Precision Synthesis of Narrow Polydispersity, Ultrahigh Molecular Weight Linear Aromatic Polymers by A$_2$ + B$_2$ Nonstoichiometric Step-Selective Polymerization

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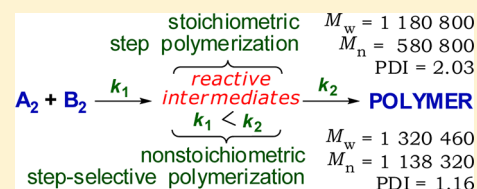
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ABSTRACT: A reliable and practical approach is offered for the two critical fundamental challenges that remain in step-growth polymerization: synthesis of narrow polydispersity and ultrahigh molecular weight polymers. The polymers are obtained by superacid catalyzed polyhydroxyalkylation involving two consecutive steps — slow and fast. Polymer syntheses with decrease in reactivity of intermediates lead to narrow polydispersity polymers, while nonstoichiometric reactions result in polymers of high and ultrahigh molecular weight. Linear aromatic polymers with ultra high molecular weight M_n > 1 000 000 and narrow polydispersity (M_w/M_n = 1.15−1.16) have been obtained. An unusual step-selective mechanism is suggested for the formation of these polymers.

stoichiometric step polymerization M_w = 1 180 800 M_n = 580 800   PDI = 2.03

A$_2$ + B$_2$ $\xrightarrow{k_1}$ *reactive intermediates* $\xrightarrow{k_2}$ **POLYMER**

$k_1 < k_2$

nonstoichiometric step-selective polymerization M_w = 1 320 460 M_n = 1 138 320   PDI = 1.16

1. INTRODUCTION

The processes of polymerization are divided into two groups known as chain-growth polymerization and step-growth polymerization (polycondensation). The discovery of "living polymerization"[1] and, particularly, the tremendous progress reported over the last 15 years in the investigations of mechanistic aspects of chain growth polymerization and development of controlled/living radical polymerization (CRP) in the early 1990s led to a number of versatile techniques for exerting precise control over polymer molecular weights, molecular-weight distributions and complex architectures.

In contrast, the basic tenets of the theory of step-growth polymerization [particularly, broad (ca. 2) polydispersity excluding controlled synthesis of well-defined structures] have remained unchanged during the last 60 years.

According to the classical theory of step-growth polymerization[2−4] all functional groups at any given stage of the polymerization are equally reactive, regardless of the size of the molecule to which they are attached (under the assumption that no intramolecular cyclization occurs). The molecular weight distribution consequently predicted is known as the "most probable" distribution with polydispersity index approaching 2 at high conversion, which means that this type of polymerization is inapplicable to the synthesis of polymers with narrow polydispersity. Moreover, although the classical Carothers−Flory theory predicts unlimited chain growth, high-molecular weights (number average, M_n, > 50 000 Da) are usually not achieved.

The factors limiting chain growth are believed to be monomer imbalance, impurities in monomers and solvents, and decomposition of the functional groups. It should be mentioned that, basically, the experimental results are in acceptable agreement with the theoretically predicted ones.

During the past 10 years, two important discoveries in the mechanism of step polymerization have been reported. Kricheldorf and co-workers have shown[5] that, in agreement with the predictions of Stepto and Gordon[6−8] in the kinetically controlled step polymerization of linear monomers, ring closure competes with propagation at any concentration at any stage of the polymerization for A$_2$ + B$_2$ and AB monomer combinations.

As a result, all reaction products are necessarily macrocycles at 100% conversion when side reactions are absent. Obviously, suppression of formation of macrocycles is necessary to obtain very high-molecular-weight linear polymers. Several years ago, Yokozawa demonstrated that by creating a difference in the
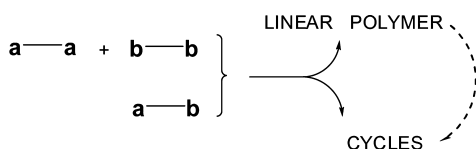
reactivity of the functional groups of specially designed monomers it is possible to transform the polymerization mechanism from step-growth to chain-growth.[9,10] This type of chain polymerization that proceeds with the formation of a low-molar-mass byproduct is called condensative chain polymerization (CCP) (IUPAC Recommendations 1996). A number of polymers with narrow polydispersity and moderate molecular weight have been obtained successfully by CCP of AB monomers.

