

Superacid-Catalyzed Polycondensation of Acenaphthenequinone with Aromatic Hydrocarbons

Mikhail G. Zolotukhin,* Serguei Fomine, Luz María Lazo, Roberto Salcedo, Luis E. Sansores, and Gerardo G. Cedillo

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

Howard M. Colquhoun

School of Chemistry, University of Reading, PO Box 224, Whiteknights, UK

Juan M. Fernandez-G.

Instituto de Química, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacan 04510, México D. F., México

Alexei F. Khalizov

Department of Chemistry, University of Waterloo, Waterloo, Canada

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ABSTRACT: A novel series of linear, high molecular weight polymers were synthesized by one-pot, superacid-catalyzed reaction of acenaphthenequinone (**1**) with aromatic hydrocarbons. The reactions were performed at room temperature in the Brønsted superacid CF₃SO₃H (trifluoromethanesulfonic acid, TFSA) and in a mixture of TFSA with methanesulfonic acid (MSA) and trifluoroacetic acid (TFA), which was used as both solvent and a medium for generation of electrophilic species from acenaphthenequinone. The polymer-forming reaction was found to be dependent greatly on the acidity of the reaction medium, as judged from the viscosity of the polymers obtained. Polycondensations of acenaphthenequinone with 4,4'-diphenoxybenzophenone (**f**), 1,3-bis(4-phenoxybenzoyl)benzene (**g**), 1,4-bis(4-phenoxybenzoyl)benzene (**h**), 1,10-bis(4-phenoxyphenyl)decane-1,10-dione (**i**), 2,6-diphenoxybenzotrile (**j**), 2,6-diphenoxybenzoic acid (**k**), and 2-(4-biphenyl)-6-phenylbenzoxazole (**l**) proceeded in a reaction medium of wide range of acidity, including pure TFSA (Hammett acidity function H_0 of pure TFSA is -14.1), whereas condensation of **1** with biphenyl, terphenyl, diphenyl ether, and 1,4-diphenoxybenzene needed a reaction medium of acidity H_0 less than -11.5 . A possible reaction mechanism is suggested. The polymers obtained were found to be soluble in the common organic solvents, and flexible transparent films could be cast from the solutions. ¹H and ¹³C NMR analyses of the polymers synthesized revealed their linear, highly regular structure. The polymers also possess high thermostability. Char yields for polymers **3a**, **3c**, **3d**, and **3l** in nitrogen were close to 80% at 1000 °C.

1. Introduction

Friedel–Crafts aromatic substitution reactions—alkylation and acylation—play an important role in organic chemistry. Besides, these reactions are widely used in polymer chemistry, and in fact, the first communication on formation of a viscous resin from the reaction of benzyl chloride and aluminum trichloride was reported more than 100 years ago by Friedel and Crafts.¹ Since then, many reports on the preparation of polymers (first mainly via polyalkylation reactions, later via polyacylation as well) have been published.^{2–5} Cheaply available monomers and the promising properties of the polymers that might be obtained have greatly stimulated interest in that field.

For a long time, however, polymer-forming Friedel–Crafts reactions were considered not to be regioselective. Indeed, such aromatic substitution reactions as alkylation and acylation basically lead to formation of isomer mixtures. In addition, Friedel–Crafts reactions (especially those catalyzed by aluminum trichloride) very often need large amounts of catalyst, which might

remain in and substantially contaminate the polymers formed. Nevertheless, over the past few decades many linear, high molecular weight Friedel–Crafts polymers have been reported, and commercial technologies have been developed for some of them, such as the polyhydroxyarylene alkylene “Xylox” and the aromatic polyketones “Stilan”, “Ultrapek”, and “Declar”.^{4,5} It seems worthwhile to note the high regioselectivity in syntheses of linear aromatic polymers of poly(phthalidylidenearylene) type^{6,7} and to report on the finding of a general approach for the design of polymers via Friedel–Crafts reactions.⁸

Traditionally, Friedel–Crafts polymer-forming electrophilic aromatic substitution reactions present interaction of electrophiles, bearing such reactive functional groups as carbocations, acylium, or sulfonium ions, with aromatic hydrocarbons in the presence of a catalyst. The type of catalyst, method of electrophile generation, and nucleophilicity of the hydrocarbon compound all dramatically affect the polymer synthesis. Thus, for example, enhancement of the nucleophilicity of the aromatic hydrocarbons allows less reactive electrophiles to be used for polymer preparation. Varying the catalysts also affects both the reactivity of the reagents and the

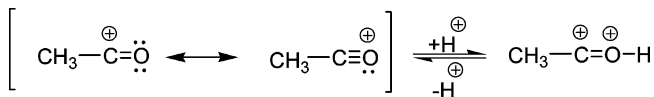
* Corresponding author. E-mail: zolotukhin@zinalco.iimatercu.unam.mx.

selectivity of the reaction products. In other words, in a Friedel–Crafts polymer preparation, a proper relationship between the electrophilicity of the cation, nucleophilicity of the aromatic hydrocarbon, and catalytic effect of a catalysts used must obtain for successful synthesis of a relatively pure specific product. Physical properties of the reaction medium and its phase state may also play important roles.

It is important to mention that, so far, only traditional types of electrophiles have been used in Friedel–Crafts polymer preparations. Obviously, the design of monomers bearing new types of electrophilic functional groups is of great importance for the advancement of Friedel–Crafts polymer chemistry.

In this respect, the theory of superelectrophilic activation, suggested recently by Olah to explain the reactivities of some electrophiles in superacid solutions, presents a promising challenge.⁹ (It should be noted that the intensive research on carbocation chemistry undertaken over the past few decades, and recently recognized by the Nobel Prize awarded to Professor Olah, has so far not resulted in very much by way of application to polymer chemistry.)

