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Electroactive and Photoactive Poly[Isoindigo-*alt*-EDOT] Synthesized Using Direct (Hetero)Arylation Polymerization in Batch and in Continuous Flow

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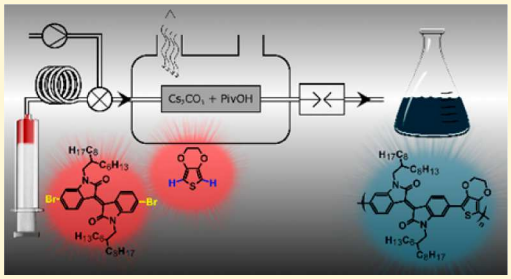
Supporting Information

ABSTRACT: In this work, a combined approach was used to obtain a low-cost material for organic electronics by focusing on inexpensive monomers, short synthetic pathway, high-yielding polymerization method, low waste, and easy scalability. To achieve this, a new material, poly[isoindigo-*alt*-3,4-ethylenedioxythiophene], was synthesized using direct (hetero)arylation polymerization (DHAP). Only a few synthetic steps are required to obtain this material, and no organometallic intermediates are used. In order to make a bigger step toward a truly inexpensive technology, continuous flow methods were applied for the first time to DHAP. This method helped solving a common problem encountered in conjugated polymers synthesis, namely, batch-to-batch variations. Electronic properties of this polymeric material were evaluated using field effect transistors ($\mu_h = 7 \times 10^{-3}$ cm^2·V^{-1}·s^{-1}) and solar cells (η = 3.0%).



Organic semiconductors are often presented as a novel alternative for the large-scale production of flexible, thin, and low-cost electronic devices. In this field, conjugated polymers play an important role as they allow the formation of high-performance devices for both organic field effect transistors (OFET) and organic photovoltaic devices (OPV) while presenting good stability and easy solution processability. Hole mobilities[1−3] over 10 cm^2·V^{-1}·s^{-1} are now reported for OFET and power conversion efficiencies over 10% are possible with OPV.[4,5] Such high performances are generally made possible by fine-tuning the polymeric material structure in order to obtain the necessary combination of ideal electronic and morphological properties.

The most efficient polymers up to now incorporate alternating electron-rich and electron-poor moieties in order to create a *push*−*pull* effect, allowing for lower frontier orbital gap materials. Their synthesis is most commonly achieved by copolymerizing two distinct monomeric units. This usually is a shorter and more versatile synthetic route, allowing the exploitation of molecular symmetry to create complex structures in fewer, simpler steps. However, polymerization methods allowing the selective coupling of two aromatic units are limited to a handful of reactions. Kumada- and Negishi-type couplings are used, but they are incompatible with many functional groups. Stille and Suzuki palladium-catalyzed cross-coupling polymerizations are now the most commonly used methods to synthesize conjugated copolymers and are compatible with a wide variety of functional groups.[6] These reactions have often proven high yielding and produce conjugated polymers with high molecular weight but generate stoichiometric amounts of organoboron or organotin waste. In the case of Stille couplings, toxic trialkyltin derivatives are released, rendering this reaction impractical for industrial purposes. Although these reactions work in most situations, there can be some monomers which cannot be functionalized or are very unstable when functionalized with the required reactive end groups.

Developments in organic chemistry can address the issues brought by existing reactions by providing new synthetic tools. This is shown by the recent application of direct arylation reactions to form well-defined conjugated polymers and molecules.[7−13] Several studies now show that materials synthesized this way can successfully be applied to fabricate organic electronic devices.[14−21] This type of reaction forms a C−C bond by coupling an aromatic C−H bond directly with an aromatic C−X (X = Br, I) bond. This allows a more efficient synthesis of conjugated copolymers as it reduces the number of synthetic steps by avoiding at least a borylation or a metalation step. It also reduces waste production and provides better atom economy as the only byproduct is H−X.[22,23] Direct (hetero)-arylation polymerization (DHAP) has also shown great potential to synthesize conjugated copolymers with high yield

