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Guzman-Gutierrez, M.T.; Ruiz-Trevino, A.; Fritsch, D.; Cuellas, D.C.;
Fernandez-G., J.M.:

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Functional Polymers**

High Performance Polymers

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What is This?

A Novel Approach to the Synthesis of High Performance and Functional Polymers

MIKHAIL G. ZOLOTUKHIN[1]
SERGUIE FOMINE
LUZ MARIA LAZO
MA. DEL CARMEN G. HERNÁNDEZ
M. T. GUZMÁN-GUTIÉRREZ
Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de Mexico, Apartado Postal 70-360, CU, Coyoacan, 04510, Mexico D.F, Mexico

ALBERTO RUIZ-TREVINO
Universidad Iberoamericana, Departamento de Ingenierias, Prol. Paseo de la Reforma No. 880, Mexico, D.F. 01210, Mexico

DETLEV FRITSCH
Institute of Polymer Research, GKSS Research Centre Geesthacht GmbH, Max-Planck-Strasse 1, D-21502, Geesthacht, Germany

DAVID CUELLAS CUELLAS
Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas, Juan de la Cierva 3, 28006, Madrid, España

JUAN M. FERNANDEZ-G.
Instituto de Quimica, Universidad Nacional Autonoma de Mexico, Apartado Postal 70-360, CU, Coyoacan 04510, Mexico D. F., Mexico
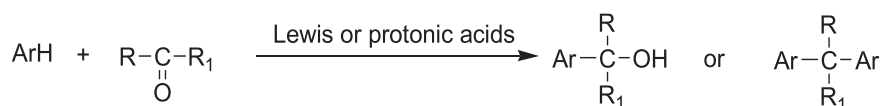
Abstract: A novel series of linear, high molecular weight high performance and functional polymers were synthesized by a one-pot, superacid-catalyzed polyhydroxylakylation reaction of carbonyl compounds containing electron-withdrawing substituents, adjacent or relatively close to a carbocation center with non-activated aromatic hydrocarbons. The reactions were performed at room temperature in the Brønsted superacid CF_3SO_3H (trifluoromethanesulfonic acid, TFSA) and in a mixture of TFSA with methylene chloride, which was used as both solvent and a medium for generation of electrophilic species from the carbonyl component. Polycondensations of 1,1,1-trifluoroacetone, 2,2,2-trifluoroacetohenone, 2,7-dinitrofluorenone, acenaphthenequinone and isatin with aromatic hydrocarbons proceed readily in the presence of superacid at room temperature. The polymers obtained were found to be soluble in the common organic solvents, and flexible transparent films could be cast from the solutions. ^{1}H and ^{13}C NMR analyses of the polymers synthesized revealed their linear, highly regular structure. The polymers also possess high thermostability.

Key Words: Superelectrophilic, hydroxyalkylation, trifluoromethanesulfonic acid, Friedel–Crafts, high performance polymers, functional polymers

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1. INTRODUCTION

Discovery of new polymer-forming reactions comprises one of the most fascinating topics of polymer chemistry. In principle, there are two basic directions in this area. The first one involves new reactions of the functional groups. The second direction involves an increase of synthetic potential of known chemical reactions by means of new catalysts, uncommon monomers, etc.

The acid-catalyzed condensation of ketones and aldehydes with aromatic compounds is known as the hydroxyalkylation reaction [1, 2]:

$$ArH \;+\; R-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-R_1 \quad\xrightarrow{\text{Lewis or protonic acids}}\quad Ar-\overset{\displaystyle R}{\underset{\displaystyle R_1}{C}}-OH \quad\text{or}\quad Ar-\overset{\displaystyle R}{\underset{\displaystyle R_1}{C}}-Ar$$

where R and R_1 are H, Alkyl, aryl

This widely used reaction has been applied to the preparation of thermosets (for example, phenol-formaldehyde resin, known as "Bakelite" was the first commercial polymer), dyes and pigments, and various monomers [2].