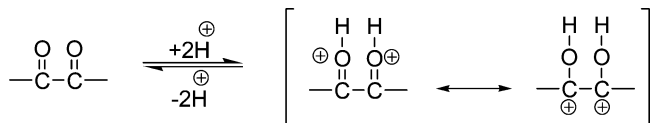
According to Olah's theory, superelectrophilic activation may occur when a cationic electrophile reacts with a Bronsted or Lewis acid to give a highly reactive dicationic electrophile. For example, protonation (protosolvation) of the acetyl cation by the superacidic HF–BF₃ system leads to the highly reactive superelectrophilic protoacetyl dication:⁹



Superelectrophiles have since been proposed or studied in numerous superacid-catalyzed reactions.^{10–12}

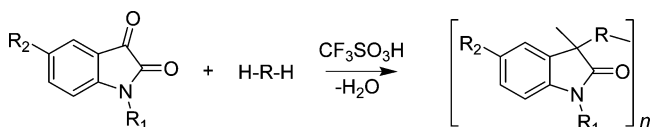
It was also found that superelectrophilic activation takes place in the Friedel–Crafts reactions of the compounds containing 1,2-dicarbonyl groups with non-activated aromatic hydrocarbons.^{13–16}

It is assumed that adjacent carbonyl groups undergo protonation to form protosolvates:^{14,15}



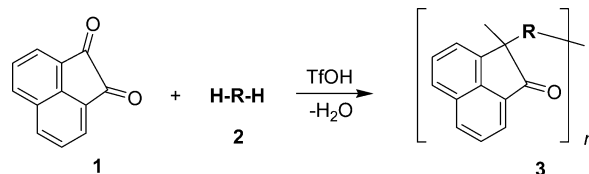
Because of the mutual electron-withdrawing effect of the protonated carbonyl groups, these intermediates may behave as highly reactive electrophiles or super-electrophiles.

In line with the superelectrophilic concept and report,¹⁵ we have recently shown that such a compound as isatin, containing nitrogen and 1,2-carbonyl groups as a part of its heterocycle, reacts in TFSA with aromatic hydrocarbons, yielding high molecular weight polymers:¹⁷



It seemed plausible that cyclic α -diketones would also likewise generate highly reactive electrophiles in TFSA,

and indeed, very recently we have found that acenaphthenequinone (**1**) reacts with aromatic hydrocarbons in a TFSA medium, yielding high molecular weight polymers:¹⁸



In the present study, we utilize this strategy to access a wide variety of novel polymers derived from acenaphthenequinone and various aromatic hydrocarbons (**2**), such as biphenyl (**a**), diphenyl ether (**b**), fluorene (**c**), terphenyl (**d**), 1,4-diphenoxybenzene (**e**), 4,4'-diphenoxybenzophenone (**f**), 1,3-bis(4-phenoxybenzoyl)benzene (**g**), 1,4-bis(4-phenoxybenzoyl)benzene (**h**), 1,10-bis(4-phenoxyphenyl)decane-1,10-dione (**i**), 2,6-diphenoxybenzocyanide (**j**), 2,6-diphenoxybenzoic acid (**k**), and 2-(4-biphenyl)-6-phenylbenzoxazole (**l**).

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

2. Experimental Section

2.1. Materials. Biphenyl, diphenyl ether, and 1,4-diphenoxybenzene were obtained from Aldrich and purified by the usual methods. Methanesulfonic acid and trifluoromethanesulfonic acid were obtained from Fluorochem Ltd. and were distilled under vacuum prior to use. The aromatic hydrocarbons 4,4'-diphenoxybenzophenone and 1,3- and 1,4-bis(4-phenoxybenzoyl)benzenes were prepared according to published methods^{19,20} and purified by recrystallization from a benzene–ethanol (1:3, v/v) mixture and NMP, respectively. 2,6-Diphenoxybenzocyanide (**j**) and 2,6-diphenoxybenzoic acid were prepared similar to a published method.²¹ Acenaphthenequinone was obtained from Aldrich and purified by sublimation followed by recrystallization with charcoal from chlorobenzene.

2.2. Characterization. The inherent viscosities of 0.2% polymer solutions in *N*-methylpyrrolidinone were measured at 25 °C using an Ubbelohde viscometer. The ¹H and ¹³C NMR spectra were recorded using a Bruker Avance 400 spectrometer, operating at 400.13 and 100 MHz for ¹H and ¹³C, respectively. Thermogravimetric analyses (TGA) were carried out in air and under nitrogen at a heating rate of 10 °C min⁻¹ on a TGA 2950 thermogravimetric analyzer, TA Instruments, and differential scanning calorimetry (DSC) measurements at 20 °C min⁻¹ on a DSC 2910 TA Instruments. Polymer films for the measurements were prepared by casting 10% (w/v) chloroform solutions of the polymers onto a glass plate followed by drying for 8 h at 80 °C in an oven.

2.3. Polymer Synthesis. A typical polymer synthesis was conducted in single-necked 10 mL flask equipped with magnetic stirrer. Acenaphthenequinone (0.764 g, 4.20 mmol), biphenyl (0.647 g, 4.20 mmol), TFA (2.25 mL), and TFSA (3.75 mL) were stirred under a dry nitrogen at room temperature for 10 h, and the resulting clear, viscous, green solution was then poured slowly into ethanol (100 mL). The yellow solid was filtered off, washed copiously with ethanol and water, and then extracted with refluxing methanol and finally with acetone, before drying at 100 °C under vacuum. The resulting yellow fibrous polymer **3a** (1.28 g, 96% yield) had an inherent viscosity (η_{inh}) of 0.41 dL g⁻¹ in NMP. ¹H NMR (400 MHz, CDCl₃, δ , ppm, Figures 2 and 3): 7.99 (d, J = 6.6 Hz, 1H, H⁴), 7.71 (t, 1H, H⁵), 8.11 (d, J = 6.9 Hz, 1H, H⁶), 7.82 (d, J = 7.3 Hz, 1H, H³), 7.61 (t, 1H, H⁹), 7.46 (d, J = 6.2 Hz, 1H, H¹⁰), 7.25 (d, J = 7.7 Hz, 4H, H¹⁴), 7.37 (d, J = 7.35 Hz, 4H, H¹⁵). ¹³C NMR (400 MHz, CDCl₃, δ , ppm): 67.1 (C¹), 203.7 (C²),

