

High- T_g Functional Aromatic Polymers

Olivia Hernández-Cruz, Mikhail G. Zolotukhin,* Serguei Fomine, Larissa Alexandrova, and Carla Aguilar-Lugo

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán 04510, México D. F., México

F. Alberto Ruiz-Treviño

Departamento de Ingeniería y de Ingeniería y Ciencias Químicas, Universidad Iberoamericana, Prol. Paseo de la Reforma No. 880, 01219 México D.F., Mexico

Gabriel Ramos-Ortiz and José Luis Maldonado

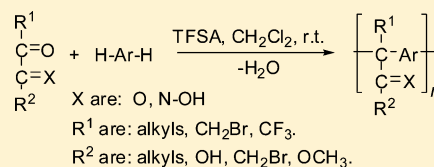
Centro de Investigaciones en Óptica A.P. 1-948, 37000 León, Gto. Mexico

Gregorio Cadenas-Pliego

Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. 140, Saltillo Coahuila 25100, Mexico

Supporting Information

ABSTRACT: A novel series of linear, high-molecular-weight polymers and copolymers were synthesized by one-pot, metal-free superacid-catalyzed polymerization of aliphatic 1,2-diketones (2,3-butanedione (**1a**), 2,3-hexadione (**1b**), 3,4-hexadione (**1c**), 2,3-butanedione monoxime (**1d**), pyruvic acid (**1e**), 1,4-dibromo-2,3-butanedione (**1f**), 2-bromopyruvic acid (**1g**), and methyl-3,3,3-trifluoropyruvate (**1h**) with linear, nonactivated, multiring aromatic hydrocarbons terphenyl (**A**), biphenyl (**B**), fluorene (**C**), and *N*-ethyl carbazole (**D**). Depending on the reaction



system, the polymerizations were carried out as stoichiometric or non stoichiometric, with direct or inverse monomer addition. Copolymers were obtained by polymerization of 1,2-diketones with a mixture of aromatic hydrocarbons. In the course of the polymerization only one carbonyl group of a 1,2-diketone reacts to form C–C bonds with aromatic fragments while the other functional groups (including the second carbonyl group) are incorporated unchanged into polymer chain. The polymerizations performed at room temperature in the Brønsted superacid CF₃SO₃H (TFSA) and in a mixture of TFSA with methylene chloride or trifluoroacetic acid (TFA) tolerant of carbonyl, acetyl, *N*-oxime, carboxy, methoxy, and bromomethyl groups. The polymers obtained were soluble in most common organic solvents, and flexible transparent, colorless films could be cast from the solutions. ¹H and ¹³C NMR analyses of the polymers synthesized revealed high regio-selectivity of the polymerizations and yielded linear structures with para-substitution in the phenylene fragments of the main chains. An electron affinity (EA) of the carbonyl component and the heterolytic C–O bond dissociation energy (DE) in carbinol **3** (correlating with the activation energy of carbocation **4** formation) have been used to rationalize the reactivity of carbonyl components. The calculations show the following reactivity order of the diketones. **1f** > **1g** ≈ **1e** > **1a** > **1d** > **1h** > **1b** > **1c** which is totally in agreement with the experimental data. The new functional polymers obtained demonstrate good processability, high T_g and thermal stability. Unexpected white light emission was observed for polymer **2gA**.

1. INTRODUCTION

Polymers containing functional groups are of great interest because the functional groups can have desirable properties or can be used to attach some moieties with desirable properties. In some cases reactions of functional groups (also called chemical modification) is the only way to obtain a polymer which otherwise is difficult or impossible to prepare directly.

Generally there are two types of functional polymers: pendant-functionalized and end-functionalized. Pendant-functionalized polymers have functional groups as side groups on

the polymer chain. End-functionalized polymers, also called telechelic polymers, have end-groups comprising or containing functional groups. Pendant-functionalized polymers usually are obtained by polymerization of a monomer containing the desired functional group. It is worth mentioning that polymer-forming reactions should be tolerant of the functional groups.

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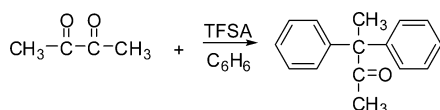
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Thus, preparation of functional polymers by step-growth polymerization is less versatile in a comparison with chain-polymerization of functional monomers. On the other hand, rather low T_g of functional polymers from chain-growth polymerization significantly limits their application. Therefore, a promising synthetic route to high T_g functional polymers would be a polymer-forming condensation reaction affording a polymer combining aromatic fragments in the main chain with side functional groups. In this respect, superacid-catalyzed condensation of aliphatic 1,2-diketones with aromatic hydrocarbons (hydroxyalkylation) presents a promising challenge.

Aliphatic 1,2-diketones are known to be versatile synthons in the formation of a variety of carbocyclic and heterocyclic structures. The presence of adjacent carbonyl functions in 1,2-diketones mutually reinforces electrophilicity of both the carbonyl atoms, which thereby renders them highly susceptible to nucleophilic reagents. Nucleophilic reactions of 1,2-diketones are generally well documented,^{1,2} whereas the acid-catalyzed reactions of 1,2-diketones with aromatic remain largely unexplored. Ohwada has shown that 1,2-dicarbonyl compounds such as 2,3-butanedione (Scheme 1) reacted with benzene in the presence of a strong acid, trifluoromethanesulfonic acid, to give *gem*-diphenylated ketones in high yield.³

Scheme 1. TFSA-Catalyzed Reaction of 2,3-Butanedione with Benzene



Recently, Klumpp described TFSA-catalyzed reactions of α -ketoacids with aromatic compounds.⁴ It therefore seemed plausible that 1,2-dicarbonyl compounds would also react with reactive aromatic compounds other than benzene to form polymeric structures.

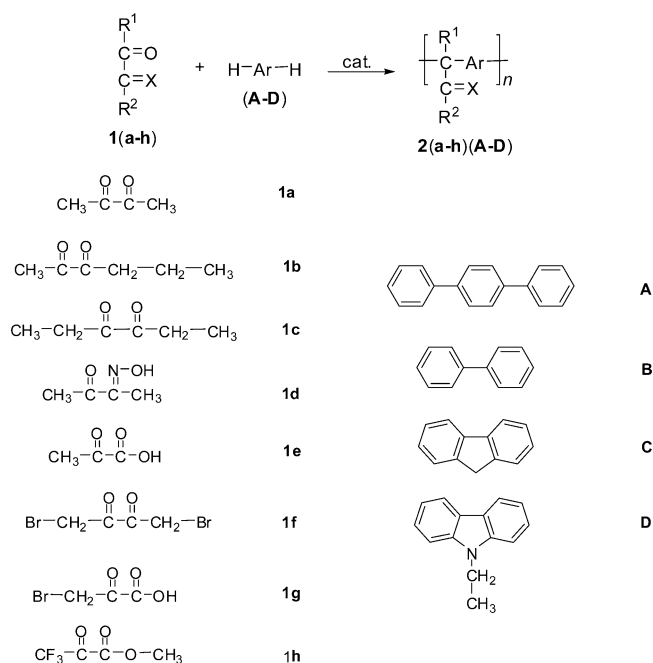
The aim of the present work was the synthesis of polymers by reaction of 2,3-butanedione, 2,3-hexadione, 3,4-hexadione, 2,3-butanedione monoxime, pyruvic acid, 1,4-dibromo-2,3-butanedione, 2-bromopyruvic acid, and methyl-3,3,3-trifluoropyruvate with aromatic hydrocarbons in a superacid medium according to Scheme 2.

The effect of the acidity of the reaction medium is highlighted. The structures of the polymers obtained, the reaction mechanism proposed, and general properties are reported. Spectral data, solubility, and the thermal properties have been determined and are discussed in relationship to chemical structure.

2. RESULTS AND DISCUSSION

2.1. Monomers. Commercially available aliphatic 1,2-diketones **1a–1h** were used for the polymerizations with aromatic hydrocarbons such as *p*-terphenyl, biphenyl, fluorene, and *N*-ethylcarbazole. These monomers are of particular interest for these reactions because: (i) they are relatively cheap, (ii) the aliphatic 1,2-diketone moiety (as a reactive site) can be a part of the molecules bearing various functional groups, (iii) direct involvement of aromatic hydrocarbons in polymer synthesis via an electrophilic substitution reaction presents a new and very promising challenge for Friedel–Crafts polymers, and (iv) incorporation of phenylene fragments in the polymers increases their glass transition temperatures, chemical

Scheme 2. Step-Growth Polymerization of 1,2-Diketones with Aromatic Hydrocarbons



inertness and thermostability. More importantly, superacid-catalyzed condensations of aliphatic 1,2-diketones with aromatic hydrocarbons are simple and an efficient way to obtain aromatic polymers bearing side reactive functional groups without main-chain heteroatoms. Such polymers are generally very difficult or impossible to prepare by other routes. This route also opens up a number of opportunities for the design of functional copolymers by treating aliphatic 1,2-diketones with mixtures of aromatic hydrocarbons. The variety of monomers described demonstrates the scope of the reaction and opens up possibilities for preparation of new polymers.

