

**“In-Water” Direct Arylation Polymerization (DARp) under
Aerobic Emulsion Conditions**

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COMMUNICATION

“In-Water” Direct Arylation Polymerization (DARp) under Aerobic Emulsion Conditions

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Despite limited reports employing sustainable solvents for Direct Arylation Polymerization (DARp), the large amount of organic waste generated from conjugated polymer synthesis requires attention. Herein, we report the first emulsion-DARp methodology to afford polymers with molecular weights up to 14.5 kg/mol with a 10-fold reduction of organic solvent utilized.

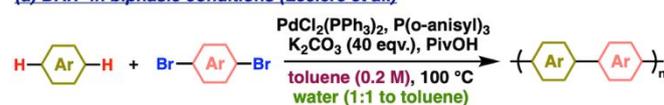
Conjugated polymers are inexpensive, lightweight, flexible semiconducting materials that have drawn considerable attention owing to their excellent processability and attractive optoelectrical properties.¹ Applications for these materials have expanded rapidly in the past decades to which include organic photovoltaics (OPVs), organic light-emitting diodes, organic field-effect transistors (OFETs), chemical sensors, electrochromic devices, batteries, and biological sensors.^{2–8} In recent years, a focus on the industrial-scale production of conjugated polymers to meet the demands for roll-to-roll printed organic electronic devices has grown, demonstrating the promising potential of these materials for commercial applications.^{9–11}

However, the development of well-defined conjugated polymers relies on conventional synthetic methods such as Stille and Suzuki polycondensations, which require multistep preparations of organostannanes or organoboranes using hazardous, pyrophoric reagents and challenging monomer purification processes.^{12,13} Additionally, the generation of stoichiometric quantities of toxic by-products (for instance, highly toxic tin waste in the case of Stille) has led to some to doubt the industrial scalability of these polymerization techniques.¹⁴ In contrast, the emergence of Direct Arylation Polymerization (DARp) has offered a robust, atom-economical synthetic approach for the preparation of conjugated polymers by only generating environmentally-benign by-products (for example, KBr).^{15–19} By accessing directly through a C-H

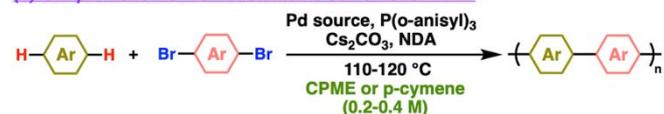
activation pathway, DARp also alleviates the necessity of utilizing organolithium reagents involved in the monomer-functionalization processes in Stille and Suzuki polymerizations.

Despite being recognized as a “greener” approach, most DARp protocols are heavily reliant on toxic, unsustainable organic solvents and therefore generate large quantities of hazardous organic waste in the production of conjugated polymers.²⁰ Recently, Leclerc et al. developed biphasic DARp conditions by introducing an equal-volume water/toluene solvent system, which allows the use of easily-accessible “wet” solvents and reagents (Scheme 1a).²¹ While these DARp conditions are more user-friendly and cost-effective, the sustainability of this protocol remains unimproved, since toxic organic solvents in these reactions are employed in near the usual amount albeit with the addition of water to the reaction mixture. Although recent advances in improving the sustainability of DARp have focused on the employment of renewable, biocompatible green solvents such as cyclopentyl methyl ether (CPME) and p-cymene (Scheme 1b),^{22–26} a new

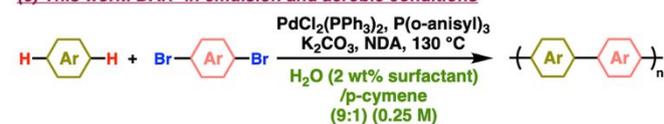
(a) DARp in biphasic conditions (Leclerc et al.)



(b) Our previous work on sustainable solvents for DARp



(c) This work: DARp in emulsion and aerobic conditions



Scheme 1. Development of DARp in water-compatible/sustainable conditions.

DARp methodology that involves a significant reduction in the required quantity of organic solvents is highly attractive.

