terphenyl (0.104 g, 0.45 mmol), methylene chloride (1.7 mL), TFA (1.0 mL), and TFSA (0.3 mL) were stirred at room temperature for 6 h and precipitated into methanol. The slightly yellow fiber formed was filtered off and washed with hot methanol. After drying, 0.155 g (96. %) of white polymer 9d with an inherent viscosity  $\eta_{\text{inh}}$  of 0.45 dL g<sup>-1</sup> (NMP) was obtained.

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