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Superelectrophiles in the synthesis of condensation monomers and polymers

A L Rusanov, V P Chebotarev, S S Lovkov

Contents

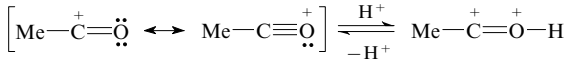
I. Introduction 547
II. Synthesis of condensation monomers and their precursors using superelectrophiles 547
III. Synthesis of condensation polymers in superacid media 548

Abstract. The carbonyl compounds activated by electron-withdrawing groups react efficiently with aromatics in superacid media. Examples of the synthesis of condensation monomers and their precursors, as well as superelectrophile-induced polymerisation transformations are considered. Particular attention is focused on properties of the polymers obtained. The bibliography includes 47 references.

I. Introduction

More than 30 years ago Olah *et al.*[1–3] found that superacids † promote electrophilic nitration and acylation reactions of aromatics. This pioneer discovery has led to the creation of a concept of superelectrophilic activation that results in superelectrophiles, *i.e.*, electrophiles of a 'double electron-deficient nature', *viz.*, dications. Reactivity of these species is much higher than that of common cationic intermediates formed in aprotic and acidic media.

According to the Olah theory, superelectrophilic activation of carbonyl compounds can occur upon interaction of a cationic electrophile with Brønsted or Lewis acids. For example, protonation of the acetyl cation with a system $HF-BF_3$ results in the formation of highly reactive superelectrophilic dication:[2]



Subsequent studies (see, for example, Refs 6–10) demonstrated wide possibilities for the application of superacid-catalysed reactions.

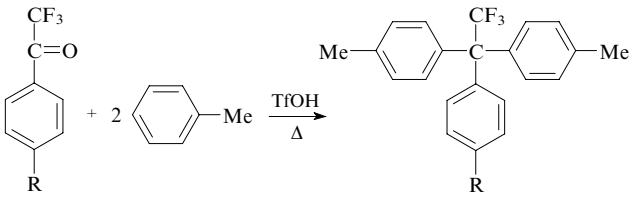
A L Rusanov A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-499) 135 50 85, tel. (7-495) 135 63 72, e-mail: alrus@ineos.ac.ru
V P Chebotarev, S S Lovkov Joint-Stock Company 'G S Petrov Research Institute of Plastics', Perovsky pr. 35, 111024 Moscow, Russian Federation. Fax (7-495) 626 84 03, tel. (7-495) 600 07 59, e-mail: tchebotarev@rambler.ru (V P Chebotarev), lovkov1@rambler.ru (S S Lovkov)

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At present, superelectrophiles are employed in the synthesis of aromatic condensation monomers and their precursors, as well as the corresponding polymers. Reactions where trifluoromethanesulfonic acid (CF_3SO_3H, TfOH) acts as a reaction medium attract the most attention. Trifluoromethanesulfonic acid with the acidity (H_0) equal to -14 (two orders of magnitude higher than that of 100% sulfuric acid)[7] is considered the strongest acid among all known organic monoacids.[11,12] This is the ideal non-oxidative medium for generation of highly reactive species in many electrophilic reactions. This review generalises the data on the application of superelectrophiles formed in trifluoromethanesulfonic acid for the synthesis of polymers with new valuable properties.

II. Synthesis of condensation monomers and their precursors using superelectrophiles

It is known (see, for example, reviews[13–15]) that carbonyl compounds containing electron-withdrawing groups form in trifluoromethanesulfonic acid highly reactive intermediates capable of subsequent transformations. In this medium, arylation of activated ketones can be carried out, which does not take place under conditions of conventional acid catalysis. For instance, 2,2,2-trifluoroacetophenone and its derivatives react with toluene in the presence of TfOH,[16] whereas acetophenone is inert under these conditions.



R = H (**a**), Me (**b**).

