

Remarkable enhancement of reactivity of carbonyl compounds for polymerizations with non-activated aromatic hydrocarbons

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Reaction of carbonyl compounds bearing electron-withdrawing substituents with non-activated aromatic hydrocarbons proceeds selectively in trifluoromethanesulfonic acid (TFSA) at room temperature to give linear, high-molecular-weight polymers.

Synthesis and investigations of reactive intermediates that possess high energies and unusual reactivities comprise one of the most fascinating topics of today's chemistry. In addition to the discovery of new reactions, enhancement of intermediate reactivity in well-known reactions also permits new products to be obtained.

For example, the acid-catalyzed condensation of ketones and aldehydes with electron-rich arenes, known as the hydroxylation reaction, is widely used in chemical syntheses.¹ It is believed that the reaction proceeds *via* formation of carboxonium intermediates. In studies of superacid systems, Olah *et al.*² found that the electrophilic solvation (or protosolvation) of electrophiles such as onium, carboxonium, and related ions involves their further interaction with Lewis or Brønsted acids. Such interactions in superacid systems like trifluoromethane sulfonic acid (TFSA) can, in some cases, lead to extremely reactive dications.

Additionally, the reactivity (electrophilicity) of the carboxonium ion can be further increased by the presence of electron-withdrawing substituents. Experimental and theoretical studies of electronegatively substituted carbocations 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.^{3–6}

Therefore, it seems plausible that the carbonyl-containing compounds bearing electron-withdrawing substituents would generate highly reactive intermediates in a TFSA medium.

Thus, acetophenone reacts with neither benzene nor toluene in the presence of TFSA, whereas 2,2,2-trifluoroacetophenone does, to give, for example, 1-phenyl-1,1-bis(*p*-tolyl)-2,2,2-trifluoroethane (43%) after boiling for 48 hours in a mixture of toluene and TFSA (20/1, v/v).⁷

We have found that stirring of an equimolar mixture of 2,2,2-trifluoroacetophenone with 4,4'-diphenoxybenzophenone in a TFSA medium at room temperature for 10 hours affords a linear, soluble, film-forming, high-molecular-weight polymer **1**. Measurements of inherent viscosity (0.2% solution in NMP, 25 °C) gave value of 0.28 dL g⁻¹, proton and ¹³C NMR (Bruker Avance 400, operating at 400.13 and 100 MHz for ¹H and ¹³C, respectively) spectra were well-resolved and fully consistent with the formation of all-*para* polymer **1**. (Fig. 1, doublets at 7.83, 7.19, 7.11 and 7.05 ppm, corresponding to the protons of phenylene fragments of the main chain). The polymer displays *T*_g at 175 °C. The yield of the polymer was close to 100%.

Remarkably, under these conditions 2,2,2-trifluoroacetophenone reacts even with biphenyl to give polymer **2**. This is the first example of a Friedel–Crafts polymerization using unsubstituted biphenyl as a comonomer. The ¹H NMR spectrum (Fig. 2) also revealed highly selective *para* substitution in the main chain (doublets at 7.09 and 6.72 ppm).

Broadened signals at 6.79 and 6.67 ppm correspond to the protons of the side phenyl group. Inherent viscosity and *T*_g were

found to be 0.32 dL g⁻¹ and 326 °C, respectively. The yield was 97%.

Quantum mechanics calculation of model reactions between acetophenone and 2,2,2-trifluoroacetophenone with biphenyl, carried out at the B3LYP/aug-cc-PVTZ(-f)//B3LYP/6-31G* level using the Poisson–Boltzman solver⁸ implemented in the Jaguar v. 5.0 suite of programs to calculate the solvation effects of TFSA acid, reveals that electron-withdrawing groups favors formation of σ -complexes (increasing stability and reducing activation energy of their formation), which is the limiting step of the electrophilic aromatic substitution reaction. This shows that the adjacent electron-withdrawing trifluoromethyl group enhances significantly the electrophilicity of the carbocation, formed from the carbonyl group, toward non-activated aromatic hydrocarbons.