2.2. Polymer Synthesis and Characterization. 2,3-Butanedione (**1a**) reacted with benzene within 5 min in the presence of TFSA at 5 °C to give 3,3-diphenyl-2-butanone in 94% yield.³ It was also shown that the reaction depends on the acidity of the medium, as judged from the yield of the product. Exploratory polymerizations were carried out adding TFSA to a mixture of terphenyl with 2,3-butanedione (**1a**) in methylene chloride at −3 °C. Attempted reactions under these conditions gave colored, low-molecular-weight products which could not be satisfactorily resolved (Table 1, entry 1). Success was achieved when diketone **1a** was added dropwise over 20 min to a cooled mixture of terphenyl, methylene chloride and TFSA (inverse addition). Thereafter, the reaction mixture was stirred for 3 h and poured into methanol. White film-forming polymers with reasonable high yield and viscosities were obtained after extraction with hot methanol and drying. (Table 1, entries 2–3). It is to be noted that TFSA is removed completely from the polymer after extraction with methanol. Neither IR and NMR spectroscopy nor TGA analysis of the product detected the presence of TFSA residue. (Polymers based on **1d** and **1g** were additionally reprecipitated from *N*-methyl-2-pyrrolidone (NMP) into methanol.)

Formation of various side products were reported in the reaction of **1a** with benzene.³ However, the NMR analyses of the polymers obtained revealed no structural irregularities (Figure 1). The chemical structure of the polymers obtained

Table 1. Polymerization Results for Polymers Based on 1,2-Diketones and Aromatics

entry	polymer code	monomer concentration (mol/L)	acid	acid ^c /ketone (mol/mol)	order	temperature (°C)	reaction time (h)	yield (%)	inherent viscosity η_{inh} (dL g ⁻¹)
1	2aA	0.4	TFSA	14.0	D ^a	-3	20 min	82.4	0.06
2	—	0.4	TFSA + TFA	7.5	I ^b	0	3	43.0	0.31
3 ^d	—	0.3	TFSA + TFA	7.5	—	0	3	75.8	0.50
4	2aB	0.35	TFSA + TFA	7.5	—	0	20	72.0	0.12
5	—	0.6	TFSA + TFA	11.0	—	0	20	89.8	0.26
6	2aAB	0.33	TFSA + TFA	7.5	—	0	6.5	86.1	0.22
7	2aC	0.5	MSA + TFA	13.0	—	0	20	82.4	0.24
8 ^d	2aD	0.4	TFA	12.0	—	0	25	93.0	0.26
9	—	0.6	TFA	12.0	—	0	4	99.1	0.59
10	2bA	0.3	TFSA + TFA	11.0	—	0	24	94.1	0.18
11	2bD	0.6	TFA	22.0	—	0	5	99.4	0.26
12	2cA	0.4	TFSA + TFA	14.0	—	0	24	66.9	0.16
13	2dA	1.0	TFSA	6.0	D ^a	r.t.	24	94.8	0.15
14	—	0.5	TFSA	19.0	—	r.t.	24	99.7	0.87
15	2eA	0.5	TFSA	11.0	—	r.t.	1 min	77.1	ins.
16	—	0.5	TFSA	4.0	—	r.t.	6 min	71.8	ins.
17	2fA	0.4	TFSA	1.5	D ^a	0	4 min	72.6	0.61
18	2fB	0.4	TFSA	3.5	D ^a	0	4.2	96.51	0.21
19	2gA	0.4	TFSA	4.0	D ^a	0	10 min	90.7	0.32
20	2hD	0.8	MSA + TFA	4.0	D ^a	0	1.3	81.0	0.56

^aD: direct addition (TFSA is added to a mixture of monomers). ^bI: inverse addition (1,2-diketone is added to a mixture of TFSA with aromatic).

^cAcid/ketone: Molar ratio of acid to ketone was calculated using TFSA for the entries 1–6, 10, 12–19; MSA for 7 and 20, TFA for 8 and 9.

^dMolecular weights (M_w , M_n) determined by GPC-MALLS, THF, for the polymers of entries 3 and 8 are 78.2, 43.4; 31.8, 15.3 kDa, respectively.

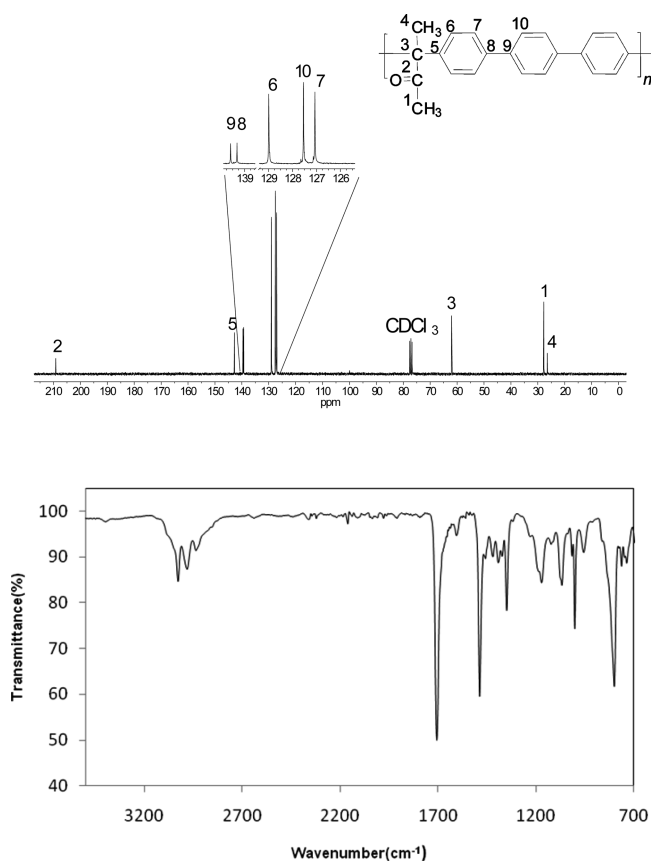


Figure 1. ¹³C NMR and IR spectra of polymer 2aA (Table 1 entry 3).

was also verified by infrared spectroscopy (Figure 1). Thus, in the IR spectrum of polymer 2aA, the bands appeared at 3031 and 2974 cm⁻¹ can be assigned to the aromatic and aliphatic C–H stretching, respectively. A characteristic sharp band at

1710 cm⁻¹ corresponds to C=O group. The bands at 1600 and 1482 cm⁻¹ are attributed to aromatic C=C stretching. Sharp bands at 1001 and 798 cm⁻¹ can be represented to deformation vibration of aromatic C–H groups.

The concentration of superacid in the reaction media has a notable impact on the polymerization rate. In an ideal case, when no side reactions take place the polymerization rate should increase with the concentration of superacid since the equilibrium concentrations of protonated ketone and carbinol increase. These species are involved in the rate limiting steps. However, superacid media can also cause a variety of side reactions negatively impacting the polymerization. Thus, in the case of active aromatic component the superacid is able to promote the protonation of the aromatic ring, thus reducing its nucleophilicity, or even cleave certain bonds of the monomers. In those cases the polymerization rate passes through a maximum with superacid concentration. If superacids are unacceptable as a catalysts due to numerous side reactions caused by them weaker acids must be employed to promote polymerization.

It is common knowledge that in electrophilic substitution reactions biphenyl is less reactive than terphenyl. Nevertheless, polymerizations of 2,3-butanedione with biphenyl were also successful (Table 1, entries 4–5). It is worth noting that polymerizations with biphenyl proceeded in the presence of a larger amount of TFSA. Similarly, polymerization of 1a with a mixture of biphenyl and terphenyl gave a linear polymer 2aAB. Although fluorene is known to give disubstituted derivatives in many Friedel–Crafts reactions, both viscosity and the yield of the polymers from the polymerizations of 1a with fluorene were not very high. Besides, significant amounts of TFSA had to be used. Deeply colored, mostly insoluble products, typical for highly reactive but not selective polymerizations, or low-molecular-weight oligomers were recovered from TFSA-catalyzed condensations of 1a with N-ethyl carbazole (D).