Recently, Beverina et al. introduced E-factor, a quantitative measure of the ratio of kg of organic waste generated per kg of conjugated polymer synthesized using Suzuki

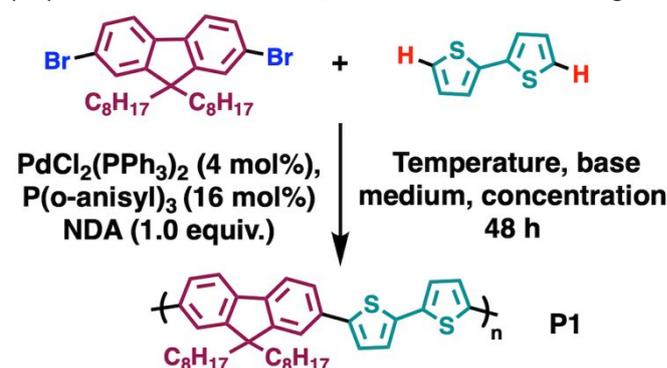
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polymerization.²⁷ By utilizing water as the main reaction medium, along with the use of minimal amount of organic solvent (9:1 water/toluene) and the presence of 2 wt% of surfactant, efficient Suzuki polymerizations were executed in an emulsion under aerobic conditions to afford conjugated polymers with M_n up to 26.9 kg/mol and yields up to 93%. Specifically, in such micro-heterogeneous reaction environments, efficient polymerizations occur in highly concentrated organic domains (known as the “hydrophobic effect”), which allows a significant enhancement in the reaction rates while enabling a 10-fold reduction of the E-factor.²⁸

Such “in-water” synthetic strategies have proven successful for the preparation of various small-molecule organic semiconductors,^{29–32} including a report by Beverina et al. focused on Pd-catalyzed direct arylation reactions between brominated benzenes and thiophene substates containing reactive C-H bonds.³³ Furthermore, the water-compatibility of certain DARp conditions in aromatic solvent (toluene) is showcased in the aforementioned report by Leclerc et al. (Scheme 1a).²¹ Therefore, in this report, we aim to extend these strategies to apply an “oil-in-water” emulsion polymerization method to DARp for the first time (Scheme 1c). By using only 10 vol% of sustainable organic solvent (p-cymene), efficient DARp protocols are carried out in water under aerobic conditions to afford conjugated polymers with good M_n (up to 14.5 kg/mol) and yields (up to 79.2%) with minimal structural defects detected.

Herein, poly(9,9-dioctylfluorene-alt-bithiophene) (P1) was selected as the target polymer for our model study (Scheme 2 and Table 1), since the synthesis of P1 has been explored in

analogous emulsion conditions using a Suzuki polymerization.²⁷ In addition, P1 was afforded with high M_n



Scheme 2. Synthesis of P1 via DARp using emulsion conditions listed in Table 1.

(42.0 kg/mol) and yield (89.2%) via DARp using the sustainable aromatic solvent, p-cymene, in our previous report.²³ Furthermore, the potentially reactive C-H bonds on the β -positions of the 2,2'-bithiophene monomer pose a significant challenge for the preparation of P1 via DARp, which makes this model study an excellent examination of possible defect-formation using the novel DARp protocol in emulsion conditions.^{34,35}

We chose $\text{PdCl}_2(\text{PPh}_3)_2$ (4 mol%) in combination with the ligand $\text{P}(\text{o-anisyl})_3$ (16 mol%) as the catalytic system for the optimization of the synthesis of P1 via DARp in emulsion conditions, since this catalytic system has been demonstrated to be water-compatible in biphasic-DARp conditions as well as being highly-efficient in the sustainable aromatic solvent, p-

Table 1. Optimization for the synthesis of P1 using emulsion conditions depicted in Scheme 2.^a

entry	reaction medium ^b	temperature (°C)	base (equiv.)	concentration (M) ^c	atm	M_n (kg/mol) ^d , Đ ^d	yield ^e (%)
1	H ₂ O	110	Cs ₂ CO ₃ (3.2)	0.25	air	-	-
2	H ₂ O/toluene 9:1	110	Cs ₂ CO ₃ (3.2)	0.25	air	8.8, 1.92	58.8
3	H ₂ O/p-cymene 9:1	110	Cs ₂ CO ₃ (3.2)	0.25	air	10.3, 2.01	63.3
4	H ₂ O/p-cymene 9:1	110	Cs ₂ CO ₃ (3.2)	0.05	air	-	0
5	H ₂ O/p-cymene 9:1	130	Cs ₂ CO ₃ (3.2)	0.25	air	11.9, 3.17	75.4
6	H ₂ O/p-cymene 9:1	130	NaO ^t Bu (3.2)	0.25	air	-	0
7	H ₂ O/p-cymene 9:1	130	K ₂ CO ₃ (3.2)	0.25	air	13.6, 3.03	79.2
8	H ₂ O/p-cymene 9:1	130	K ₂ CO ₃ (3.2)	0.25	N ₂	12.9, 2.63	76.3
9 ^f	H ₂ O/p-cymene 9:1	130	K ₂ CO ₃ (40)	0.25	air	-	0
10	H ₂ O/p-cymene 9:1 (Aliquat 336)	130	K ₂ CO ₃ (3.2)	0.25	air	-	0
11	H ₂ O/p-cymene 9:1 (TBAB)	130	K ₂ CO ₃ (3.2)	0.25	air	7.0, 1.92	59.1
12 ^g	H ₂ O/p-cymene 9:1	130	K ₂ CO ₃ (3.2)	0.25	air	8.7, 2.52	69.1