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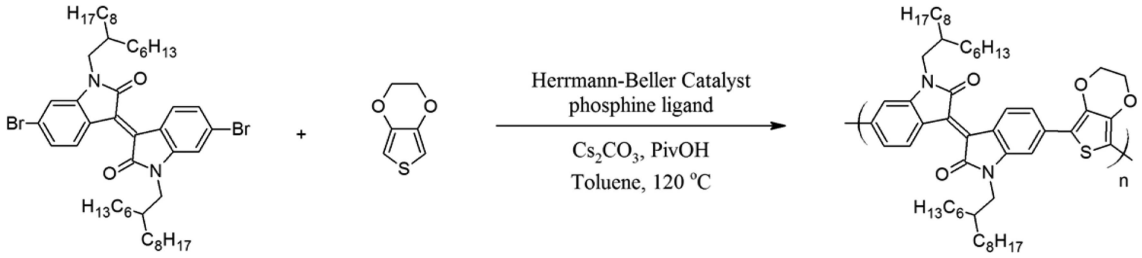
Scheme 1. Synthesis of PiIEDOT



and molecular weight.[13,24,25] Some examples even demonstrated improved molecular weights when compared with traditional synthetic methods,[24−28] and, as was previously highlighted,[29−33] high molecular weights are essential to high-performance materials.

Although an economical reaction yielding high molecular weights is desirable, scalability of the reaction can be an issue. This brings up the often highlighted challenge of conjugated polymer synthesis and also its biggest criticism: reproducibility. Batch-to-batch variation is a common problem with these materials, and trying to scale up the reaction usually proves difficult in this regard. Changes in reaction time, heat transfer of the reactor, agitation of the mixture, and partial solvent evaporation can influence the reaction rate. This necessitates the optimization of reaction conditions when the reaction scale changes. A way to reduce such inconsistencies is to use a method where the reaction conditions are always exactly the same, regardless of the scale. Continuous-flow methods allow such control, using a reactor with fixed reaction conditions.[34−36] The reactants enter and exit the reactor at a controlled rate using a pump. Increase in reaction scale is achieved very simply by using larger amounts of reactant solutions. It is thus possible to obtain greater reproducibility and scalability for target reactions.

Although several studies report polymer synthesis using continuous flow chemistry, only a few showcase the synthesis of conjugated polymers. Grignard metathesis,[37] Rieke,[38] and Suzuki[39] polymerizations were studied with success, but DHAP has never been studied in continuous flow. In this study, a new donor−acceptor polymer was synthesized using DHAP. The commercially available 3,4-ethylenedioxythiophene (EDOT) was used as a strong electron-donating moiety, which has shown great potential to yield low band gap polymers when copolymerized with electron-accepting monomers.[40] This monomer has also proven to be quite reactive in DHAP, yielding high-molecular-weight polymers.[41−45] Isoindigo (iI) was used in conjunction with EDOT. This electron-accepting unit has already proven its usefulness in OPV, with power conversion efficiencies over 7% achievable.[46−48] OFET devices are also promising with very high hole mobility in excess of 2 $cm^2 \cdot V^{-1} \cdot s^{-1}$ reported.[49,50] Furthermore, successful examples of DHAP on iI are already described in the literature,[27,51,52] and a iI and EDOT copolymer has already shown good air stability when applied to fabricate nonvolatile memory devices.[53]

In this work, a combined approach was used where the reaction conditions were optimized in order to obtain a polymerization method usable in continuous flow. Following this, continuous-flow synthesis was achieved by using a stationary phase containing the reagents insoluble in the reaction solvent. Hole mobility of the resulting polymer, poly[isoindigo-*alt*-EDOT] (PiIEDOT), was measured using OFET devices fabricated by direct solution processing. This polymer was also used in conjunction with phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) in order to make bulk heterojunction solar cells. Atomic force microscopy (AFM) was used to correlate solar cell performance with nanoscale phase separation induced by processing additives.

■ RESULTS

Synthesis of the Monomer. Isoindigo is easy to synthesize and can be obtained using the simple two-step synthesis first published by Reynolds et al.[54] in conjunction with a slightly altered purification method.[27] A simple condensation in acid conditions of 6-bromooxindole and 6-bromoisatin, followed by an alkylation in DMF at high temperature, affords the brominated monomer in good yield, ready to be used in DHAP. EDOT, on the other hand, was bought directly from Sigma-Aldrich and was purified using column chromatography on silica using a 1:2 mixture of dichloromethane and hexanes as the eluent.