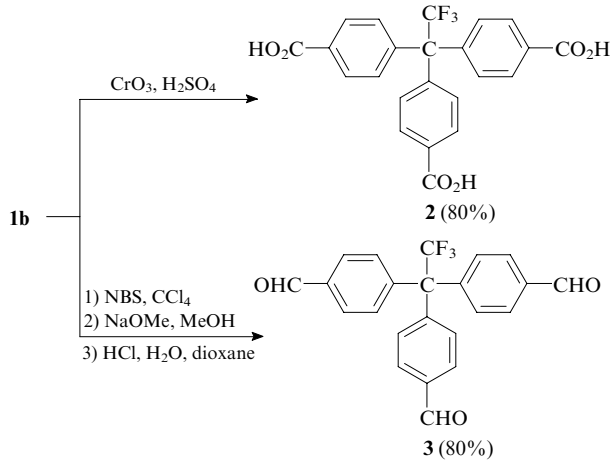
1a,**b** (50%)

If ethylbenzene is used instead of toluene, the reaction is complicated by side processes, which seem to involve the ethyl group. At the same time, replacement of 4-methyltrifluoroacetophenone by 4-methylheptafluorobutyrophenone leads to

† Acids that are stronger than $AlCl_3$ (in the case of Lewis acids[4]) or 100% H_2SO_4 (in the case of Brønsted acids[5]) are termed as superacids.

incomplete condensation of the reactants: only 1,1-bis(4-tolyl)heptafluorobutan-1-ol was isolated from resinous products.[16]

Bis- and tris(4-tolyl)-2,2,2-trifluoroethanes **1a**,**b** are of interest as precursors for the preparation of well-soluble condensation monomers because they contain fluoroalkyl and methyl substituents. The latter can be easily transformed to other functional groups. Thus 1,1,1-tris(4-tolyl)-2,2,2-trifluoroethane **1b** is oxidised under the action of CrO_3 to give 1,1,1-tris(4-carboxyphenyl)-2,2,2-trifluoroethane **2**; 1,1,1-tris(4-formylphenyl)-2,2,2-trifluoroethane **3** can be obtained from compound **1b** by multistep transformations.[16]

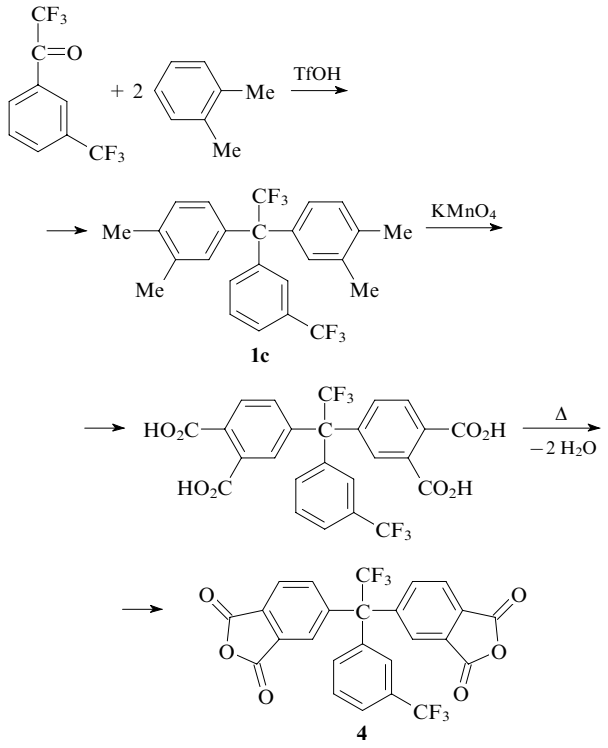


NBS is *N*-bromosuccinimide.

The reaction of 2,2,2-trifluoro-3′-(trifluoromethyl)acetophenone with an excess of *o*-xylene in the presence of trifluoromethanesulfonic acid gives 1,1-bis(3,4-dimethylphenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane **1c**,[17] which is then transformed to the corresponding dianhydride **4** upon oxidation with permanganate.

Dianhydride **4** was used for the synthesis of polyimides well-soluble in organic solvents. These polymers are characterised by high heat stability (the glass transition temperature, T_g, is $\leqslant 322$ °C) and heat resistance (the destruction temperature, T_d, is 500–530 °C), as well as relatively low values of dielectric constants ($\varepsilon = 2.75-3.02$).[17]

1,1-Bis[4-(4-nitrophenoxy)phenyl]-1-[3,5-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane **5** was synthesised from 2,2,2-trifluoro-3′,5′-bis(trifluoromethyl)acetophenone and 4-nitrodiphenyl oxide in the presence of trifluoromethanesulfonic acid; then **5** was reduced to 1,1-bis[4-(4-aminophenoxy)-



phenyl]-1-[3,5-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane **6** (Scheme 1).[18]