Despite these important and inspiring achievements, controlled reactions based on simple monomers yielding high molecular weight polymers with narrow polydispersity and bearing functional groups remain a principal task in step-growth polymerizations.

One promising way to achieve this aim is the development of new polymer-forming reactions. One recent example is the acid-catalyzed condensation of ketones and aldehydes with aromatic compounds, known as hydroxyalkylation (Scheme 1),[11,12] where R and R[1] are H, alkyl, aryl.
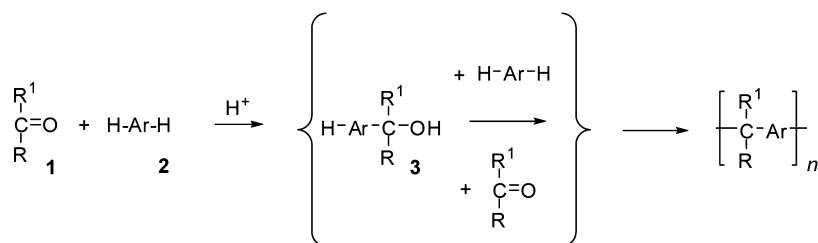
Scheme 1. Hydroxyalkylation
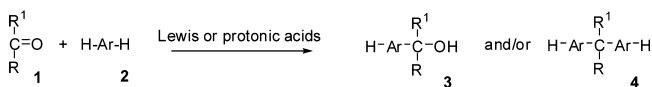
Depending on the monomer structures and reaction conditions, an alcohol, a diaryl-compound or a mixture of these can be obtained.

Although hydroxyalkylation has been known for a long time,[13] these Friedel–Crafts-type reactions have not been studied to the same extent as the corresponding reactions involving alcohols, alkyl halides or aryl halides. The main reason for such neglect is probably the generally lower yields and the formation of oligomeric byproducts. The concept of super-electrophilic activation proposed by Nobel Prize winner Olah and co-workers to explain the high reactivities of electrophilic species in superacidic media,[14] and its application for hydroxyalkylation reactions, turned out to be remarkably successful. Numerous hydroxyalkylation reactions have been carried out using superacids [mostly trifluoromethanesulfonic acid (TFSA)] as catalysts or as a reaction medium.[15–17] Recently, for the first time, superacid-catalyzed hydroxyalkylation reactions of carbonyl compounds with nonactivated aromatic hydrocarbons were applied to produce high molecular weight polymers (Scheme 2).

Despite their apparent complexity (two consecutive steps of the polymer-forming reaction with an intermediate carbinol potentially capable of various transformations) the polyhydroxyalkylations appeared to be very efficient. Successful preparation of linear[18–22] and hyperbranched[23–30] polymers, dendrons and dendrimers[31] have been reported. Generally, molecular weights (M_n) of the polymers from superacid-catalyzed hydroxylakylation ranged from 30 000 to 100 000 Da.

Very recently, dramatic acceleration of superacid-catalyzed polyhydroxylakylation in the presence of a small excess of the carbonyl compound (so-called "nonstoichiometric polycondensation") was demonstrated.[32] The origin of the "nonstoichiometric" effect is owing to a large difference in reactivity between the initial, relatively unreactive carbonyl compound and the highly reactive intermediate carbinol formed after the first reaction step. To the best of our knowledge this is the largest nonstoichiometric effect (in terms of increase of molecular weight) reported in step polymerization so far.[33–36] Matrix assisted laser desorption time of flight (MALDI–TOF) spectroscopy measurements revealed two important features of this process:[32]

(1) Samples from both stoichiometric and nonstoichiometric reactions contain aryl-terminated linear chains:
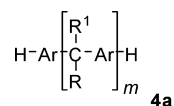
This is additional evidence that the second reaction is faster than that of the first one and that aryl-terminated intermediates **4a** prevail in the course of the polymerization.

(2) A small fraction of macrocycles has been detected in both reactions; however, the proportion of macrocyles in nonstoichiometric syntheses is essentially less. (A decrease in the proportion of macrocyles in the nonstoichiometric polymerization of bisphenol A with excess of methylene bromide was also reported by Hay.[35])

Since oligomers and polymers having two aryl end groups cannot cyclize, their predominance in the reaction mixture reduces the influence of cyclization. A large concentration of these nucleophiles favors the reactions and leads to the formation of linear chains at the expense of macrocyclization. These are the following practically important features of nonstoichiometric polyhydroxyalkylation: (i) increase in molecular weight of the polymer, (ii) decrease of the macrocycle fraction, (iii) decrease in reaction time, and (iv) use of low-reactivity monomers.