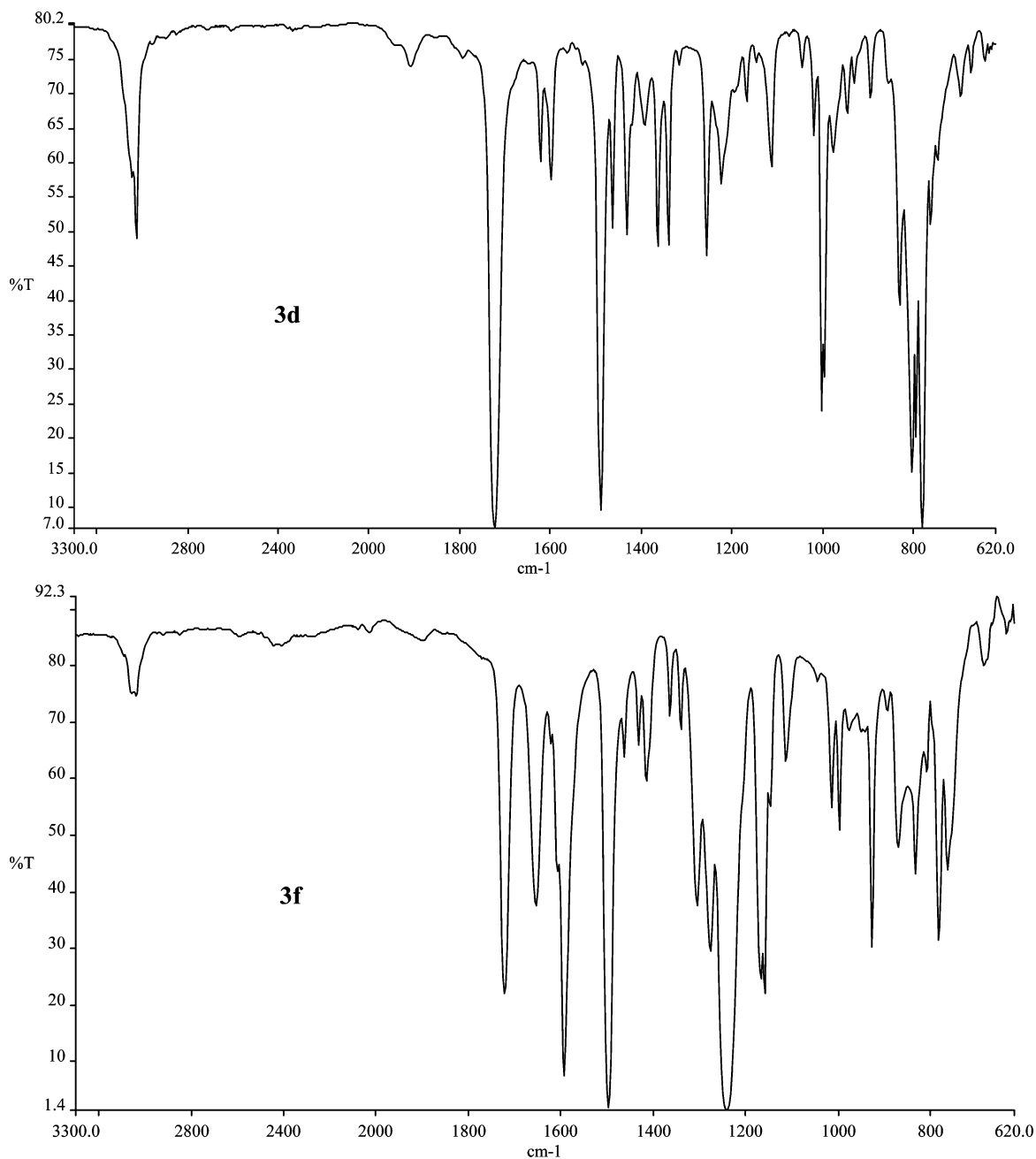


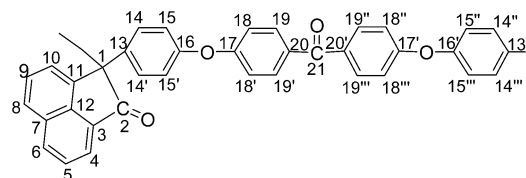
Figure 1. IR spectra of polymers **3d** and **3f** (films).

132.2 (C³), 122.9 (C⁴), 128.6 (C⁵), 131.9 (C⁶), 130.9 (C⁷), 124.3- (C⁸), 128.8 (C⁹), 122.8 (C¹⁰), 142.8 (C¹¹), 141.1 (C¹²), 141.4 (C¹³), 129.0 (C¹⁴), 126.9 (C¹⁵), 139.3 (C¹⁶). NMR spectra of the polymer are given in Figures 2 and 3.

Preparation of 3f. Acenaphthenequinone (0.182 g, 0.001 mol) and 4,4'-diphenoxybenzophenone (0.366 g, 0.001 mol) were added to a vigorously stirred mixture of TFSA (5 mL) and MSA (2 mL). The reaction mixture was stirred for 5 h at room temperature and poured into water. The slightly green fiber formed was filtered off, washed with water, and extracted with hot methanol and acetone. After drying, 0.51 g (96%) of white fiberlike polymer **3f** was obtained. The inherent viscosities of the 0.2% solutions of the polymer in NMP and concentrated sulfuric acid were 0.54 and 0.78 dL g⁻¹, respectively.

¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.07 (d, *J* = 7.0 Hz, 1H, H⁴), 7.81 (t, *J* = 7.6 Hz, 1H, H⁵), 8.19 (d, *J* = 8.1 Hz, 1H, H⁶), 7.91 (d, *J* = 8.3 Hz, 1H, H⁸), 7.71 (t, *J* = 7.8 Hz, 1H, H⁹), 7.50 (d, *J* = 6.8 Hz, 1H, H¹⁰), 7.29 (d, *J* = 8.8 Hz, 4H, H¹⁴), 6.98 (d, *J* = 8.5 Hz, 4H, H¹⁵), 7.00 (d, *J* = 6.8 Hz, 4H, H¹⁸), 7.74 (d, *J* = 8.8 Hz, 4H, H¹⁹).

¹³C NMR (400 MHz, CDCl₃, δ, ppm): 66.7 (C¹), 203.9 (C²), 132.3 (C³), 123.3 (C⁴), 128.9 (C⁵), 132.4 (C⁶), 131.2 (C⁷), 124.8 (C⁸), 129.1 (C⁹), 123.0 (C¹⁰), 142.9 (C¹¹), 141.3 (C¹²), 138.6 (C¹³), 130.5 (C¹⁴), 119.9 (C¹⁵), 155.0 (C¹⁶), 161.1 (C¹⁷), 117.6 (C¹⁸), 132.4 (C¹⁹), 132.6 (C²⁰), 194.3 (C²¹).



