Green Solvent Processed Amide-Functionalized Conjugated Polymers Prepared via Direct Arylation Polymerization (DArP)

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ABSTRACT: Organic electroactive materials that can be processed using simple-alcohols, such as ethanol and 1-butanol, are highly desired, since these solvents can be sourced from biomass and present lower hazards for human and environmental health. Herein, we report the first class of poly (3-alkylamidethiophenes) (P3AAT) synthesized via the sustainable method of direct arylation polymerization (DArP) that can be processed using green, sustainable solvents. The unprecedented synthesis of P3AAT reveals the superiority of DArP, as P3AAT can be readily prepared in only three simple steps with M_n up to 15.4 kDa and yields up to 90% exclusively with this methodology. The tertiary amide, poly(N-hexyl-N-methylthiophene-3-carboxamide-2,5-diyl) (P1) has excellent solubility in the green solvents ethanol, 1-butanol, and anisole. Processing of P1 in 1-butanol is shown to provide comparable SCLC hole mobility versus dichlorobenzene and commensurate photophysical properties. Also, the secondary amide, poly(N-(2-ethylhexyl)thiophene-3-carboxamide-2,5-diyl) (P2) was

successfully synthesized, demonstrating excellent functional-group-tolerance for DArP, while showing hydrogen bonding features and similar SCLC hole mobility as P1. This study provides a facile synthetic strategy for a novel structural motif that can be processed in sustainable solvents without a compromise in performance, which can easily be extended to other valuable areas of organic electronics and bioelectronic.

Conjugated polymers have emerged as promising low-cost, non-toxic materials compared to their inorganic counterparts for applications such as organic photovoltaics (OPVs), organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), chemical sensors, bioelectronics, and biological cell imaging.[1–6] However, solution processing of conjugated polymers often requires the use of highly toxic, carcinogenic halogenated solvents such as chloroform, and 1,2-dichlorobenzene (DCB). Aside from water, as shown in Figure 1, the best choice for green solvents for processing conjugated polymers are simple alcohols, such as ethanol and 1-butanol, or anisole, which can be sourced from biomass.[7] Typically, it has been thought that ionic or highly polar terminal groups such as ammonium, sulfonate, phosphonate (class 1), or functional side chains such as oligo(ethylene glycol) (class 2) need to be incorporated to enhance solubilities of conjugated polymers in green solvents.[8–11] The introduction of these ionic/ polar terminal groups on the side chains were found to be detrimental to the performances of devices and also significantly complicated monomer synthesis.[9,10]