In the present study, we utilize these promising findings to resolve two basic problems of step growth polymer chemistry:

Scheme 2. Polyhydroxyalkylation

(a) synthesis of high- and ultrahigh molecular weight (UHMW) polymers; (b) synthesis of polymers of narrow polydispersity.

2. RESULTS AND DISCUSSION

2.1. Polymer Syntheses. Having demonstrated a strong nonstoichiometric acceleration in condensation of 1,1,1-trifluoroacetone with 4,4′-diphenoxybenzophenone,[32] we hoped to increase molecular weight of the polymers by increasing of reaction time and monomer imbalance. Indeed, molecular weights of the resulting polymers have been increasing, however, broad polydispersity, sometimes partial solubility and NMR spectra of these products pointed to a significant proportion of side reactions. It is very likely that these reactions are due to alkylation in the phenyl ether fragment. We therefore turned our attention to polymerization of 1,1,1-trifluoroacetone with biphenyl, which is less reactive and reacts more selective. Unexpectedly, in the course of optimization of reaction conditions, the stoichiometric polymerization of 1,1,1-trifluoroacetone with biphenyl gave polymer **5** with viscosity η_{inh} of 2.57 dL/g and M_w, M_n, and PDI 1 180 000, 580 800, and 2.03, respectively. To the best of our knowledge, this is the first example of direct preparation of linear aromatic UHMW polymer by step-polymerization. It is worth noting that the formation of a very viscous solution of polymer **5** in chloroform at concentrations 3−5% (w/v) and reprecipitation of 1% polymer solution into methanol as a monofiber also confirm high molecular weight of the product. Spectral studies have revealed high regioselectivity of the polymer-forming reaction (Figure 1).
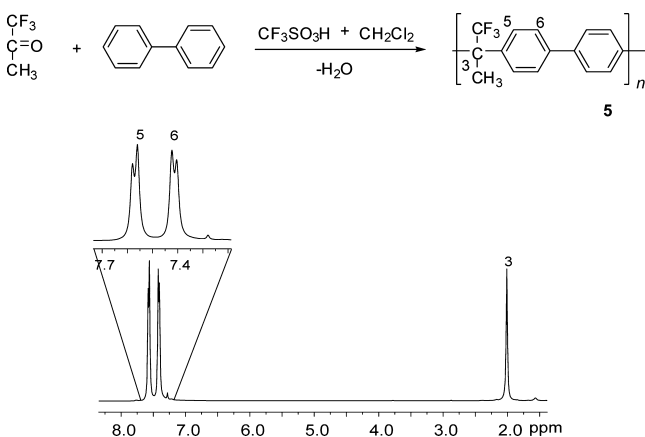

Figure 1. ^{1}H NMR spectrum of polymer **5** (solution in CDCl$_3$). A small peak at 7.21 ppm corresponds to residue chloroform.

Interestingly, that spectral patterns of this polymers were identical with that of polymer **5** with M_w 55 000. The reactions proceeded as "precipitation polycondensations",[37,38] when the polymer formed precipitated from the initially homogeneous solution and polymer-forming reaction continues in the precipitate. At first sight, such synthetic efficiency could be attributable to the high local concentration of functional groups in the "reactive gel" (precipitated polymer). However, neither known precipitation polycondensations nor polycondensations in the melt produce polymers of so high a molecular weight.

Theoretical studies of the consecutive steps of superacid-catalyzed polymerization of 1,1,1-trifluoroacetone with benzene revealed that the rate of the second reaction is faster than that

of the first.[32] This finding indicates that similar situation will be held for biphenyl monomer as well. Therefore, it is very likely that a combination of high local monomer concentration in the reactive gel and suppression of cyclization are the main reasons for the formation of UHMW polymer. Nonstoichiometric polymerizations of biphenyl with an excess of 1,1,1-trifluoroacetone proceeded much faster, affording UHMW polymer **5** in 6 h instead of 24 h for stoichiometric synthesis, but further increase of the reaction time basically resulted to broad polydispersity and partial insolubility of the polymer obtained. High molecular weight polymers were also obtained successfully from polymerizations of 1,1,1-trifluoroacetone and 2,2,2-trifluoracetophenone with terphenyl and a mixture of biphenyl and terphenyl. In all cases the PDI index was close to 2. When analyzing known examples of superacid catalyzed polyhydroxyalkylations, we have noticed that stoichiometric reactions involving as a carbonyl component isatin and acenaphthene-quinone [containing heteroatoms (oxygen, nitrogen) that do not participate directly in the reaction] basically result in polymers with polydispersity c.a. 1.5 or even less, which is very unusual for step-polymerization. Inspired by these results we decide to explore this challenge.