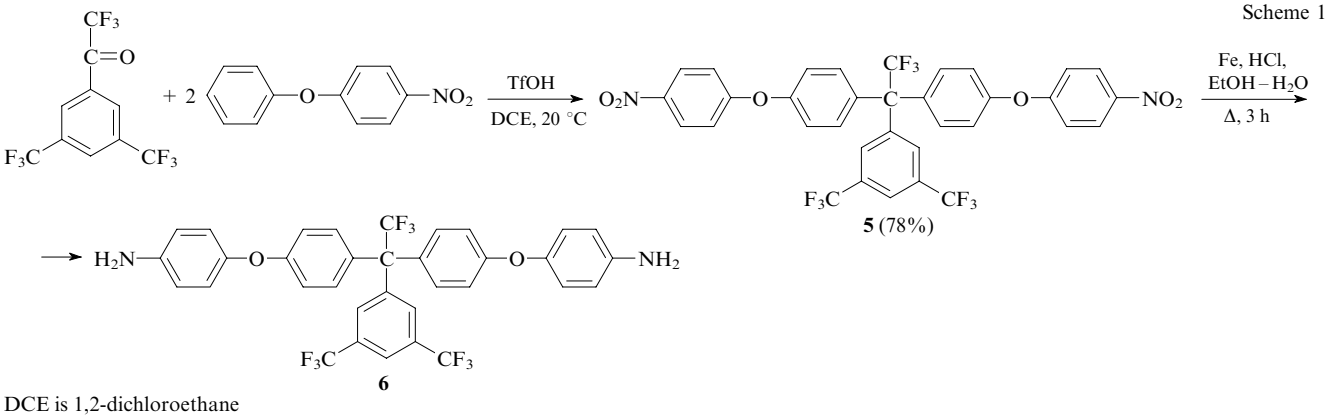
Polycondensation of diamine **6** obtained with dianhydrides of aromatic tetracarboxylic acids results in polyimides well-soluble in THF, *N*-methylpyrrolidone, *N*,*N*-dimethylacetamide and characterised by high values of heat stability and heat resistance ($T_g = 223-225$ °C, $T_d = 535-568$ °C) combined with high deformation-strength characteristics.[18]

Good solubility of polyimides obtained from monomers **4** and **6** in organic solvents is in accordance with the existing concepts on the relationship between the structure and solubility of these polymers.[19–21]

III. Synthesis of condensation polymers in superacid media

In addition to the synthesis of condensation monomers, electrophile-involving reactions are successfully used for the synthesis of macromolecular compounds.[22–24] There are examples of quantum chemical calculations of polycondensa-

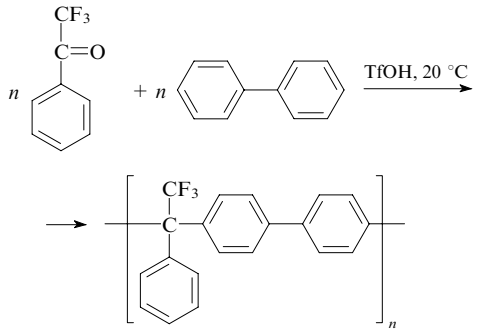
Scheme 1



DCE is 1,2-dichloroethane

tion reactions of different activated ketones with aromatics in the presence of trifluoromethanesulfonic acid.[25]

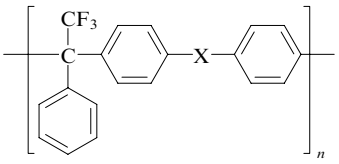
Although reactions of aldehydes and ketones with electron-enriched arenes are widely used in organic synthesis,[26,27] the first example of the successful introduction of biphenyl into the Friedel–Crafts polycondensation has been reported only recently.[23] The reaction of equimolar amounts of 2,2,2-trifluoroacetophenone and biphenyl occurs at room temperature in the presence of trifluoromethanesulfonic acid.