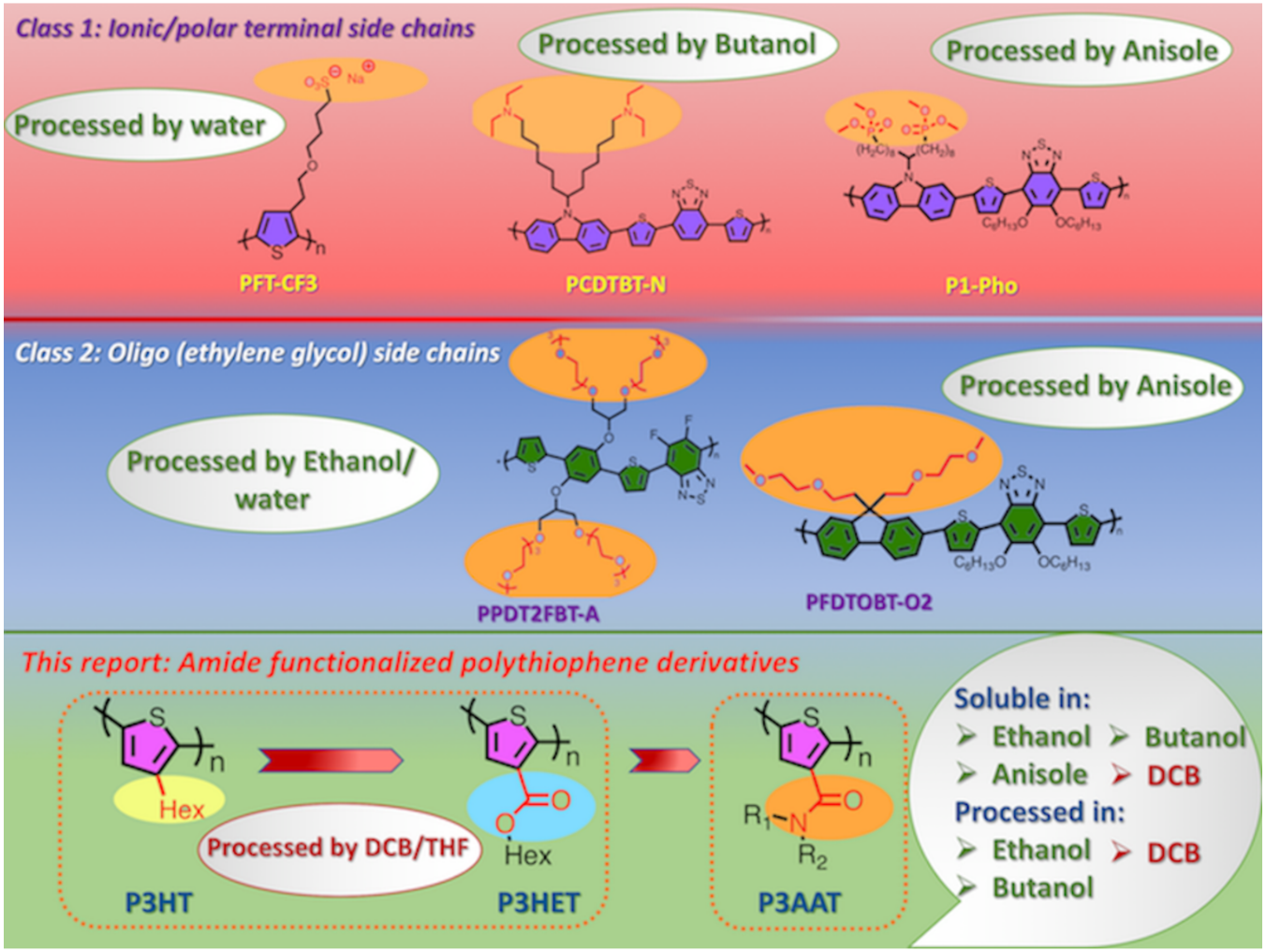


Figure 1. Summary of different approaches towards green solvent processing of conjugated polymers.

Poly(alkylthiophenes) (P3AT) and related analogs are a class of conjugated polymers that attract great interest, due to their relative ease of synthesis, desirable electronic properties, and highly modular functionalization.[12–14] For example, polythiophenes with a tethered amide functional group have been electrochemically polymerized for applications as biological DNA binders and sensors.[15,16] In an effort to simplify the structures of conjugated polymers capable of green solvent processing, we were emboldened to devise a simple, scalable monomer, and developed the amide functionalized polythiophenes, poly(N-hexyl-N-methylthiophene-3-carboxamide-2,5-diyl) (P1) and poly(N-(2-ethylhexyl)thiophene-3-carboxamide-2,5-diyl) (P2), depicted in Figure 1 and Scheme 1. It is worth-noting that synthesizing P3AAT via Stille-polymerization requires

extremely challenging (if not impossible) synthesis and purification of the stannyl-monomers. More importantly, for secondary-amide functionalized P2 with an N-H bond, stannylating the monomer using a strong base such as LDA or application of polymerization methods such as Grignard metathesis (GRIM) will react with the secondary amide functional group. Therefore, we concluded that these polymers can only be prepared via direct arylation polymerization (DArP) to target highly regio-regular amide-functionalized polythiophenes, which would provide a streamlined synthetic pathway that does not incorporate any functionalization of monomer and the use of highly toxic alkylstannanes.[17–25] Herein, we report the first conjugated polymer (P1) prepared by DArP that demonstrates green-solvents-solubility and processability, and the first