Polymerizations based on isatin and aromatic hydrocarbons were shown to be wide in scope and especially efficient.[39] The homogeneous polymerization of isatin with biphenyl (Scheme 3) was chosen for detailed study.

Scheme 3. Superacid-Catalyzed Polymerization of Isatin with Biphenyl
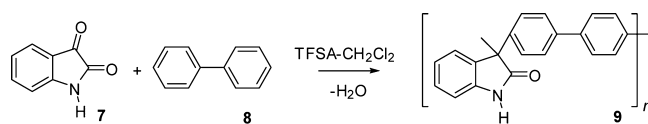
Optimization of the reaction conditions of stoichiometric reactions of isatin with biphenyl has revealed a monomer concentration range (0.15−0.20 mol/L) that affords polymers with polydispersity less than 1.5.

Nonstoichiometric polymerizations under these conditions gave polymers with ultrahigh molecular weight and remarkably narrow polydispersity (Table 1, entries 2, 3). The analyses of

**Table 1. Nonstoichiometric Polymerizations of Isatin with Biphenyl**

entry no.	isatin/biphenyl (mol/mol)	$M_w \times 10^{-3}$ Da	$M_n \times 10^{-3}$ Da	PDI	η_{inh} (dL/)^a
1	1.00	90.95	80.40	1.18	0.76
2	1.10	770.84	670.73	1.15	2.37
3	1.15	1320.46	1138.32	1.16	3.02
4	1.30	1220.30	810.40	1.50	2.98
5	1.70	1170.20	720.95	1.61	2.78
6	2.00	1030.20	580.45	1.76	2.97

^{a}0.2% polymer solutions in 1-methyl-2-pyrrolidinone (NMP).

these samples revealed no structural irregularities. It is incredible that the molecular weights of these polymers remain very high and polydispersity relatively narrow, even with a large excess of isatin (entries 5, 6).

It is important to note that the polydispersity of the polymer samples remains practically unchanged in the course of polymerizations with a small excess of isatin (entries 1−3),

Scheme 4. Step-Selective Mechanism of Polymerization of Isatin with Biphenyl
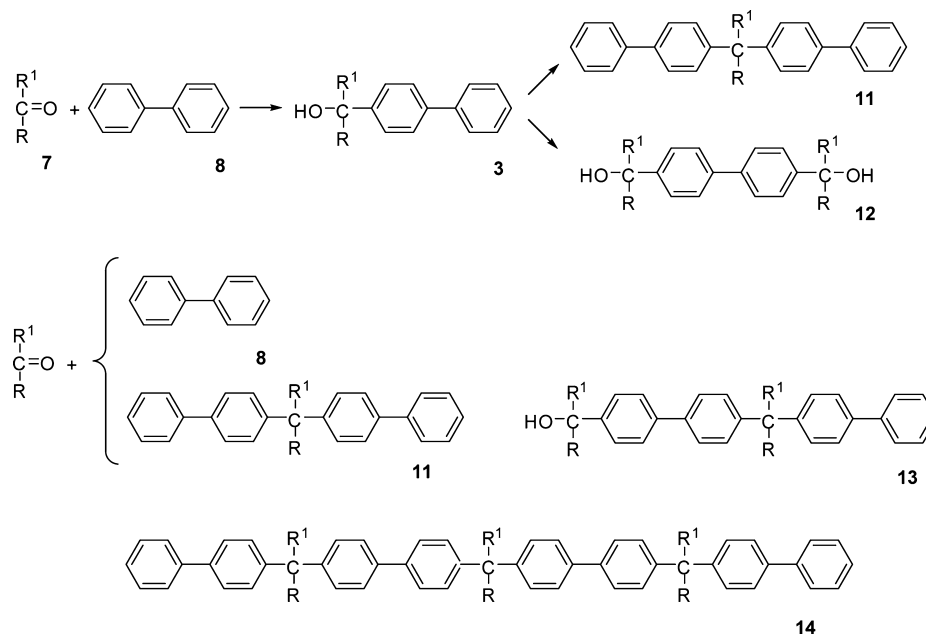
while in polymerizations with a large excess (entries 4−6) a gradual increase of PDI was observed. Polymer yield in all cases exceeded 95%.

