

Linear, Single-Strand Heteroaromatic Polymers from Superacid-Catalyzed Step-Growth Polymerization of Ketones with Bisphenols

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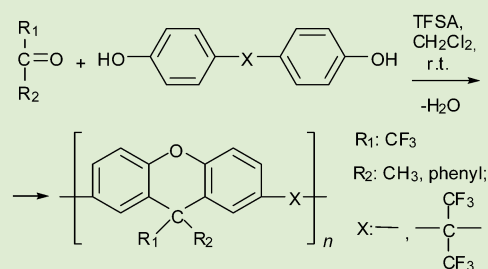
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S Supporting Information

ABSTRACT: Novel, linear, high-molecular-weight single-strand heteroaromatic polymers and copolymers containing 9*H*-xanthene moieties in the backbone were synthesized by metal-free superacid-catalyzed stoichiometric and nonstoichiometric step-growth polymerizations of carbonyl compounds bearing electron-withdrawing substituents with bisphenols. The electrophilic aromatic substitution reactions of ketones with phenol fragments occur exclusively in *ortho*-positions to the hydroxy phenol group and followed by highly efficient cyclodehydration reaction of hydroxyl-containing intermediates to give corresponding substituted 9*H*-xanthene-2,7-diyl polymers. The polymerizations were performed at room temperature in the Brønsted superacid trifluoromethanesulfonic acid (CF₃SO₃H, TFSA) and in a mixture of TFSA with methylene chloride and nitrobenzene.



Bisphenols are widely used for the preparation of various types of polymers. These commercially available monomers, and the promising properties of the many polymers that can be produced from them, offer high incentives for polymer chemists to pursue the development of new polymer-forming reactions involving bisphenols. Thus, a new class of semi-fluorinated polymers was developed from the nucleophilic addition of bisphenols and aromatic trifluorovinyl ether monomers.¹ As a continuation of this work, new semi-fluorinated aromatic ether polymers containing perfluorocyclopentenyl and perfluorocyclohexenyl (PFCP) enchainment were prepared from the step-growth polycondensation of commercial bisphenols and octafluorocyclopentene (decafluorocyclohexene) in the presence of triethylamine.^{2,3}

Recently, the reactions of trifluoromethylaryl ketones with catechol, resorcinol, and hydroquinone (in the ratio 1 mol of ketone/2 mol of phenol) in the presence of TFSA have been reported.⁴ While the reaction with catechol affords tetraphenols without any byproducts, resorcinol and hydroquinone form substituted 9*H*-xanthenediols in high yield. Therefore, it seemed plausible that trifluoromethylaryl ketones would react with bisphenols to form macromolecules.

Exploratory reactions were carried out by treating 4,4'-biphenol (A) with equimolar quantities of 2,2,2-trifluoroacetophenone (1) in a mixture of trifluoromethanesulfonic acid (TFSA) and methylene chloride at room temperature, in a manner similar to superacid-catalyzed polyhydroxyalkylation.⁵ Various reaction conditions were explored before a successful

polymerization was achieved. The reaction proceeds as a solution step-growth polycondensation. The polymer obtained (1A) after being isolated from the reaction medium, washed, and dried has the appearance of white fiber. The polymer is completely soluble in chloroform, DMFA, NMP, DMAAC, THF, and pyridine, and flexible transparent films could be cast from the solutions. The polymer had an inherent viscosity η_{inh} of 1.06 dL g⁻¹ in NMP. The high solubility of the polymer allowed us to perform reliable spectral studies to delineate its structure.

The ¹H NMR spectrum of the polymer presents obvious overlapping of many signals and is therefore unsuitable for structural analysis (Figure 1). However, the ¹³C NMR spectrum is very well resolved and shows clean signals corresponding to the structure 1A (Scheme 1, Figure 2).

It is to be noted that the signals corresponding to carbons C-4a and C-1 are split. It is known that xanthene units are folded along the connecting line through the oxygen atom and the xanthene carbon atom C-9 so that the planes of the two benzenoid rings of the xanthene unit form an angle of 156°. Therefore, the formation of stereoisomers is the reason for the splitting of the signals in the ¹³C MNR spectrum and for observed multiple signals in the ¹H NMR spectrum.

