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ARTICLE

Novel, Metal-Free, Superacid-Catalyzed "Click" Reactions of Isatins with Linear, Nonactivated, Multiring Aromatic Hydrocarbons

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ABSTRACT: A novel series of linear, high-molecular-weight polymers was synthesized by one-pot, metal-free superacid-catalyzed reaction of isatins (**1a−d**) with linear, nonactivated, multiring aromatic hydrocarbons: biphenyl (**A**), *p*-terphenyl (**B**), *p*-quaterphenyl (**C**), 2-(4-biphenylyl)-6-phenylbenzoxazole (**D**), 9*H*-fluorene (**E**), 9,9-dimethyl-9*H*-fluorene (**F**), 2,2′-[2,5-bis(trifluoromethyl)-1,4-phenylene]bis(9,9-dimethyl-9*H*-fluorene) (**G**), oligo-9,9-bis(2,6-ethylhexyl)-9*H*-fluorene (**H**), biphenol (**I**), and bi-2-napththol (**J**). The reactions were performed at room temperature in the Brønsted superacid trifluoromethanesulfonic acid (CF_3SO_3H, TFSA) and in a mixture of TFSA with methylene chloride or TFA tolerant of hydroxyl, carboxy, and cyano groups. The polymers obtained were soluble in most common organic solvents, and flexible transparent films could be cast from the solutions. ^1H and ^{13}C NMR analyses of the polymers synthesized revealed their linear structure with *para*-substitution in the phenylene fragments of the main chain. The molecular weights M_w and M_n of the polymers ranged from 54200 to 742000 and from 40140 to 438500 g/mol, respectively. Most of the polymers also possess narrow polydispersity (1.15−1.50). The oxindole groups of the polymers react smoothly with alkyl bromides under basic conditions in *N*-methylpyrrolidinone (NMP). The amount of "click"able allyl- and propargyl- functionalities is readily controlled by adjusting the reaction ratio of polymer to alkyl bromides. The demonstrated efficiency and orthogonality of isatin-based polymer chemistry shows it to be an essential addition to the family of polymer "click" reactions.

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 functional groups. The second direction involves an increase of synthetic potential of known chemical reactions by means of new catalysts, uncommon monomers, etc. It should be noted that synthetic methodologies used in organic chemistry are not always applicable to polymer chemistry. Only regioselective and highly efficient reactions give rise to high-molecular-weight polymers. (Highly pure monomers are absolutely necessary in order to obtain the desired macromolecules.) This is why development of new polymer-forming reactions presents a promising but challenging area.

One recent example is Cu(I) catalysis of the Huisgen 1,3-dipolar cycloaddition reaction of organic azides and alkynes (also termed CuAAc) introduced by Meldal and Sharpless.[1,2] Because of high efficiency, regio-specificity and excellent tolerance toward functional groups, this reaction (and this type of chemistry) was defined by Sharpless as "Click" reaction (chemistry).[3] In recent years, "click" chemistry has attracted increasing attention and, since 2004, has been extended to polymer science.[4] (It should be noted that some existing polymer-forming reactions meet the criteria needed for "click" polymer chemistry.[8])

It is really remarkable how popular CuAAC reactions became for polymer syntheses (including macromolecules of complex topologies) and coupling of polymer fragments into block copolymers. It has also been used for grafting and surface modifications. More than 20 reviews and three "click" chemistry themed journal issues have been published (see refs 5−7 and references cited therein).

It is also important that the success of click chemistry helped to create new strategies of click-assisted, one-pot, multistep reactions[8] and created a strong drive to develop organic reactions

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offering efficiency and versatility so that they can be incorporated into the field of materials science.[5-7,9-11]

Despite the numerous advantages that made the copper-catalyzed, azide–alkyne click reaction a universal tool for orthogonal conjugations, several limitations and precautions should always be taken into account. First, monomer syntheses (in particular, preparation of potentially explosive azides using sodium azide, a very well-known explosive component of airbag formulations) are potentially hazardous; second, the presence of copper salt residues in terms of polymer properties (including biocompatibility and cytotoxicity) is questionable; third, the formation of strongly basic triazole fragments is sometimes an undesirable element in the design of polymer structure and properties; and fourth, azide–alkyne click reactions are not applicable for the syntheses of crystalline or even semicrystalline polymers. Despite these potential problems, research and development in this field are increasing exponentially.

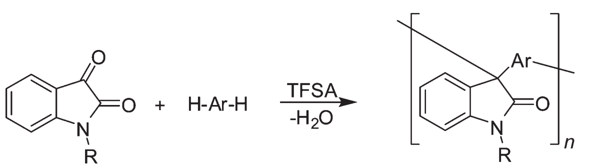
In this respect, the theory of superelectrophilic activation, suggested recently by Olah to explain the reactivities of some electrophiles in superacid solutions, presents a promising challenge.[12] (It should be noted that the intensive research on carbocation chemistry undertaken over the past few decades, and recognized by the Nobel Prize awarded to Professor Olah, has so far led to few applications to polymer chemistry.) According to Olah's theory, superelectrophilic activation may occur when a cationic electrophile reacts with a Brønsted or Lewis acid to give a highly reactive dicationic electrophile.[13]

Realization of this idea has allowed numerous superacid catalyzed reactions (including hydroxyalkylation) to be successfully performed.[14]

In line with the superelectrophilic concept and report[15] we have recently shown that isatin reacts in TFSA with aromatic hydrocarbons bearing terminal phenoxy groups to yield linear, high-molecular-weight polymers.[16] Superacid-catalyzed self-polymerization of isatin derivatives with phenoxy-terminated aromatic compounds gave 100% hyperbranched polymers.[17-20] Dendrons and dendrimers were convergently prepared using phenoxy-isatin derivatives as AB_2 monomers by superelectrophilic arylation in TFSA.[21] This strategy has the advantage that incomplete reactions of the AB_2 monomers are minimized, which essentially simplifies purification, the most difficult step in dendron (dendrimer) syntheses.

However, reactions of isatin itself with biphenyl and terphenyl lead to low-molecular-weight, structurally nonhomogeneous products.[16]

Since development of simple, efficient reagents for click coupling reactions between nonactivated aromatic 'substances' is of high importance, the aim of the present work was to devise a flexible, one-step preparation of a family of novel polyarylenes from the superacid-catalyzed reactions of isatin with linear, nonactivated, multiring aromatic hydrocarbons according to the following scheme:



1a-d **2(a-d)Ar**

Here R are H (**a**), phenyl (**b**), *m*-(trifluoromethyl)phenyl (**c**), 3,5-bis(trifluoromethyl)phenyl (**d**). H–Ar–H has Ar as biphenyl (**A**), *p*-terphenyl (**B**), *p*-quaterphenyl (**C**), 2-(4-biphenylyl)-6-phenylbenzoxazole (**D**), 9*H*-fluorene (**E**), 9,9-dimethyl-9*H*-fluorene (**F**), 2,2′-[2,5-bis(trifluoromethyl)-1,4-phenylene]bis(9,9-dimethyl-9*H*-fluorene) (**G**), oligo-9,9-bis(2,6-ethylhexyl)-9*H*-fluorene (**H**), biphenol (**I**), and bi-2-napththol (**J**).

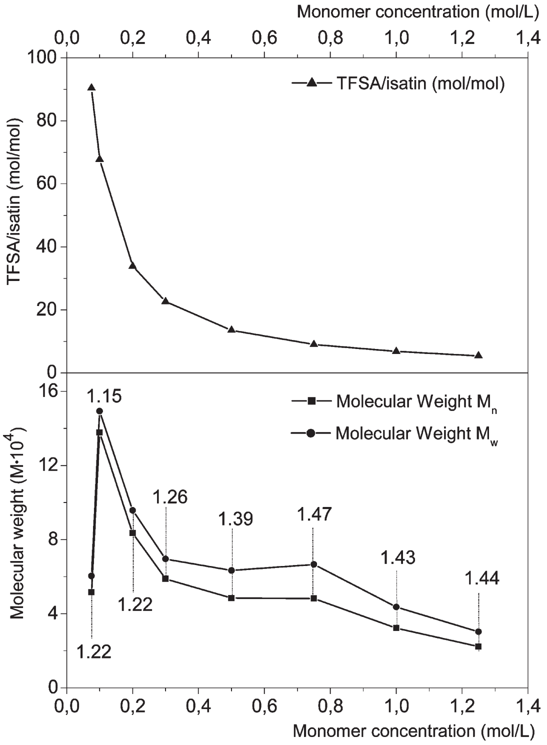
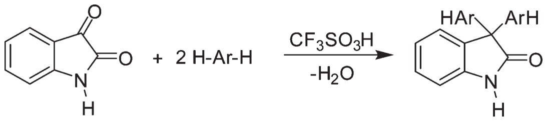


Figure 1. Dependence of polymer molecular weights and polydispersity (bottom) and the TFSA/isatin ratio (top) on monomer concentration in polycondensation of isatin with biphenyl.