Synthesis of the Polymers in Batch. The polymer PiIEDOT (see Scheme 1) was synthesized using direct (hetero)arylation polymerization (DHAP) methods. A brief optimization of reaction conditions was done in order to obtain high-molecular-weight PiIEDOT. Additional considerations taken into account are the limitations of continuous flow methods. The flow chemistry system used in this work, a Vaportec R2+R4 unit (see Supporting Information (SI) for details), pushes the reagent solutions using HPLC pumps that do not tolerate solid particles. A major problem with this is that the most efficient DHAP methods published to-date use bases such as carbonates, carboxylate salts and alkoxides. Such bases are usually soluble in the reaction mixture if polar solvents such as water, *N*,*N*-dimethylformamide, or dimethyl sulfoxide are used. Yet, these are usually poor solvents for conjugated polymers and monomers, resulting in lower molecular weights or heterogeneous solutions with partially solubilized monomers. On the other hand, solvents such as tetrahydrofuran and toluene offer excellent solubility of the polymers at high temperature, but they are poor solvents for bases commonly used in DHAP. The resulting heterogeneous reaction mixtures are impossible to pump in a continuous flow reactor. However, this insolubility can also be exploited. For example, this allows the use of a stationary phase containing the base and a mobile phase containing the rest of the reactants.

For these reasons, batch polymerization methods in toluene were studied. Using reaction conditions based on previously reported publications,[24,25] PiIEDOT was synthesized using the Herrmann−Beller catalyst[55] with cesium carbonate as the base and pivalic acid (PivOH) as the additive (see Scheme 1).

Three different ligands were tested: $PCy_3 \cdot HBF_4$, $P(t\text{-}Bu)_3 \cdot HBF_4$ and $P(o\text{-anysil})_3$. The $P(o\text{-anysil})_3$ ligand allowed the

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formation of the highest-molecular-weight material (see Table 1, entries 1 to 3). After Soxhlet extractions with acetone and hexanes, a polymer with a number-average molecular weight (M_n) of 93 kg/mol and a weight-average molecular weight (M_w) of 210 kg/mol, soluble in chloroform, was obtained. A very small amount of material was found insoluble in hot chloroform. Nonetheless, isolated yield was very high at 95%. In total, 80% of the initial monomer mass was converted to isolated polymer, with HBr being the main byproduct. Molecular weights were obtained from high-temperature (110 °C) size-exclusion chromatography (SEC) in 1,2,4-trichlorobenzene.

Table 1. Optimization of DHAP Conditions for PiIEDOT

entry	ligand	reaction time (h)	M_n (kg/mol)	M_w (kg/mol)	PD	yield (%)
1	PCy_3 HBF_4	24	19	41	2.2	63
2	P(*t*-Bu)$_3$ HBF_4	24	7	14	2.0	61
3	P(*o*-anysil)$_3$	24	93	210	2.3	95

A study was conducted in order to determine molecular weights obtained with PiIEDOT as a function of polymerization time. For this study, optimal reaction conditions determined earlier were used. Polymerizations were started simultaneously and stopped every 30 min, with a control experiment stopped after 24 h. They were then precipitated in methanol, filtered, and extracted. Acetone was used to remove monomers, inorganic materials, and catalytic impurities. The polymer was then extracted directly with chloroform without removing small molecular weight material beforehand.

Results shown in Figure 1 demonstrate that molecular weight increases rapidly until a molecular weight plateau is reached after 4 h. After that time, significant batch-to-batch variation occurs. During initial optimization, several samples polymerized for 22 h showed molecular weights ranging from $M_n \approx 80$ to 100 kg/mol and $M_w \approx 200$ to 350 kg/mol. It seems that once this reaction time is reached, the reaction stops because the polymer solubility decreases to the point it forms a gel with the reaction solvent. This gel shows great cohesive strength and is almost insoluble in boiling chloroform, though the material swells a lot and becomes soft. When such insoluble materials are obtained, previous publications and reviews on DHAP usually blamed cross-linking of the material.[56] However, the high-molecular-weight material obtained in this work can be completely solubilized in 1,2-dichlorobenzene (*o*-DCB) at 100 °C. In fact, it is necessary to do so before any further processing is done. After precipitation of the polymer from *o*-DCB using methanol, the material obtained can then be solubilized using boiling chloroform. This gel formation can cause problems when scaling up reactions as it slows or stops the agitation of the reaction mixture. Being a heterogeneous reaction, it is possible that the base could be trapped in the polymer gel, thus stopping or slowing the polymerization prematurely. This would in turn cause a broadening of the mass distribution of the polymer at larger reaction scales. Fortunately, using a continuous flow method can render such problems irrelevant. However, special care must be taken in controlling the reaction parameters rigorously to avoid blockage of the reactor.