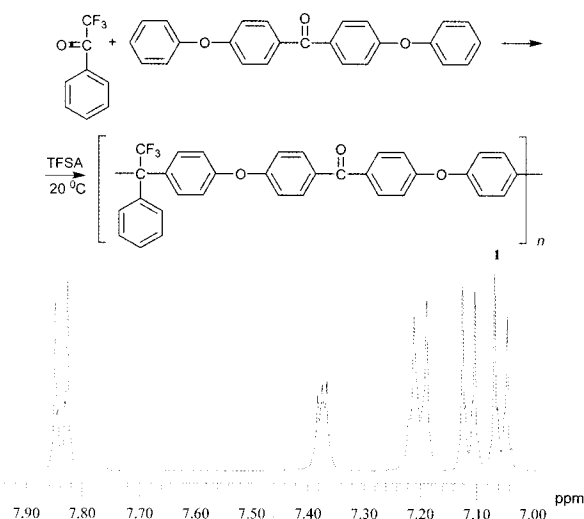


Fig. 1 ¹H NMR spectrum of polymer **1** (solution in CDCl₃).

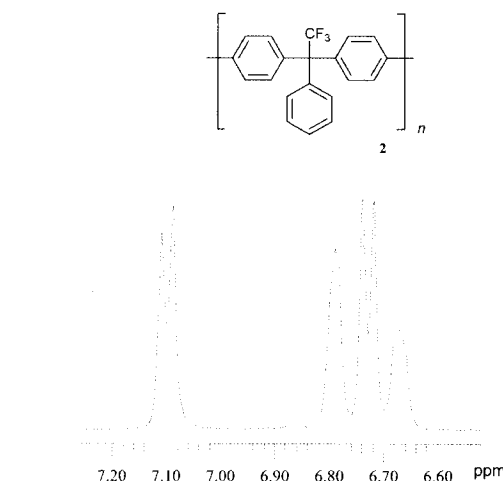


Fig. 2 ¹H NMR spectrum of polymer **2** (solution in CDCl₃).

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 reacted with 4,4'-diphenoxybenzophenone to produce, in virtually quantitative yield, the high-molecular-weight polymer **3** with an inherent viscosity of 0.38 dL g⁻¹. The well-resolved ¹H NMR spectrum of the polymer points to high regioselectivity of the polymer-forming reaction (Fig. 3).

It should be noted that NMR spectra of the polymers **1–3** do not reveal signals which could be attributed to end groups. The glass transition temperature of polymer **3** was found to be 270 °C. Although viscosity values of the polymers obtained are not very

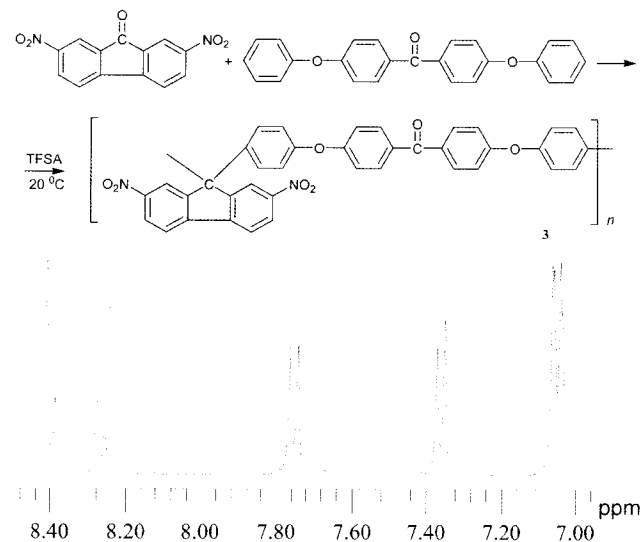


Fig. 3 ¹H NMR spectrum of polymer **3** (solution in THF-*d*₈).

high, flexible, transparent, colourless (for **1** and **2**, yellow for **3**) films could be cast from the polymer solutions in common organic solvents.

Clearly, the presence of the electron-withdrawing substituents (nitro groups) appears to be very significant for activation of the carbonyl group. One may predict that many carbonyl compounds could similarly be used for reactions with aromatic hydrocarbons.

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.

In summary, we have demonstrated that enhancement of the reactivity of carbonyl compounds can be achieved by the presence of electron withdrawing substituents, adjacent or relatively close to a carbocation center. Condensation of these carbonyl compounds with non-activated aromatic hydrocarbons, carried out in a TFSA medium at room temperature, affords linear, high-molecular-weight polymers.

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