Successful attempts to obtain polymers of even higher molecular weight by increasing of acidity of the reaction medium have been made, however, reliable characterizations of these polymers by GPC turned out to be problematic due to the high viscosity of the polymer solutions.

The results presented in the table are in a total disagreement with a classical step-growth polymerization producing polymers with polydispersity ca. 2, which means that the mechanism of the formation of narrow polydispersity polymers is different from that of traditional step-growth process.

2.2. Reaction Mechanism. On the basis of experimental results, there are two important features of the mechanism:

(i) the first step of the hydroxyalkylation reaction is slower than the second one;

(ii) the growing polymer chains have narrow polydispersity.

Thus, the polymerization mechanism can be postulated as follows (Scheme 4).

A carbonyl compound [e.g., isatin (**7**)] in the presence of TFSA and trifluoroacetic acid (TFA) reacts with biphenyl (**8**) to give a carbinol derivative (**3**). This intermediate may react with either another molecule of biphenyl to form diaryl-derivative (dimer **11**) or the carbonyl compound to produce the dicarbinol (**12**). Since the carbinol (**3**) is more reactive than (**7**), a dimer (**11**) will be obtained. Next, the carbonyl compound may react with either biphenyl or the dimer (**11**). The reaction with biphenyl would give another molecule of dimer (**11**), which thereby maintains narrow polydispersity, whereas reaction of the carbonyl compound with dimer (**11**), leading to carbinol (**13**), would broaden molecular-weight distribution.

Therefore, molecules of the carbonyl compound (**7**) should preferentially react with biphenyl to give dimers. Subsequently, all biphenyl will be converted into dimer (**11**), in a similar manner; carbonyl compounds would react gradually with dimers (**11**), tetramers (**14**), octamers, etc. This is the only way

to obtain polymer with narrow polydispersity. Obviously, this step-selective reaction mechanism implies a decrease in reactivity (nucleophilicity) of the oligomers formed. The larger the molecules, the less reactive they are in reactions with the carbonyl compound.

It is common knowledge that nucleophilicity of aromatic compounds is determined by their ionization potential (IP). According to Koopman's theorem, IP = −HOMO (highest energy occupied molecular orbital) energy. It has been demonstrated that the nucleophilicity in general and that of the aromatic component in the reaction of superacid-catalyzed hydroxyalkylation correlates with HOMO energy.[40,41]

Therefore, HOMO energy can be used as an indicator of nucleophilicity (reactivity). Figure 2 shows the evolution of HOMO energy with molecular weight of the polymers **5** and **9** up to 32-mers.

It can be observed that HOMO energy for polymer **5** is essentially independent of the molecular weight, which means
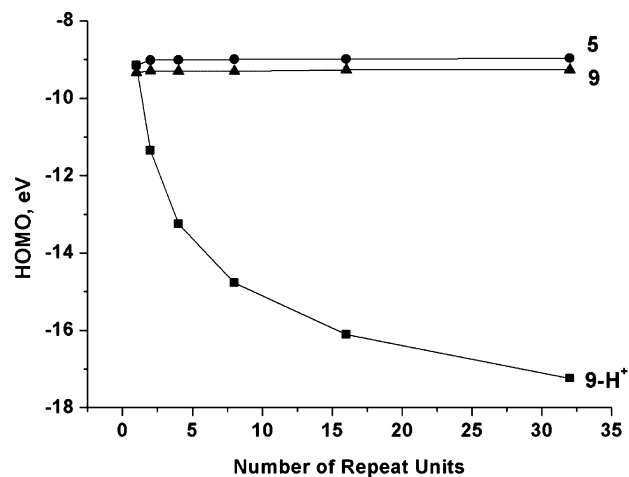

Figure 2. Evolution of HOMO energies of optimized oligomers obtained at PM6 level.