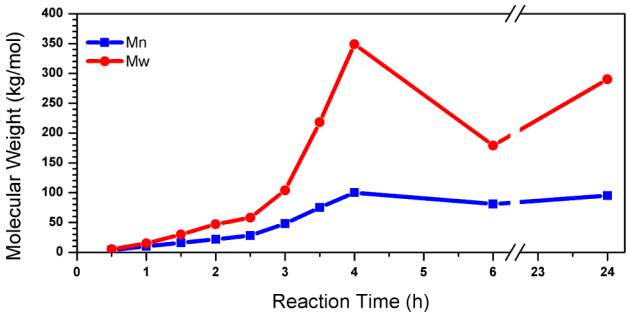

Figure 1. Molecular weight of PiIEDOT as a function of polymerization time.

Synthesis of the Polymers in Continuous Flow. With optimal batch conditions determined, an attempt was made to synthesize PiIEDOT in continuous flow. A benchtop vaportec R4+R2 unit was used to perform these tests (see SI for detailed setup). The polymerization conditions used mimicked as closely as possible the flask conditions. However, the HPLC pumps in the Vaportec unit preclude the use of solids in suspension, in our case, cesium carbonate in toluene. For this reason, we used column reactors filled with cesium carbonate dispersed in diatomaceous earth (Celite(TM) 545 Filter Aid). The monomers, catalyst, additive, and ligand were solubilized in anhydrous, degassed toluene before being injected in the flow reactor's injection loop under anaerobic conditions (Figure 2).

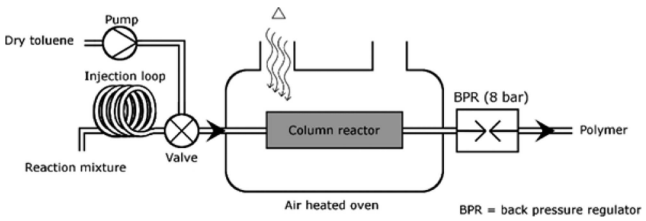

Figure 2. Continuous flow synthesis of PiIEDOT.

The reaction conditions and packing procedure of the reactor are described in details in the electronic SI. When the reaction mixture flowed through the reactor, the polymerization only proceeded on the very first few millimeters of the column, yielding only oligomers. This indicates that the pivalic acid, when deprotonated by cesium carbonate, was insoluble in toluene. As a result, effective polymerization time was extremely short. To solve this problem, the packing material was modified. A mixture of 0.3 equiv of PivOH with 2.3 equiv of Cs_2CO_3 was heated at 140 °C for 2 h. As a result, the pivalic acid melted and was instantly deprotonated by the cesium carbonate. The mixture is then crushed into a fine powder and mixed with diatomaceous earth. Following this modification to the column packing, the reaction proceeded all through the reactor.

As the reaction path in the reactor is quite small (1 cm in diameter by 5−6 cm long), polymerization time was very short. Even by reducing the flow rate to 0.06 mL/min, which was the minimum rate the pump could handle in our case, the residence time was only about 25 min. This resulted in limited molecular weight of M_n = 21 kg/mol (see Table 2). An additional column reactor was added in series and a total reaction time of approximately 60 min was obtained. It is important to note that the polymer spends a small amount of time in a connecting tube linking the two reactors, meaning that actual reaction time is probably closer to 50 or 55 min. Nevertheless, molecular weights increased and a M_n of 33 kg/mol was obtained. Scaling up of the reaction was done by doubling and quadrupling the

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Table 2. Results of Continuous Flow Polymerizations Depending on the Number of Columns Used and Reaction Scale

entry	number of columns	reaction time (min)	scale[a] (mmol)	M_n (kg/mol)	M_w (kg/mol)	PD	Y[b] (%)
1	1	25	0.2 mmol	21	67	3.2	35
2	2	60	0.2 mmol	33	97	2.9	60
3	2	60	0.4 mmol	30	90	3.0	64
4	2	60	0.8 mmol	34	88	2.6	72
5	2	60	0.2 mmol (triplicate)	38 ± 5	108 ± 10	2.8 ± 0.1	64 ± 2
6	4	>240	0.2 mmol	42	124	3.0	71

[a]Quantity of each monomer. [b]Yield of the chloroform extract only.

reaction scale. Molecular weights were very similar between batches, but a steady increase in yield was observed. By doing bigger batches, the diffusion of the monomers in the column is diminished. When diluted, the polymerization proceeds slowly, if at all, and lower molecular weight material is obtained for the diluted fractions at start and finish of the run. This, in turn, reduces chloroform extract yield for smaller scale reactions.