In this work we report an application of the hydroxyalkylation reaction for the preparation of linear, high molecular weight, high performance and functional polymers.

2. EXPERIMENTAL

2.1. Materials

Biphenyl and diphenyl ether were obtained from Aldrich and purified by the standard methods. Trifluoromethane sulfonic acid was obtained from Fluorochem Ltd. and was distilled under vacuum prior to use. 4,4′-Diphenoxybenzophenone were prepared according to published methods [3, 4] and purified by recrystallization from a benzene–ethanol (1 : 3, v/v) mixture. Acenaphthenequinone was obtained from Aldrich and purified by sublimation followed by recrystallization with charcoal from chlorobenzene. Isatin was obtained from Aldrich and purified by recrystallization with charcoal from ethanol.

2.2. Characterization

The inherent viscosities of 0.2% polymer solutions in *N*-methylpyrrolidinone were measured at 25°C using an Ubbelohde viscometer. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 spectrometer, operating at 400.13 and 100 MHz for ^{1}H and ^{13}C, respectively. The SEC-MALS measurements were performed at 25°C using a separation system consisting of two size exclusion columns, Waters HSPgel HR MB-L and HR MB-B with a range from 5×10^2 to 7×10^5 and from 1×10^3 to 4×10^6, respec-

tively, connected in series. The light-scattering photometer was a DAWN EOS multi-angle light-scattering (MALS) instrument (Wyatt Technology, Santa Barbara, CA, USA). Simultaneous concentration detection was performed using an Optilab REX interfero-metric refractometer (Wyatt Technology). Both detectors used a wavelength of 690 nm. Thermogravimetric analyses (TGA) were carried out in air and under nitrogen at a heat-ing 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).

2.3. Polymer syntheses

2.3.1. Syntesis of polymer 1

A typical polymer synthesis was conducted in single-necked 10 mL flask equipped with magnetic stirrer. Trifluoromethane sulfonic acid (TFSA) (1.4 mL) was added to an ice-cooled mixture of 0.144 g (1.28 mmol) 1,1,1,-trifluoroacetone, 0.470 g (1.28 mmol) 4,4′-diphenoxybenzophenone and 0.4 mL methylene chloride with vigorous stirring. After the addition of the reagents, the cooling bath was removed. The reaction mixture was stirred at room temperature for 10 h. The yellow–orange viscous solution was poured into methanol, the fibrous precipitate formed was washed copiously with methanol, and then extracted with refluxing methanol for 12 h before drying at 100°C under vacuum. The re-sulting white polymer **1** (0.55 g, 94% yield) has M_w and M_n of 45 290 and 15 550 $g\,mol^{-1}$, respectively. The ^1H NMR spectrum of the polymer is presented in figure 1.

2.3.2. Syntesis of polymer 3

TFSA (8.0 mL) was added to an ice-cooled mixture of 2,2,2,-trifluoroacetophenone (1.537 g, 8.82 mmol), biphenyl (1.360 g 8.82 mmol) and methylene chloride (7.0 mL), with vigorous stirring. After the addition of the reagents, the cooling bath was removed. The reaction mixture was stirred at room temperature for 3 days. The dark blue, elas-tic precipitate was shredded and washed copiously with methanol, and then extracted with refluxing methanol for 12 h before drying at 100°C under vacuum. The resulting white polymer **3** (2.62 g, 96% yield) has molecular weights M_w and M_n of 128 600 and 47 360 $g\,mol^{-1}$, respectively.