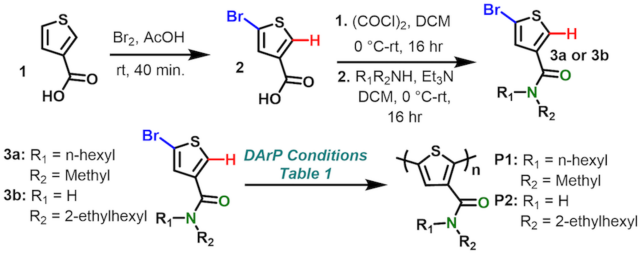
Table 1. DArP conditions and polymerization results.

Entry	Polymer	Solvent[a]	Pd source[b] (Mol%)[b]	Base[c]	Time (h)	M_n (kDa)[d], Đ[d]	Yield[e] (%)
1	P1	THF	Pd_2dba_3 (4)	Cs_2CO_3	16	NP	NP
2	P1	THF	$PdCl_2(PPh_3)_2$ (4)	Cs_2CO_3	16	10.4, 1.7	70
3	P1	CPME	$PdCl_2(PPh_3)_2$ (4)	K_2CO_3	48	8.1, 1.6	76
4	P1	CPME	$PdCl_2(PPh_3)_2$ (4)	Cs_2CO_3	48	8.3, 1.5	85
5	P1	CPME	$PdCl_2(PPh_3)_2$ (6)	Cs_2CO_3	72	15.4, 1.5	77
6	P1	CPME	$Pd(OAc)_2$ (3)	K_2CO_3	24	10.8, 2.0	80
7	P1	CPME	$Pd(OAc)_2$ (5)	K_2CO_3	24	13.5, 1.5	73
8	P2	CPME	$PdCl_2(PPh_3)_2$ (4)	Cs_2CO_3	48	7.9, 1.5	90
9	P2	CPME	$Pd(OAc)_2$ (3)	K_2CO_3	24	11.6, 1.9	53[f]

[a]All polymerizations were conducted with 0.2 M concentration and reaction temperature of 110 °C. [b]For Pd_2dba_3 and $PdCl_2(PPh_3)_2$, tris(o-methoxyphenylphosphine) was used with Pd: ligand ratio of 1:4; For $Pd(OAc)_2$, $P(t\text{-}Bu)_2Me\text{-}HBF_4$ was used with Pd: ligand ratio of 1:2. 0.5 equivalents of neodecanoic acid was used for all polymerizations. [c]1.5 equivalence of base was employed. [d]NP indicates no polymer formation. [e]Determined after purification via Soxhlet extraction. [f]insoluble material was obtained from this polymerization after Soxhlet extraction, which is not included in the calculation for yield.

secondary-amide functionalized conjugated polymer synthesized via DArP (P2) that shows hydrogen bonding, which can be potentially useful for controlling polymer self-assembly and morphorlogy.[26,27] Significantly, this study can be extended via DArP to the synthesis of more complex copolymer structures such as donor-acceptor (D-A) alternating copolymers or random copolymers, providing conjugated polymers with exciting new properties such as green-solvent-processability or hydrogen-bonding.[28,29] This study presents a simple methodology for developing simple, low-cost, easy-to-prepare conjugated polymers, which can be readily synthesized in only three simple steps (Scheme 1) with good M_n, yields, and structural fidelity.

Complete synthetic procedures and characterization for the monomers and polymers can be found in the supporting information (SI). As shown in Table 1, using conditions originally developed by Ozawa and Leclerc, our first attempt for the synthesis of P1 was performed by using Pd_2dba_3 as



Scheme 1. Synthesis of P1 and P2 via DArP.