To verify the reproducibility of this method, three consecutive reactions were performed using two freshly prepared columns. Results were satisfactory, with M_n of 38 ± 5 kg/mol and M_w of 108 ± 10 kg/mol obtained, a very reasonable variation between batches considering the precision of the SEC analysis itself (see Table 2, entry 4). An attempt was made to further improve molecular weight. By using a total of four columns connected in series, reaction time could be increased to over 4 h. However, the molecular weight only increased slightly to a M_n of 42 kg/mol. This reaction time was unexpectedly high and is due to the polymer partially adhering to the solid phase. This might also explain why molecular weight was limited. As a result, this causes a diffusion of the monomers in the columns, which could limit molecular weights due to the dilution of the reaction mixture. It is also possible that higher molecular weight material partially precipitates in the column when the reaction mixture is concentrated. An evidence of this possibility is that columns are stained with polymer after the polymerization is complete in continuous flow. However, very few polymeric material remain in the column after the run is complete, thus analysis of the trapped polymer is very difficult. We have shown that continuous flow methods can be applied to reproducibly scale up reactions with minimal batch-to-batch variation.

Characterization of the Polymers. The optical and electronic properties of PiIEDOT were measured using UV−vis spectroscopy and cyclic voltammetry. UV−vis absorption spectra were obtained both in chloroform solution and as a thin film on glass substrate. The resulting UV−vis spectra of a high-molecular-weight sample (M_n = 90 kg/mol, M_w = 260 kg/mol) are shown in Figure 3a. In thin film, PiIEDOT showed a strong absorption with a maximum at 735 nm with a well-defined shoulder peak at 675 nm. The optical HOMO−LUMO gap of this material was calculated using the absorption onset in thin film. PiIEDOT has a reduced frontier orbital gap of 1.55 eV, identical to what was reported by Reynolds's group[57] in 2010 for a very similar copolymer of isoindigo and propylene-3,4-dioxythiophene. It is notably lower than the 1.68 eV HOMO−LUMO gap exhibited by the analogous poly-[isoindigo-*alt*-3,4-ethylenedithiathiophene] previously reported by Yang's group.[58] High-molecular-weight PiIEDOT did not show any frontier orbital gap shift when in solution in chloroform, though band maxima were slightly red-shifted (see Figure 3a).

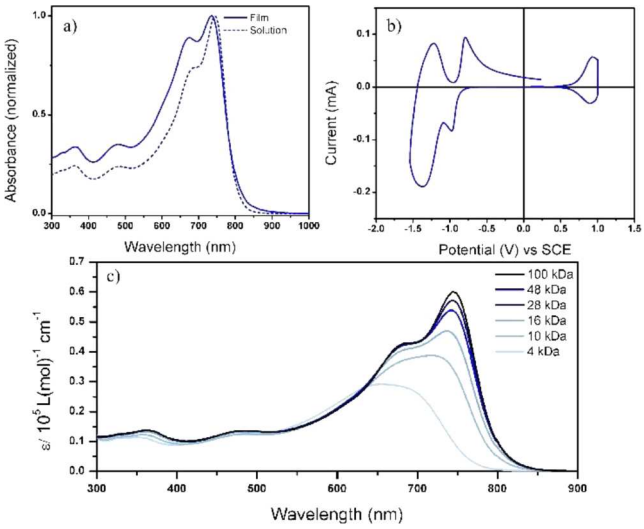

Figure 3. (a) UV−vis absorption spectra of PiIEDOT both in thin film and in solution in chloroform. (b) Cyclic voltammetry performed on PiIEDOT. (c) Extinction coefficients of batches having various molecular weights (M_n) of PiIEDOT in solution in chloroform (moles calculated using the repeat unit).