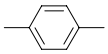
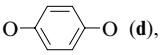
7a

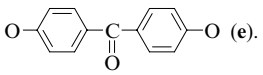
This reaction results in polymer **7a**, which is characterised by low inherent viscosity (η_{inh} = 0.32 dl g^{-1}) and has T_g = 326 °C.[23] This compound is of potential interest as a material with low dielectric permeability because it contains no polar groups and consists of fragments responsible for the hydrophobic nature and large free volume of the macromolecule.[28–30]

Under similar conditions, high-molecular-mass compounds **7b–e** containing (trifluoromethyl)phenylmethane fragments were synthesised from 2,2,2-trifluoroacetophenone and diphenyl oxide, terphenyl, 1,4-diphenoxybenzene or 4,4′-diphenoxybenzophenone.



7b–e

X = O (**b**),  (**c**),  (**d**),



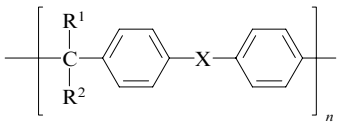
(**e**).

Poly(ether ether ketone) **7e** synthesised[31] from 2,2,2-trifluoroacetophenone and 4,4′-diphenoxybenzophenone is well-soluble in common organic solvents; inherent viscosity of its 0.2% solution in *N*-methylpyrrolidone is 0.28 dl g^{-1}, T_g = 175 °C.

Sulfonation and phosphorylation of polymers **7a–e** gave novel materials[32] that can be used as proton-exchange membranes for fuel cells.

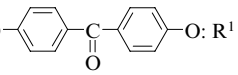
A series of fluoro-containing aromatic condensation high-molecular-mass materials have recently been synthesised for the first time.[24]

Polycondensation of fluorinated carbonyl compounds with aromatic hydrocarbons (biphenyl, terphenyl, diphenyl ether, 4,4′-diphenoxybenzophenone) was carried out at room temperature in the presence of trifluoromethanesulfonic acid or its mixture with dichloromethane. In addition to 2,2,2-trifluoroacetophenone, 1,1,1-trifluoroacetone, 2,3,4,5,6-pentafluorobenzaldehyde, octafluoroacetophenone were also used. (Note that in the case of hexafluoroacetone, no polymers could be synthesised.) The polymers formed are characterised by high heat resistance and by good solubility in organic solvents. Transparent colourless films can be cast from polymer solutions. According to the ^{1}H and ^{13}C NMR data, these high-molecular-mass polymers have linear highly ordered structures. Molecular masses and thermal characteristics of compounds **7f–i** are presented in Table 1.



7f–i

X is absent: R^1 = CF_3, R^2 = Me (**f**); R^1 = H, R^2 = C_6F_5 (**g**);

X =  : R^1 = CF_3, R^2 = Me (**h**);

R^1 = CF_3, R^2 = C_6F_5 (**i**); *etc.*

Table 1. Characteristics of polymers **7f–i**.[24]

Compound **7**	M_w	M_n	T_g/°C	T_d/°C (in N_2)
f	38 200	17 400	280	527
g	65 550	12 890	230	480
h	45 290	15 550	155	517
i	22 630	15 850	180	444

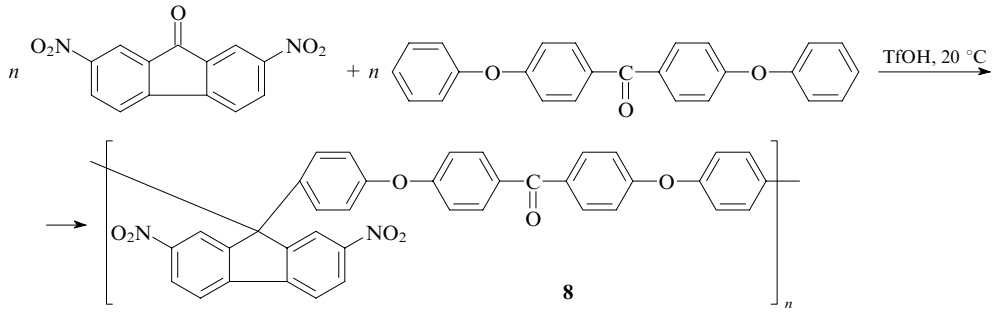
Quantum chemical calculations of reactive intermediates involved in acid-catalysed polycondensation of benzene and biphenyl with carbonyl compounds of the general formula $R^1C(O)R^2$ (R^1 = H, Me, CF_3; R^2 = Ph, Me, CF_3) have been performed.[33] It was shown that in superacid media both monocations and the products of their further protonation, superelectrophilic dications, can be intermediate species. The calculations demonstrate that, although dications are more reactive, the energy of their formation is higher than the energy released in the course of reactions involving these electrophiles. The mechanism including only monocationic intermediates was suggested for the reaction of benzene with benzaldehyde in the presence of trifluoromethanesulfonic acid.