Pd catalyst source using high-pressure THF (Table 1, Entry 1). [30,31] This did not lead to polymer formation, which suggested that Pd_2dba_3 is not an efficient Pd-catalyst source for this particular monomer. By changing to $PdCl_2(PPh_3)_2$, which has been shown as an efficient catalyst for polythiophene synthesis via DArP, the desired polymer was obtained in good M_n (10.4 kDa) and satisfactory yield (70%) (Entry 2).[32,33] Our previous study investigated the use of sustainable solvent cyclopentyl methyl ether (CPME), which shows great compatibility with DArP.[24]

However, the replacement of THF with CPME reduced the molecular weight to 8.1 kDa, albeit with a slight increase in yield (76%) (Entry 3). Cs_2CO_3 improved M_n (8.3 kDa) and yield (85%) slightly (Entry 4). Increasing $PdCl_2(PPh_3)_2$ catalyst loading to 6 mol%, while prolonging reaction time provided the best molecular weight as it almost doubled the M_n from Entry 4 to 15.4 kDa (Entry 5). As an alternative route, $Pd(OAc)_2$ with a phosphine ligand was demonstrated by Sommer et al. and Wang et al. as an efficient DArP condition, thus, we explored the use of $Pd(OAc)_2$ with $P(tBu)_2Me$-HBF_4 as a ligand (Entry 6).[21,34] We found this reaction condition in CPME to be highly efficient as the polymerization was completed in only 24 hours (due to precipitation of polymer and decomposition of palladium catalyst "palladium black" observed), providing polymer with high M_n (10.8 kDa) and good yield (80%). Increasing the loading of $Pd(OAc)_2$ to 5 mol%, which is the catalyst loading reported by Wang et al., increased the M_n to 13.5 kDa with good yield (73%) (Entry 7).

For the synthesis of P2, application of a condition used for P1 (Entry 3) provided lower M_n polymer (7.9 kDa) (Entry 8), albeit in excellent yield (90%). We were, however, concerned about the use of Cs_2CO_3 as a base, since this has been shown by Buchwald et al. to facilitate aryl-amination reactions, which may lead to defects embedded within the polymer for P2.[35] Although it has been shown in a small molecule study that secondary amides can be preserved in a direct arylation reaction, transcribing to polymerizations still exhibits great synthetic challenges, such as the use of unbalance stoichiometric aryl bromides (2:1 to substrate), and unfavorable solvents for conjugated polymer synthesis (2 wt % SPGS-550-M in water).[36] Unlike small molecule syntheses, even a small degree of side-reaction can result in major defects embedded in the polymer structure, which cannot be removed in a purification (such as Soxhlet extraction) and can be easily evidenced from

^{1}HNMR. In fact, ^{1}H-NMR studies (see SI and discussion below) of this polymer (Entry 8) show impurities in the aliphatic region (Figure S12), which we believe to be resultant of N-arylation of the secondary amide. Therefore, instead of applying the optimal condition for P1 (Entry 5) to the synthesis of P2, we concluded that the reaction condition needed to be altered to improve polymer purity. Employing $Pd(OAc)_2$ with $P(t\text{-}Bu)_2Me\text{-}HBF_4$ as a ligand and K_2CO_3 as a base, provided P2 with a satisfactory M_n (11.6 kDa) and yield (53%) (Entry 9). The decrease in yield (53%) was due to a fraction of insoluble polymer, which is likely due to lower solubility from intramolecular hydrogen bonding as described by previous reports.[26,37,38] Also, the ^{1}H-NMR shows no apparent impurity in the aliphatic region, and N-H resonance (δ 5.82 ppm) remains after polymerization (Figure S13). It is important to note that $CHCl_3$ soluble fraction of P2 (Entry 9) exhibits good