that reactivity of the oligomers does not change in the course of the synthesis. As a result, ultrahigh-molecular-weight, but broad-polydispersity polymers are obtained. For polymer (9-H^{+}) (Table 1, Scheme 3) in protonated form (the estimation of ΔG of protonation in TFSA of amide carbonyl of 3,3-diphenylindolin-2-one using theoretical model described earlier[42] gave −5.1 kcal/mol) HOMO energy continuously and strongly decreases with molecular weight, which thereby indicates decreased oligomer reactivity.
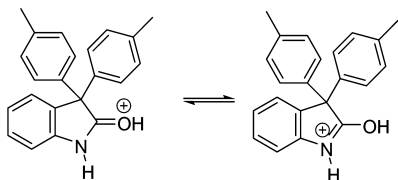
Protonation of indole fragments creates a net positive charge that reduces the nucleophilicity of the whole unit. This effect reflects in a drop of HOMO energy for protonated oligomers and their reactivity decreases with molecular weight, which contributes to the narrowing of polydispersity until all n-mers are consumed and no reaction occurs with $n + 1$-mers due to reduced reactivity.

The protonation of indole fragments appears to be a crucial factor that controls the reactivity of the oligomers, and this affords narrow polydispersity. It is worth noting that HOMO energies for nonprotonated oligomers of polymer (9) are practically equal to that of polymer (5). The protonation, or, to be more exact, nonprotonation of the aromatic fragments is the reason for typical for step-growth polymerization broad polydispersity of the polymer 5. In our opinion, although mechanism of the formation of narrow polydispersity polymers (see Scheme 4) is a step process, it is different from classical step-growth polymerization. At the same time, the reaction does not proceed as a condensative chain polymerization. Possibly, the term "step-selective polymerization" can be applied to define this rare case of polymerization. Obviously, more studies have to be done to clarify all the details of this polymerization; however, at the moment; the scheme suggested is an agreement with available theoretical and experimental results.

3. CONCLUSIONS

What is truly new in this work:

(i) Linear, ultra high molecular weight aromatic polymers have been obtained for the first time by $A_2 + B_2$ stoichiometric precipitation step polymerization involving two consecutive steps—slow and fast,.

(ii) Narrow polydispersity, UHMW polymers have been obtained by nonstoichiometric solution step-selective polymerization.

(iii) On the basis of the results obtained, a reaction mechanism for step-selective polymerization is suggested.

A synthesis involving two consecutive reactions of initial compounds of low reactivity and highly reactive intermediates appears to be good a strategy for a solution of fundamental long-standing problems of step-polymerization. One of these syntheses is superacid-catalyzed polyhydroxyalkylations. The reactions performed at room temperature in the Brønsted superacid CF_3SO_3H and in a mixture of TFSA with methylene chloride or TFA are wide in scope and include simple reaction conditions, readily available starting materials and reagents, and

generation of an inoffensive byproduct (water). The reactions also are tolerant of such functional groups as hydroxyl, carboxy, sulfoxy, amino, and cyano. The modification of structural factors and the acidity of the reaction medium allow for tuning of the reactivity of carbonyl and aromatic components; thereby, reaction kinetics are controlled.

The strategies outlined here allow for the efficient solutions of the following principal tasks of step growth polymer chemistry:

Synthesis of UHMW polymers by means of stoichiometric and nonstoichiometric step-polymerizations at high monomer concentration using reactions with a large difference between the reactivities of the first and second steps,

Synthesis of polymers with molecular weights up to 100 000−300 000 Da and narrow polydispersity using stoichiometric step-selective polymerization,

Controlled synthesis of narrow polydispersity, UHMW polymers by nonstoichiometric step-selective polymerization.

The strategy can be extended to both known and new polymer syntheses capable of nonstoichiometric acceleration, and to various polymer families (polyamides, polyketones, polyesters, etc.) using hydroxyalkyaltion or other efficient nonstoichiometric reactions as a coupling step.

Finally, it is certain that design of new efficient nonstoichiometric polymerizations will offer many opportunities to gain ready access to large collections of complex molecular architectures.