The effect of molecular weight on the extinction coefficient of PiIEDOT in solution in chloroform was studied using the materials obtained with various polymerization times. As shown in Figure 3c, the absorption edge changes significantly from 767 to 802 nm for samples between 4 kg/mol and 28 kg/mol. The associated shift in frontier orbital gap is from 1.62 to 1.55 eV. Most striking is the shift in absorption maxima, from 655 to 743 nm, an 88 nm shift. When molecular weight increases beyond 28 kg/mol, the optical properties are mostly saturated, with only the 743 nm peak slowly increasing in intensity, but with no HOMO−LUMO gap or band maximum change. As a result, samples obtained in continuous flow, despite their lower molecular weight, retain most of the optical properties of high-molecular-weight materials obtained in batch.

Cyclic voltammetry of high-molecular-weight (M_n = 90 kg/mol, M_w = 260 kg/mol) PiIEDOT was performed by depositing polymer films on platinum electrodes. An electrode of Ag/Ag^+ (0.1 M of $AgNO_3$ in acetonitrile) was used as a pseudoreference electrode. This Ag/Ag^+ pseudoreference electrode, whose potential can vary slightly with age, was calibrated against the ferrocene−ferrocenium redox couple using a saturated calomel electrode (SCE). The resulting voltammogram, presented versus SCE, is shown in Figure 3b. Energy levels were estimated using the onsets of the reduction (LUMO level) and oxidation (HOMO level) peaks, assuming that SCE electrode is −4.70 eV from vacuum.[59,60] The reduction and oxidation onsets were respectively of −0.76 and 0.64 eV vs SCE. Calculated LUMO and HOMO energy

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levels are −3.94 eV and −5.34 eV. Both the first oxidation and reduction processes show a high degree of reversibility (see Figure S1 in the SI), and it is possible to observe a second well-defined reduction peak.

Organic Field Effect Transistor Performance. To evaluate the carrier mobility of the polymer, organic field-effect transistors (OFET) were fabricated using high-molecular-weight (M_n = 90 kg/mol, M_w = 260 kg/mol) PiIEDOT. Top contact OFETs were fabricated on pretreated SiO_2/Si substrates as described in the SI. Typical transfer and output curves for PiIEDOT are shown in Figure 4. Best results were

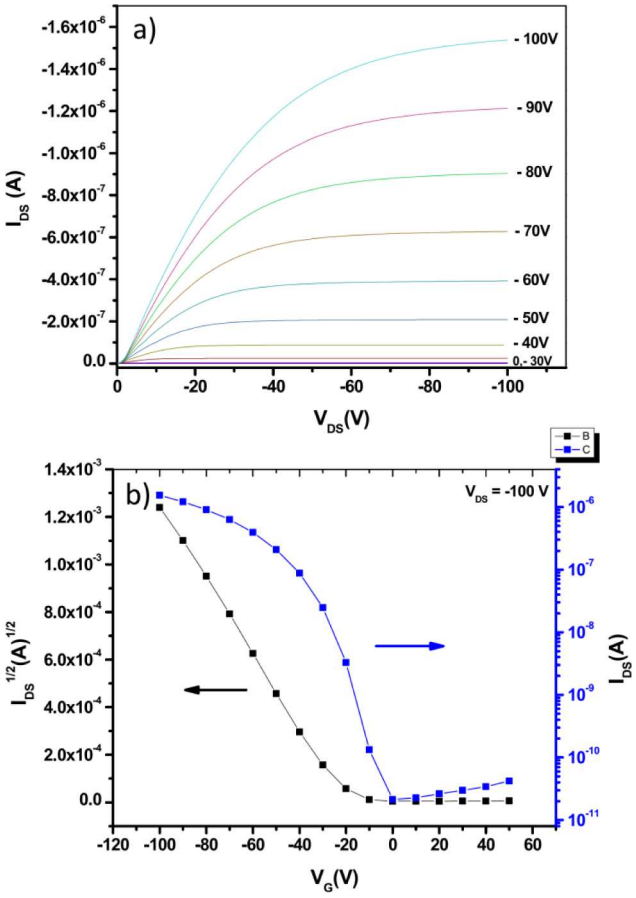

Figure 4. OFET characteristics of PiIEDOT measured in air: (a) output curves taken at different gate voltage; (b) transfer curve displaying the saturation regime for V_{DS} = −100 V.

obtained by treating the surface of the Si/SiO_2 with octyltriclorosilane (OTS) and annealing the films at 150 °C for 30 min (see Table S1 in the SI). A mobility of $\mu_h = 7.0 \times 10^{-3}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$ with an On/Off ratio of 9×10^3 was obtained.