3. RESULTS AND DISCUSSION

The acid-catalyzed addition reactions of aldehydes and ketones have been known for a long time. For instance, the condensation of chloral with benzene in the presence of sulfuric acid was reported by A. Bayer as early as 1872 [5]. Nevertheless, these Friedel–Crafts-type reactions have not been studied to the same extent as the correspond-
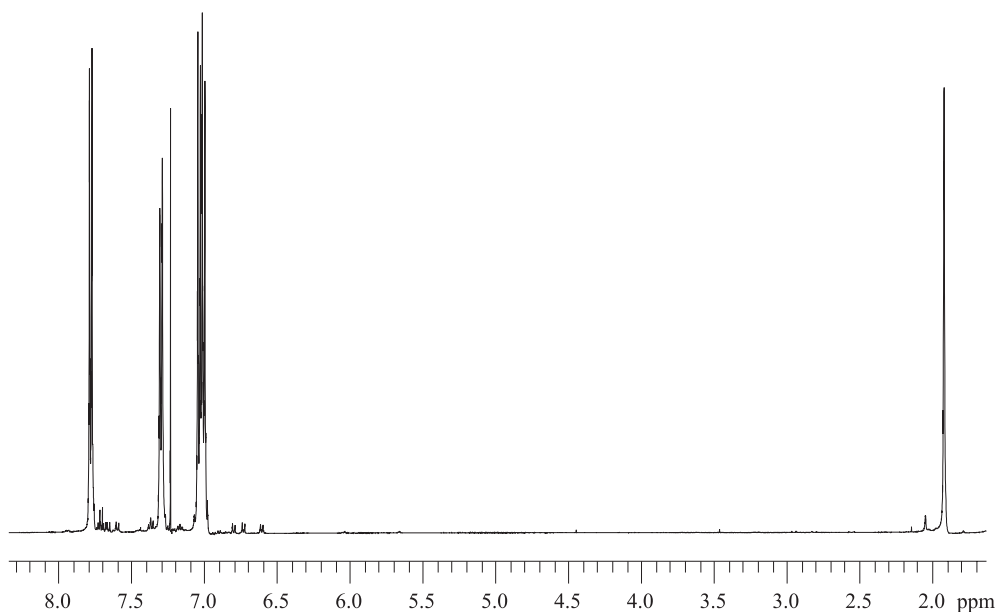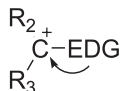
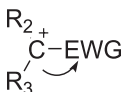Figure 1. ^{1}H NMR spectrum of polymer **1**.

ing reactions involving alcohols, alkyl halides or aryl halides. Probably, the main reason for such neglect is the generally lower yields and the formation of oligomeric by-products.

It is believed that the attacking species in the hydroxyalkylation reaction are carbocations, formed from the aldehyde or ketone and the acid catalyst (except when the reaction is carried out in basic solution). A fundamental dogma in the carbocation area holds that since this intermediate is intrinsically electron-deficient, electron-donating groups stabilize a carbocation:

$$\begin{array}{c} R_2 \\ \overset{+}{C}-EDG \\ R_3 \end{array}$$

where EDG is an electron donating group;

while carbocations containing electron-withdrawing groups adjacent to a carbocation:

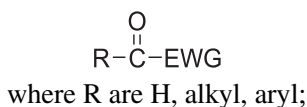$$\begin{array}{c} R_2 \\ \overset{+}{C}-EWG \\ R_3 \end{array}$$

where EWG is an electron-withdrawing group,

are intrinsically unstable and therefore would form 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 demonstrated 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 [6–8].
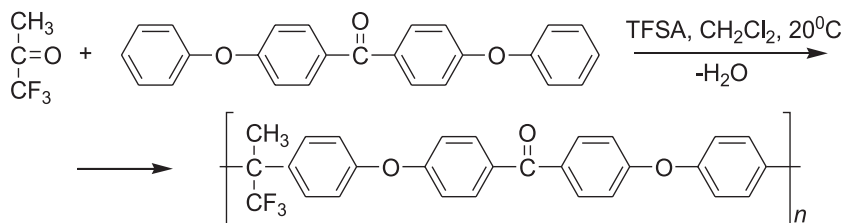
Recent progress in the chemistry of electrophilic intermediates, especially the major contribution to this field by group of Nobel prize winner, G. A. Olah, led to the superelectrophilic hydroxylation reactions, in which carboxonium intermediates react with Lewis or Bronsted acids to give extremely reactive dications, (which, in fact, can be considered as carbocations containing adjacent electron-withdrawing groups, i.e. another carbocation centers) [9]. One can expect that electron-withdrawing substituents, such as CF_3, NO_2, or another CO-group will enhance reactivity of the cations formed from the carbonyl group and desactivate once reacted aromatic nuclei (as a nucleophile) towards further reactions. Olah has also shown that low-viscosity, nonoxidative TFSA (superacid, which is 10^3 times stronger than sulfuric acid) is a convenient medium for syntheses involving superelectrophiles.