The failure in the synthesis of polymers based on acetophenone and hexafluoroacetone can be explained by the fact that, in the former case, rather stable low reactive cations are formed, while in the second case, no protonation of the carbonyl group takes place because this process is energetically unfavourable.

It is shown[31] that electron-withdrawing substituents that are not bound directly to the carbocationic centre, can also enhance electrophilicity of the substrate. Thus, in contrast to unsubstituted fluorenone, 2,7-dinitrofluorenone readily reacts with 4,4′-diphenoxybenzophenone to give high-molecular-mass polymer **8** (Scheme 2).

Poly(ether ketone) **8** obtained has η_{inh} = 0.38 dl g^{-1} and T_g = 270 °C; flexible films can be cast from its solutions in common organic solvents.[31] Polymer **8** was also involved into silfonation and phosphorylation reactions in order to obtain systems with protogenic substituents.[32]

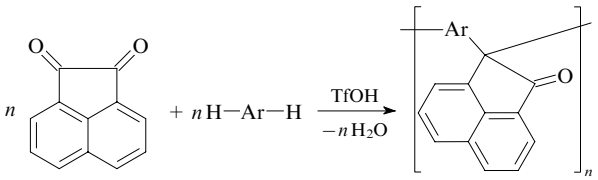
Scheme 2



Note that macromolecules **8** based on 2,7-dinitrofluorenone are cardo (loop-like) polymers.[34–36] Polymers prepared from acenaphthenequinone[37,38] and isatin[39] also belong to this class of polymers.

Reactions of acenaphthenequinone and its derivatives with different electrophiles have been comprehensively studied.[40,41] Thus acenaphthenequinone reacts readily with benzene in trifluoromethanesulfonic acid at room temperature to form 1,1-diphenyl-2-acenaphthenone in high yield.[13]

Syntheses of polymers **9a–l** based on acenaphthenequinone and such aromatic hydrocarbons as biphenyl, fluorene, *p*-terphenyl, diphenyl oxide, 1,4-diphenoxybenzene, 4,4′-diphenoxybenzophenone, 1,3-bis(4-phenoxybenzoyl)benzene, 1,4-bis-(4-phenoxybenzoyl)benzene, 1,10-bis(4-phenoxyphenyl)decane-1,10-dione, 2,6-diphenoxybenzonitrile, 2,6-diphenoxybenzoic acid and 2-(4-biphenylyl)-6-phenylbenzoxazole have been described[38].



Condensation of acenaphthenequinone with biphenyl, terphenyl, diphenyl oxide and 1,4-diphenoxybenzene was performed in a mixture of trifluoromethanesulfonic acid with methanesulfonic or trifluoroacetic acid, *i.e.*, in a less acidic medium. As a result, high-molecular-mass organo-soluble film-forming polymers **9a–e** were obtained, which have characteristics listed in Table 2. The attempts to conduct this reaction in pure TfOH resulted in deeply coloured insoluble products or oligomers.

Table 2. Characteristics of polymers **9a–l**.[38]

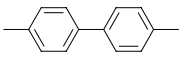
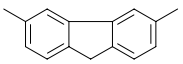
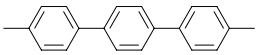
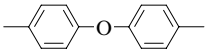
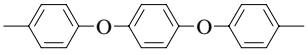
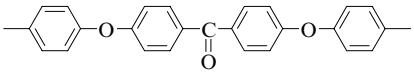
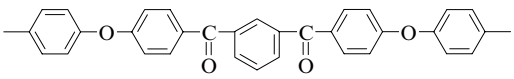
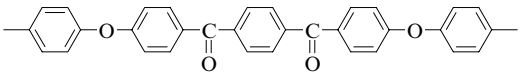
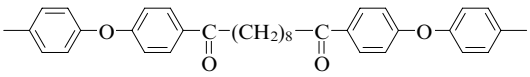
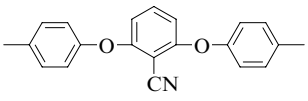
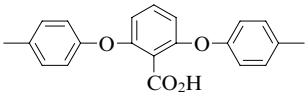
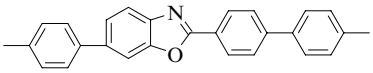
Compound **9**	Ar	η_{inh} /dl g^{-1} (see [a])	T_g /°C	T_d /°C	
				in air	in nitrogen
a		0.40	> 450	525	530
b		0.52	> 450	510	525
c		0.53	> 450	540	546
d		1.34	296	515	522
e		0.40	244	–	–
f		0.54	240	525	535
g		0.44	191	525	530
h		0.87	225	530	535
i		0.66	132	440	464
j		1.08	272	520	522