OFET performances measurements were also performed using flask and flow samples with similar molecular weights of M_n = 48 kg/mol and M_n = 42 kg/mol, respectively. The obtained results are very similar, with hole mobilities about 2×10^{-3} $cm^2 \cdot V^{-1} \cdot s^{-1}$, independently of the synthetic method. The observations are also consistent with our expectations, with slightly decreased performances for lower molecular weight samples.[30,31] However, hole mobilities of all polymers are still of the same order of magnitude.

Organic Photovoltaic Performance. The energy levels of PiIEDOT are near ideal for organic solar cells, with a LUMO level 0.3−0.4 eV above that of phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$)[61]. The reduced HOMO−LUMO gap of 1.55 eV is also ideal to obtain efficient single junction solar cells. In order to investigate the potential of this polymer in solar cell applications, bulk heterojunction (BHJ) solar cells were fabricated using a conventional device architecture with a structure of ITO/PEDOT:PSS/PiIEDOT:$PC_{71}BM$/BCP/Al (see SI for more details). The active area of each solar-cell device was 1.0 cm^2 with an active layer thickness of 85 ± 5 nm. A high-molecular-weight sample synthesized using flask conditions was first studied (M_n = 90 kg/mol, M_w = 260 kg/mol). The active layer was deposited by spin-coating a polymer/$PC_{71}BM$ blend (weight ratio 1:2) from *o*-DCB with and without processing additives. The *J*−*V* curves and EQE spectra obtained are shown in Figure 5a,b, respectively. The electrical parameters are summarized in Table 3.

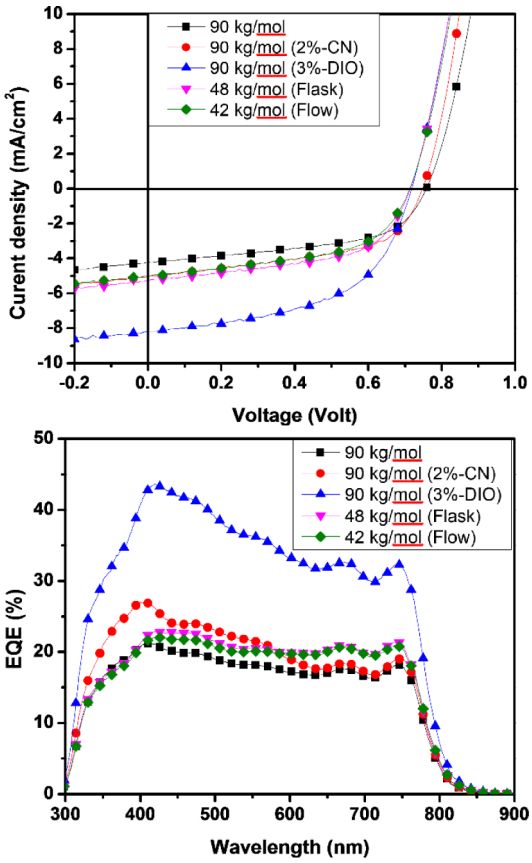

Figure 5. (a) Photovoltaic *J*−*V* characteristics of PiIEDOT: $PC_{71}BM$ BHJ solar cells made using different molecular weights without and with processing additives (2%CN or 3%DIO) (b) Corresponding EQE for each solar cells.

When using the additives 1-chloronaphtalene (CN, 2 vol %) or 1,8-diiodooctane (DIO, 3 vol %), a significant improvement of the PCE, up to 3.0%, was observed with an EQE up to 45%. This increase is mainly due to an improved J_{sc}, with little change to the V_{oc} and FF. To further investigate the effect of the additives, the topography of the active layer was analyzed by AFM (see Figure S3 in the SI). The BHJ film realized with *o*-DCB as solvent is composed of large isolated domains, hundreds of nanometers in size, which can explain the lower current and performances obtained. The topography of BHJ films deposited with CN and DIO additives show inter-connected domains and a much smaller nanoscale phase