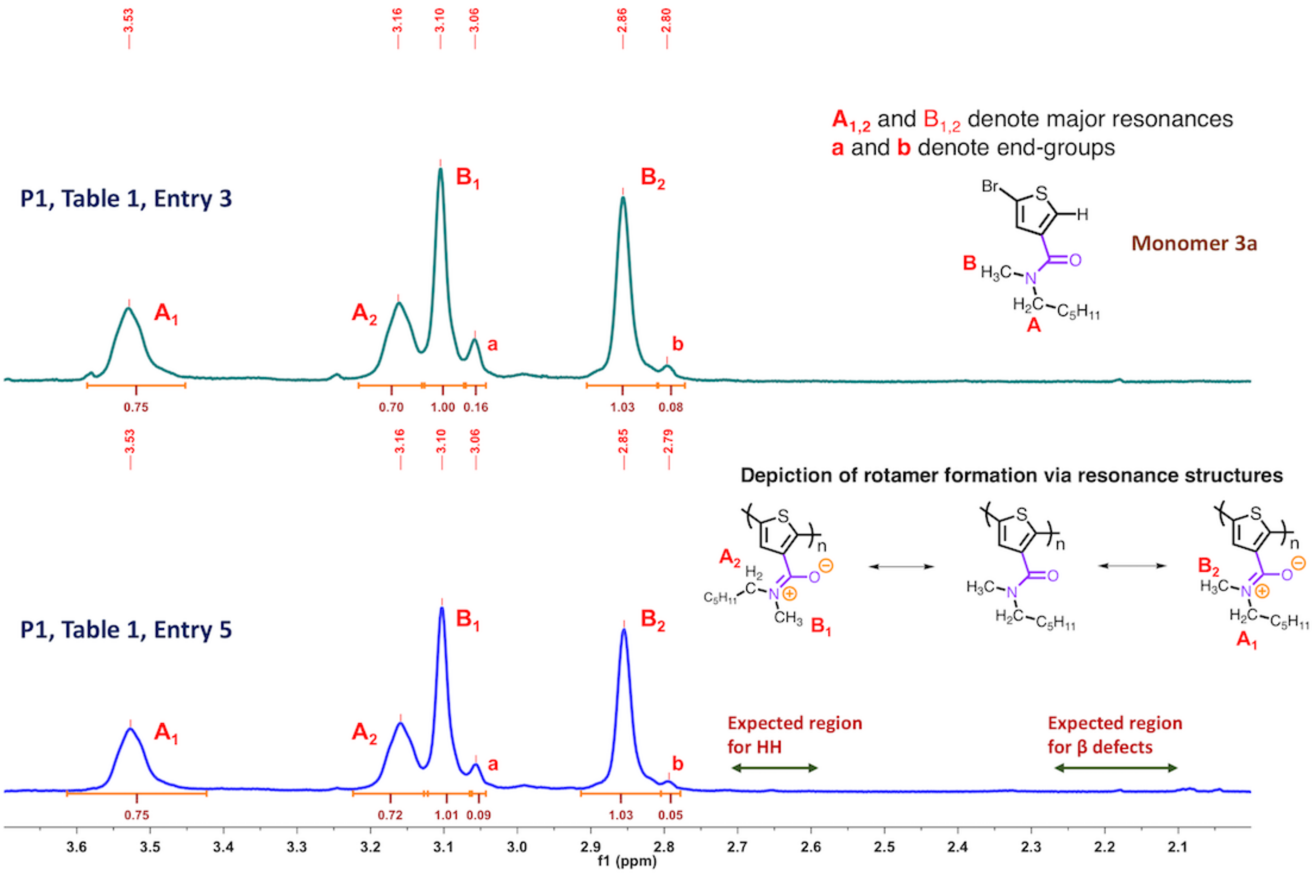


Figure 2. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C) of DArP polymers P1 (Table 1, Entry 3, top) and P1 (Table 1, Entry 5, bottom).

solubility in halogenated organic solvents. The synthesis of P2 marks an unprecedented conjugated polymer synthesis of a homo-polymer containing secondary amide with N-H bonds preserved, exhibiting superior functional group tolerance for these DArP conditions.