We therefore turned our attention to weaker catalysts such as MSA and TFA. The latter turned out to be more effective. We have also found that **1a** in this reaction should be employed at more than one equivalent of **D**. According to the classical theory of step-growth polymerization the highest molecular weight of linear polymer is obtained when exactly stoichiometric amounts of the monomers are present. Recently, a strong enhancement of stoichiometrically imbalanced, super-acid-catalyzed polyhydroxyalkylation has been demonstrated.⁵ 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. Very likely, this is the situation for the polymerizations of **1a** with **D**. Nonstoichiometric polymerizations of **1a** with **D** gave high-molecular-weight polymers. The polymers obtained were soluble in most common organic solvents and flexible transparent films could be cast from the solutions (Figure 2, Supporting Information).

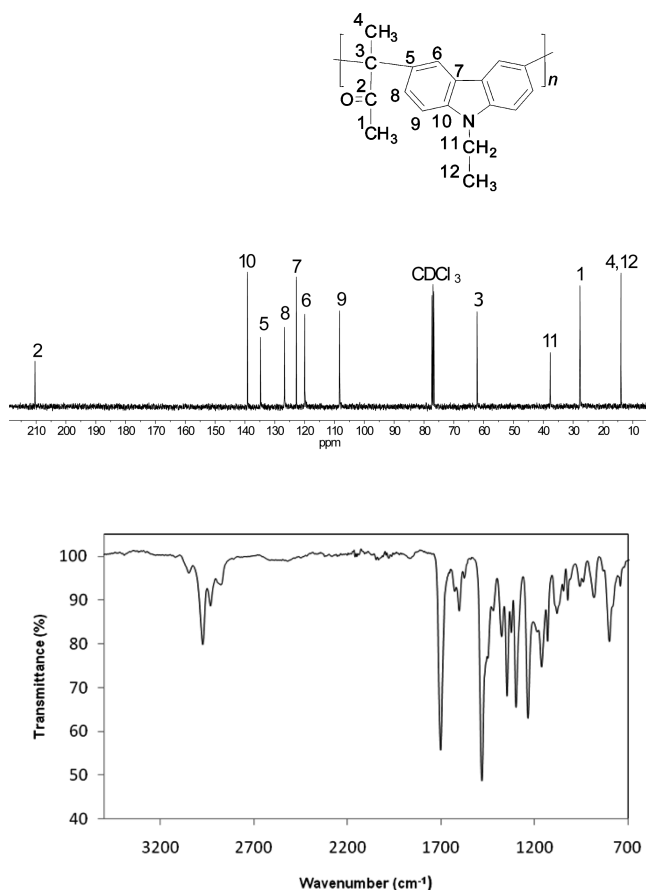


Figure 2. ¹³C NMR (solution in CDCl₃) and IR spectra of polymer **2aD** (Table 1 entry 9).

Polymerizations involving 1,2-diketones bearing longer aliphatic fragments [2,3-hexadione (**1b**), 3,4-hexadione (**1c**)] were less successful than that of 2,3-butanedione judging by viscosity values (Table 1, entries 10–12). 2,3-Butanedione monoxime (**1d**) reacted with benzene in the presence of large amount of TFSA (100 equiv) to give after 5 min at 5 °C the monophenylated oxime and diphenylated oxime in 58% and 37% yield, respectively.³ A much longer time (72 h) is required to obtain diphenylated oxime in 64% yield.³

Surprisingly, the polymerization of **1d** with terphenyl at room temperature afforded in 24 h a nearly quantitative yield of linear, high-molecular-weight polymer (Table 1, entries 13–14).

¹³C NMR-Spectroscopy has revealed all aromatic resonances anticipated for the all *para* polymer **2dA**, and no other resonances can be observed (Figure 3). The proton NMR spectrum of this polymer similarly showed a highly resolved pattern with no evidence of *ortho*- or *meta*-substitution.

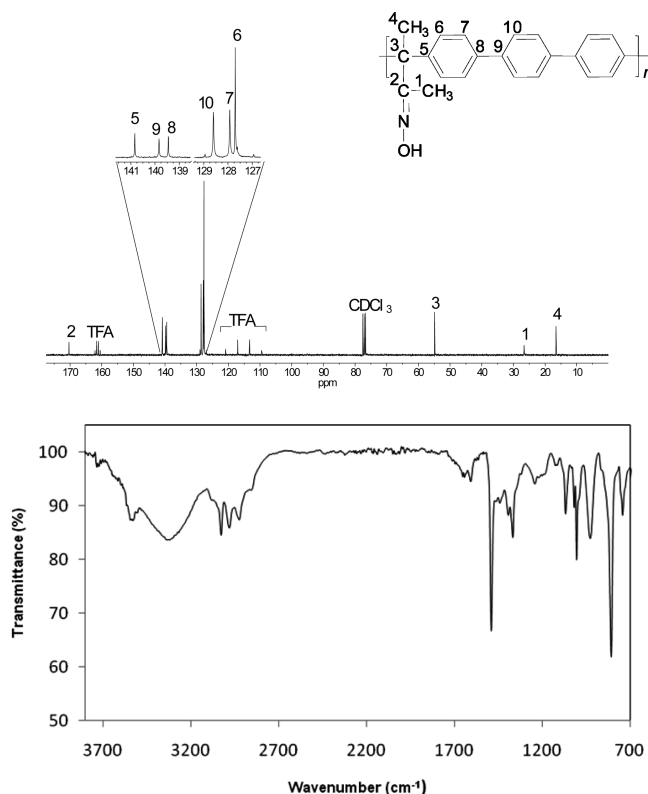
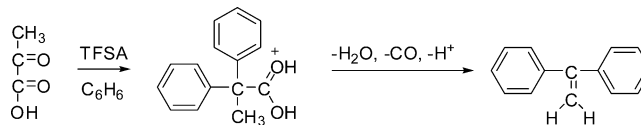


Figure 3. ¹³C NMR (solution in CDCl₃-trifluoroacetic acid) and IR spectra of polymer **2dA** (Table 1 entry 14).

When pyruvic acid is reacted with benzene in TFSA (Scheme 3), 1,1-diphenylethylene is formed as the major product.⁴ The reaction proceeds with decarbonylation of intermediate acylation.

Scheme 3. Reaction of Pyruvic Acid with Benzene



A TFSA-catalyzed polymerization of pyruvic acid **1e** with terphenyl at room temperature gave apparently polymeric but insoluble product. An evolution of a gas in the course of the synthesis was observed. IR spectrum of the polymer does not show the presence of carbonyl groups (Figure 4).

Thermogravimetric analysis of the polymer both in air and in a nitrogen atmosphere revealed two-step weight loss expected for the aromatic polymers containing aliphatic (olefinic) fragments. Very likely that in a manner similar to the reaction

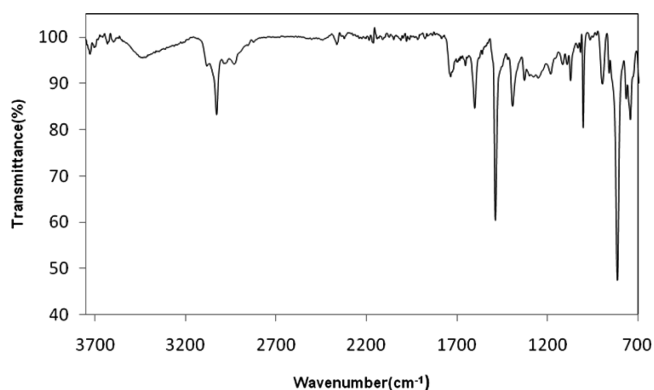
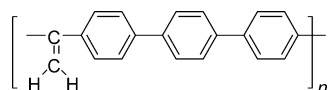


Figure 4. IR spectra of polymer **2eA**. (Table 1 entry 15).

of pyruvic acid with benzene the polymer obtained bears ethylene side groups.



1,4-Dibromo-2,3-butanedione (**1f**) turned out to be the most reactive monomer. Polymerizations of **1f** with aromatic compounds proceed in the presence of smaller amounts of TFSA Table 1, (entries 17 and 18); the reaction is very fast with no decarbonylation. The polymerization reaction was complete within a few minutes and the viscous reaction solution formed was precipitated into methanol.