Scheme 1. Synthesis of 3,3-Diphenyloxindole



The effect of the reaction conditions is highlighted. The structure and general properties of the polymers obtained, the "click" incorporation in the polymers allyl and propargyl functionalities are reported.

2. Results and Discussion

Isatin, a heterocyclic 1,2-dicarbonyl compound, was reported[15] to condense readily with benzene and substituted aromatics such as alkylbenzenes or chlorobenzene in TFSA to give 3,3-diaryloxindoles (**2**) in high yield (Scheme 1).

Theoretical study of this reaction revealed that isatin is easily protonated in TFSA media.[22] The first protonation occurs at the amide carbonyl group ($\Delta G = -0.70$ kcal/mol) while the second protonation takes place at the ketone carbonyl ($\Delta G = 1.79$ kcal/mol). For the nitrogen atom, which is the least basic site, the free Gibbs protonation energy is 8.5 kcal/mol. The protonation energies of isatin and reaction activation energies of aromatic electrophilic substitution of isatin and nonactivated aromatic hydrocarbons have been estimated using a PBE0/6-31+G** model for the geometry optimizations and larger aug-cc-pvtz basis set for single point energy estimation. This method is described in detail in[23] and reproduces pK_a of acids within one pK_a unit. Calculations revealed that the free Gibbs protonation energy of isatin at the ketone oxygen is significantly lower than that for 2,2,2-trifluoracetophenone. Moreover, the free Gibbs activation energies for the electrophilic aromatic substitution reaction between an isatin molecule protonated at the ketone carbonyl and a biphenyl molecule in TFSA media are less than

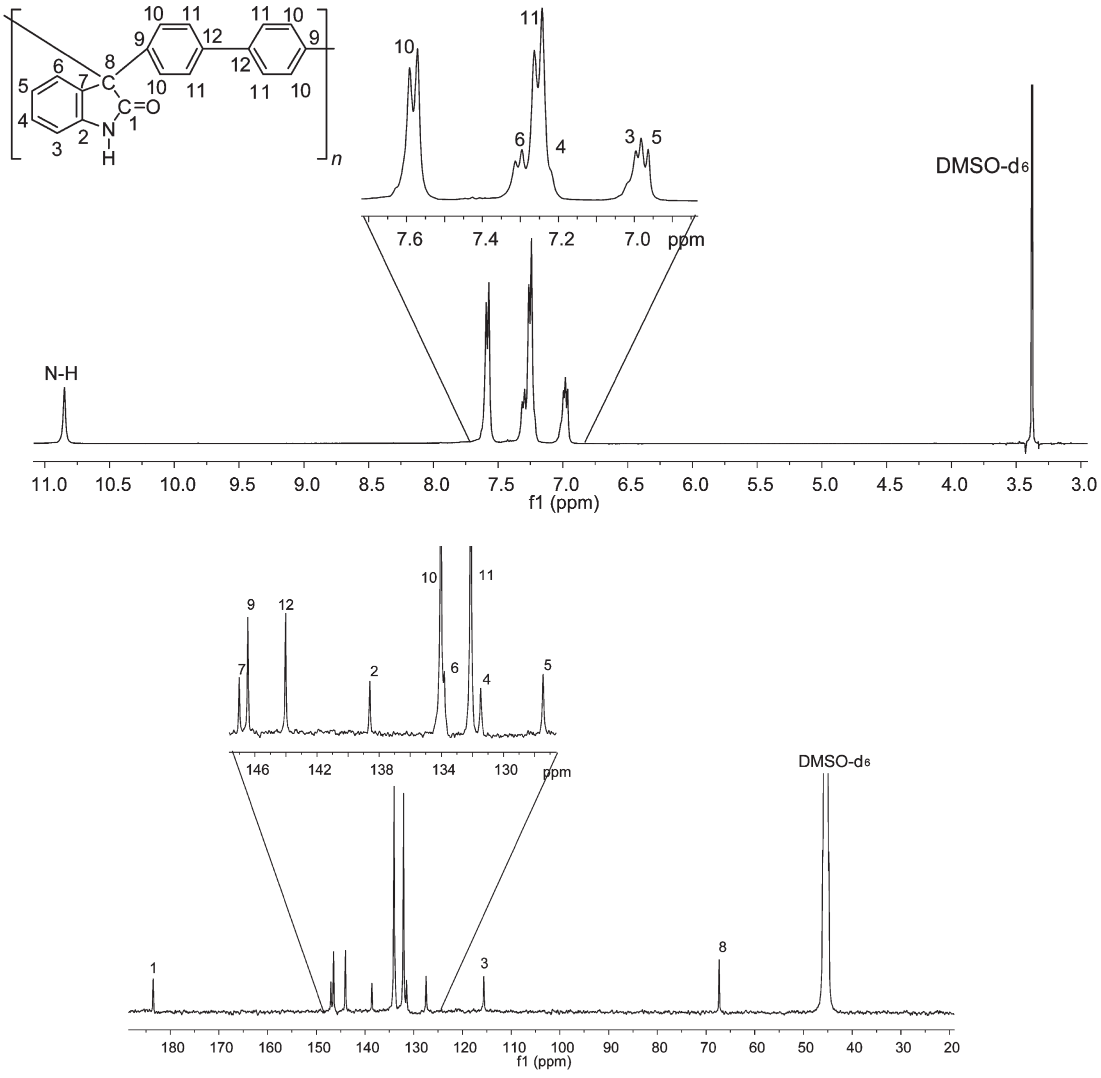


Figure 2. ^{1}H and ^{13}C NMR spectra of polymer **2aA** (solution in DMSO-d_6).

Table 1. Reaction Conditions, Inherent Viscosities and Molecular Weights Determined for the Polymers Reported in This Work

polymer code	isatins **1a−d**	aromatic hydrocarbons H−Ar−H	TFSA: isatin (mol/mol)	monomer concentration (mol/L)	reaction time	inherent viscosity $\eta_{\text{inh.}}$ dL g^{-1}, (NMP)	molecular weight, (g/mol), $M_w \times 10^4$	molecular weight, (g/mol), $M_n \times 10^4$	M_w/M_n
2aA	**a**	biphenyl	9.04	0.79	1 h 40 min	0.85	14.940	12.970	1.15
2aD	**a**	2-(4-biphenylyl)-6-phenylbenzoxazole	19.78	0.57	25 h	0.44	5.420	4.014	1.35
2aB	**a**	*p*-terphenyl	6.78	0.47	55 min	1.44	10.780	9.320	1.16
2c(D/N)	**c**	*p*-quaterphenyl/diphenoxybenzophenone	7.73	0.15	6 h	1.51	18.890	13.492	1.40
2aE	**a**	fluorene	6.33	0.40	29 h	0.59	7.875	6.504	1.21
2aF	**a**	9,9-dimethyl-*9H-fluorene*	3.62	0.46	29 h 30 min	0.92	74.200	43.850	1.69
2aG	**a**	2,2′-(2,5-bis(trifluoromethyl)-1,4-phenylene)-bis(9,9-dimethyl-9*H*-fluorene)	9.89	0.27	5 min	1.69	23.445	15.424	1.52
2aH	**a**	oligofluorene	14.13	0.02	24 h	0.31	1.350	0.740	1.82
2aI	**a**	2,2′-dihydroxy-1,1′-biphenyl	2.09	0.66	8 h	1.74	20.880	15.787	1.32
2aJ	**a**	1,1′-bi-2-napththol	5.02	0.67	16 min	0.35	8.560	6.440	1.33

that for 2,2,2-trifluoracetophenone, which is known to produce smoothly high-molecular-weight polymers with non activated aromatic hydrocarbons in TFSA media.[24] Therefore, isatin and its derivatives could be considered as promising monomers for polymer syntheses and could be good candidates for "click" chemistry, due to the low activation energies estimated for hydroxyalkylation reactions involving protonated isatin species.

Linear, nonactivated, multiring aromatic hydrocarbons, such as biphenyl, terphenyl, 2-(4-biphenylyl)-6-phenylbenzoxazole, *p*-quaterphenyl, 2,2′-[2,5-bis(trifluoromethyl)-1,4-phenylene]bis-(9,9-dimethyl-9*H*-fluorene), oligo-9*H*-fluorene, biphenol, and bi-2-napththol were chosen for reactions with isatin. This monomer selection allows for the estimation of the scope of the reaction and preparation of new polymers.