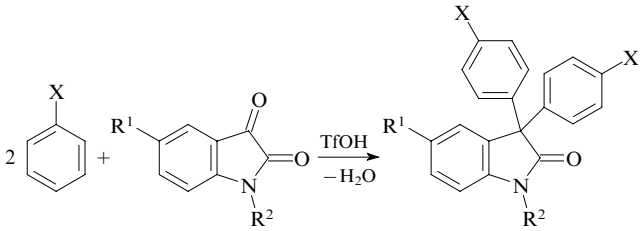
Table 2 (continued).

Compound **9**	Ar	η_{inh} /dl g^{-1} (see [a])	T_g /°C	T_d /°C	
				in air	in nitrogen
k		0.27	300	400	415
l		0.35	>450	505	508

[a] In *N*-methylpyrrolidone.

At the same time, condensation reactions of acenaphthenequinone with arenes containing electron-withdrawing groups, 4,4′-diphenoxybenzophenone, 1,3- and 1,4-bis(4-phenoxybenzoyl)benzene, 1,10-bis(4-phenoxyphenyl)decane-1,10-dione, 2,6-diphenoxybenzonitrile, 2,6-diphenoxybenzoic acid and 2-(4-biphenylyl)-6-phenylbenzoxazole, occur readily in media of different acidities, in particular, in pure trifluoromethanesulfonic acid. Macromolecular products **9f**–**l** are also well-soluble in chlorinated solvents, aprotic bipolar solvents, strong acids. These results [38] confirm the dependence of the direction of reactions involving superelectrophiles on the acidity of the reaction medium found earlier.[42–44]

The reaction of isatin and its derivatives with aromatics to form *p*-substituted 3,3-diaryloxindoles is reported.[45]

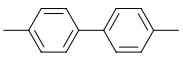
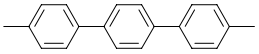
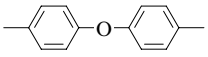
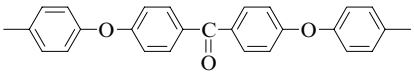
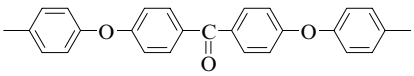
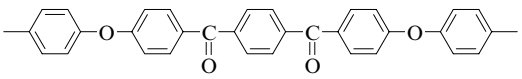
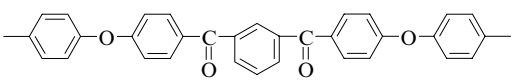


X = H, Me, Cl; R^1 = H, NO_2; R^2 = H, Ph.

By analogy with this reaction, polycondensation of isatin with equimolar amounts of different aromatic compounds has been performed.[39]