To confirm the desired polymer structures for P1 and P2, ^{1}H-NMR analysis was performed (complete polymer NMR spectra provided in the SI, see Figure S6-S18). Regarding the assignments of P1, the spectra shown in Figure 2 depicts that both α-protons adjacent to amide functional group, N-CH_2 (A_1 and A_2) and N-CH_3 (B_1 and B_2) form rotamers, which are observed for alkyl amides, resulting in two distinct singlets for each of the aforementioned protons.[39,40] Specifically, the rotamer resonances attributed to the N-CH_2 in monomer 3a (δ 3.46 and 3.32 ppm, Figure S2), are assigned to the resonances at δ 3.53 and 3.16 ppm in the polymer. A similar pattern was observed for the N-CH_3 (methyl) with monomer 3a at δ 3.03 ppm (Figure S2), the resonances in the corresponding polymer P1 are assigned to B_1 and B_2 at δ = 3.10 ppm and δ = 2.86 ppm (Figure 2). Structural fidelity is critical for polymers composed of unsymmetrical repeat units, since defects can negatively influence the electronic and physical properties of the polymer.[41,42] Previous reports on poly(3-hexylthiophene) (P3HT) and poly(3-hexylesterthiophene) (P3HET) showed that the ratios of head-to-head (HH) and branching (β) defects content can be readily determined from the aliphatic region in ^{1}H-NMR.[30,43] It is well-studied that for P3HT, while the desired head-to-tail (HT) couplings are found δ = 2.82 ppm, HH and β-branching signals are found in the range of δ = 2.56-2.58 ppm and δ = 2.18-2.38 ppm respectively.[44] Similarly, HT coupling of P3HET is detected at δ = 4.30 ppm, with HH coupling shows at δ = 4.13 ppm.[45] Therefore, a similar shift upfield is expected if any HH coupling (~ 0.2 ppm) or β defects (~ 0.6 – 0.8 ppm) are to occur. As shown in Figure 2, P1 exhibits no quantifiable signal of homocoupling or β defects in

the expected regions, indicating a highly regio-regular polymer structure. With regards to end-groups, we observe a correlation between the GPC-M_n and the relative integrations for resonances assigned to a, b with the major resonances (Figure 2). Specifically, we observe a decrease in integration ratio by roughly half the original value when the M_n of P1 nearly doubles from 8.1 kDa (Table 1, Entry 3) to 15.4 kDa (Table 1, Entry 5). A similar trend was observed for other entries as well (see SI for annotated spectra), providing further evidence for a and b as likely end-groups.[46]

To confirm the presence and retention of the N-H bond for P2, FT-IR spectroscopy was obtained (Figure S19), which shows a broad N-H stretch between 3300 cm^{-1} to 3700 cm^{-1}. To confirm the presence of hydrogen bonding, VT-NMR experiments were performed (Figure S14-S17). The ^{1}H-

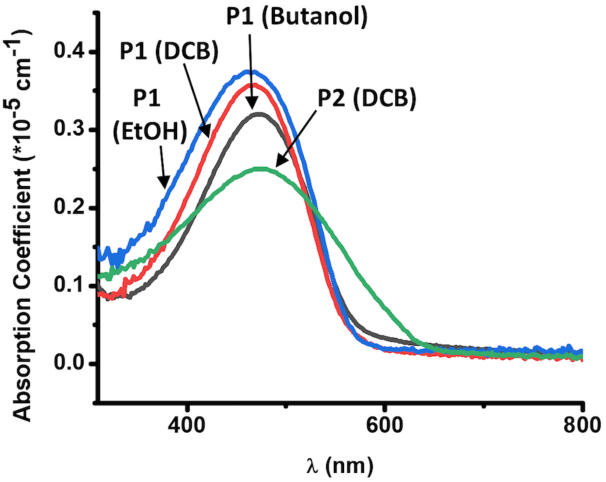


Figure 3. UV-vis absorbance for films of polymers P1 (DCB, ethanol, and butanol) and P2 (DCB). See SI for complete details.

