Superelectrophiles in Polymer Chemistry. A Novel, One-Pot Synthesis of High-T_g, High-Temperature Polymers

Mikhail G. Zolotukhin,* Luydmila Fomina, Roberto Salcedo, and Luis E. Sansores

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

Howard M. Colquhoun

School of Chemistry, University of Reading, P.O. Box 224, Whiteknights, UK

Leonard M. Khalilov

*Institute of Oil Chemistry and Catalysis, Prospekt Oktyabrya 141, Ufa 450054, Russia*

Introduction. It has been more than 25 years since Olah's group reported that electrophilic nitration and acylations are facilitated by superacids.[1] These pioneer studies led to the proposal of superelectrophilic activation due to the formation of superelectrophiles, that is, electrophiles of doubly electron-deficient (dipositive) nature whose reactivity exceeds greatly that of their parent compounds in aprotic or conventional acidic media. Superelectrophiles have since been proposed or studied in numerous superacid-catalyzed reactions.[2−5] It was also found that 1,2-dicarbonyl groups form highly reactive intermediates in superacidic trifluoromethanesulfonic acid.[5−7]

Recently, we reported the first application of superelectrophilic chemistry for polymer preparation having synthesized poly(arylene oxindole)s by reaction of isatin containing 1,2-dicarbonyl groups with aromatic hydrocarbons in a TFSA medium.[8] Very recently, the superelectrophile-based approach was used successfully for the synthesis of hyperbranched poly(arylene oxindole).[9]

1,2-Dicarbonyl groups in isatin present a part of the N-containing heterocycle. Therefore, it seemed plausible that such compounds, as 1,2-quinones, would also likewise generate highly reactive electrophiles in TFSA.

The aim of the present work was the synthesis of polymers by reaction of acenaphthenequinone with aromatic hydrocarbons in a superacid medium.

Results and Discussion. It has long been known that acenaphthenequinone reacts under heating with benzene in the presence of aluminum trichloride. Using excess benzene as solvent, the resulting 1,1-diphenyl-2-acenaphthenone was obtained in moderate yield:[10]
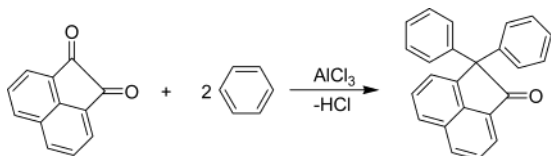
It was shown recently that condensation of acenaphthenequinone with benzene carried out in a TFSA

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

medium at room temperature affords excellent yield of 1,1-diphenyl-2-acenaphthenone.[11] Following these data, we expected that the condensations of acenaphthenequinone with aromatic hydrocarbons, performed similar to the condensations of isatin with aromatic in a TFSA medium[8] at room temperature, would afford polymeric products according to the following scheme
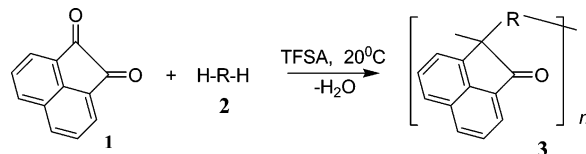
where H−R−H (**2**) are biphenyl (**a**), phenyl ether (**b**), fluorene (**c**), terphenyl (**d**), 1,4-diphenoxybenzene (**e**), and diphenoxybenzophenone (**f**). However, our attempts to obtain high molecular weight, linear polymers in such a way failed. Deeply colored, mostly insoluble products, typical for highly reactive but not selective polymerizations, were recovered from these experiments, in a sharp contrast to white polymers resulting from condensations involving isatin.

Acenaphthenequinone, in contrast to isatin, does not contain a nitrogen adjacent to the carbonyl group. It is very likely that the partial deactivation of the "amide-type" carbonyl by delocalization of electron density from nitrogen decreases the reactivity of isatin. Therefore, decrease of the reactivity of acenaphthenequinone might be a key to the problem.