A fundamental dogma in the superelectrophilic chemistry holds that increase of acid strength favors formation of protosolvated superelectrophilic intermediates, which thereby favors superacid-catalyzed hydroxylkyation. Additionally, such traditional

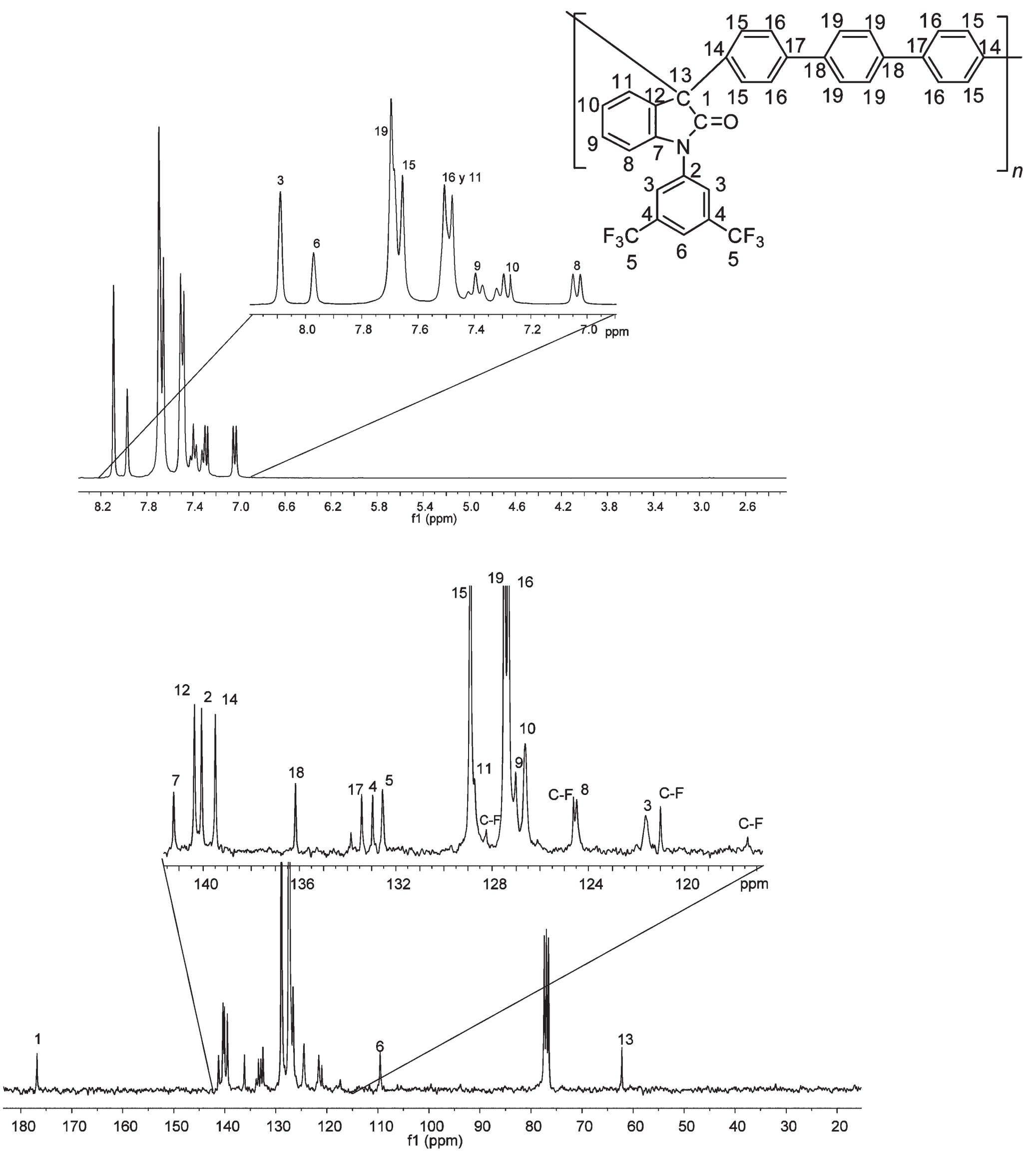


Figure 3. ^{1}H and ^{13}C NMR spectra of polymer **2dB** (solution in $CDCl_3$).

factors of step-growth polymerization as homogeneity of the reaction medium, reaction temperature and time, and monomer concentrations affect polymer syntheses.

We have shown that reactions of isatin with biphenyl at room temperature in a mixture of TFSA with methylene chloride afford soluble, polymeric products. Figure 1 shows the influence of the monomer concentration on the polymer molecular weight in the course of this reaction. Yields of the polymers obtained were close to quantitative (95−98%). Basically, in homogeneous step-growth polymerization, an increase in monomer concentration increases the molecular weight of the polymers. However, for the reaction of isatin with biphenyl, maximum molecular weight values were obtained with a monomer concentration 0.1 mol/L; less concentrated solutions resulted in a drastic decrease of molecular weight (Figure 1). This contradiction can be explained by increase of TFSA/isatin ratio with decrease of the monomer concentration. Most likely, the reason for the formation of low-molecular-weight products at monomer concentrations less than 0.1 mol/L is domination of cyclization reactions.[25]

Friedel−Crafts electrophilic aromatic substitution reactions are known to be not very selective. Thus, such reactions as alkylation and acylation basically lead to formation of isomer mixtures. It is also difficult to achieve high regioselectivity in acid-catalyzed hydxyalkylation, even more difficult in polyhydroxyalkylation. This is why the structural analysis of the polymers synthesized being an important element of the present work, has received a particular attention. Fortunately, the high solubility of the polymers allowed us to perform reliable spectral studies to delineate their structure.

Surprisingly, NMR analyses of the polymers based on isatin and biphenyl revealed no structural irregularities. The NMR spectra of the polymer (**2aA**) in DMSO-d_6 (Figure 2) are well resolved and the resonances anticipated for oxindole and *para*-substituted biphenyl moieties are all evident.

Very likely, the high regioselectivity of the reaction is due to bulky isatin-containing electrophilic intermediates.

However, the most striking feature of the condensation of isatin with biphenyl is the very low polydispersities of the polymers obtained. Remarkably, it is close to 1 (1.15) for the polymer obtained with a monomer concentration of 0.1 mol/L!

It is worth mentioning that, generally, biphenyl is considered to be a monomer of low reactivity for Friedel−Crafts polymerizations. Moreover, the first reaction of biphenyl with an electrophilic intermediate (which results in the formation of an electron-withdrawing oxindole substituent) decreases of nucleophilicity (and reactivity) of the second nonreacted

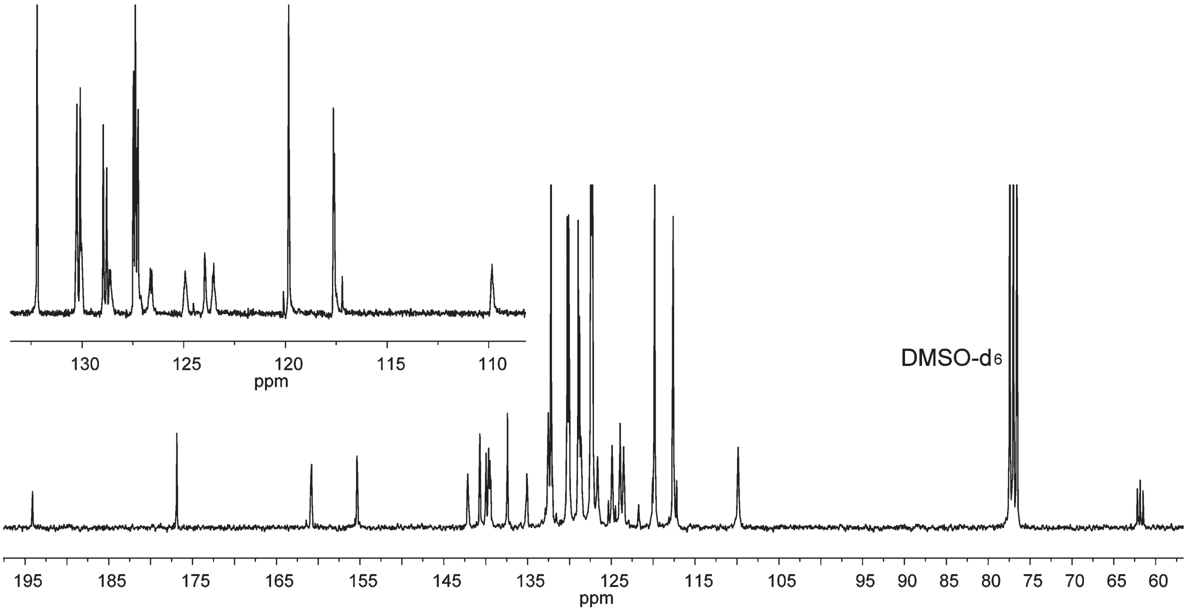
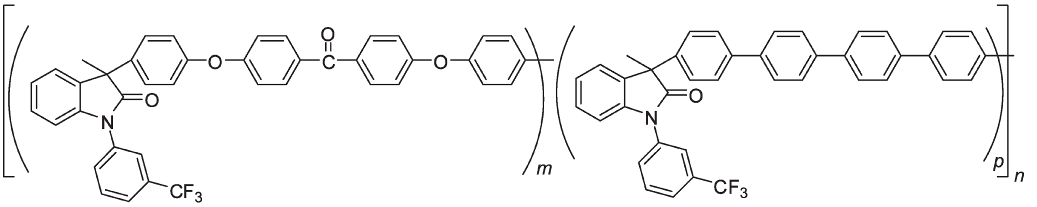
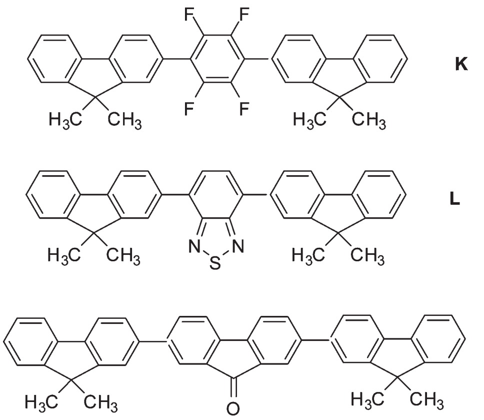