Therefore, it seems plausible that the carbonyl-containing compounds bearing electron-withdrawing substituents

$$R-\overset{\overset{\textstyle O}{\|}}{C}-EWG$$

where R are H, alkyl, aryl;

would generate highly reactive intermediates in a TFSA medium and the reactions of these electrophiles with aromatic fragments capable of di-substitution would lead to the highly regio-selective polymer-forming polyhydroxyalkylation.

Indeed, 1,1,1-trifluoroacetone reacts with diphenoxybenzophenone in the presence of TFSA at room temperature to give high molecular weight polymer (**1**):

The NMR spectrum of the polymer in $CDCl_3$ (figure 2) is well resolved and the aromatic resonances anticipated for methyl and diphenoxybenzophenone are all evident.
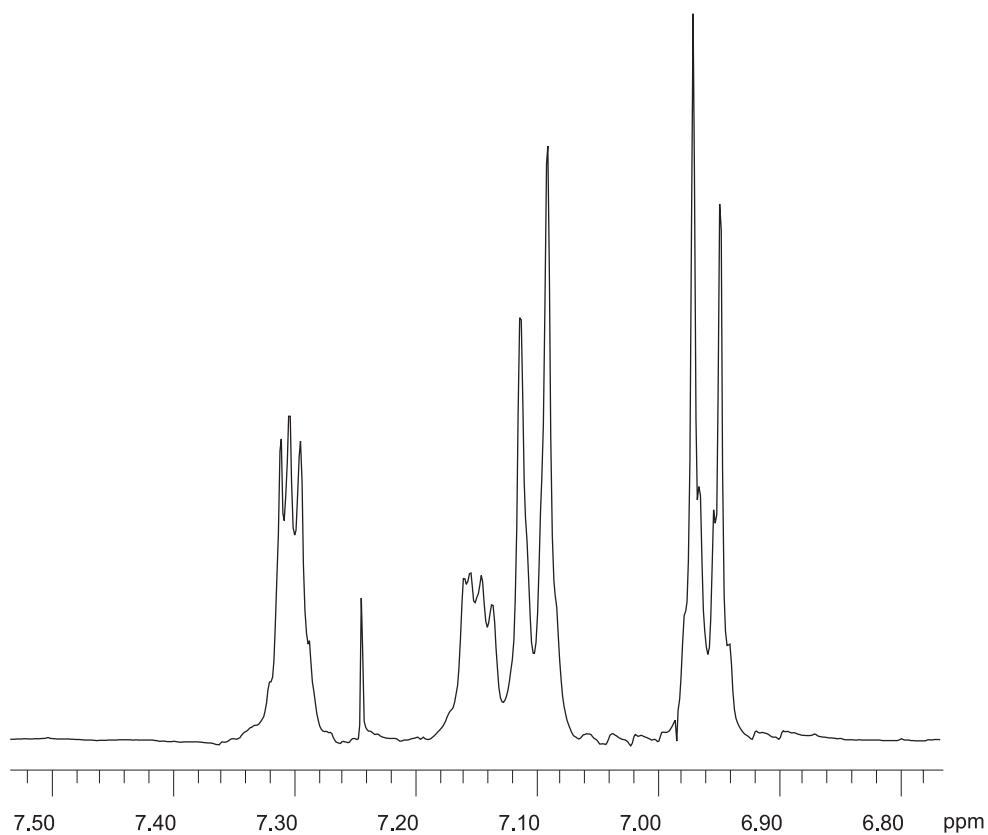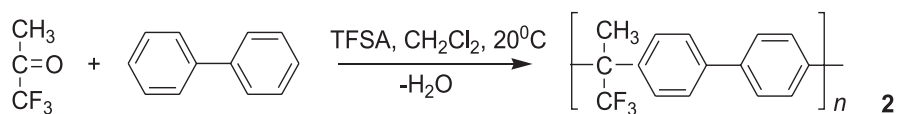
Figure 2. ^{1}H NMR spectrum of polymer **3** (in CDCl$_3$).