One of remarkable pecularities of suprelectrophilic chemistry is a dependence of a reaction on the acidity of the reaction medium (generally, judging from the products yield).[12−14] The acidity function of the reaction media was found to be tuned easily by dilution of pure trifluoromethanesulfonic acid with solvents like trifluoroacetic or methanesulfonic acids.

We found that polymer syntheses carried out in mixtures of TFSA with MSA afford high molecular weight, linear polymers, fully soluble in common organic solvents. All the polymer preparations 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. Yield of the polymers obtained was close to quantitative. The IR spectra of the polymer films revealed the expected presence of the band at 1723 cm^{-1} corresponding to the carbonyl group of the diarylacenaphthenone fragment and a set of bands typical for aromatic hydrocarbons. The good solubility of the polymers has allowed analysis of their structures by NMR spectroscopy. The ^{1}H NMR spectrum of polymer **3f**, obtained by reaction of acenaphthenequinone with 4,4′-diphenoxybenzophenone, is given in Figure 1. The spectrum is well resolved, the aromatic resonances anticipated for the diphenoxybenzophenone (doublets at 7.76, 7.31, 7.17, and 7.00 ppm) and acenaphthenone fragments (doublets at 8.21, 8.08, 7.92, and 7.52 ppm, triplets at 7.82 and 7.72 ppm) are all evident, and no other resonances can be observed.

It is often difficult to achieve high regiospecificity in polyalkylation reactions, and more surprising is the fact that polymer-forming electrophilic substitution reaction
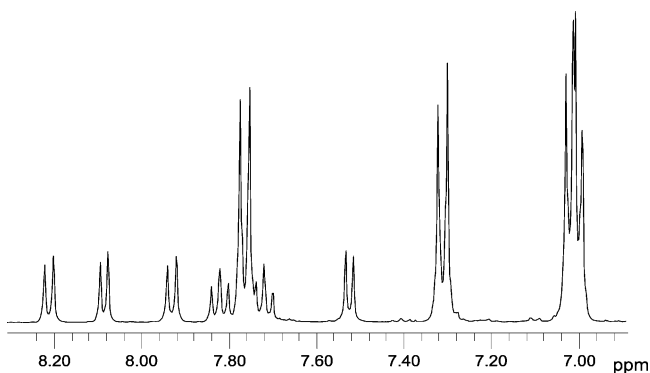
Figure 1. ^{1}H NMR spectrum of polymer **3f** in CDCl$_3$.

Table 1. Synthesis and Characterization Data for Poly(arylene acenaphthenone)s

polymer **3**	η_{inh}, dL g^{-1} (NMP)	T_g, °C	dec temp in air (TGA onset, °C)
a	0.40	>450	525
b	1.34	296	510
c	0.52	>450	480
d	0.53	>450	525
e	0.40	244	420
f	0.54 (0.78)^a	240	525

^{a} Measured for 0.2% solutions of the polymers in concentrated sulfuric acid.

proceeds only with aromatic hydrocarbons, but with acenaphthenone residue. It is likely that large steric bulk and (in superacid solution) the positive charge associated with a protonated acenaphthenone fragment inhibits further substitution of the alkylated rings.

It is even more surprising that condensation of acenaphthenequinone with biphenyl was also 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. (Synthesis of wholly aromatic polyketones through polyacylation of 2,2′-dimethoxybiphenyl has, however, been reported.[15]) This approach appeared also to be successful when such highly reactive compounds as 1,4-diphenoxybenzene and phenyl ether were used.

The majority of the polymers obtained are fully soluble in chlorinated and aprotic solvents and strong acids (except **3a** and **3d**). Polymers are not soluble in alcohols, aromatic hydrocarbons, or ethers. Transparent, strong, flexible films could be cast from the polymer solutions. Some properties of the polymers are presented in Table 1. Most of the polymers synthesized possess high values of inherent viscosity. DSC analysis of the polymers revealed glass transitions temperature ranging from 240 to 296 °C and the absence of heat transitions for polymers **3a**, **3c**, and **3d** up to 450 °C. The polymers obtained also possess high thermostability, particularly, polymers **3a**, **3d**, and **3f**. Obviously, the combination of these properties is of great interest for potential use of the polymers in the area of membrane separation processes, microelectronics, and high-performance functional polymer-based materials.