Figure 4. ^{13}C NMR spectrum (bottom) with DEPT 135 (top) of polymer **2c(D/N)** (solution in CDCl$_3$).

Scheme 2. Chemical Composition of Copolymer 2c(D/N)



Scheme 3. Chemical Composition of Monomes of D−A−D (Donor−Acceptor−Donor) Type



aromatic nuclei. Nevertheless, even such desactivated nuclei continue to react to yield high-molecular-weight products. Thus, although the protonation of the benzoxazole fragment of 2-(4-biphenylyl)-6-phenylbenzoxazole in the reaction medium also decreases the nucleophilicity of terminal aromatic nuclei, high-molecular-weight polymer **2aD** is obtained (Table 1).

p-Terphenyl is also known to be more reactive than biphenyl in Friedel-Crafts reactions. Isatin (and *N*-alkyl or N-aryl) derivatives readily react with *p*-terphenyl to give linear polymers with para-substitution in the main chain. The ^{1}H NMR spectrum of polymer **2 dB** (Figure 3) confirms a linear structure with *para*-substituted terphenylene fragments alternating with oxindole groups.

Figure 5. IR spectra of polymer **2bG**.

The GPC analysis of polymer **2aB** has revealed the high values of molecular weights and very low polydispersity (Table1).

Remarkably, isatin reacts even with *p*-quaterphenyl. Because of limited solubility, *p*-quaterphenyl is seldom if ever used for direct Friedel−Crafts polymerizations. Indeed, reactions of isatin with *p*-quaterphenyl gave apparently polymeric but insoluble products. Attempts to obtain soluble polymers using N-[*m*-(trifluoromethyl)phenyl]isatin (**c**) in the hope that bulky *m*-trifluoromethyl side groups would increase polymer solubility also failed. We therefore turned our attention to the copolycondensation of N-[*m*-(trifluoromethyl)phenyl]isatin with *p*-quaterphenyl and 4,4′-diphenoxybenzophenone (**N**).

These reactions gave polymers that were soluble in a wide range of solvents, including chloroform, methylene chloride and DMFA. The signals of the proton spectrum of polymer **2c(D/N)** are overlapped, however, the ^{13}C NMR is resolved very well (Figure 4).

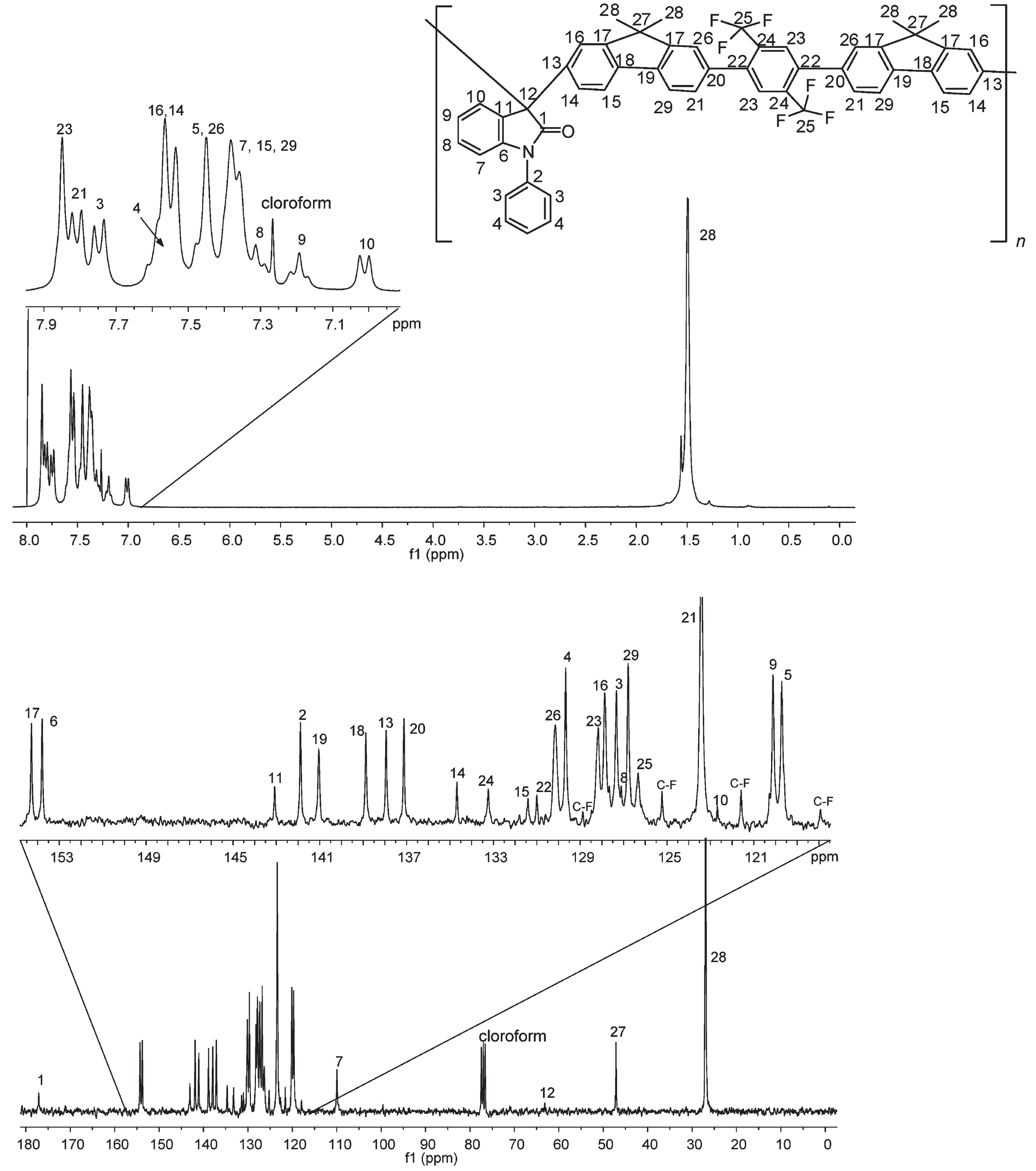


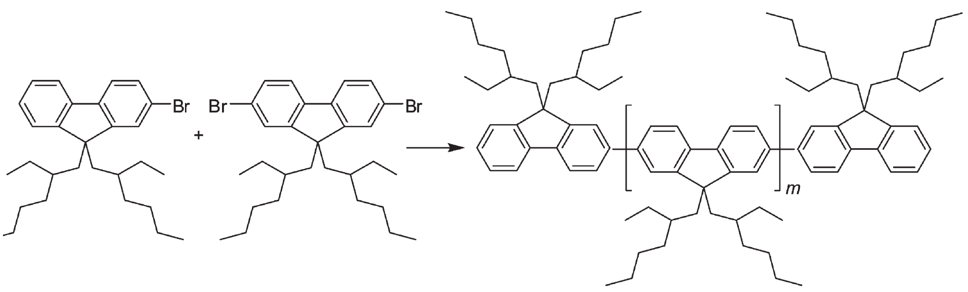
Figure 6. ^1H and ^{13}C NMR spectra of polymer **2bG** (solution in $CDCl_3$).