NMR signal of the N-H peak was observed to shift upfield with increasing temperature: δ = 5.82 ppm at T = 348 K, δ = 5.80 ppm at T = 373 K, δ = 5.78 ppm at T = 398 K (Figure S18). The signal intensities of this peak increased significantly upon the elevation of temperature. This observation, previously observed in polymers containing amides or other hydrogen-bonding contents, confirms

the formation of hydrogen bonding in P2.[37,38] Interestingly, the major aromatic peak shifts downfield (δ = 7.50 ppm at T = 348 K; δ = 7.54 ppm at T = 373 K; δ = 7.58 ppm at T = 398 K) as the temperature increases, which is in agreement with previous literature.[38] This can be explained by the reduction of hydrogen-bonding interactions between polymer side chains upon the elevation of temperature,[37,38] thus removing electron density from the aromatic C-H bond and resulting in a deshielding effect. It should be noted that DSC and GIXRD experiments indicate these polymers (P1 and P2) to be fully amorphous, as no T_m, T_c, or diffraction pattern was observed (See Figure S37-S40).

For both P1 and P2 the electrochemical HOMO, UV-vis absorption, and space-charge limited current (SCLC) mobilities were measured (see SI for tabulated data and experimental conditions). Similar to P3HET (-5.98 eV), both P1 (-5.96 eV) and P2 (-5.90 eV) exhibit much deeper HOMO levels compared to P3HT (5.27 eV).[44,45] In addition to DCB, P1 was found to have excellent solubility in the green solvents ethanol, 1-butanol, and anisole (Figure S20), allowing for the formation of thin-films via spin-coating (Figure S21). To better quantify the solubility of P1 in green solvents, the maximum solubilities of P1 with the highest M_n (Table 1, Entry 5, M_n = 15.4 kDa) in green solvents were measured and summarized in Table S1. Outstanding maximum solubility of P1 was found in 1-butanol (18 mg/mL), while ethanol and anisole also gave good solubility results (9 mg/mL for ethanol and 14 mg/mL for anisole). For P1 with an M_n of 10.4 kDa (Table 1, Entry 2), solubility in ethanol was found to be 15 mg/ml and with even lower molecular weight (Table 1, Entry 3, M_n = 8.1 kDa), good solubility in ethanol/water (88:12) of 5 mg/mL was found. However, we found 1-butanol and ethanol provided uniform films, while anisole and ethanol/water mixtures did not (Figure S21). P2 was found to only be soluble in chlorinated

solvents, such as DCB.

UV-Vis absorbance spectroscopy experiments were conducted by spin-casting solutions of P1 and P2 (Figure 3). With regards to optical bandgap, λ_{max}, and absorption coefficient, films of P1 prepared from solutions of ethanol (2.16 eV, 468 nm, and 37.4×10^{-3} cm^{-1}) and 1-butanol (2.18 eV, 471 nm, and 32.1×10^{-3} cm^{-1}) gave similar results to those prepared from DCB (2.18 eV, 468 nm, and 35.7×10^{-3} cm^{-1}). P2 (1.89 eV, 475 nm, and 35.7×10^{-3} cm^{-1}) provided a narrower bandgap, comparable λ_{max}, but lower absorption coefficient than P1, respectively. As previously observed in conjugated polymers containing secondary amides, the decrease in absorption intensity of P2 compared to P1 can be attributed to the disruption of π-stacking and aggregation due to the introduction of hydrogen-bonding side-chain interactions.[37] UV-Vis absorbance spectroscopy data was also collected for P1 and P2 in solution (For P1, DCB, ethanol, and 1-butanol; For P2, DCB). By comparison, both thin-film and solution measurements gave similar UV-Vis spectra and comparable results for λ_{max} (See Figure S22-26, Table S2 for details).