The ^1H NMR and ^{13}C NMR spectra (Figure 5) of washed and dried polymer clearly indicate resonances of biphenyl and bromomethyl fragments. It is to be noted that reactivity of the

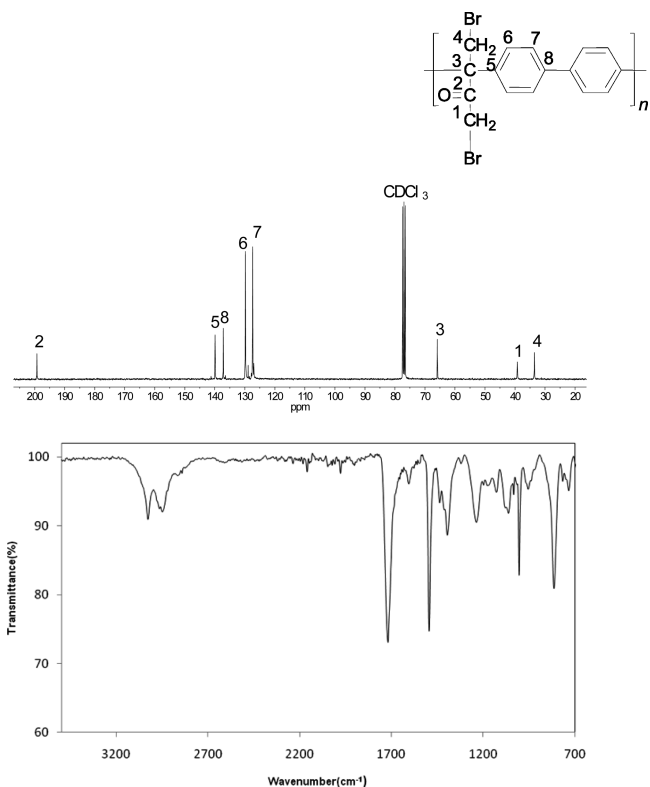


Figure 5. ^{13}C NMR (solution in CDCl_3) and IR spectra of polymer **2fB**. (Table 1 entry 18).

bromomethyl functional groups (in nucleophilic substitution reactions) should be different.

In a manner analogous to the reaction of diketone **1f**, 3-bromopyruvic acid **1g** reacts smoothly with polyaromatic compounds to form high-molecular-weight polymers. NMR analyses of the polymer revealed no structural irregularities (Figure 6). All the NMR spectra are well resolved and the

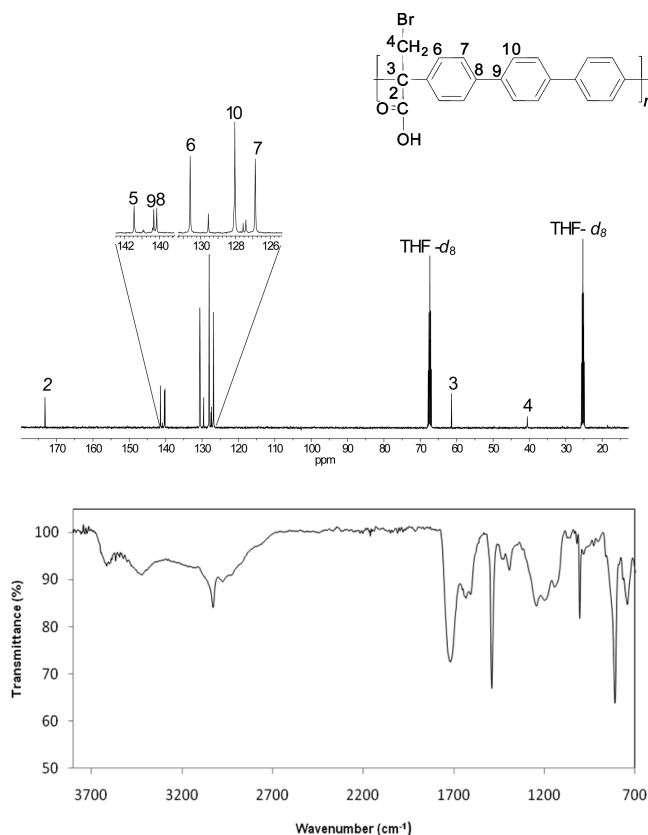


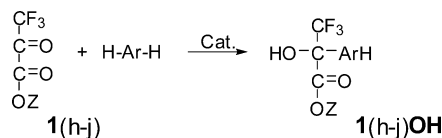
Figure 6. ^{13}C NMR (solution in $\text{THF-}d_8$) and IR spectra of polymer **2gA**. (Table 1 entry 19).

resonances anticipated are all evident. Remarkably, the polymer obtained (**2gA**) bears two functional groups (bromomethyl- and carboxy-) which is very promising for the application of the polymer (and oligomer) as macroinitiators in ATRP polymerizations.

Methyl and ethyl-3,3,3-trifluoropyruvates (Scheme 4) were reported to react with activated aromatic in the presence of acids yielding carbinols.^{6,7}

Thus, methyl-3,3,3-trifluoropyruvate (**1h**) reacts with aniline and anisole derivatives at room temperature in water in the presence of $\text{In}(\text{OTf})_3$ to give carbinol.⁶ TFSA- and $\text{Ga}(\text{OTf})_3$ -catalyzed reactions of ethyl-3,3,3-trifluoropyruvate (**1j**) with

Scheme 4. Condensations of Methyl and Ethyl 3,3,3-Trifluoropyruvates with Aromatic Hydrocarbons



Z = Me (h), Et (j)

toluene gave high yield of carbinol **1jOH**. Ga(OTf)₃-catalyzed reactions of **1j** with highly activated heteroaromatic (such as indole, pyrrole, and *N*-methyl pyrrole) at room temperature and condensations with benzene, anisole and xylol at 90 °C also afforded excellent yields of the hydroxyl trifluoromethyl aromatic acetic esters.⁷ Reactions are usually completed within 1–2 h.

Therefore, it was expected that attempts to obtain polymeric products from the condensations involving methyl 3,3,3-trifluoropyruvate (**1h**) would be unsuccessful. Surprisingly, TFA-catalyzed polymerization of **1h** with *N*-ethyl carbazole gave high-molecular-weight polymer (Figure 7), whereas polymerizations of **1h** with **A** and **B** resulted in oligomers.

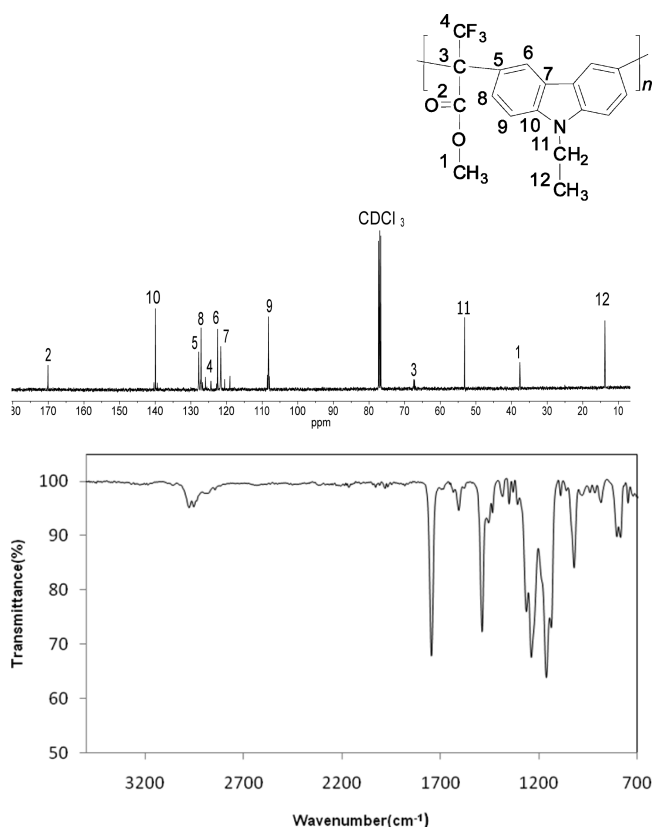


Figure 7. ¹³C NMR (solution in CDCl₃) and IR spectra of polymer **2hD**. (Table 1 entry 20).

Thus, the experimental results demonstrate a high efficiency of the polymerizations of aliphatic 1,2-diketones with aromatic hydrocarbons. To obtain deeper insight into the reactivity of 1,2-diketones in the hydroxyalkylation reaction, we estimated important reactivity indexes for those components; the intermediates responsible for the formation of carbocations, the electron affinities and C–O bond strength in the corresponding carbinols and electrophilic species responsible

for the second reaction step. The experimentally observed reactivities of 1,2-diketones has been rationalized in terms of those reactivity indexes.

2.3. Mechanistic Aspects. Although the acid-catalyzed addition reactions of aldehydes and ketones have been known for a long time these Friedel–Crafts-type reactions have not been studied to the same extent as the corresponding reactions involving alcohols, alkyl halides or aryl halides.⁸ The main reason for such neglect is probably 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 and its application for hydroxyalkylation reactions turned out to be remarkably successful.^{9,10}

Numerous reactions have been carried out using superacids as a reaction medium [mostly trifluoromethanesulfonic acid (TFSA)].^{11–13} Superacid-catalyzed polyhydroxyalkylations have also been reported^{14–18} (and references cited therein).