Preparation of 3g. Acenaphthenequinone (0.182 g, 1.00 mmol), 1,3-bis(4-phenoxybenzoyl)benzene (0.470 g, 1.00 mmol), and TFSA (7.0 mL) were stirred under a dry nitrogen at room temperature for 8 h, and the resulting viscous, green solution was then poured slowly into water (200 mL). The pale brown fibers were filtered off, washed copiously with water, and then

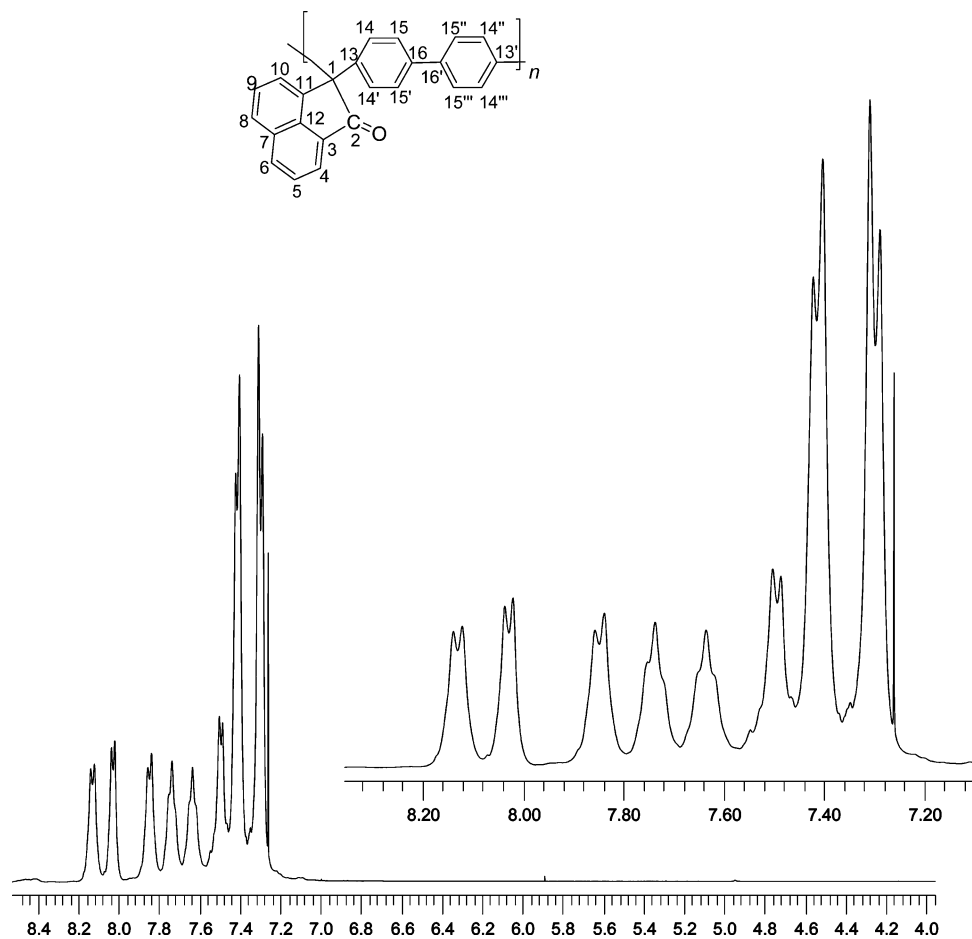


Figure 2. ^1H NMR spectrum of polymer **3a** (solution in CDCl_3).

extracted with refluxing methanol and finally with acetone, before drying at $100\text{ }^\circ\text{C}$ under vacuum. The resulting fibrous polymer **3g** (0.62 g, 97% yield) had an inherent viscosity (η_{inh}) of 0.44 dL g^{-1} in NMP.

Preparation of 3k. Acenaphthenequinone (0.228 g, 1.25 mmol), 2,6-diphenoxybenzoic acid (0.383 g, 1.25 mmol), methylene chloride (0.6 mL), and TFSA (1.5 mL) were stirred under a dry nitrogen at room temperature for 9 h, and the resulting viscous solution was then poured slowly into ethanol. The pale yellow fibers were filtered off, washed copiously with water, and then extracted with refluxing methanol and finally with acetone, before drying at $100\text{ }^\circ\text{C}$ under vacuum. The resulting fibrous polymer **3k** (0.59 g, 98% yield) had an inherent viscosity (η_{inh}) of 0.27 dL g^{-1} in NMP.

^1H NMR (400 MHz, CDCl_3 , δ , ppm, Figure 4): 8.07 (d, $J = 6.9\text{ Hz}$, 1H, H^4), 7.90 (t, $J = 7.5\text{ Hz}$, 1H, H^5), 8.37 (d, $J = 8.4\text{ Hz}$, 1H, H^6), 8.04 (d, $J = 8.4\text{ Hz}$, 1H, H^8), 7.76 (t, $J = 7.7\text{ Hz}$, 1H, H^9), 7.62 (d, $J = 6.9\text{ Hz}$, 1H, H^{10}), 7.16 (d, $J = 8.8\text{ Hz}$, 4H, H^{14}), 7.00 (d, $J = 8.8\text{ Hz}$, 4H, H^{15}), 6.59 (d, $J = 8.4\text{ Hz}$, 2H, H^{19}), 7.74 (t, $J = 8.0\text{ Hz}$, 1H, H^{20}), 7.43 (s, 1H, -COOH), 7.82 (s, 1H, COOH).

^{13}C NMR (400 MHz, CDCl_3 , δ , ppm): 65.8 (C^1), 203.1 (C^2), 131.2 (C^3), 123.1 (C^4), 129.1 (C^5), 132.7 (C^6), 130.5 (C^7), 124.7 (C^8), 129.2 (C^9), 123.0 (C^{10}), 142.3 (C^{11}), 140.2 (C^{12}), 137.1 (C^{13}), 129.7 (C^{14}), 118.7 (C^{15}), 155.8 (C^{16}), 153.8 (C^{17}), 123.6 (C^{18}), 113.7 (C^{19}), 130.1 (C^{20}), 164.8 (C^{21}).

3. Results and Discussion

3.1. Polymer Synthesis. The reactions of acenaphthenequinone and its derivatives with different nucleophiles and organic and inorganic reagents are well documented and have been reviewed recently.²² Surprisingly, there is only one publication concerning the Friedel–Crafts reaction of acenaphthenequinone with

benzene in the presence of aluminum trichloride. With excess benzene as solvent the resulting 2,2-diphenylacenaphthen-1-one was obtained in moderate yield²³ (Scheme 1). It was shown more recently that condensation of acenaphthenequinone with benzene carried out in the medium of trifluoromethanesulfonic acid, which has been often acclaimed as the strongest of all known monoprotic organic acids,^{24,25} at room temperature affords excellent yield of 1,1-diphenyl-2-acenaphthene.¹² TFSA has extreme thermal stability and resistance to both reductive and oxidative cleavage. Clearly, too, the nonoxidizing nature of TFSA can be beneficial in minimizing or eliminating side reactions. TFSA has also successfully been used as a solvent–catalyst for the preparation of aromatic polyketones in reactions of aromatic acids with aromatic hydrocarbons.^{26–29} Following these data, we expected that the condensations of acenaphthenequinone with aromatic hydrocarbons listed in Table 1, performed similar to the condensations of isatin with aromatic in a TFSA medium,¹⁷ at room temperature would afford polymeric products.

However, to our surprise, first attempts to obtain high molecular weight, linear polymers in such a way failed. Deeply colored, mostly insoluble products, typical for highly reactive but not selective polymerizations, or low molecular weight oligomers were recovered from condensations of acenaphthenequinone with compounds **2a–2e**.

