Superelectrophiles in Aromatic Polymer Chemistry

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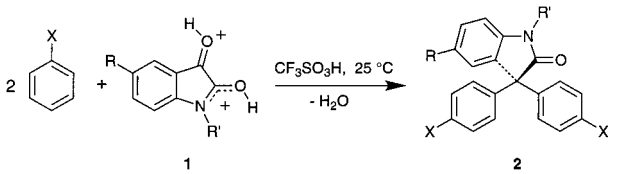
Introduction

The concept of a superelectrophile was originally introduced by Olah[1,2] to account for the very high reactivity of certain electrophilic species in superacidic media, where protonation of a conventional, monocationic electrophile can lead to formation of a doubly charged and therefore more reactive species.[3] Isatin, a heterocyclic 1,2-dicarbonyl compound, is also doubly protonated in trifluoromethanesulfonic acid and the resulting superelectrophile **1** condenses readily with aromatic compounds to give 3,3-diaryloxindoles **2** in high yield and with good regioselectivity for *para*-substitution.[4] As indicated in Scheme 1, the "amide-type" carbonyl group in **1** is itself *de*activated by delocalization of electron density from the nitrogen, but the overall positive charge associated with the protonated amide unit *activates* the adjacent (protonated) carbonyl group so that the latter behaves as a superelectrophilic center. Here we report the first applications of such chemistry to polymer synthesis and in particular to the synthesis of a new class of aromatic polymers, the polyaryleneoxindoles.

Results and Discussion

Exploratory reactions were carried out treating simple polynuclear aromatics such as diphenyl ether, biphenyl, or *p*-terphenyl, with equimolar quantities of isatin in trifluoromethanesulfonic acid solution at room temperature. The resulting polymers, isolated by precipitation into water, showed very high glass transition temperatures (337 °C for the polymer from diphenyl ether, and >400 °C for those based on biphenyl and *p*-terphenyl) and the materials obtained were of high molar mass, with inherent viscosities (η_{inh}) in the range 0.31−0.73 dL g^{-1}. Surprisingly, however, in view of the high regioselectivity reported for small-molecule chemistry of this type,[4] the ^{1}H and ^{13}C NMR spectra of these polymers included a number of weak resonances which could not be assigned on the basis of a linear, all-*para* substitution pattern. We therefore turned our attention to monomers such as 4,4′-diphenoxybenzophenone and 1,4-bis(4-phenoxybenzoyl)benzene (Scheme 2) which show very good selectivity for linear, *para*-substitution in electrophilic poly*acylation* reactions,[5] as a result of inductive deactivation of the *ortho*-positions of the terminal aromatic rings.[6] Although it is often difficult to achieve high regiospecificity in polyalkylation reactions,[7] it seemed possible that the large steric bulk and (in superacid solution) the positive charge associated with a protonated oxindole residue would inhibit further substitution of the alkylated rings. In practice, we discovered that such ether−ketone-type monomers exhibited very high selectivity indeed for linear, all-*para* polycondensation with isatin and moreover afforded polyaryleneoxindoles of very high inherent viscosity (up to 1.8 dL g^{-1}).

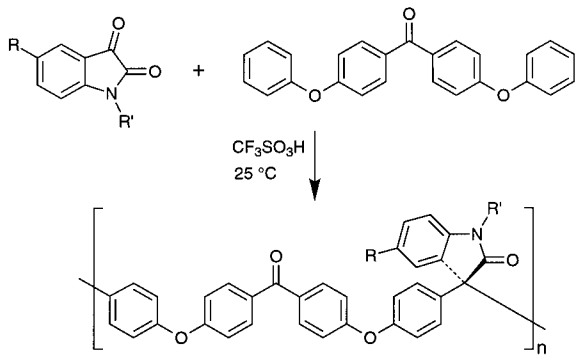
Scheme 1. Condensation of Isatins 1 (R = H, NO$_2$; R′ = H, Ph) with Aromatic Compounds (X = H, Me, Cl) in Trifluoromethanesulfonic Acid to Give 3,3′-Diaryloxindoles 2 (95−99% Isolated Yield; Ref 4)[a]



1 2

[a] The isatin nucleus is shown in its doubly protonated, superelectrophilic form.