A fundamental dogma in the carbocation area holds that since this intermediate is intrinsically electron-deficient, electron-donating groups stabilize a carbocation, while carbocations containing electron-withdrawing groups adjacent to a carbocation are intrinsically unstable and therefore would form and react only with great reluctance and only under forcing conditions.

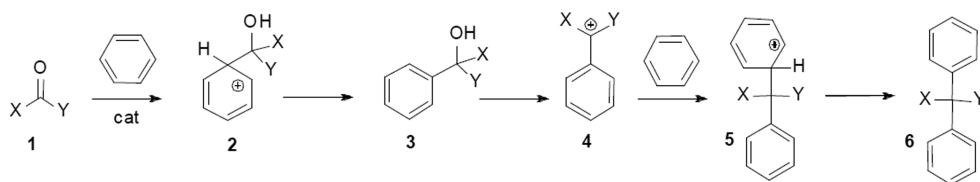
Contrary to earlier views, experimental and theoretical studies of electron-negatively substituted carbocations conducted in a number of laboratories have shown a facile formation of these electron-deficient carbonium ions and have led to the general premise that a genuine electron-withdrawing substituent on the cationic center increases its electrophilicity toward aromatics.^{19–21}

Recent progress in the chemistry of electrophilic intermediates, especially the major contribution to this field by Olah, led to the superelectrophilic hydroxylation reactions, in which reactivity of carbonyl compounds is increased by the presence of electron withdrawing substituents, adjacent or relatively close to a carbocation center. Because of the mutual electron-withdrawing effect of the protonated carbonyl groups in α -diketones, these intermediates may behave as highly reactive electrophiles or superelectrophiles.

The schematic representation of the reaction mechanism for the acid-mediated hydroxyalkylation reaction between aromatics and ketones bearing electron-withdrawing substituent adjacent to a carbonyl group is shown in Scheme 5 where groups X can be methyl, ethyl, or trifluoromethyl among others and Y is an electron-withdrawing fragment which can include another carbonyl.

The first step of the hydroxyalkylation reaction is the activation of carbonyl group by the interaction with acid catalysts. This step involves partial or total protonation of the carbonyl group. Depending on the acid strength and the nature of the carbonyl component monoprotonation, multiple

Scheme 5. Mechanism of Hydroxyalkylation Reaction



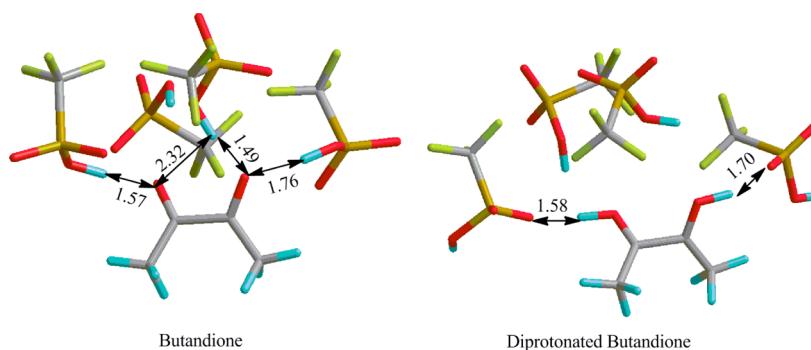


Figure 8. Optimized geometry of butanedione and diprotonated butanedione solvated with TFSA. Distances in Å.

protonation or only hydrogen-bond formation is possible. It is believed that α -diketones are diprotonated in the medium of superacids.^{3,4,7,22–25}

Thus, Ohwada has estimated that in TFSA ($(H_0) - 14$) the content of 2,3-butanedione dications can reach 10^{-3} – 10^{-5} . It is worth mentioning that diprotonated species have been detected in solutions of α -diketones in magic acid ($\text{HOSO}_2\text{F}-\text{SbF}_5$) using NMR-spectroscopy.³ On the other hand, theoretical calculations demonstrated that in case of monoketones activated with electron withdrawing groups no protonation of carbonyl groups occurs in TFSA.²⁶

Considering those facts we decided to estimate the theoretical possibility for 2,3-butanedione protonation in TFSA. The cluster solvation model has been used for calculations. The inner solvation sphere consisted of four TFSA molecules, while the outer sphere used SMD polarized continuum methods. Dielectric constant of 77.4 and solvent radii of 2.59 Å were applied for the outer solvation sphere.²⁷ As seen from Figure 8 no proton transfer from TFSA to 2,3-butanedione occurs in the neutral state; instead, tight hydrogen bonds are formed between TFSA and diketone molecules. According to the calculations diprotonation of 2,3-butanedione in TFSA is highly endergonic process with free Gibbs energy of 31.2 kcal/mol which corresponds to negligibly low equilibrium concentration of diprotonated species in TFSA solution (about 10^{-23} M).

Therefore, according to the calculations no appreciable concentration of protonated or diprotonated species exists in solutions of diketones in TFSA due to low basicity of vicinal carbonyl groups. According to this finding it seems reasonable to use a continuum model and neutral diketone molecules to compare their reactivities in hydroxyalkylation reactions.

After having been activated by the solvation with acid ketone **1** forms the tetrahedral intermediate **2**. This step is considered to be the rate-determining step of the aromatic electrophilic substitution.²⁸ The tetrahedral intermediate is then aromatized producing carbinol **3**. The next step is the cleavage of carbinol C–O bond to give carbocation **4**. The carbocation **4** reacts with another aromatic molecule to generate tetrahedral intermediate **5** giving the final product **6** after the aromatization. Although this mechanism is correct in most of the cases, there are exceptions where the rate-determining step is not the tetrahedral intermediate formation but the cleavage of carbinol C–O bond producing carbocation **4**. This mechanism has been first suggested by D. Klumpp who demonstrated that the reaction between aromatics and carbonyl components bearing strong electron-withdrawing groups often stops at the carbinol formation step.²⁹ An electron-withdrawing group in the

carbonyl component has different effect on the first and second substitution steps; it decreases the activation energy of formation of the tetrahedral intermediate **2** and simultaneously increases the activation energy of carbocation **4** formation.²⁶ The mechanism of this effect is related to the increasing of electrophilicity of carbonyl carbon facilitating the first electrophilic attack, at the same time electron withdrawing substituent destabilizes carbocation **4**, thus strengthening C–O bond in carbinol **3**. The reactivity of the carbonyl component in the first reaction step and the carbinol formation is governed by the electrophilicity of the carbonyl carbon where directed the nucleophilic attack of aromatic molecule. In a series of papers exploring the mechanism of superacid mediated hydroxyalkylation reaction, various reactivity descriptors have been developed to rationalize the reactivity of carbonyl components.^{30,31} Among them are the global electrophilicity of carbonyl component, the difference of global electrophilicities of carbonyl and aromatic components, and LUMO energies of carbonyl component. It turns out that the best correlation with the reactivity was observed for differences between the electron affinity (EA) of carbonyl component and the ionization potential (IP) of the aromatics. Therefore, for a given aromatic molecule EA is the best parameter, which correlates with the reactivity of carbonyl compound. EA is closely related with the electrophilicity of carbonyl carbon. On the other hand, the heterolytic C–O bond dissociation energy (DE) in carbinol **3** correlates with the activation energy of carbocation **4** formation.²⁶ Therefore, those two quantities; EA and DE can be used to rationalize the reactivity of ketones in the reaction of hydroxyalkylation. We estimated adiabatic electron affinities (EAs) of carbonyl compounds **1a–1g** and the corresponding C–O bond dissociation energies (DE) which are listed in (Table 2). The calculations were carried out using a model

Table 2. Heterolytic C–O Dissociation Energies and Electron Affinities Calculated for Diketone Monomers

monomer	DE (kcal/mol)	EA (eV)
1a	82.0	3.22
1b	81.6	3.06
1c	82.4	3.04
1d	76.9	2.90
1d^a	86.5	3.17
1e	89.3	3.27
1f	90.5	3.47
1g	91.0	3.30
1h	98.7	3.64

^aComplex with one TFSA molecule.

applied in our earlier paper: M06-2X functional in combination with 6-311+G(d,p) basis set and SMD solvation model implemented in Gaussian 09 suit of program²⁷ were used for the optimization and energy evaluation. Dielectric constant of 77.4 and solvent radius of 2.6 Å have been used to model solvation in TFSA.