Even more surprising, condensations of acenaphthenequinone with 4,4'-diphenoxybenzophenone (**f**), a compound which is obviously less nucleophilic (and, therefore, less reactive, in a comparison, for example,

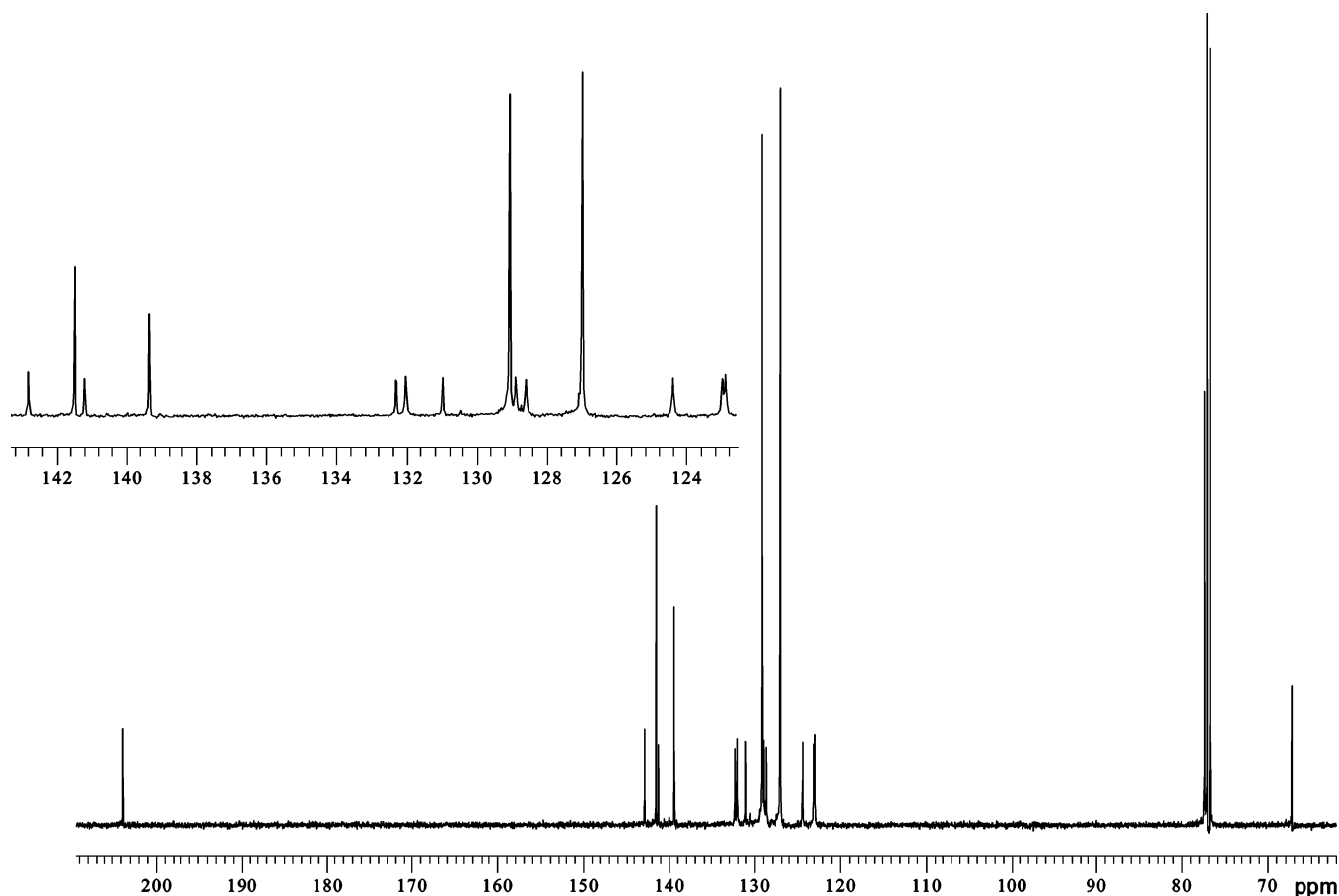


Figure 3. ^{13}C NMR spectrum of polymer **3a** (solution in CDCl_3).

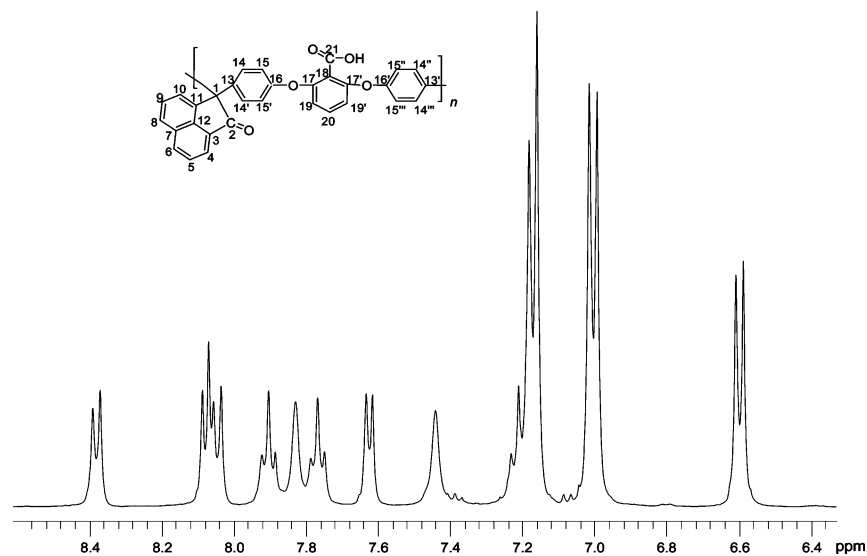
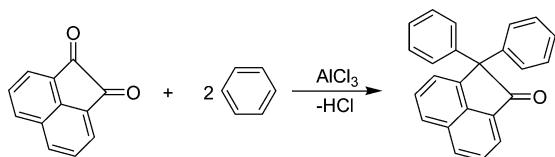


Figure 4. ^1H NMR spectrum of polymer **3k** (solution in $\text{DMSO}-d_6$).