The molecular weights, M_w and M_n, of the polymer were 45 290 and 15 550 g mol^{-1}, respectively. The T_g of polymer **1** was 155°C.
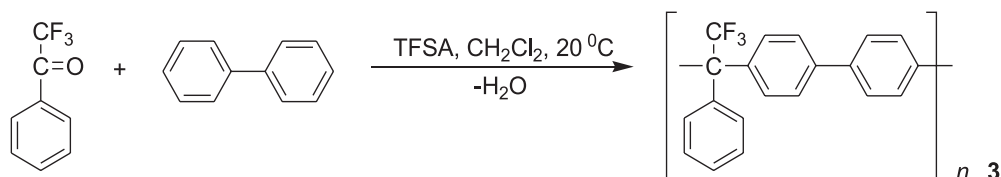
Interestingly, 1,1,1-trifluoroacetone reacts even with biphenyl to give a linear polymer:

^{1}H and ^{13}C NMR spectroscopy confirms highly regular structure of polymer **2**.

The molecular weights, M_w and M_n, of the polymer were 38 200 and 17 400, respectively; the T_g of polymer **2** is 280°C. Surprisingly, polymers based on 1,1,1,-trifluoroacetone and aromatic hydrocarbons possess very high thermostability. The decomposition temperatures (onset) of polymers **1** and **2** under nitrogen are 517 and 527°C.

Similar to 1,1,1-trifluoroacetone, 2,2,2-trifluoroacetophenone reacts with aromatic hydrocarbons, such as biphenyl, phenyl ether to give linear polymers [10]:
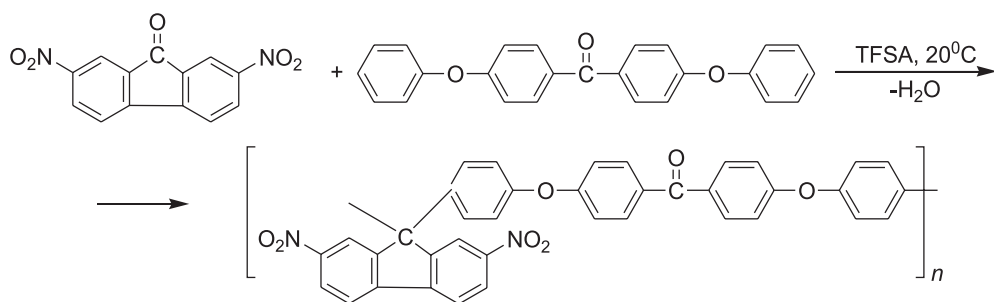