Table 2 shows estimated EAs and DE for monomers **1a–1h**. Since monomer **1d** has a basic oxime nitrogen atom which is definitely protonated in TFSA media, EA and DE in this case have been estimated for a complex between **1d** and TFSA (Figure 9).

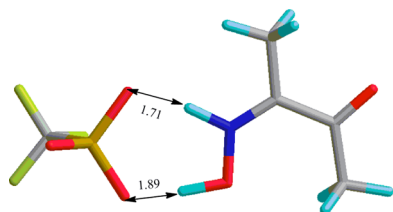


Figure 9. Optimized geometry of **1d**–TFSA complex. Distances in Å.

The highest EA is for **1h**, however, at the same time **1h** has highest DE. This means that even though **1h** has the most electrophilic carbonyl carbon, due to the influence of CF₃ group, the cleavage of the very strong C–O bond in carbinol **4** is the reason for relatively low reactivity of this monomer. Monomers **1e**, **1g**, and **1f** have close EAs and DE and significantly lower DE than that of **1h**. Those monomers are the most reactive ones suggesting that for **1h** the rate-determining step is the cleavage of C–O bond in carbinol **4**, while for **1e** and **1g** the rate-limiting step is the formation of tetrahedral intermediate **3**. Out of three reactive monomers **1e**, **1g** and **1f**, the last one **1f** is especially reactive due to high EA and relatively low DE. Monomer **1e**, however, undergoes a side reaction during the polymerization process accompanied by gas evolution, which is assumed to be a decarboxylation. **1a** is slightly less reactive compared to **1g**, **1e**, and **1f** due to lower electrophilicity (lower EA). As seen from Table 1, EA and DE for **1d** depend notably on whether it is protonated or not by TFSA. As seen the interaction with TFSA leads to increase of both EA and DE due enhancing of the electron-withdrawing properties of oxime group on protonation. The protonation of **1d** is important to explain the relatively high reactivity of **1d**, just below of **1f**, **1g**, **1e**, and **1a**. Unprotonated **1d** has the lowest EA out of all monomers which corresponds to the lowest electrophilicity of carbonyl carbon and therefore the lowest reactivity in the reaction of hydroxyalkylation which is not true. The monomers **1b** and **1c** are the less reactive ones, **1b** being slightly more reactive than **1c**, which corresponds their relative EA values. Therefore, the reactivity of carbonyl compounds **1a–1h** can be understood taking into account 2-fold influence of electron-withdrawing groups. The electron-withdrawing group reduces the activation energy of tetrahedral intermediate **3** formation and increases the activation energy of C–O bond cleavage in carbinol **4**. When the activation energy of C–O bond cleavage in carbinol **4** exceeds that for the tetrahedral intermediate formation **3**, the electron-withdrawing groups starts decrease the total reactivity of carbonyl compound in hydroxyalkylation reaction. Therefore, the reactivity order of the carbonyl components: **1f** > **1g** ≈ **1e** > **1a** > **1d** > **1h** > **1b** > **1c** is explained by the 2-fold influence of electron-withdrawing groups in carbonyl molecules.

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. The qualitative solubility properties of the polymers are reported in Table 2. As can be seen from Table 3, the majority of the polymers obtained possess good solubility in chlorinated and aprotic solvents.

Table 3. Solubility^a of Polymers

solvent	polymer							
	2aA	2aD	2dA	2eA	2fA	2fB	2gA	2hD
methylene chloride	+	+	–	–	+	+	–	+
dichloroethane	+	+	–	–	+	+	–	+
chloroform	+	+	–	–	+	+	*	+
H ₂ SO ₄	–	–	–	–	–	–	–	–
DMF	–	+	+	–	+	+	*	+
NMP	+	+	+	–	+	+	*	+
THF	+	+	–	–	+	+	+	+
DMSO	+	+	–	–	+	+	*	+
DMAA	–	+	+	–	+	+	*	+
pyridine	+	+	+	–	+	+	*	+
cyclohexanone	–	+	–	–	+	+	+	+
1,4-dioxane	+	–	+	–	+	+	+	+

^aKey: (+) soluble at room temperature; (–) insoluble; (*) partial solubility and precipitation at room temperature.

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 3. The polymers obtained also possess relatively high thermostability (Table 4, Figure 10, Supporting Information). DSC analysis did not reveal glass transition temperatures below decomposition temperatures.

Table 4. Thermal Properties of the Polymers

polymer code	onset (°C)		char yield, 800 °C (wt %) in N ₂
	air	nitrogen	
2aA	391	395	36
2aD	385	404	40
2dA	241	277	43
2eA	178	183	48
2fA	211	214	50
2fB	210	212	44
2gA	168	170	57
2hD	347	418	56

It is important that functional groups in the polymers remain their reactivity. To prove the accessibility and reactivity of the functional groups reduction of carbonyl groups to methylene groups by use of triethylsilane in trifluoroacetic acid media at room temperature was carried out according to the following scheme: simply by dissolving polymer **2aA** in a mixture of methylene chloride and trifluoroacetic acid, adding triethylsilane, and stirring overnight. The product, which remained in solution at the end of the reaction period, was recovered by precipitation into ethanol. The progress of reduction was estimated by sampling the reaction at intervals and analyzing the product by FT-IR spectroscopy (disappearance of the carbonyl band near 1670 cm⁻¹), Figure 11.

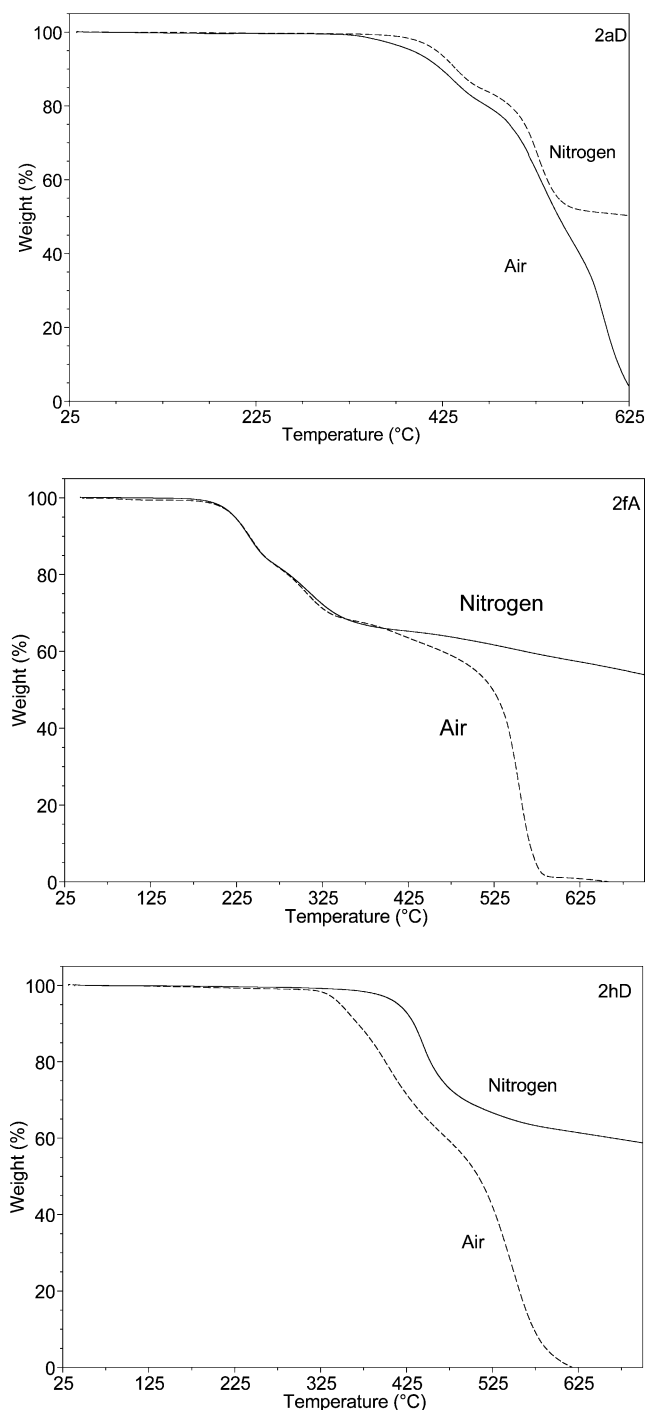


Figure 10. TGA thermograms of polymers.

By taking into account the generally high intensity of the band, it is clear that reduction is essentially quantitative.