A triplet at 63 ppm points to the presents in the macromolecule three triads characteristic for the statistic copolymer: quaterphenyl−isatin−quaterphenyl, diphenoxybenzophenone−isatin−diphenoxybenzophenone, and quaterphenyl−isatin−diphenoxybenzophenone. The ^{13}C NMR spectrum with DEPT 135 showing CH-carbons, reveals eight relatively small signals corresponding to CH atoms of oxindole ring and *m*-(trifluoromethyl)phenyl group, and eight intensive signals of CH atoms in phenylene fragments of the main chain.

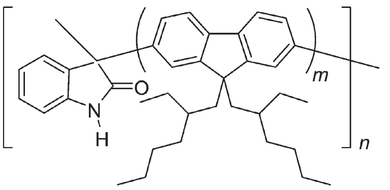
A linear polymer structure with *para*-substituted aromatic fragments is obvious (Scheme 2). It should be mentioned that breaking of substitution symmetry (*ortho*- and *meta*-substitution) would raise inevitably the amount of the signals in both ^1H and ^{13}C NMR spectra.

9*H*-Fluorene is known to be a more reactive nucleophile than biphenyl or terphenyl in the reaction of electrophilic aromatic substitution. Indeed, condensations of isatin with 9*H*-fluorene proceed smoothly to give high-molecular-weight polymer (**2aE**).

Scheme 4. Synthesis of Oligo-9,9-bis(2,6-ethylhexyl)-9*H*-fluorene



Scheme 5. Chemical Composition of Polymer 2aH



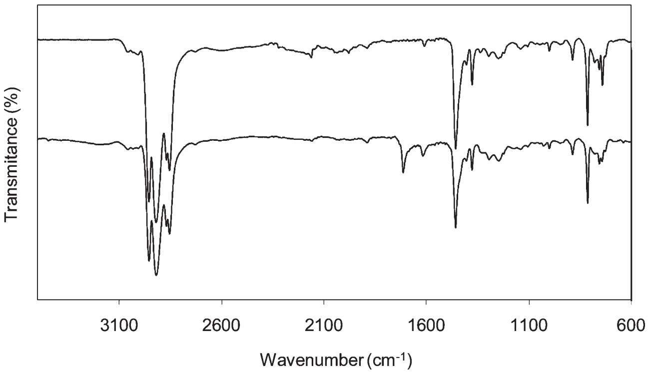


Figure 7. IR spectra of oligofluorene (top) and polymer **2aH** (bottom).

Again, the polydispersity of the polymer is very low. Reaction of isatin with 9,9-dimethyl-9*H*-fluorene is even more efficient (Table 1, **2aF**). This monomer turned out to be a convenient terminal group to design DAD (donor−aceptor−donor) monomers for the reaction with isatin. Thus, high-molecular-weight polymer was obtained from reaction *N*-phenylisatin (**1b**) with 2,2′-[2,5-bis(trifluoromethyl)-1,4-phenylene]bis(9,9-dimethyl-9*H*-fluorene) (**G**) (Figures 5 and 6).

It is worthy to mention that the polycondensation of *N*-methylisatin with 1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene (**K**) gave a polymer with promising properties for use as matrix material of phosphorescent OLEDs (PhoLEDs)[26] (Scheme 3).

The synthesis and investigation of polymers from the reactions of *N*-phenyl isatin with 4,7-bis[2′-(9′,9′-dimethyl)fluorenyl]-benzo[1,2,5]thiadiazole (**L**) and 2,7-bis[2′-(9′,9′-dimethyl)-fluorenyl]-9*H*-fluoren-9-one (**M**) has shown that this approach allows for the fine-tuning of third-order nonlinear optical properties of the polymers by means incorporation into the main chain highly polarizable individual fragments.[27]

It seemed plausible that because of high regioselectivity in these polymer-forming reactions, highly nucleophilic aromatic compounds would also react with isatin. To test the idea we synthesized the oligofluorene precursor blocks with hydrogens in the terminal 2,7-positions. The compounds have been generated in a routine Yamamoto coupling of 2,7-dibromo-9,9-bis(2,6-ethylhexyl)-9*H*-fluorene as bifunctional monomer and 2-bromo-9,9-bis(2,6-ethylhexyl)-9*H*-fluorene as monofunctional end-capper (Scheme 4) followed by fractionation.

A fraction of the polymer with relatively low polydispersity (M_w = 6000, M_n = 4000) was used for the reaction with isatin. Analyses of the resulting polymer **2aH** showed a 2-fold enhancement of inherent viscosity (from 0.17 until 0.31 dL g, (TCE), increase of the molecular weights (M_w = 13500, M_n = 7400) and the presence, in the IR spectrum of the polymer, of a characteristic peak of the carbonyl group of the oxindole residue at 1732 cm^{-1} (Figure 7, Scheme 5).

These results point to the high efficiency of isatin in these coupling reactions.

Finally, condensations of isatin with aromatic hydrocarbons bearing functional groups were carried out. Reaction of isatin with 2,2′-dihydroxy-1,1′-biphenyl proceeded smoothly to give a linear, soluble polymer (**2aI**). Even more surprisingly, isatin condensations with 1,1′-bi-2-napththol also turned out to be highly regioselective. Structural analysis (Figure 8-9) has revealed the chemical compositions of these polymers with functional hydroxyl groups.

It is known that superacid-catalyzed polyhydroxyalkylations show significant dependence upon acid strength. Increase of the amount of TFSA causes rapid molecular-weight growth. Therefore, a strongly acidic media (or pure TFSA) is recommended for polymerizations involving relatively weak nucleophiles (2-(4-biphenylyl)-6-phenylbenzoxazole) and an essentially less acidic one for polymerizations involving biphenols.

It is worth mentioning that superacid-catalyzed polyhydroxyalkylations involving 2,6-diphenoxybenzonitrile and 6-diphenoxybenzoic acid as a nucleophilic component afforded linear polymers containing pendant functional cyano- and carboxygroups.[28] Therefore, one can expect similar orthogonality in polycondensations involving isatin.

One can expect that the polymers obtained in the presence of superacid would form strong complexes with these acid significantly affecting polymer properties. It turned out that an extraction with hot methanol of a polymer precipitated as thin fiber removes completely TFSA residues. Analysis of IR, NMR and, particularly, TGA data of these polymer-fibers do not reveal any presence of TFSA-containing products. A polymer, precipitated as a thick fiber may contain 3−5% of TFSA residues. However, the second reprecipitation of the polymer from a solution in aprotic solvents (DMFA or NMP) followed by methanol extraction removes the acid impurities below the detectable level of the above-mentioned methods.

It was shown that oxindole fragments in hyperbranched polymers polymers obtained by self-condensation of 6-(4-phenoxybenzoyl)isatin react with *tert*-butyl bromoacetate in dimethylformamide (DMFA).[19] We have found that the polymers synthesized are readily alkylated with bromoalkyls, such as propargyl bromide (**e**) and allyl bromide (**f**), in *N*-methylpyrrolidone (NMP) with K_2CO_3 as base at room temperature for 24 h. The reactions proceeded quantitatively (Scheme 6).