4. EXPERIMENTAL PART

4.1. Characterization. NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating at 400.13 and 100 MHz for ^{1}H and ^{13}C respectively. Chloroform-d (CDCl$_3$) and dimethyl sulfoxide-d_6 were used as solvents. Infrared (IR) spectra were measured on a Nicolet FT-IR-ATR spectrometer. 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). The chromatographic setup used consists of a 717 plus Autosampler HPLC Waters separation module having a vacuum degassing facility on online, 515 HPLC pump, and a Waters 410 differential refractometer. N,N-Dimethylformamide (DMF) was used as the eluent at flow rate of 0.8 mL/min, and analysis time per sample was 40 min. A bank of two Styragel columns, HR 4E, and HR 5E (dimensions 7.8 mm × 300 mm), both with a mixed-bed pore size (50 Å to 1.0 × 10^6 Å), and particle size 3 and 5 μm was used. The temperature of the columns was controlled at 50 °C by the thermostat.

The GPC was used on line with the following multidetector system supplied by Wyatt Technology Co. (Santa Barbara, CA): a multiangle light scattering (MALS) Dawn EOS photometer, with a wavelength of 690 nm. The calibration constant was 8.457 × 10^{-6} Vcm^{-1} and Rayleigh factor of 9.78 × 10^{-5} cm^{-1}. The normalization of the photodiodes was performed by measuring the scattering intensity of PSt 3.0 × 10^4 and 2.0 × 10^5 g/mol in DMF, with value (dn/dc) = 0.159 mL/g, assuming isotropic scattering. ViscoStar viscometer detectors for measuring the differential pressure in a four-capillary bridge, the dimensions of the capillary tube are 0.010 in. internal diameter and 26 in. length. An interferometer refractometer detector (Optilab rEX) as a concentration detector, with wavelength of the equipment is 685 nm.

The refractive index increment (dn/dc) value is measured using the calibrated differential refractive index (DRI) detector OptiLab rEX. Six different concentrations of polymer solution (sample), in a range of 0.1 to 6.0 mg/mL were prepared and injected at 35 °C. The obtained dn/dc value was 0.2456 mL/g. The precision error on the dn/dc value,

when calculated from the DRI detector response, is about ±0.0005 mL/g. A workstation was used to empower the following software: ASTRA V for Windows (Wyatt Technology, version 5.3.2.10)

4.2. Materials. All starting materials were obtained from Aldrich. Biphenyl was used as received. Methylene chloride, TFA, biphenyl, and 1,1,1-trifluoroacetone were distilled, and isatin was purified by recrystallization with charcoal from ethanol. TFSA was distilled prior to use.

4.3. Polymer syntheses. As an example, in a typical synthesis to produce poly[[1,1′-biphenyl]-4,4′-diyl[1-(trifluoromethyl)-ethylidene]] (polymer **5**), a 10 mL flask equipped with a mechanical stirrer was charged with trifluoroacetone (0.504 g, 4.49 mmol), biphenyl (0.6936 g, 4.49 mmol), and methylene chloride (3.3 mL). The solution was cooled to 5 °C, and TFSA (3.3 mL) was added in one portion to the solution and the reaction mixture was stirred for 30 min. Thereafter, the temperature was raised to 20 °C over 1 h and reaction was continued at this temperature for 25 h. The resulting dark-brown, gel-like mass was then shredded and poured slowly into methanol. The precipitated, white solid was filtered, extracted with methanol and dried in air overnight and at 100 °C under vacuum. The resulting pure white fibrous polymer (**5**) reprecipitated from NMP into methanol, extracted with refluxing methanol and dried (0.971 g, 87% yield) had an inherent viscosity of 2.57 dL/g . Molecular weights M_w and M_n were found to be 1 180 000 and 580 800 Da, respectively.

Preparation of Poly[(2,3-dihydro-2-oxo-1H-indole-3,3-diyl)[1,1′-biphenyl]-4,4′-diyl] (9) (Table 1, Entry 2). A typical example of polymer preparation is as follows. TFSA (1.8 mL) was added to a mixture of isatin (0.0728 g, 0.495 mmol) and biphenyl (0.0694 g, 0.45 mmol) in TFA acid (1.2 mL). The reaction mixture was stirred at room temperature for 10 h and precipitated into methanol. The nearly white fiber formed was filtered off and washed with hot methanol. After drying, 0.1269 g (99.6%) of white, fiber-like polymer (**9**) was obtained. The inherent viscosity η_{inh} of the polymer was found to be 2.37 dL g^{-1} at 25 °C. Molecular weights M_w and M_n were found to be 770 840 and 670 000 Da, respectively.

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Notes
The authors declare no competing financial interest.

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