Oligomers and polymers bearing bromomethyl groups are promising candidates for the preparation of quaternary ammonium-functionalized materials, for initiation and grafting using ATRP chemistry. Besides, bromomethyl functionality in combination with thermo- and chemically stable main chains opens up large possibilities for further chemical modifications proceeding at elevated temperature in the presence of bases or acids. It is very important to note that due to high T_g of the polymers obtained these chemical transformation at elevated

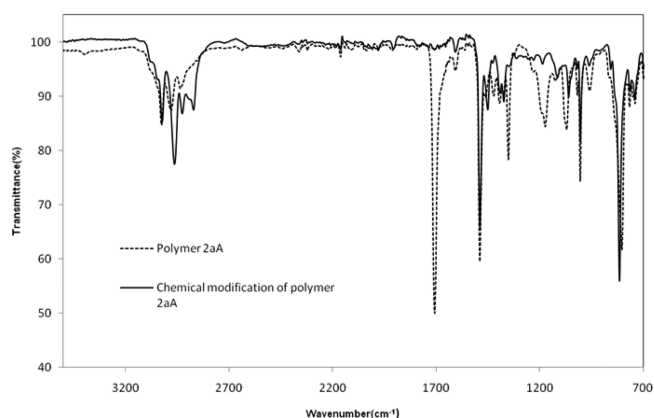


Figure 11. IR spectra of polymer 2aA before and after reduction.

temperatures can be performed with such polymer materials as films and fibers.

Finally, functionalization of aromatic polymers will offer many opportunities to fine-tuning of polymers properties and unexpected findings.

Thus, we have found that polymer 2gA possess white-light emission (Figure 12).

In order to get white light emission the general strategy is to use a blend as the emissive layer, such as a polymer–polymer blend, polymer–small molecule blend, or polymer–organometallic-complex blend. White light emission from a single, high-molecular-weight polymer is interesting and rather rare phenomenon. It is very likely that more promising effects will be found by studying new functional polymers.

3. CONCLUSION

In summary, we have demonstrated for the first time a simple and reliable preparation of a novel series of linear, high-molecular-weight polymers and copolymers by one-pot, metal-free superacid-catalyzed polymerization of aliphatic 1,2-diketones with linear, nonactivated, multiring aromatic hydrocarbons terphenyl (A), biphenyl (B), fluorene (C), and *N*-ethyl carbazole (D). Depending on the reaction system, the polymerizations were carried out as stoichiometric or non-stoichiometric, with direct or inverse monomer addition. Copolymers were obtained by polymerization of 1,2-diketones with a mixture of aromatic hydrocarbons. In the course of the polymerization only one carbonyl group of the 1,2-diketones reacts to form C–C bonds with aromatic fragments while the other functional groups (including the second carbonyl group) are incorporated unchanged into the polymer chain.

The polymerizations performed at room temperature in the Brønsted superacid CF₃SO₃H and in a mixture of TFSA with methylene chloride or TFA tolerant of carbonyl, acetyl, *N*-oxime, carboxy, methoxy, and bromomethyl groups demonstrate wide applicability and include simple reaction conditions, readily available starting materials and reagents, and generation of an inoffensive byproduct (water). In spite of the strong acidity of TFSA, no hydrolysis of the methoxy, carboxy, or *N*-oxime groups were observed during the reaction. The polymers obtained were soluble in most common organic solvents, and flexible transparent, colorless films could be cast from the solutions. ¹H and ¹³C NMR analyses of the polymers synthesized revealed high regio-selectivity of the polymerizations yielding linear structures with *para*-substitution in the phenylene fragments of the main chains.

Scheme 6. Reduction of Carbonyl Groups of Polymer 2aA

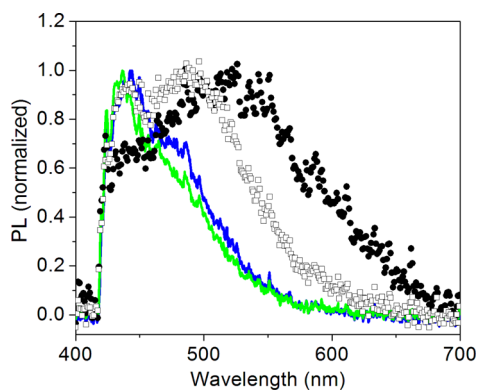
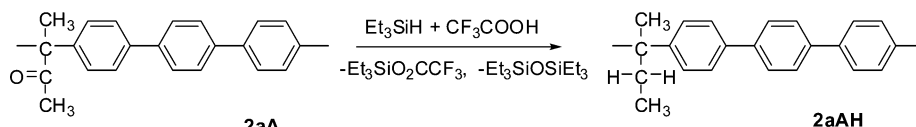


Figure 12. Photoluminescence spectra of polymer **2gA** in THF solution at low concentration (green line) and at high concentration (blue line), in THF at high concentration after 3 days (open squares), and **2gA** in solid (filled circles).

Theoretical and experimental studies of the reactivity of the diketones have revealed 2-fold influence of electron-withdrawing carbonyl group adjacent to the cation center, which reduce the activation energy of tetrahedral intermediate **3** formation and increase the activation energy of C–O bond cleavage in carbinol **4**. When the activation energy of the C–O bond cleavage in carbinol **4** exceeds that for the tetrahedral intermediate formation **3**, the electron-withdrawing groups starts decrease the total reactivity of carbonyl compound in hydroxyalkylation reaction.

An electron affinity (EA) of carbonyl component and the heterolytic C–O bond dissociation energy (DE) in carbinol **3** (correlating with the activation energy of carbocation **4** formation) have been used to rationalize the reactivity of carbonyl components. The calculations show the following reactivity order of the diketones. $\mathbf{1f} > \mathbf{1g} \approx \mathbf{1e} > \mathbf{1a} > \mathbf{1d} > \mathbf{1h} > \mathbf{1b} > \mathbf{1c}$ which coincides with the experimental data.

These new functional polymers obtained demonstrate good processability, high T_g and thermal stability. Unexpected white light emission was observed for polymer **2gA**.

The results obtained can also be considered to be the basis for the design of multifunctional polymers (copolymers) containing simultaneously various functional groups.

4. EXPERIMENTAL PART

Characterization. NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating at 400.13 and 100 MHz for ^1H and ^{13}C respectively. Chloroform- d (CDCl_3), THF- d_6 , and a mixture of chloroform- d /TFA were used as a solvent. Infrared (IR) spectra were measured on a Thermo Scientific FT-IR-ATR spectrometer. The inherent viscosities of 0.2% polymer solutions in 1-methyl-2-pyrrolidinone (NMP) and tetrahydrofuran (THF) were measured at 25 °C using an Ubbelohde viscometer. Thermogravimetric analyses (TGA) were carried out in air and under nitrogen at heating rate of 10 °C/min on a TGA Q5000 TA Instruments analyzer. The T_g was evaluated by differential scanning calorimetry (DSC) measured at 10 °C/min on DSC Q100 TA Instruments. Molecular weights were determined by gel permeation chromatography (GPC-MALLS) according to the published method.¹⁸

Materials. All starting materials were obtained from Aldrich. 2,3-Butanedione monoxime, pyruvic acid, bromopyruvic acid, 1,2-dibromo-2,3-butanedione, methyl-3,3,3-trifluoropyruvate, biphenyl and *p*-terphenyl were used as received. *N*-Ethylcarbazole was purified by recrystallization with charcoal from ethanol. 2,3-Butanedione, 2,3-hexanedione, and 3,4-hexanedione were distilled under reduced pressure. Methylene chloride, TFA, TFSA were distilled prior to use.

Polymer Syntheses. Synthesis of Polymer 2aA (Direct Addition). 2,3-Butanedione (0.13 mL, 1.5 mmol), *p*-terphenyl (0.3455 g, 1.5 mmol), methylene chloride (2.0 mL), and TFSA (2.0 mL) were stirred in a nitrogen/ethanol bath and kept in a –3 °C freezer for 20 min. The reaction mixture was precipitated into methanol. A brown powder (**2aA**) (0.3688 g, 82.4%) with an inherent viscosity η_{inh} of 0.06 dL g^{-1} (NMP) was obtained after precipitation, filtration and drying.

Synthesis of Polymer 2aA (Inverse Addition). To a mixture of *p*-terphenyl (0.3455 g, 1.5 mmol), methylene chloride (1 mL), TFA (1.5 mL) and TFSA (2.8 mL) under ice water bath was added a solution of 2,3-butanedione (0.13 mL, 1.5 mmol) in methylene chloride (1.0 mL). The solution was slowly added dropwise over a period of 30 min. The reaction mixture was stirred in an ice water bath for 2 h and precipitated into methanol. The slightly yellow fiber formed was filtered off and washed with refluxing methanol and dried. The resulting slightly yellow fiber **2aA** (0.3394 g, 75.8%) had an inherent viscosity η_{inh} of 0.5 dL g^{-1} in NMP.