The substitution reaction was monitored by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectrum (Figure 10) clearly indicate

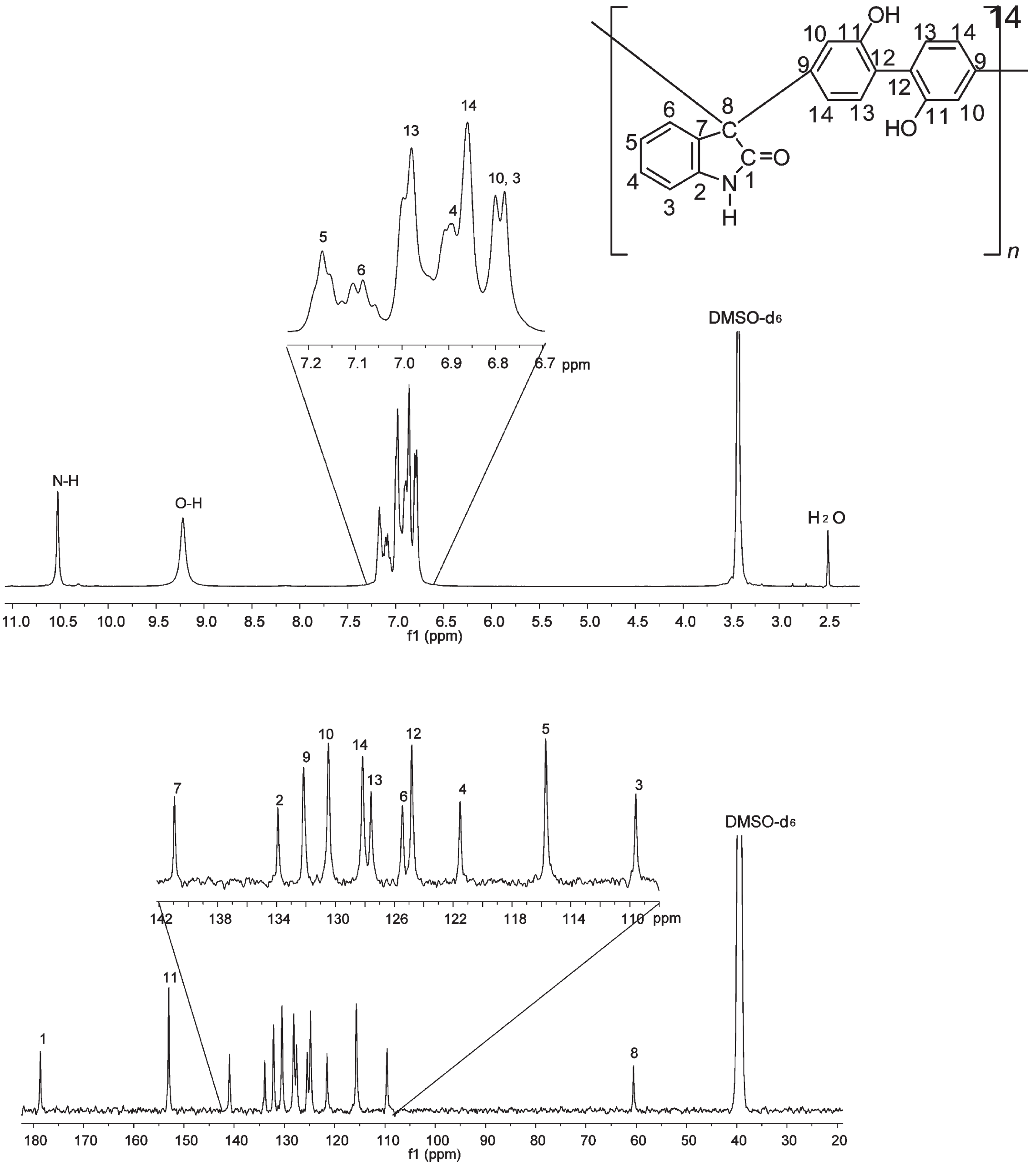


Figure 8. ^{1}H and ^{13}C NMR spectra of polymer **2aI** (solution in DMSO-d_6.

disappearance of resonances of proton at 10.5 ppm of initial polymer **2aA** and appearance of resonances of propargyl group of the modified polymer **3eA**.

Similarly, polymer **3fA** bearing allyl groups has been obtained. It is important that the degree of substitution can be easily controlled by the amount of alkylating compound. GPC analysis has revealed an increase of the molecular weight of the polymer functionalized.

After separation from the reaction media, washing, and drying, most of the polymers obtained appear as pure white fibrous powders. All polymers obtained were completely soluble in organic solvents and formed transparent and flexible films due to their high molecular weights. Polymers containing *N*-alkyl or *N*-alkyl-substituted oxindole groups were soluble in chlorinated and aprotic solvents, while nonsubstituted N−H polymers were soluble in aprotic solvents.

DSC analysis of the nonmodified polymers did not reveal glass transitions until 400 °C; fully aromatic polymers (*N*-aryl substituted) exhibited a similar TGA pattern with no significant weight loss below 520 °C both in air and in nitrogen atmosphere.

The polymer syntheses demonstrated suggest that a large variety of new polymers may be obtained similarly. Aromatic high-band gap polymer with high triplet energy as a matrix material of phosphorescent OLEDs (PhoLEDs) have been reported recently.[26] Polymers with promising nonlineal optical properties,[27] and donor−acceptor polymers for solar energy conversion can be obtained as well. Simple preparation, incorporation of rigid aromatic blocks in the main chain, and the presence of bulky side groups that inhibit conformational change all point to the large potential of these polymers for membrane separation processes. It is to be noted that although the superacid catalyzed reactions were carried out only with a few isatins and several hydrocarbons, it is evident that a large variety of aromatics (including oligomers and polymers) can react with isatins to give well-defined polymers.

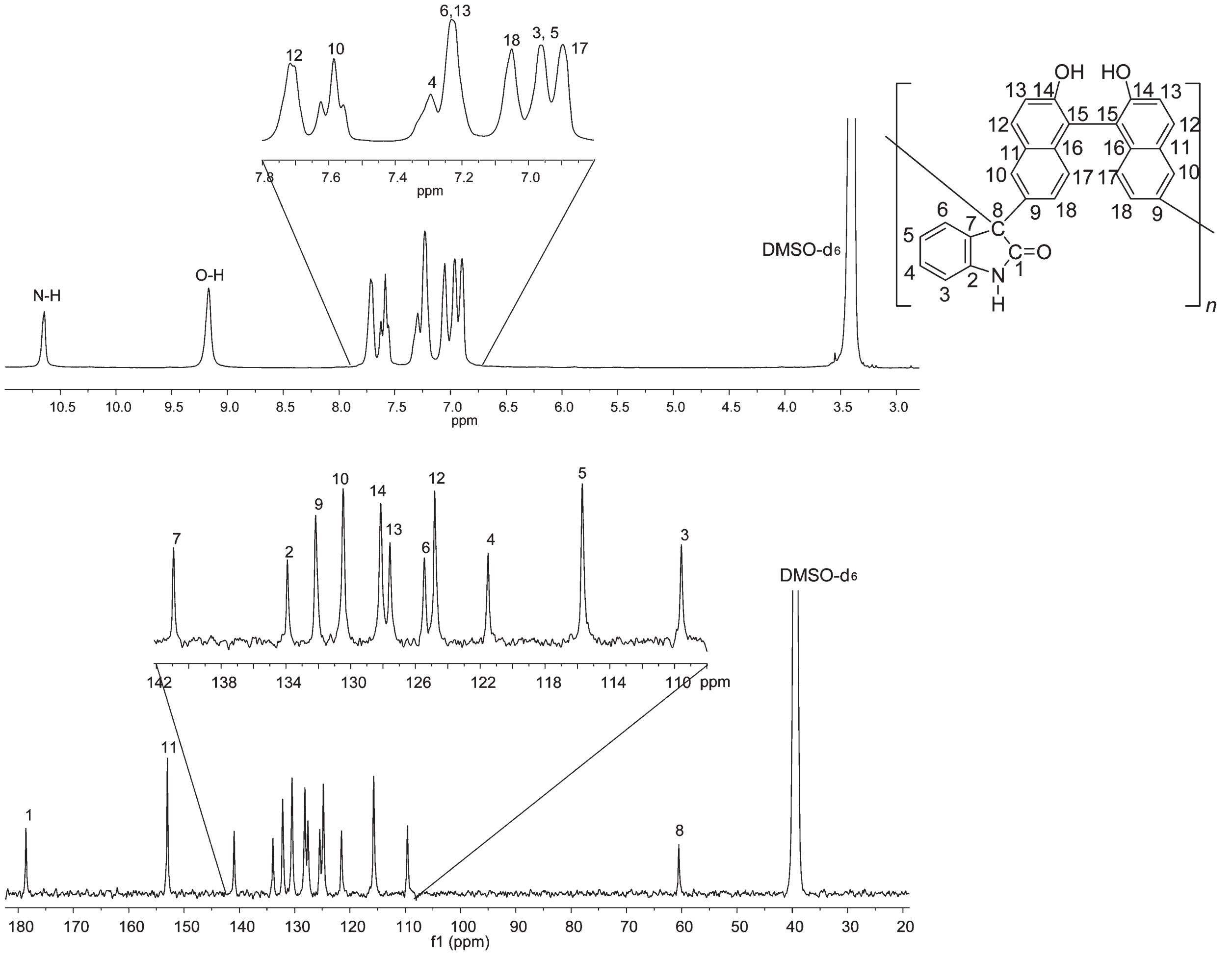
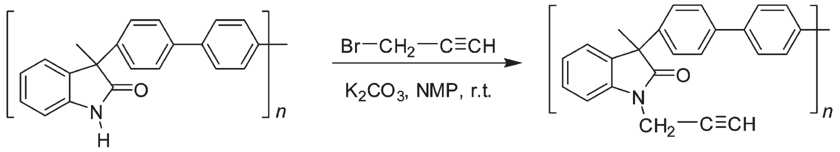


Figure 9. ^{1}H and ^{13}C NMR spectra of polymer **2aJ** (solution in DMSO-d_6).