The molecular weights, M_w and M_n, of the polymer were 128 600 and 47 360 g mol^{-1}, respectively; the T_g of polymer **3** was 326°C. One can mention that the polydispersities of the polymers are rather broad. The data are repeatable during gel permeation chromatography measurements, detailed structure studies to clarify the phenomenon are in progress now.
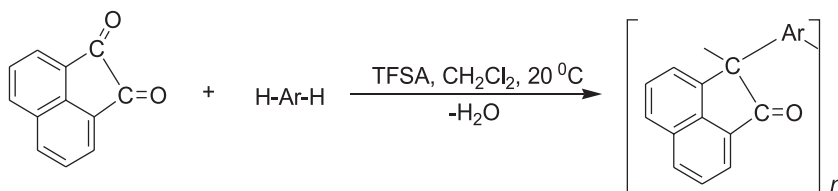
Reactions of 2,2,2-trifluoroacetophenone with biphenyl, terphenyl or fluorene in a mixture of TFSA with CH$_2$Cl$_2$ proceeded as "precipitation polycondensations", when the polymer formed precipitates from the initially homogeneous solution as a colored, elastic mass ("reactive gel"). It is generally accepted that premature polymer in polycondensation syntheses prevents further macromolecular chain growth reactions. It has, however, been found that under certain conditions polymer-forming reactions can occur in the precipitate, i.e. after phase separation, yielding high molecular weight polymers [3,4,11]. After completion of the reaction, the precipitates formed are isolated from the reaction medium, shredded and washed thoroughly with methanol and dried overnight in air. After re-precipitation from chloroform into methanol, which was followed by filtration and washing, white fibrous polymers were extracted with refluxing methanol before drying at 100°C under vacuum. Yields of the polymers obtained were close to quantitative. (It should be noted that all the polymerizations were carried out under non-optimized conditions.)

It is worth mentioning that electron-withdrawing substituents (particularly, trifluoromethyl groups) in carbonyl compounds eventually become substituents in polymer chains, which will afford new polymer structures and properties. Thus, the incorporation of fluorine atoms (or groups containing fluorine atoms) into macromolecules leads to polymers with increased solubility, glass transition temperature, thermal stability and chemical resistance, while also leading to decreased moisture absorption, dielectric constant and color.
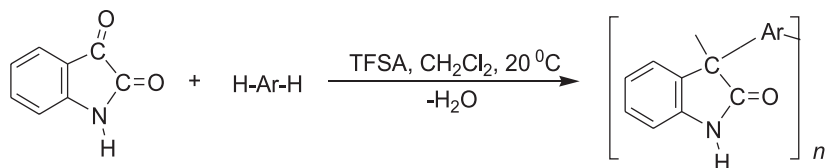
Remarkably, we found that electron-withdrawing groups, non-adjacent to the carbocation center, may also increase the electrophilicity of the carbocation. For example, 9-fluorenone, like acetophenone, did not react with 4,4′-diphenoxybenzophenone in a TFSA medium at room temperature. However, 2,7-dinitro-9-fluorenone reacts with 4,4′-diphenoxybenzophenone to produce, in virtually quantitative yield, the high molecular-weight polymer **4** with an inherent viscosity of 0.38 dL g^{-1}.
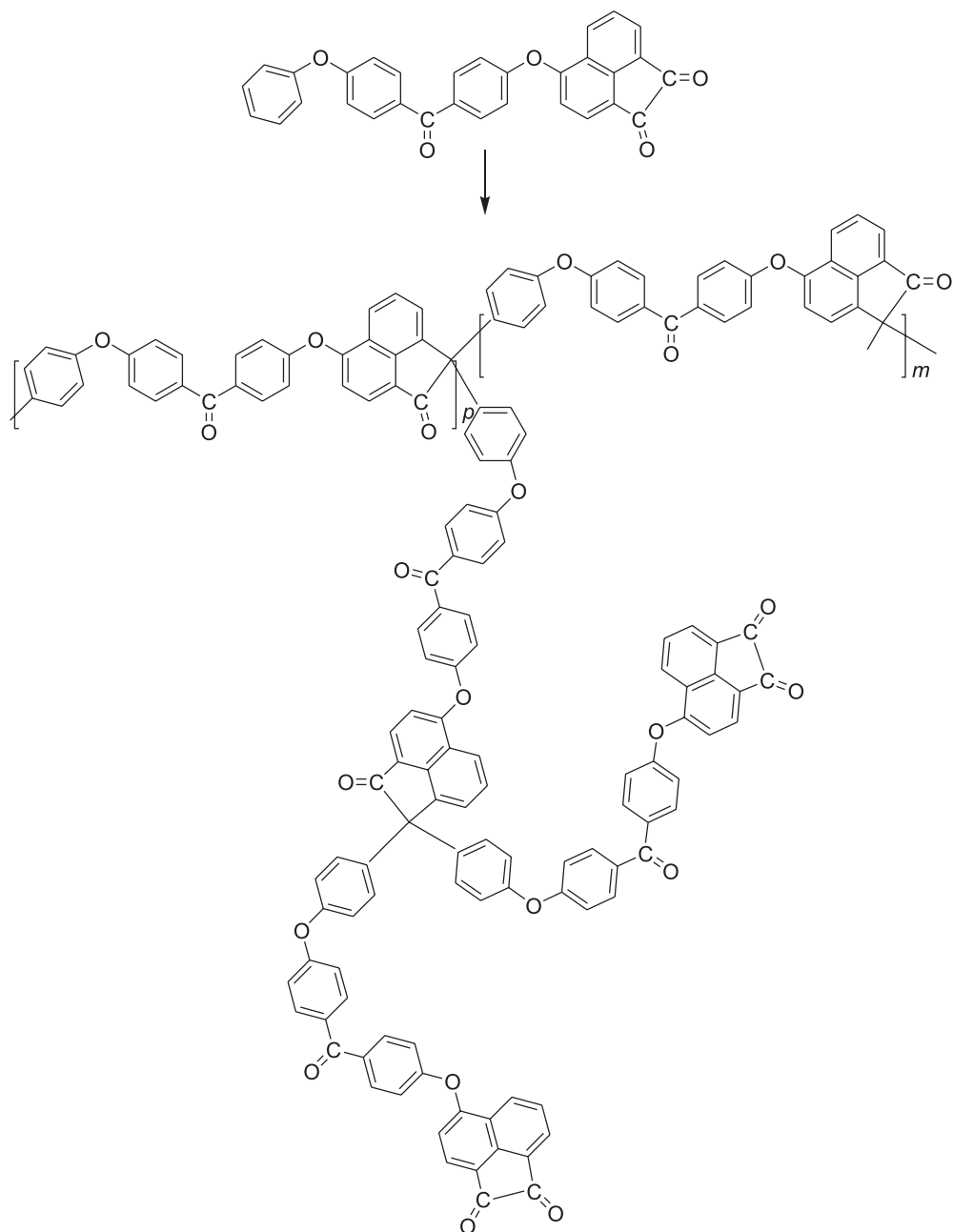