Scheme 1. Condensation of Acenaphthenequinone with Benzene

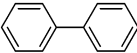
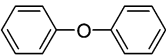
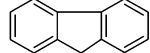
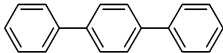
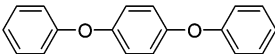
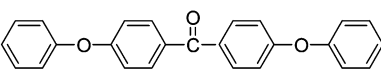
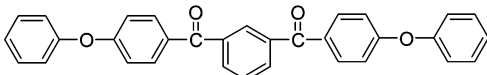
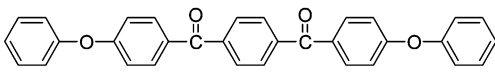
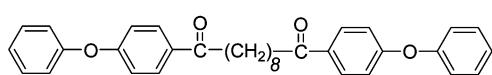
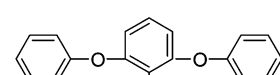
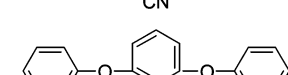
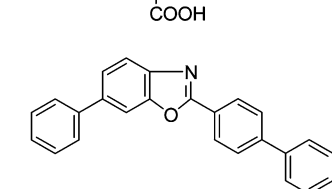


with diphenyl ether (**2b**) or diphenoxybenzene (**2e**), produced linear high molecular weight, film-forming polymer. The polymer preparation proceeded at room

temperature in homogeneous solution. The polymer, precipitated after reaction into water, formed a slightly green fiber, which, after hot extraction with methanol and acetone, changed color to slightly yellow. The yield of the polymer was close to quantitative. Reactions of acenaphthenequinone with **2h** and **2i** also yielded polymeric products.

One of the remarkable peculiarities of superelectrophilic chemistry is a dependence of a reaction on the acidity of the reaction medium (generally, judging from the products yield).^{30–32}

Table 1. Aromatic Hydrocarbons Used for Condensations with Acenaphthenequinone

Hydrocarbons 2	Structure
a	
b	
c	
d	
e	
f	
g	
h	
i	
j	
k	
l	

A fundamental dogma in the superelectrophilic chemistry holds that increase of acid strength favors formation of protosolvated superelectrophilic intermediates.^{9–12,33}

On the other hand, nucleophiles, such as aromatic hydrocarbons, may also undergo protonation. Obviously, that protonation of the aromatic would decrease its nucleophilicity and, therefore, prohibit an electrophilic substitution reaction. It is also true that decrease of the acid strength would decrease protonation probability. To check the assumption, we have performed condensations of acenaphthenequinone with aromatic in the less acidic medium using a mixture of TFSA with MSA and TFA. (Obviously, we should expect a decrease in reactivity of the components as well.) Nevertheless, condensation of acenaphthenequinone with **2f** carried out in a mixture of TFSA with MSA (74/26, w/w) afforded a polymer **3f** having viscosity value similar to the polymer obtained in pure TFSA.

Preparation of polymer **3f** in a mixture of TFSA with TFA (44/56, w/w) was also successful. But what is more important is that condensations of acenaphthenequinone with hydrocarbons **2a–2e** carried out in a mixture of TFSA with TFA gave linear, high molecular weight products. It is worthy to mention that H_0 (Hammett acidity function) of pure TFSA is -14.1 , while the acidity of the mixture TFSA with TFA (44/56, w/w) used was -11.5 .^{15,34}

Therefore, reaction media of acid strength of H_0 equal to or slightly less than -11.5 are necessary for polycondensations of acenaphthenequinone with hydrocarbons **2a–2e**.

Theoretical calculations³⁵ show that such a remarkable difference between the reactivity of aromatic molecules resides in their protonation preferences. Thus, in the case of biphenyl, terphenyl, and diphenyl ether the first protonation occurs at C4 carbons, while for 4,4'-diphenoxybenzophenone the first protonation site is

carbonyl. Therefore, in the case of first three monomers their protonation impedes polymerization while the last monomer maintains its polymerizability when protonated. The decrease in acidity of reaction media decreases aromatic substrates protonation of the first three monomers and, therefore, favors the polymer-forming reaction.

Remarkably, that polymer syntheses involving acenaphthenequinone allow also for the one-step preparation of polymers containing pendant functional groups. For example, condensations of acenaphthenequinone with 2,6-diphenoxybenzonitril (**j**) and 2,6-diphenoxybenzoic acid (**k**) carried out in a mixture of TFSA with TFA (70/30, w/w) afforded fully soluble, linear polymers. It is worth mentioning that both nitrile and carboxylic groups may react in pure TFSA with phenoxy groups. Nevertheless, structural analysis (see below) has confirmed expected chemical composition of the polymers bearing functional groups.

Similar to the later two structures, polymer **3l** was obtained by condensation of acenaphthenequinone with 2-(4-biphenyl)-6-phenylbenzoxazole.

Despite the big difference in structure and reactivity of the monomers **2a–2l**, soluble, film-forming polymers were obtained in all cases. Even condensation of biphenyl with acenaphthenequinone was successful. To the best of our knowledge, this is the first example of direct involvement of a nonsubstituted biphenyl in polymer synthesis via an electrophilic substitution reaction.

Generally, the polymer syntheses took 6–10 h. We have found that increasing the reaction time gave more highly colored, and sometimes even cross-linked, products. This may very likely be accounted for by high reactivity of the superelectrophilic intermediates.

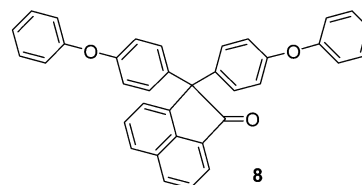
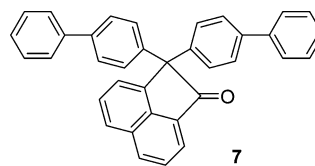
Thus, fine-tuning of the acidity of the reaction medium allows for the variety of the polymers (including ones bearing functional groups) to be obtained. Metal-free catalytic systems applied afford highly pure polymers.

3.2. Polymer Structure. Fortunately, the high solubility of polymers **3a–3l** allowed us to perform reliable spectral studies to delineate their structure.

The high-resolution IR spectra of the polymers obtained revealed the expected presence of the band at 1723 cm^{-1} corresponding to the carbonyl group of the diarylacenaphthen-1-one fragment and a set of bands typical for aromatic hydrocarbons (Figure 1). It is to be noted that the spectra of polymers **3a**, **3c**, and **3d** exhibit intensive aromatic C–H stretching bands around 3000 cm^{-1} and strong absorption bands at $782\text{--}804\text{ cm}^{-1}$, which are attributed to out-of-plane bending of the ring C–H bonds. As can be seen from Figure 1, the intensities of these bands are significantly lower in the spectrum of polymer **3f** (as well as in the spectra of rest of the polymers) and, in fact, are more typical of those for aromatic polymers.

Interestingly, IR spectra of two model compounds, **7** and **8**, calculated by means the Gaussian 98 code at the hybrid B3LYP level, which combines the exact Hartree–Fock exchange with Becke's and uses the Lee–Yang–Parr correlation function in order to include the most important correlation effects, also show highly intensive aromatic C–H bands for **7**.