Scheme 6. Modification of Polymer 2aA



2aA **3eA**

A "click" incorporation in the isatin/aromatic structures of alkene or alkyne functionalities, followed by their "click" reactions, opens up a potential array of new structures.

Conclusions. A series of novel, wholly aromatic, high-molecular-weight polymers was readily obtained for the first time by superacid-catalyzed condensation of isatin with linear, nonactivated, multiring aromatic hydrocarbons. The reactions performed at room temperature in the Brønsted superacid CF_3SO_3H and in a mixture of TFSA with methylene chloride or TFA wide in scope and include simple reaction conditions, readily available starting materials and reagents, and generation of an inoffensive byproduct (water). The reactivity of isatin can be fine-tuned easily by the isatin:TFSA ratio in the reaction media. The reactions also are tolerant of such functional groups as hydroxyl, carboxy, and cyano.

NMR studies have shown the existence of high regioselectivity in polymer-forming reactions.

The weight-average and number-average molar masses of the polymers, determined by gel permeation chromatography and multiangle laser light scattering, ranged from 54 200 to 742 000, and from 40 140 to 438 500 g/mol, respectively. Most of the polymers possess narrow polydispersity (1.15–1.50). The polymers based on isatin and aromatic substances reacted quantitatively with propargyl and allyl bromides. The incorporation of "click"able alkyne and alkene functionalities can be readily controlled by adjusting the reaction ratio of polymer to alkyl bromides.

Finally, it should be noted that in contrast to most reported polymer click reactions, which involve the formation of carbon–heteroatom (mostly N, O, and S) bonds, isatin-based reactions are in the march of modern synthetic organic chemistry that emphasizes formation of carbon–carbon bonds.

On the whole, we conclude that superacid-catalyzed reactions of isatin with linear, nonactivated, multiring aromatic hydrocarbons meet the criteria needed for "click" polymer chemistry and will be a significant addition to that field.

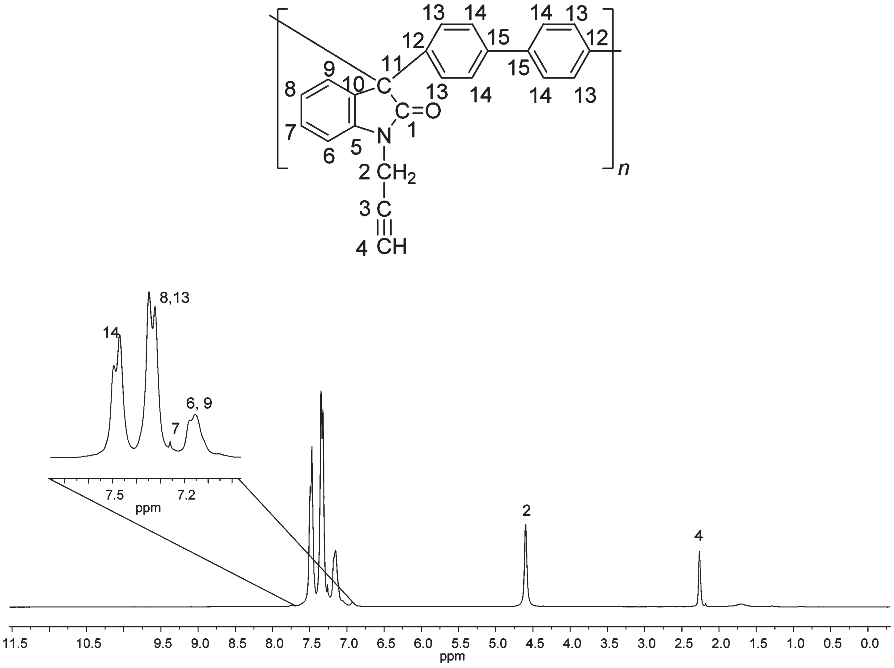


Figure 10. ^{1}H spectrum of polymer **3eA** (solution in CDCl$_3$).

3. Experimental Part

3.1. Characterization. NMR spectra were recorded on Bruker Avance 400 Spectrometer, operating at 400.13 and 100 MHz for ^{1}H and ^{13}C respectively. Chloroform-*d* (CDCl3) and dimethyl sulfoxide-d_6 were used as solvents. Infrared (IR) spectra were measured on a Nicolet FT-IR-ATR spectrometrer. The inherent viscosities of 0.2% polymer solutions in 1-methyl-2-pyrrolidinone (NMP) were measured at 25 °C using an Ubbelohde viscometer. Molecular weights were determined by gel permeation chromatography (GPC-MALLS) according to the published method.[26] Thermogravimetric analyses (TGA) were carried out in air and under nitrogen at a heating rate of 10 °C/min on a DuPont 951 Thermogravimetric Analyzer. The T_g was evaluated by differential scanning calorimetry (DSC) measured at 10 °C/min on DuPont 910.

3.2. Materials. All starting materials were obtained from Aldrich. *p*-Terphenyl, 9*H*-fluorene, and *p*-quaterphenyl were used as received. Methylene chloride, TFA, TFSA, and biphenyl were distilled, and isatin, *N*-phenylisatin, 2-(4-biphenylyl)-6-phenylbenzoxazole, biphenol and bi-2-napththol were purified by recrystallization with charcoal from ethanol, ethanol, toluene, aqueous methanol and ethanol, respectively. *N*-*m*-(Trifluoromethyl)phenylisatin and 3,5-bis(trifluoromethyl)phenylisatin were obtained by the published method.[29]

Synthesis of 9,9-Dimethylfluorene-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The monomer was prepared according to known method.[30]A 1.6 M solution of *n*-BuLi in hexane (0.92 g, 14.3 mmol) was added dropwise at 78 °C to a solution of 2-bromo-9,9-dimethylfluorene (3.0 g, 11.0 mmol) in dry THF (40 mL). The mixture was stirred for 1 h at −78 °C. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.66 g, 14.3 mmol) was slowly added and stirred for another 15 min at −78 °C. Afterward, the solution was allowed to return to room temperature and then stirred for 24 h before being poured into water. The aqueous phase was then extracted with dichloromethane, the collected organic layers were dried over MgSO$_4$, and the solvent was removed by rotary evaporation. After recrystallization of the residue from heptane, 2.3 g (65%) of a colorless solid was obtained. ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$, 32 °C): 7.82 (s, 1H), 7.75 (dd, 1H, J = 0.7 Hz, J = 7.6 Hz), 7.70 (m, 1H), 7.66 (d, 1H, J = 7.6 Hz), 7.39 (td, 1H, J = 3.5 Hz, J = 7.5 Hz), 7.28 (m, 2H), 1.45 (s, 6H), 1.30 (s, 12H) ppm. ^{13}C NMR (100 MHz, C$_2$D$_2$Cl$_4$, 32 °C): 154.5, 153.0, 142.3, 139.1, 134.1, 129.1, 128.2, 127.2, 123.0, 120.8, 119.6, 84.0, 47.1, 27.4, 25.3 ppm. Anal. Calcd for C$_{21}$H$_{25}$BO$_2$: C 78.76; H 7.87. Found: C 78.73; H 8.22. FD−MS: 320 (M$^+$). Melting point: 133 °C.

Preparation of 2,2′-(2,5-Bis(trifluoromethyl)-1,4-phenylene)-bis(9,9-dimethyl-9H-fluorene) (***G***). A 100 mL Schlenk-tube was charged with 1,4-dibromo-2,5-bis(trifluoromethyl)benzene (2,0 g, 5,4 mmol), 9,9-Dimethylfluorene-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3,96 g, 12.4 mmol), tetrakis(triphenylphosphino)−Pd (93 mg, 0.1 mmol), and Na$_2$CO$_3$ (2,57 g, 24.2 mmol). Then degassed toluene (50 mL), and degassed water (25 mL) were added, and the mixture was stirred under argon at 80 °C for 12 h. The reaction was quenched by adding 30 mL of 2 M aqueous HCl and 50 mL of chloroform. The mixture was subsequently washed with concentrated Na$_2$CO$_3$, concentrated titriplex solution, and brine and dried over Na$_2$SO$_4$, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography over silica gel (petrol ether/ethyl acetate 9:1) to obtain 2.1 g (66%) of a colorless solid. ^{1}H NMR (400 MHz, CDCl$_3$, 32 °C): 7.88 (s, 2H), 7.87−7.77 (m, 4H), 7.55−7.47 (m, 4H), 7.45−7.36 (m, 6H), 1.58 (s, 12H) ppm. ^{19}F NMR (376 MHz, CDCl$_3$, 32 °C): −57.54 (s) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 32 °C): 153.9, 153.4, 141.1, 139.4, 138.6, 137.0, 130.2, 130.2, 127.8, 127.7, 127.1, 123.4, 122.7, 120.3, 119.6, 100.0, 47.0, 27.1 ppm. Mass (APLI−(TOF)MS): calculated, 598.2095; found, 598.1982.