Scheme 2. Polycondensation of Isatins (R = H, Br; R′ = H, Ph) with 4,4′-Diphenoxybenzophenone in Trifluoromethanesulfonic Acid, Affording High Molar Mass Polyaryleneoxindoles



3 (R = H, R′ = H), **4** (R = H, R′ = Ph), **5** (R = Br, R′ = H)

The ^{13}C NMR spectrum of polymer **3**, formed by reaction of 4,4′-diphenoxybenzophenone with isatin (Scheme 2), is given with selected assignments in Figure 1. The 16 aromatic resonances anticipated for the all-*para* polymer **3** are all evident, and no other resonances can be observed, at a signal-to-noise ratio of 150:1. The proton NMR spectrum of this polymer similarly showed a highly resolved pattern with no evidence of *ortho*-substitution. Polycondensations of 4,4-diphenoxybenzophenone with *N*-phenylisatin and 5-bromoisatin also gave high molar mass, linear polyaryleneoxindoles, and a number of successful polycondensations were achieved with other ether−ketone monomers including 1,3- and 1,4-bis(4-phenoxybenzoyl)benzene (Table 1). Full ^{1}H and ^{13}C NMR data, with assignments, for all of the new polymers are reported in the Supporting Information.

Polymers **3** and **5**−**11** are insoluble in hydrocarbon or chlorocarbon solvents, consistent with the presence of significant interchain hydrogen bonding, but are soluble in dipolar solvents such as NMP and DMAc. The basic character of these new polymers, arising from the

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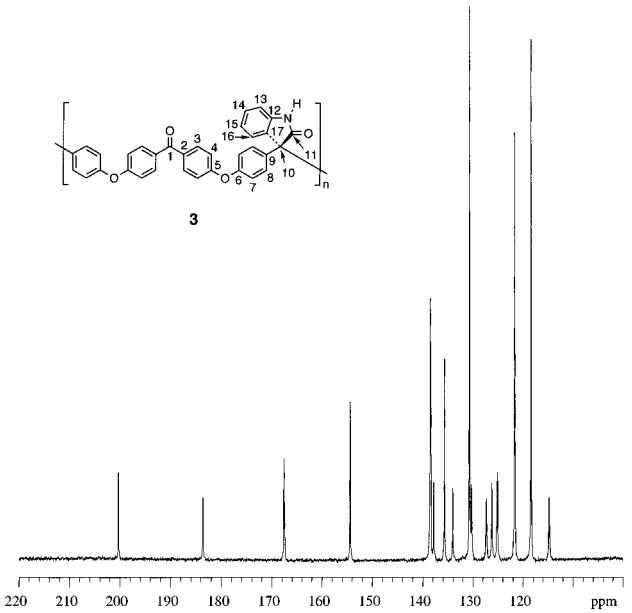
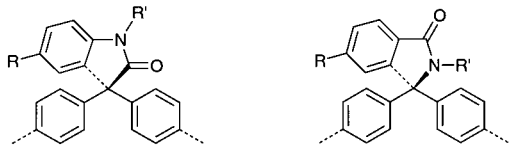


Figure 1. ^{13}C NMR spectrum (aromatic region) of polymer **3**, in CD_2Cl_2/CH_3SO_3H (2:1) as solvent. Selected assignments: δ 114.79 (C13), 118.46 (C7), 121.74 (C4), 130.78 (C8), 131.14 (C2), 135.76 (C3,9), 137.84 (C17), 138.57 (C12), 154.41 (C6), 167.59 (C5), 183.62 (C11), 200.30 (C1).

presence of both ketone and oxindole units, also makes them soluble in strong acids such as trifluoroacetic acid/chloroform mixtures and in concentrated sulfuric acid. Polymer **4**, derived from *N*-phenylisatin, additionally proved soluble in chlorinated aliphatic solvents such as dichloromethane, from which strong, transparent, flexible films could be cast. The infrared spectrum of this type of film was highly resolved and showed two very strong carbonyl bands, at 1728 and 1656 cm^{-1}, assigned to oxindole and aryl ketone groups, respectively. The TGA onset-temperature for decomposition of the *N*-phenyl substituted polymer **4** is noticeably higher than for the corresponding polymers derived from isatin itself (Table 1), presumably reflecting the absence of amidic hydrogen.