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Table 3. Electrical Parameters of PiIEDOT:$PC_{70}BM$ BHJ OPV Devices Fabricated Using Different Solvent Conditions and Mean PCEs Obtained

sample molecular weight (M_n)	processing additive	J_{sc} (J–V) (mA·cm^{-2})	J_{sc} (EQE) (mA·cm^{-2})	V_{oc} (V)	FF (%)	PCE (J–V) (%)
90 kg/mol (flask sample)	---	4.2	4.7	0.76	54	1.56 ± 0.19
90 kg/mol (flask sample)	2 vol % CN	5.0	5.4	0.74	54	1.54 ± 0.37
90 kg/mol (flask sample)	3 vol % of DIO	8.2	9.1	0.71	54	3.00 ± 0.16
48 kg/mol (flask sample)	3 vol % of DIO	5.3	5.4	0.71	55	1.74 ± 0.22
42 kg/mol (flow sample)	3 vol % of DIO	5.0	5.2	0.71	54	1.80 ± 0.12

separation, which correlates well with the increased J_{sc} and PCE of the devices.

The efficiency of materials synthesized in flask and in flow was also compared. The devices were realized using the same conditions and layer thicknesses (85 ± 5 nm) as were used for the high-molecular-weight sample. Materials with molecular weights as close as possible were used. PiIEDOT synthesized in flask with a M_n of 48 kg/mol and M_w of 104 kg/mol (Figure 1, 3 h polymerization time) was compared with a material synthesized using flow methods with a M_n of 42 kg/mol and M_w of 124 kg/mol (Table 2, entry 6). Solar cell efficiencies for the two samples are comparable, with PCE of 1.74 and 1.80%, respectively. The V_{oc} and FF of these samples are nearly identical to the high-molecular-weight material, but a reduction in J_{sc} results in lower efficiencies. This reduction in photocurrent generation is commonly reported for lower molecular weights materials.[30,32,33] AFM studies of the active layers show very similar morphology organization between all samples using the DIO additive, regardless of the molecular weights tested. This could explain the similarity of the V_{oc} and the FF between all samples. We thus conclude that materials obtained using continuous flow methods are similar to those obtained in flask conditions, as long as molecular weights are similar.

■ CONCLUSION

In summary, isoindigo and 3,4-ethylenedioxythiophene, two inexpensive monomers, were copolymerized using direct (hetero)arylation methods in high yield and molecular weight (M_n = 93 kg/mol). However, reproducibility of these reactions in flask is not ideal. To solve these issues, we demonstrated for the first time the utilization of continuous flow methods to synthesize conjugated polymers by direct (hetero)arylation. A column reactor was used with a stationary phase comprised of the nonsoluble reagents necessary to perform the polymerization. As a result, reproducibility and scalability of the method was improved. However, molecular weights were limited to M_n = 42 kg/mol.

Samples with similar molecular weights made using flask or continuous flow methods were also compared. Results from both transistors and solar cells were consistent between samples having the same molecular weights. This demonstrates the usefulness of continuous flow methods to synthesize conjugated polymers using direct arylation polymerization in a reliable and scalable manner.

■ ASSOCIATED CONTENT

Supporting Information

Detailed polymerization methods, characterization details, device fabrication, figures S1 and S2, Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

DHAP, direct (hetero)arylation polymerization; o-DCB, 1,2-dichlorobenzene; SEC, size-exclusion chromatography; OFET, organic field-effect transistor; OPV, organic photovoltaic; M_n, number-average molecular weight; M_w, weight-average molecular weight; PD, polydispersity; Y, Yield; V_{DS}, Voltage drain to source; V_{th}, threshold voltage; J_{sc}, short-circuit current; V_{oc}, open circuit voltage; FF, fill factor; PCE, power conversion efficiency; EQE, external quantum efficiency; V_g, gate voltage; OTS, octadecyltrichlorosilane; DIO, 1,8-diiodooctane; CN, 1-chloronaphtalene; PiIEDOT, poly[isoindigo-*alt*-3,4-ethylenedioxythiophene]; $PC_{71}BM$, phenyl-C_{71}-butyric acid methyl ester; BHJ, bulk heterojunction; μ_h, hole mobility; AFM, atomic force microscopy; SCE, saturated calomel electrode; iI, isoindigo; EDOT, ethylene-3,4-dioxythiophene

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