Analysis of the ^1H and ^{13}C NMR spectra of polymers in CDCl_3 solution has confirmed the anticipated structure of the polymers obtained. Although the resonances in the ^1H NMR spectra of polymers containing only phenylene fragments in the main chain **3a**, **3c**, and **3d**



are somewhat broadened, the pattern of the signals is still quite clear. For example, sharp doublets at 7.43 and 7.31 ppm of polymer **3a** (Figure 2) point to the strictly para-substitution in the biphenyl segments of the main chain. The ^{13}C NMR spectrum of polymer **3a** (Figure 3) showed all 16 anticipated resonances. ^1H spectra of polymers **3b** and **3e–3l** are better resolved (Figure 4), and the assignment was made without any particular difficulty.

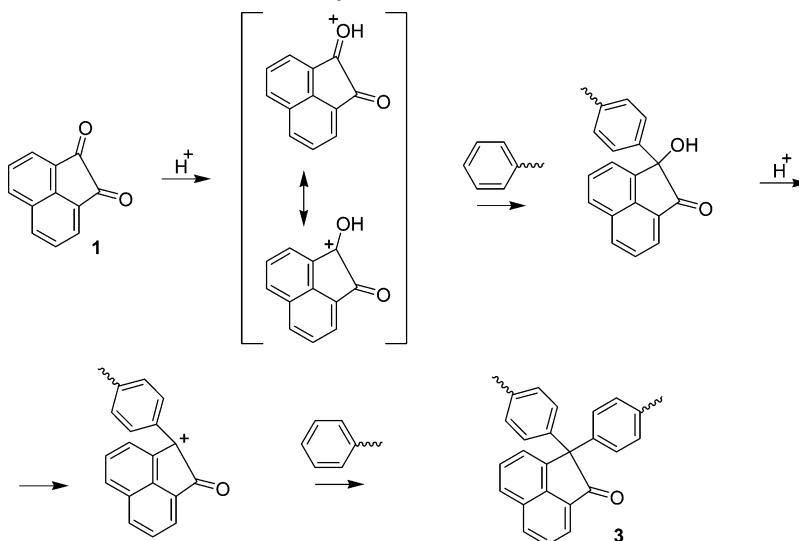
Thus, NMR studies have shown the existence of high regioselectivity in polymer-forming reactions. In the spectra of polymers **3b** and **3e**, additional weak signals, most likely arising from side structures, can be seen. Taking into account the high activity of hydrocarbons **2b** and **2e** in electrophilic substitution reactions, the appearance of these signals is not surprising. It should be also mentioned that the polymers were obtained without particular attention to rigorous optimization of the conditions for their synthesis.

3.3. Reaction Mechanism. Structural studies of the products obtained have shown unambiguously that superacid-catalyzed condensations of acenaphthenequinone with aromatic hydrocarbons result in high molecular weight, linear, fully soluble polymers. NMR investigations of polymer **3a** revealed no any essential indications of structural irregularity.

In accordance with the concept of superelectrophilic activation in superacids,⁹ one may assume that, similarly to the case of reactions of linear α -diketones,¹⁴ two adjacent carbonyl groups of acenaphthenequinone in TFSA acid undergo protonation to form protosolvates. Because of the mutual electron-withdrawing effect of the protonated carbonyl groups, these intermediates may behave as highly reactive electrophiles or super-electrophiles.

The presence of adjacent protonated groups mutually increases their reactivity toward aromatic groups. To obtain deeper insight into the reaction mechanism, the energies of mono- and diprotonation of acenaphthenequinone were calculated theoretically using B3LYP/6-31G* optimized molecular geometries and a single point energy calculation using larger aug-ccpvtz(-f) basis set. Solvation was taken into account using continuum Poisson–Boltzmann solver implemented in Jaguar v 5.5 suit of program at the same theoretical level. Calculations show that first protonation occurs at carbonyl oxygen, and the second proton goes to another carbonyl group. The energy of first protonation is $-3.38\text{ kcal mol}^{-1}$ while the second protonation is endothermic with an energy of $11.0\text{ kcal mol}^{-1}$. Therefore, we assume that diprotonated species barely contribute to the reaction mechanism, and the reaction of acenaphthenequinone with aromatic hydrocarbons can be represented by Scheme 2.

Scheme 2. Polymer Reaction Mechanism

Table 2. Solubility^a of Polymers 3a–3l

solvent	polymers 3a–3l											
	a	b	c	d	e	f	g	h	i	j	k	l
methylene chloride	±	+	±	+	+	+	+	+	+	+	–	±
dichloroethane	±	±	–	–	+	±	+	+	+	+	–	±
chloroform	+	+	+	+	+	+	+	+	+	+	–	+
TCE	+	+	+	+	+	+	+	+	+	+	+†	+
H ₂ SO ₄	–	+	+	–	+	+	+	+	+	+†	+	+
DCAA	±	+	+	–	+	+	+	+	+	+	+	+
DMFA	±	±	±	±	+	±	+	±	+†	+	+	–
NMP	+	+	+	+	+	+	+	+	+	+	+	+
DMSO	±	+	±	±	+	+‡	+‡	+‡	–	±	+	–
DMAA	±	±	±	±	+‡	+	+	+	+	+‡	+	±
nitrobenzene	+	+	+	+	+	+	+	+	+	+	+‡	+

^a +, soluble at room temperature; ±, swells; +†, soluble on heating; +‡, soluble on heating and precipitate on cooling; –, insoluble.

3.4. Polymer Properties. It was stated above that the polymers obtained present the appearance, after separation from the reaction media followed by washing and drying, of white or yellow-white fiberlike fibrous powders. All polymers obtained were completely soluble in organic solvents. The qualitative solubility properties of polymers 3a–3l are reported in Table 2.

As can be seen from the table, the majority of the polymers obtained possess good solubility in chlorinated and aprotic solvents and strong acids. Interestingly, polymers with high aromatic content (3a and 3d) are not soluble in sulfuric acid. Polymers are not soluble in alcohols, aromatic hydrocarbons, or ethers. In general, solubility of the polymers is somewhat similar, except for polymer 3k, containing a carboxy group. Transparent, strong, flexible films could be cast from the polymer solutions. Some properties of the polymers are presented in Tables 2 and 3. Most of the polymers synthesized possess high values of intrinsic viscosity: the viscosity data for polymers 3f–3h, measured in concentrated sulfuric acid, correspond to high molecular weight polyketones. DSC analysis of the polymers revealed glass transitions ranging from 191 to 300 °C. Although no transitions are present until 450 °C for polymers 3a, 3c, and 3d, containing rigid biphenylene and terphenylene fragments in the main chain, we assume that these polymers are amorphous as well. Obviously, this increase in the glass transition temperature (in comparison with linear aromatic polyketones such as PEEK or PEKK) is due to the presence of bulky side groups.