Synthesis of Polymer 2aB (Inverse Addition). To a mixture of biphenyl (0.1850 g, 1.2 mmol), TFA (0.3 mL), and TFSA (1.2 mL) into an ice water bath was added dropwise a solution of 2,3-butanedione (0.10 mL, 1.2 mmol) in methylene chloride (0.5 mL) over 5 min. The reaction mixture was stirred in an ice water bath for 20 h and precipitated into methanol. White oligomers (**2aB**) (0.2395 g, 89.8%) with an inherent viscosity η_{inh} of 0.26 dL g^{-1} (NMP) were obtained after precipitation, filtration and drying.

Synthesis of Copolymer of 2,3-Butanedione with Biphenyl and *p*-Terphenyl (2aAB). A solution of 2,3-butanedione (0.13 mL, 1.5 mmol) in methylene chloride (0.5 mL) was added dropwise to a mixture of biphenyl (0.0771 g, 0.5 mmol), *p*-terphenyl (0.2303 g, 1.0 mmol), TFA (1.5 mL), and TFSA (1.0 mL) while the temperature was kept at 0 °C by ice water bath. The reaction mixture was stirred in an ice water bath for 6 h 30 min and precipitated into methanol. The copolymer formed was filtered off, washed with methanol and dried. After drying, 0.3526 g (86.1%) of copolymer **2aAB** with an inherent viscosity η_{inh} of 0.22 dL g^{-1} in NMP.

Synthesis of Polymer 2aC (Inverse Addition). To a mixture of fluorene (0.2493 g, 1.5 mmol), methylene chloride (0.75 mL), TFA (1.5 mL), and MSA (0.5 mL) under ice water bath was added a solution dropwise of 2,3-butanedione (0.13 mL, 1.5 mmol) in methylene chloride (0.75 mL). The reaction mixture was stirred in an ice water bath for 20 h and precipitated into methanol. The white oligomer formed were filtered off, washed with methanol and dried. The resulting white oligomer **2aC** (0.3257 g, 82.4%) had an inherent viscosity η_{inh} of 0.24 dL g^{-1} in NMP.

Synthesis of Polymer 2aD. To a mixture of *N*-ethylcarbazole (0.3515, 1.8 mmol) and TFA (2 mL) into ice water bath was added dropwise a solution consisting of 2,3-butanedione (0.18 mL, 2.3 mmol) in methylene chloride (1 mL) over 5 min. The reaction mixture was stirred for 4 h in an ice water bath and then poured into methanol. The white fiber formed was filtered off and washed with hot methanol. After drying, 0.4700 g (99.1%) of white fiber with an inherent viscosity η_{inh} of 0.59 dL g^{-1} (NMP) was obtained.

Synthesis of Polymer 2bA (Inverse Addition). A solution of 2,3-hexanedione (0.24 mL, 2.0 mmol) in methylene chloride (1 mL) was added dropwise to a mixture of *p*-terphenyl (0.4606 g, 2.0 mmol),

TFA (0.5 mL) and TFSA (2.0 mL) while the temperature was kept at 0 °C by ice water bath. The reaction mixture was stirred in an ice water bath for 24 h and precipitated into methanol. The green fibrous powder formed was filtered off and extracted with hot methanol. The beige fibrous (0.6148 g, 94.1%) with an inherent viscosity η_{inh} of 0.18 dL g⁻¹ in NMP was obtained.

Synthesis of Polymer 2bD (Inverse Addition). To a mixture of *N*-ethylcarbazole (0.2343g, 1.2 mmol) and TFA (2.5 mL) into ice water bath was added dropwise a solution consisting of 2,3-hexanedione (0.19 mL, 1.5 mmol) in methylene chloride (0.5 mL) over 5 min. The reaction mixture was stirred for 5 h in an ice water bath and then poured into methanol. The green fibrous powder formed was filtered off, washed with methanol and dried. The resulting fibrous powder 2bD (0.3300 g, 99.4%) had an inherent viscosity η_{inh} of 0.26 dL g⁻¹ in NMP.

Synthesis of Polymer 2cA (Inverse Addition). A solution of 3,4-hexanedione (0.19 mL, 1.6 mmol) in methylene chloride (1 mL) was added dropwise to a mixture of *p*-terphenyl (0.3293 g, 1.4 mmol), TFA (1.0 mL), and TFSA (2.0 mL) while the temperature was kept at 0 °C by ice water bath. The reaction mixture was stirred in an ice water bath for 24 h and precipitated into methanol. The green powder formed was filtered off and washed with methanol. After drying, 0.3127 g (66.9%) of green powder with an inherent viscosity η_{inh} of 0.16 dL g⁻¹ (NMP) was obtained.

Synthesis of Polymer 2dA (Direct Addition). 2,3-Butanedione monoxime (0.1516g, 1.5 mmol), *p*-terphenyl (0.3454g, 1.5 mmol), methylene chloride (0.5 mL), and TFSA (2.5 mL) were stirred at room temperature for 24 h. The reaction mixture was precipitated into methanol. The white fiber formed was filtered off and washed with hot methanol. The resulting white fibrous 2dA (0.4688 g, 99.7%) had an inherent viscosity η_{inh} of 0.87 dL g⁻¹ in NMP.

Synthesis of Polymer 2eA (Direct Addition). Pyruvic acid (0.10 mL, 1.5 mmol), *p*-terphenyl (0.3454 g, 1.5 mmol), methylene chloride (2 mL) and TFSA (1 mL) were stirred at room temperature for 1 h. The reaction mixture was precipitated into water. The slightly green fiber formed was filtered off and washed with methanol and dried. The resulting fiber 2eA (0.3432 g, 76.7%) was insoluble in common solvents.

Synthesis of Polymer 2fA (Direct Addition). 2-Dibromo-2,3-butanedione (0.3658 g, 1.5 mmol), *p*-terphenyl (0.3462 g, 1.5 mmol), methylene chloride (3.2 mL), and TFSA (0.2 mL) were stirred for 4 min under ice water bath and then poured into methanol. The slightly yellow fiber formed was filtered off and washed with hot methanol. The resulting fiber 2fA (0.4978 g, 72.6%) had an inherent viscosity η_{inh} of 0.61 dL g⁻¹ in NMP.

Synthesis of Polymer 2fB (Direct Addition). 2-Dibromo-2,3-butanedione (0.3658g, 1.5 mmol), biphenyl (0.2313 g, 1.5 mmol), methylene chloride (3.0 mL) and TFSA (0.45 mL) were stirred for 4.20 min under ice water bath and then poured into methanol. A slightly yellow fiber (2fB) (0.5502 g, 96.5%) with an inherent viscosity η_{inh} of 0.21 dL g⁻¹(NMP) was obtained after precipitation, filtration and drying.

Synthesis of Polymer 2gA (Direct Addition). A mixture of bromopyruvic acid (0.2410g, 1.5 mmol), *p*-terphenyl (0.3462 g, 1.5 mmol) methylene chloride (3 mL), and TFSA (0.45 mL) was stirred for 10 min under ice water bath and then poured into methanol. The white fiber formed was filtered off and washed with hot methanol. After drying, 0.5171 g (90.7%) of white fibrous polymer with an inherent viscosity η_{inh} of 0.32 dL g⁻¹(THF) was obtained.

Synthesis of Polymer 2hD (Direct Addition). Methyl-3,3,3-trifluoropyruvate (0.2293 g, 1.5 mmol), *N*-ethylcarbazole (0.2343 g, 1.2 mmol), methylene chloride (0.5 mL), TFA (0.7 mL), and MSA (0.7 mL) were slowly stirred at room temperature for 1.30 h. The reaction mixture was precipitated into methanol. White fibrous polymer (2hD) with an inherent viscosity η_{inh} of 0.56 dL g⁻¹ (NMP) was obtained after precipitation, extraction with methanol and drying (0.3404, 85.0%).

Chemical Modification of Polymer 2aA. To a mixture of polymer 2aA (0.100 mg), methylene chloride (0.5 mL) and MSA (1 mL) was added dropwise triethylsilane (1 mL) over 3 min. The reaction mixture

was stirred at room temperature for 24 and the poured into methanol. A precipitated polymer was filtered off and washed with methanol (0.0808 g, 81.0%). The resulting polymer was insoluble in common solvents.

■ ASSOCIATED CONTENT

● Supporting Information

¹H and ¹³C NMR spectra, TGA thermograms, FTIR spectra, and photo of polymer film 2aA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*(M.G.Z.) E-mail: zolutukhin@iim.unam.mx.

Notes

The authors declare no competing financial interest.

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