Thus, polycondensations of acenaphthenequinone with aromatic hydrocarbons (including nonactivated ones), carried out in a TFSA/MSA medium at room temperature, leads to linear, high-molecular-weight polymers. Structural studies revealed high regioselectivity in the polymer-forming reaction. Simple, one-pot preparation method based on available reagents affords new aromatic polymers with promising properties.

Experimental Section. a. Materials. Biphenyl, phenyl ether, and 1,4-diphenoxybenzene were obtained from Aldrich and purified by the usual methods. Acenaphthenequinone was obtained from Aldrich and purified by sublimation followed by recrystallization from chlorobenzene. Diphenoxybenzophenone was prepared according to published methods[16,17] and purified by recrystallization from a benzene−ethanol 20/80 (v/v) mixture. Methanesulfonic acid and trifluoromethanesulfonic acid were obtained from Fluorochem Ltd. and distilled under vacuum prior to use.

b. 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. Thermogravimetric analyses (TGA) were carried out in air and under nitrogen at a heating rate of 20 °C min^{-1} on a Mettler DTG 760 instrument and differential scanning calorimetry (DSC) measurements at 20 °C min^{-1} on a Mettler DSC 20 system.

c. Polymer Synthesis. A typical example of polymer preparation was as follows. Acenaphthenequinone (0.182 g, 0.001 mol) and 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 viscosity of the 0.2% solution of the polymer in NMP was 0.54 dL/g. The ^{1}H NMR spectrum of the polymer is presented in Figure 1.

References and Notes

(1) Olah, G. A.; Germain, H. C.; Lin, H. C.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 2928.
(2) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.
(3) Ohwada, T. *Rev. Heterat. Chem.* **1995**, *12*, 179.
(4) Sato, Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 3037.
(5) Klumpp, D. A. *Rec. Res. Dev. Org. Chem.* **2001**, *5*, 193.
(6) Yamazaki, T.; Saito, S.; Ohwada, T.; Shudo, K. *Tetrahedron Lett.* **1995**, *36*, 5749.
(7) Klumpp, D. A.; Baek, D. N.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1997**, *62*, 6667.
(8) Colquhoun, H. M.; Zolotukhin, M. G.; Khalilov, L. M.; Dzhemilev, U. M. *Macromolecules* **2001**, *34*, 1122.
(9) Smet, M.; Schacht, E.; Dehaen, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4547.
(10) Zsuffa, M. *Chem. Ber.* **1910**, *43*, 2918.
(11) Klumpp, D. A. *Rec. Res. Dev. Org. Chem.* **2001**, *5*, 194.
(12) Yamazaki, T.; Saito, S.; Ohwada, T.; Shudo, K. *Tetrahedron Lett.* **1995**, *36*, 5749.
(13) Suzuki, T.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1997**, *119*, 6774.
(14) Klumpp, D. A.; Lau, S. *J. Org. Chem.*, **1999**, *64*, 7309.
(15) Yonezawa, N.; Miyata, S.; Nakamura, T.; Mori, S.; Ueha, Y.; Katakai, R. *Macromolecules* **1993**, *26*, 5262.
(16) Zolotukhin, M. G.; Dosiere, M.; Fougnies, C.; Villers, D.; Gileva, N. G. *Polymer* **1995**, *36*, 3575.
(17) Zolotukhin, M. G.; Rueda, D. R.; Balta Calleja, F. J.; Cagiao, M. E.; Bruix, M.; Sedova, E. A.; Gileva, N. G. *Polymer* **1997**, *38*, 1471.

MA0495902