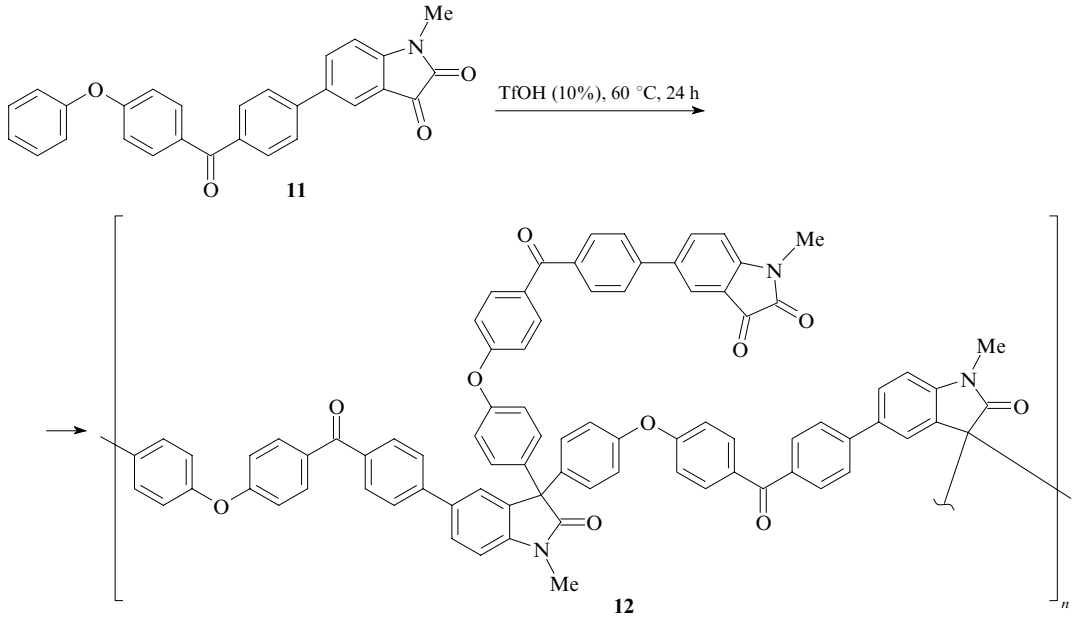
The reaction of isatin with such aromatic compounds as biphenyl, *p*-terphenyl and diphenyl oxide in trifluoromethanesulfonic acid at room temperature results in polymers **10a**–**c** (Table 3).

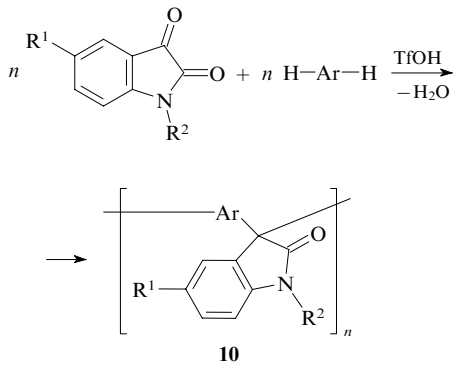
Table 3. Characteristics of polyoxindoles **10a**–**g** (R^1 = H).[39]

Compound **10**	Ar	R	η_{inh} /dl g^{-1} (see [a])	T_g /°C	T_d /°C (in air)
a		H	0.31	>400	–
b		H	0.73	>400	490
c		H	0.64	337	460
d		H	1.80	264	485
e		Ph	1.24	231	525
f		H	1.04	243	500
g		H	1.11	225	490

[a] In *N*,*N*-dimethylacetamide.

Scheme 3





$R^1 = R^2 = H$; $R^1 = H$, $R^2 = Ph$; $R^1 = Br$, $R^2 = H$.

However, the selectivity of these reactions, according to the NMR spectroscopic data, is not high. If 4,4′-diphenoxybenzophenone and 1,4-bis(phenoxybenzoyl)benzene, which are characterised by high regioselectivity in polyacylation reactions,[46] are used as comonomers for isatin, polymers **10d**–**g** are formed in higher yields (see Table 3).

Polyoxindoles **10a**–**g** exhibit good viscosity and thermal characteristics, they are insoluble in hydrocarbons and chlorinated hydrocarbons, but are soluble in dipolar solvents like *N*-methylpyrrolidone and *N*,*N*-dimethylacetamide, as well as in strong acids.

In continuation of works on the synthesis of linear polyaryleneoxindoles in superacid media, Smet *et al.*[47] performed homocondensation of monomer **11** by the AB_2 type and synthesised a highly branched polymer **12** (Scheme 3) containing 3,3-diaryloxindole groups as dendrite fragments and isatin residues as peripheral groups. Dendrimer **12** has $M_n = 7100$ and $M_w = 20\,000$; unlike linear polyoxindoles, it is soluble in chloroform, dichloromethane and toluene. The glass transition temperature of polymer **12** is 190 °C, *i.e.*, it is significantly lower than that of linear polyoxindoles.[39]

* * *

At present, the data on the synthesis of condensation monomers and polymers in superacid media are few in number. The analysis of these data indicates the efficiency of application of these reactions in macromolecular chemistry. The most probable trends in the development of this field consist of the introduction of novel polymers based on compounds with reactive carbonyl groups into polycondensation processes or in polymer-analogous transformations of polyketones containing electron-withdrawing groups.

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