3.3. Polymer Syntheses. *Preparation of Poly[(2,3-dihydro-2-oxo-1H-indole-3,3-diyl)[1,1′-biphenyl]-4,4′-diyl]* (***2aA***). A typical example of polymer preparation is as follows. TFA acid (9.3 mL) and TFSA (16 mL) were added to a mixture of isatin (2.943 g, 20 mmol) and biphenyl (3.084 g, 20 mmol). The reaction mixture was stirred at room temperature for 1 h 40 min and precipitated into methanol. The slightly yellow fiber formed was filtered off and washed with hot methanol. After drying, 5.440 g (96%) of white fiber like polymer (**2aA**) was obtained. The inherent viscosity $\eta_{\text{inh.}}$ of the 0.2% solution of the polymer in NMP was found to be 0.85 dL g^{-1}.

Synthesis of Poly[2,6-benzoxazolediyl-1,4-phenylene-2,3-dihydro-2-oxo-1H-indole-3,3-diyl)[1,1′-biphenyl]-4,4′-diyl] (***2aD***). A solution of isatin (0.294 g, 2 mmol) and 2-(4-biphenylyl)-6-phenylbenzoxazole (0.695 g, 2 mmol) in TFSA (3.5 mL) was stirred at room temperature for 25 h and precipitated into methanol. The fibrous powder formed was filtered off and extracted with hot methanol. After drying, 0.772 g (81.1%) of slightly beige fibrous polymer **2aD** with an inherent viscosity $\eta_{\text{inh.}}$ of 0.44 dL g^{-1} (NMP) was obtained.

*Synthesis of Poly[(2,3-dihydro-2-oxo-1H-indole-3,3-diyl)[1,1′:4′,1″-terphenyl]-4,4″-diyl] (**2aB**).* Isatin (0.221 g, 1.5 mmol), *p*-terphenyl (0.345 g, 1.5 mmol), methylene chloride (2 mL), TFA (1.2 mL), and TFSA (1 mL) were stirred at room temperature for 55 min and precipitated into methanol. The slightly yellow fiber formed was filtered off and washed with hot methanol. After drying, 0.757 g (88.3%) of white polymer **2aB** with an inherent viscosity $\eta_{\text{inh.}}$ of 1.44 dL g^{-1} (NMP) was obtained.

*Synthesis of the Copolymer of Isatin with p-Quaterphenyl and 4,4′-Diphenoxybenzophenone (**2c(D/N)**).* (*N*-3-Trifluoromethylphenyl)isatin (0.341 g, 1.17 mmol), *p*-quaterphenyl (0.138 g, 0.45 mmol), 4,4′-diphenoxybenzophenone (0.165 g, 0.45 mmol), methylene chloride (5.2 mL), and TFSA (0.8 mL) were stirred at room temperature for 5.8 h and precipitated into methanol. The slightly yellow fiber formed was filtered off and extracted with hot methanol. After drying, 0.450 g (82.0%) of white fibrous polymer **2c(D/N)** with an inherent viscosity $\eta_{\text{inh.}}$ of 1.51 dL g^{-1} (NMP) was obtained.

*Preparation of (**2aE**).* Isatin (0.736 g, 5 mmol), 9*H*-fluorene (0.831 g, 5 mmol), TFA (9.8 mL), and TFSA (2.8 mL) were stirred at room temperature for 29 h and precipitated into methanol. White fibrous polymer (**2aE**) (1.435 g, 97.2%) with an inherent viscosity $\eta_{\text{inh.}}$ of 0.59 dL g^{-1} (NMP) was obtained after precipitation, extraction with hot methanol and drying.

*Preparation of (**2aF**).* A mixture of isatin (0.276 g, 1.87 mmol), 9,9-dimethyl-9*H*-fluorene (0.364 g, 1.87 mmol), TFA (3.45 mL), and TFSA (0.6 mL) was stirred at room temperature for 29 h 30 min and precipitated into methanol. The white fiber formed was filtered off and extracted with refluxing methanol and dried. The resulting white fibrous polymer **2aF** (0.52 g, 85.9%) had an inherent viscosity $\eta_{\text{inh.}}$ of 0.92 dL g^{-1} in NMP.

*Synthesis of Poly[(2,3-dihydro-2-oxo-1-phenyl-1H-indole-3,3-diyl)(9,9-dimethyl-9H-fluorene-2,7-diyl)[2,5-bis(trifluoromethyl)-1,4-phenylene](9,9-dimethyl-9H-fluorene-2,7-diyl)] (**2aG**).* A mixture of isatin (0.178 g, 0.80 mmol), 2,2′-(2,5-bis(trifluoromethyl)-1,4-phenylene)bis(9,9-dimethyl-9*H*-fluorene) (0.479 g, 0.80 mmol), methylene chloride (2.3 mL), and TFSA (0.7 mL) were stirred at room temperature for 5 min and precipitated into methanol. The white fiber formed was filtered off and washed with hot methanol. After drying, 0.594 g (95.2%) of white fiber-like polymer was obtained. The polymers had an inherent viscosity $\eta_{\text{inh}} = 1.69$ dL g^{-1} (NMP).

*Preparation of (**2aH**).* Isatin (0.0106 g, 0.07 mmol), oligo-9,9-di(heptan-3-yl)-9*H*-fluorene (0.2 g, 0.04 mmol), methylene chloride (2.5 mL) and TFSAc acid (0.05 mL) were stirred at room temperature for 24 h and precipitated into methanol. The slightly beige powder formed was filtered off and washed with hot methanol. After drying, 0.174 g (87%) of beige powder was obtained

*Synthesis of Poly[(2,3-dihydro-1-methyl-2-oxo-1H-indole-3,3-diyl)[2,2′-dihydroxy-1,1′-biphenyl]-4,4′-diyl] (**2aI**).* A mixture of isatin (0.199 g, 1.35 mmol), 2,2′,-dihydroxy-1,1′-biphenyl (0.251 g, 1.35 mmol), methylene chloride (0.9 mL), TFA (0.9 mL), and TFSA(0.25 mL) was stirred at room temperature for 8 h and precipitated into water. The slightly pink fiber formed was filtered off and washed copiously with water. After drying, 0.399 g (93.7%) of gray fiber-like polymer with an inherent viscosity $\eta_{\text{inh.}}$ of 1.74 dL g^{-1} (NMP) was obtained.

*Preparation of (**2aJ**).* Isatin (0.255 g, 1.35 mmol), 1,1′-bi-2-naphthol (0.386 g, 1.35 mmol), methylene chloride (1.4 mL) and TFSA (0.6 mL) were stirred at room temperature for 46 min and precipitated into methanol. The slightly orange fiber formed was filtered off and extracted with hot methanol. After drying, 0.458 g (81.7%) of orange fiber like polymer with an inherent viscosity $\eta_{\text{inh.}}$ of 0.35 dL g^{-1} (NMP) was obtained.

Chemical Modification with Propargyl Bromide. To the solution of polymer **2aA** (0.500 g, 1.77 mmol) in NMP (9.5 mL) were added potassium carbonate (1.051 g, 8.83 mmol) and propargyl bromide (0.79 mL, 8.83 mmol). After stirring at room temperature for 24 h, the mixture was poured into methanol. The slightly yellow fiber precipitated was filtered off and washed with hot methanol. After drying, the resulting white fiber-like polymer **3eA** (0.512 g, 90.3%) had an inherent viscosity $\eta_{\text{inh.}}$ of 0.76 dL g^{-1} (NMP).

Chemical Modification with Allyl Bromide. To the solution of polymer **2aA** (0.300 g, 1.25 mmol) in NMP (5.7 mL) were added allyl bromide (1.1 mL, 5.02 mmol) and potassium carbonate (0.694 g, 5.02 mmol). After stirring at room temperature for 24 h, the mixture was poured into methanol. The slightly yellow fiber precipitated was filtered off and washed with hot methanol. After drying, the resulting white fiber-like polymer **3fA** (0.304 g, 88.8%) had an inherent viscosity $\eta_{\text{inh.}}$ of 0.92 dL g^{-1} (NMP).

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