Table 3. Characterization of the Polymers

polymer 3	η_{inh} (dL g ⁻¹) (NMP)	T_g (°C) ^a	polymer 3	η_{inh} (dL g ⁻¹) (NMP)	T_g (°C) ^b
a	0.40	>450	g	0.44 (1.08) ^a	191
b	1.34	296	h	0.87 (1.26) ^a	225
c	0.52	>450	i	0.66	132
d	0.53	>450	j	1.08	272
e	0.40	244	k	0.27	300
f	0.54 (0.78) ^a	240	l	0.35	>450

^a Measured for 0.2% solutions of the polymers in concentrated sulfuric acid. ^b Midpoint temperature of baseline shift on the heating DSC heating trace (rate 20 °C) of the sample after quenching from 400 °C.

On the whole, the properties of the polymers synthesized can be considered as exemplifying the concept of “cardo-”polymers advanced by Korshak,³⁶ according to which bulky side groups provide solubility and increase the glass transition of the polymers.

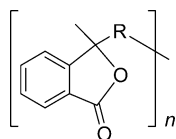
The thermal properties of the polymers were investigated by TGA analysis. The results are given in Table 4.

All of the polymers synthesized exhibited a similar TGA pattern with no significant weight loss below 500 °C both in air and in nitrogen atmosphere. There is a large window between T_g and the decomposition temperature of each polymer, which could be advantageous in the processing of these polymers by the thermoforming technique.

The amount of carbonized residue (char yield) of these polymers depends on the chemical composition of the

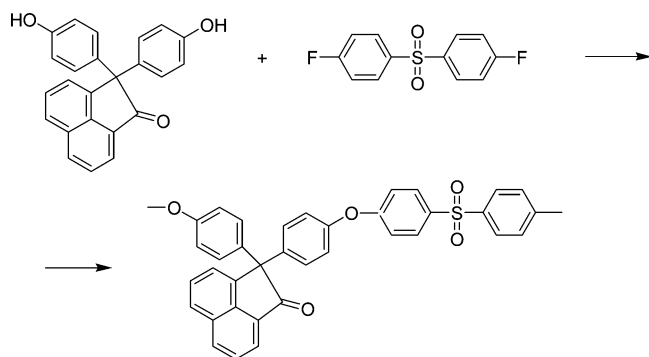
polymers. Remarkably, that char yields for polymers **3a**, **3c**, **3d**, and **3l** under nitrogen was close to 80% at 1000 °C. The high char yields of these polymers can be ascribed to their high aromatic content. This outstanding thermal stability also renders advantages in various applications.

In many way, the properties of the polymers somewhat resemble those of poly(phthalidylidenearylene)s^{6,7} of the following chemical composition:



where $-R-$ are aromatic hydrocarbon residues, such as biphenyl, diphenyl ether, fluorene, etc. Poly(phthalidylidenearylene)s are also obtained by Friedel–Crafts electrophilic substitution reactions. These polymers also possess good solubility in the common organic solvents. However, the thermostability of poly(phthalidylidenearylene)s is not as high as that of acenaphthenequinone-based polymers. Basically, decomposition of poly(phthalidylidenearylene)s (onset) starts around 460–470 °C.³⁶ Obviously, this relatively lower thermostability is due to the presence of an ether oxygen in the phthalide cycle. It is worthy of note that synthesis of poly(phthalidylidenearylene)s requires several steps, whereas polymers derived from acenaphthenequinone are obtained in one step. The absolute average molar masses of poly(3,3-phthalidylidene-4,4'-biphenylene) contained in the main-chain biphenylene fragments were measured.³⁷ Therefore, one may roughly estimate that polymer **3a** with similar viscosities value has M_w of 35 000–40 000.

In principle, polymers similar to **3b** and **3f–3h** can be obtained by other routes, for example, through nucleophilic aromatic substitution:



However, only oligomers were obtained from this reaction.³⁸

Thus, practical utilization of the theory of superelectrophilic activation opens up new possibilities for Friedel–Crafts polymer chemistry, and undoubtedly, many new polymers will be obtained by this route.

4. Conclusions

Olah's concept of superelectrophilic activation was successfully applied for the preparation via electrophilic substitution of new linear, soluble, film-forming aromatic polymers derived from acenaphthenequinone and aromatic hydrocarbons. Aromatic hydrocarbons of different structure and different nucleophilicity were used

Table 4. Thermal Properties of the Polymers

polymers	dec temp (TGA onset, °C) ^a		char yield, 700 °C (wt %) ^b
	air	nitrogen	nitrogen
a	525	530	85 (77)
b	515	522	68 (59)
c	510	525	80 (75)
d	540	546	86 (79)
3f	525	535	71 (63)
3g	525	530	68
3h	530	535	71
3i	440	464	26 (18)
3j	520	522	74(70)
3k	400	415	61 (43)
3l	505	508	83 (80)

^a Decomposition temperature, recorded via TGA at a heating rate 10 °C/min. ^b Residual weight percentage at 1000 °C (in parentheses).

as acylated substrates. The polymer-forming reaction of acenaphthenequinone and hydrocarbons depends greatly on the acidity of the reaction medium. Thus, condensations of **1** with aromatic hydrocarbons of relatively low nucleophilicity, such as diphenoxybenzophenone (**f**), 1,3-bis(4-phenoxybenzoyl)benzene (**g**), 1,4-bis(4-phenoxybenzoyl)benzene (**h**), and 1,10-bis(4-phenoxyphenyl)decane-1,10-dione, can be performed in a reaction medium of both moderate and high acidity, even in pure TFSA. Reactions with highly nucleophilic compounds (biphenyl (**a**), phenyl ether (**b**), fluorene (**c**), terphenyl (**d**), 1,4-diphenoxybenzene) must be carried out in a reaction medium having Hammett acidity function H_0 less than -12 . Mixtures of TFSA with MSA and TFA, covering wide range of acidity, were used successfully for the polymer preparations involving these highly nucleophilic compounds.

Polymers bearing pendent functional groups, such as nitrile and carboxy, are also readily obtained by condensations of acenaphthenequinone with functionalized monomers **2j** and **2k**. Structural studies revealed high regioselectivity in the polymer-forming reaction. New aromatic polymers of poly(aryl ether), poly(aryl ether ketone), and polyarylene classes with promising properties were obtained.

The simple, one-pot preparation method based on available reagents affords new aromatic polymers with promising properties.

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