SCLC hole mobility measurements were conducted for P1 and P2, and are provided in Table S3 (see SI for representative J-V curves and fabrication details). The SCLC device architecture was chosen for hole mobility measurements because the same technique is reported for measuring hole mobilities of P3HET and alcohol-processed conjugated polymers have been evaluated via the SCLC device architecture.[11,45] P1 and P2 were found to have similar hole mobilites for films processed from DCB (4.74×10^{-6} and 5.42×10^{-6} cm^2 V^{-1} s^{-1}, repsectively). For P1 in 1-butanol, hole mobilities were found to be comparable (8.48×10^{-6} cm V^{-1} s^{-1}), but working devices could not be obtained using ethanol. Additionally, the μ_{hmax} for P1 processed in 1-butanol (2.74×10^{-5}

$cm^2\ V^{-1}\ s^{-1}$) is comparable to that of P3HET prepared via Stille and processed using DCB ($2.09 \times 10^{-5}\ cm^2\ V^{-1}\ s^{-1}$).[45]

In conclusion, we have developed a sustainable, simple route to novel amide-functionalized conjugated polymers (P1 and P2) with M_n values up to 15.4 kDa and yields up to 90%. This is the first report of amide functionalized polythiophenes (P3AAT) being successfully synthesized via DArP, including a secondary amide, displaying an unprecedented functional group tolerance for DArP. ^{1}H-NMR analysis reveals a highly regio-regular polymer structure of P1, and FT-IR and NMR for P2 indicate the presence of hydrogen bonding. P1 is shown to be the first conjugated polymer prepared via DArP that has good solubility and processability in green-solvents, such as ethanol and 1-butanol, providing similar absorption properties and SCLC mobility results when compared to DCB. P2 is the first conjugated homo-polymer containing a secondary amide ever synthesized, and was found to retain good hole mobility with the introduction of N-H bonds. This study provides a simple pathway for the preparation of conjugated polymers capable of green-solvent-processing and hydrogen bonding, which will provide significant impact in organic electronic and bioelectronic applications. Future work will focus on extending P3AAT homo-polymers to D-A alternating copolymers or random copolymers incorporating a certain percentage of monomers 3a or 3b to obtain desired new properties and effective charge mobilities and crystallinity in conjugated polymers.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures including the synthesis and characterization for all monomers and polymers are included in the supporting information (SI). This material is available free of charge via the internet at http://pubs.acs.org.

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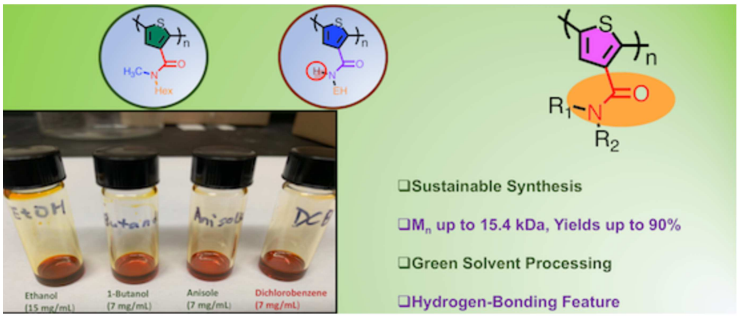
Ethanol
(15 mg/mL)
1-Butanol
(7 mg/mL)
Anisole
(7 mg/mL)
Dichlorobenzene
(7 mg/mL)
❑Sustainable Synthesis
❑M_n up to 15.4 kDa, Yields up to 90%
❑Green Solvent Processing
❑Hydrogen-Bonding Feature