As shown in Scheme 3, the polyaryleneoxindoles (**12**) reported here are isomeric with the polyarylenephthalimidines (**13**),[8] a known type of polymer obtained by amination of polymers containing 3,3-diarylphthalide residues, or by polycondensation of phthalimidine-derived bisphenols with activated aromatic dihalides.[9] The physical properties of **12** and **13** are generally quite similar, but the simplicity of the direct, superelectrophilic polycondensations reported here contrasts strongly with the complex multistep reactions involved in the synthesis of many polyarylenephthalimidines.[8,9] Moreover, the thermooxidative decomposition temperatures recorded here for the polyaryleneoxindoles are noticeably higher than those given in the literature for polyarylenephthalimidines,[10] perhaps reflecting both an inherently greater chemical stability for the oxindole ring and an absence of the defect structures that can accumulate during multistage polymer syntheses. The versatile, one-step route to polyaryleneoxindoles described in the present work clearly offers significant advantages in this respect.

Scheme 3. Isomeric Relationship between Polyaryleneoxindoles (12) and Polyarylene−Phthalimidines (13)



Experimental Section

Materials and Measurements. Trifluoromethanesulfonic acid was obtained from Fluorochem Ltd and was distilled under dry nitrogen before use. Isatin, *N*-phenylisatin, and 5-bromoisatin were obtained from Aldrich and were recrystallized from ethanol. The aromatic ether−ketones 4,4′-diphenoxybenzophenone and 1,3- and 1,4-bis(4-phenoxybenzoyl)-benzene were prepared by Friedel−Crafts reactions of diphenyl ether with phosgene, isophthaloyl chloride, and terephthaloyl chloride repectively.[11] The melting points of all reagents, after recrystallization, were consistent with literature values. Proton and ^{13}C NMR spectra were run on Bruker AMX-300 and Varian Inova-300 spectrometers with polymer solutions in either $CDCl_3$, $CDCl_3/CF_3COOH$ (1:1, v/v), or CD_2Cl_2/CH_3SO_3H (2:1 v/v). Thermogravimetric analyses (TGA) were carried out in air at 20 °C min^{-1} heating rate on a Mettler DTG 760 instrument, and differential scanning calorimetry (DSC) measurements at 20 °C min^{-1} on a Mettler DSC 20 system. Inherent viscosities were measured at 25 °C on 0.2% (w/v) polymer solutions using a Schott-Geräte CT 150 semiautomated viscometer.

Synthesis of Polyaryleneoxindoles. In a typical synthesis, isatin (0.368 g, 2.50 mmol), 1,3-bis(4-phenoxybenzoyl)-benzene (1.175 g, 2.50 mmol), and trifluoromethanesulfonic acid (8.0 mL) were stirred under dry nitrogen at room temperature for 9 h, and the resulting clear, viscous, orange solution was then poured slowly into water (200 mL). The pale yellow solid was filtered off, washed copiously with water, and then extracted with refluxing methanol and finally with acetone, before drying at 100 °C under vacuum. The resulting pure white fibrous polymer **7** (1.45 g, 97% yield) had an inherent viscosity (η_{inh}) of 1.11 dL g^{-1} in concentrated sulfuric acid. Polymers **3**−**6** and **8**−**11** were obtained by entirely analogous procedures.

Table 1. Synthesis and Characterization Data for Polyaryleneoxindoles

polymer	monomers[a]	η_{inh} (dL g^{-1})[b]	T_g (°C)[c]	dec temp in air (TGA onset, °C)[d]
3	ArOArCOArOAr/isatin	1.80	264	485
4	ArOArCOArOAr/N-phenylisatin	1.24	231	525
5	ArOArCOArOAr/5-bromoisatin	1.25	289	485
6	ArOArCO-1,4-ArCOArOAr/isatin	1.04	243	500
7	ArOArCO-1,3-ArCOArOAr/isatin	1.11	225	490
8	ArOAr/isatin	0.64	337	460
9	biphenyl/isatin	0.31	>400	
10	*p*-terphenyl/isatin	0.73	>400	490
11	$ArOArSO_2ArOAr$/isatin	0.50	281	465

[a] Ar = phenyl or 1,4-phenylene (other than the 1,3-substituted ring in polymer **7**). [b] Measured in 98% sulfuric acid or (for polymer **8** only) in DMAc. [c] Onset temperature by DSC, at a heating rate of 20 °C/min. [d] Heating rate 20 °C/min.

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Supporting Information Available: Text giving ^{1}H and ^{13}C NMR spectral data, with assignments, for polymers **3**−**7**, and figures showing ^{1}H and ^{13}C NMR spectra for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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