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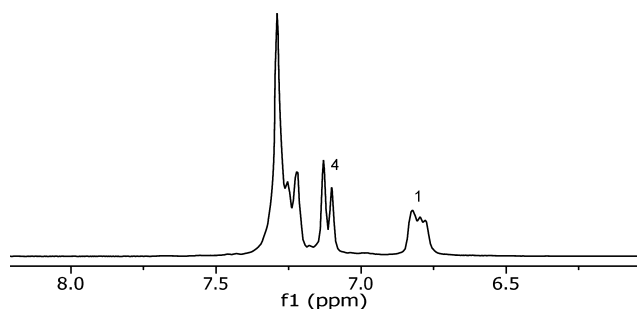


Figure 1. ^1H NMR (400.13 MHz) spectrum of polymer 1A (in CDCl_3).

Scheme 1. Reaction of 2,2,2-Trifluoroacetophenone with 4,4'-Biphenol

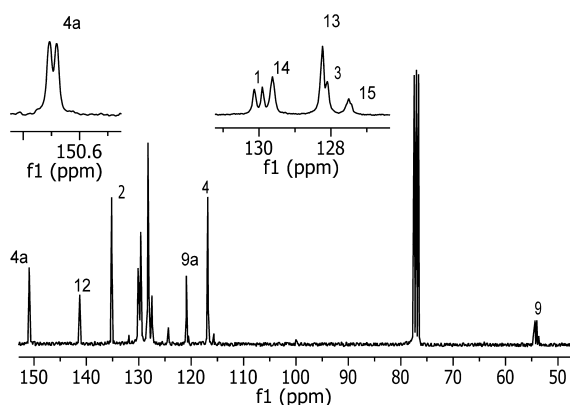
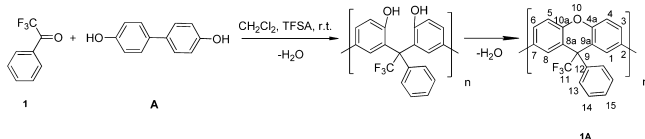


Figure 2. ^{13}C NMR spectrum of polymer 1A (in CDCl_3).

It is often difficult to achieve high regiospecificity in polyalkylation reactions, and more surprising is the fact that the polymer-forming electrophilic aromatic substitution reaction of 2,2,2-trifluoroacetophenone with 4,4'-biphenol involving two steps (the first one is a reaction of the ketone with phenol, and the second one is a reaction of the carbinol formed with phenol) proceeds exclusively in the *ortho*-position to the hydroxy group.

Remarkably, neither IR spectroscopy (Figure 3) nor NMR spectroscopy nor TGA analysis of the product detected the

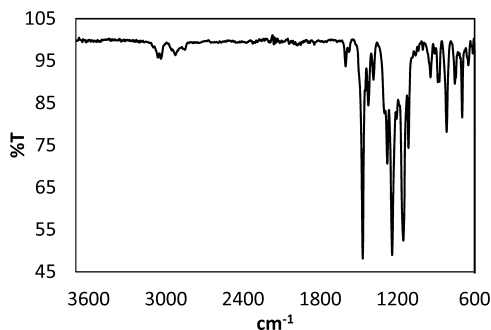


Figure 3. IR spectrum of polymer 1A.

presence of phenolic groups, which points to high efficiency of the cyclodehydration reaction that leads to the formation of 9H-xanthene fragments.

The thermal analysis of the polymer revealed a glass transition at 349 °C and decomposition temperatures in air and N_2 (onset) of 489 and 496 °C, respectively.

We were inspired by this result to polymerize 2,2,2-trifluoroacetophenone with bisphenol AF [(hexafluoroisopropylidene) diphenol]. It is known that because of the presence of the strong electron-withdrawing hexafluoroisopropylidene groups the reactivity of bisphenol AF in electrophilic aromatic substitution reactions is comparatively low.

As expected, we found that the reduced nucleophilicity of the aromatic nuclei of bisphenol AF required longer reaction times for complete conversion and produced polymer 1B with viscosity η_{inh} of 0.34 dL g^{-1} in 7 days. Therefore, we have performed a nonstoichiometric polymerization of 1 with bisphenol AF.