The carbonyl group itself, being an efficient electron-withdrawing substituent, can also activate a carbocation center. Thus a variety of new polymers was obtained from reactions of acenapthenequinone with aromatic hydrocarbons [12]:

Hetrerocyclic diketones, such as isatin, *N*-methyl isatin or *N*-phenylisatin also readily react with aromatic-affording linear, fully soluble polymers [13]:

Recently, an application of superacid catalyzed polyhydroxyalkylation for the preparation of hyperbrunched polymer with functional terminal groups was demonstrated [14]:

All of these examples show that the scope of polyhydroxyalkylation is very ample allowing for the design of new polymeric architectures that are unavailable by other methods or requiring multiple synthetic steps.

4. CONCLUSION

Thus, the superacid-catalyzed polyhydroxyalkylation reaction presents a powerful tool for the preparation of new high performance and functional polymers. These Friedel–Crafts-type aromatic electrophilic substitution reactions proceed selectively at room temperature in TFSA and mixtures of TFSA with methylene chloride to give linear, amorphous, high-molecular weight polymers.

Simple, practical, metal-free, one-pot reactions of carbonyl compounds with non-activated aromatic hydrocarbons open up wide possibilities for constructing new polymers using commercially available monomers.

NOTE

1.   Author to whom correspondence should be addressed: e-mail: zolotukhin@iim.unam.mx

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