According to the classical theory of step-growth polymerization the highest molecular weight of a linear polymer is obtained when exactly stoichiometric amounts of the monomers are present. Recently, a strong enhancement of stoichiometrically imbalanced, superacid-catalyzed polyhydroxyalkylation has been demonstrated.⁷ The origin of the “nonstoichiometric” effect is owing to a large difference in reactivity between the initial, relatively unreactive carbonyl compound and the highly reactive intermediate carbinol formed after the first reaction step. As a result, polymers of higher molecular weight are obtained in a shorter time. This is very likely the situation for the polymerizations of 1 with B. Nonstoichiometric polymerization of 1 with B (in a relation of 1.3:1) gave in 24 h a polymer with viscosity η_{inh} of 0.51 dL g^{-1} and $T_g = 240$ °C (Figure 4, Table 1). The polymer obtained

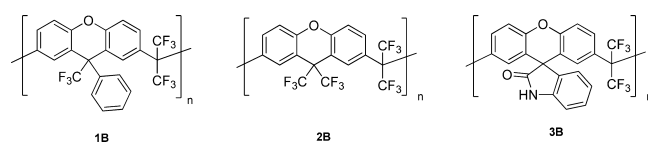


Figure 4. Structures of polymers 1B, 2B, and 3B.

exhibits an exceptional solubility: it is fully soluble in such solvents as acetone, THF, chloroform, methylene chloride, DMAAC, and DMFA, and elastic transparent films can be formed by casting from the solutions.

Condensations of trifluoroacetone with bisphenol AF proceeded with precipitation of the polymer formed from the reaction medium. There are many polymer syntheses when the polymer-forming reaction continues in the precipitate (precipitation polycondensation).

Unfortunately, in this case the precipitation resulted in low-molecular-weight oligomers.

However, we found that addition of nitrobenzene to the mixture of methylene chloride with TFSA homogenizes the reaction medium to give in 24 h a polymer (2B) with viscosity η_{inh} of 0.34 dL g^{-1} .

Successful polymerizations involving trifluoromethylalkyl and trifluoromethylaryl ketones imply that other ketones reactive in superacid-catalyzed polyhydroxyalkylation⁷ would react with bisphenols to give polymers. Indeed, polymerization of isatin (3) with B yields a polymer (3B) with viscosity η_{inh} of 0.75 dL g^{-1} .

Table 1. Polymer-Forming Reactions

entry	ketone	bisphenol	conditions ^a	polymer ^b	viscosity ^c (η_{inh}) dL g ⁻¹	T _d onset ^d (°C)	T _g (°C) ^e
1	1	A	ST	1A	0.82	497	349
2	1	B	NST	1B^f	0.51	511	240
3	2	B	NST	2B	0.35	512	215
4	3	B	ST	3B^f	0.76	400	>400

^aST: stoichiometric polycondensation. NST: nonstoichiometric polycondensation. Conditions Entry 1: **1A**, **1** (2.4 mmol), **A** (2.4 mmol), TFSA (0.5 mL), 5 h. Entry 2: **2A**, **2** (3.14 mmol), **A** (2.4 mmol), TFSA (2.0 mL), 24 h. Entry 3: **2B**, **2** (3.2 mmol), **B** (2.4 mmol), TFSA (0.5 mL), 24 h. Entry 4: **3B**, **3** (2.4 mmol), **B** (2.4 mmol), TFSA (1.0 mL), 15 days. ^bPolymer yield exceeds 85%. ^cNMP, 25 °C. ^dTGA (heating rate 10 °C/min) in nitrogen atmosphere. ^eDSC taken at 10 °C/min rate under N₂. ^fMolecular weights (M_w , M_n) determined by GPC-MALLS, THF, for the polymers **1B** and **3B** are 4.69×10^5 , 2.73×10^5 , 2.73×10^5 , 1.69×10^5 kDa, with a PD of 1.7 and 1.6, respectively.

In summary, we have demonstrated that ketones bearing electron-withdrawing substituents adjacent or relatively close to a carbocation center react with bisphenols to form high-molecular-weight linear, single-strand heteroaromatic polymers containing xanthene moieties in the backbone. The stoichiometric and nonstoichiometric polymerizations were performed at room temperature in the Brønsted superacid trifluoromethanesulfonic acid (TFSA) and in a mixture of TFSA with methylene chloride or nitrobenzene. The electrophilic aromatic substitution reactions of ketones with phenol fragments occur exclusively in *ortho*-positions to the hydroxy phenol group, followed by highly efficient cyclodehydration reaction of hydroxyl-containing intermediates to give the corresponding substituted 9*H*-xanthene-2,7-diyl polymers. These results also suggest that a large variety of new polyxanthenes may be obtained similarly.

This work expands the scope of both aromatic cation mediated and bisphenol-based polymer chemistries. Besides, the high chemoselectivity of the electrophilic aromatic substitution reaction followed by the cyclodehydration and the possibility of nonstoichiometric polymerization (which does not need strictly stoichiometric amounts of the reagents) offer a new, simple, and efficient coupling method for phenol-terminated oligomers and polymers.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures for all polymers as well as supporting spectra may be found. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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