^aAll polymerizations were conducted using the general conditions shown in Scheme 2, unless otherwise denoted. ^b2 wt% of K-EL (Kolliphor EL) was added to all reaction media as a surfactant. Additives in parenthesis were used in the amount of 0.3 equiv. TBAB, tetrabutylammonium bromide. ^cConcentration of each polymerization was calculated based on the total volume of the reaction medium added. ^dEstimated by GPC (140 °C, 1,2,4-trichlorobenzene) calibrated with polystyrene standards. ^ePolymer products were purified via Soxhlet extraction using MeOH, hexanes, and collected by CHCl₃. ^fThis polymerization was not performed due to the breakage of the emulsion. ^g1 mol% of Pd(PPh₃)₂Cl₂ and 4 mol% of P(o-anisyl)₃ were added.

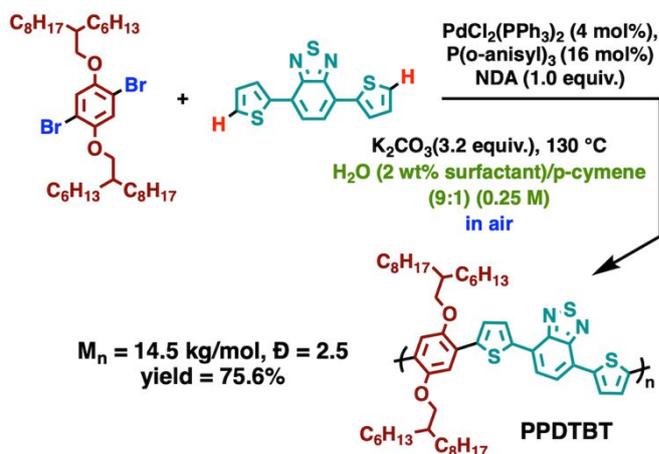
cymene with DArP.^{21,23} All polymerizations were performed using 48 hours of reaction time, which is the same reaction time reported for the Suzuki polymerization in emulsion conditions.²⁷ Beverina et al. utilized Kolliphor EL (K-EL) as the surfactant, which is a nonionic surfactant prepared by reacting castor oil with ethylene oxide, to form and stabilize micellar solutions or emulsions in water. Specifically, the use of 2 wt% of K-EL in deionized water allows the formation of micellar solutions, in which effective Suzuki polymerization was carried out giving good M_n (15.9 kg/mol) and yield (70%) of P1 at room temperature (25 °C) even without the use of organic solvent. However, such micellar solutions are unstable at the high temperatures usually required for DArP (100–120 °C), which disrupts the uniform dispersion of the colloids in water suspension and results in thermally induced phase separation.³³ Presumably due to these reasons, DArP attempted using H₂O (with 2 wt% K-EL surfactant) as the reaction medium was unsuccessful at 110 °C (Table 1, entry 1), in contrast to the result reported by Beverina et al. using Suzuki polymerization at 25 °C.²⁷

To overcome this challenge, a small amount of organic solvent, such as toluene (10 vol%), is often added to the reaction medium, which effectively converts the micellar solutions into thermally-stable emulsions.^{27–33} Dynamic Light Scattering (DLS) measurements by Beverina et al. revealed that the addition of toluene increases the diameter of the micelles from 12 nm to the 1 μm regime.³⁰ This improves the stability of the medium during the polymerization by avoiding the phase separation of the organic domain due to the low solubility of the synthesized polymer.³⁰ The effectiveness of this strategy was further proven by our experiment using DArP, which afforded P1 with M_n of 8.8 kg/mol and yield of 58.8% (Table 1, entry 2) under aerobic conditions with 9:1 H₂O/toluene emulsion. The lower M_n and yield compared to the Suzuki polymerization counterpart (M_n = 20.7 kg/mol, yield = 72%) might be attributed to the necessity of direct arylation to employ stronger inorganic carbonate bases (such as K₂CO₃ or Cs₂CO₃),¹⁹ which in an emulsion reaction condition, are exclusively soluble in the aqueous domain and are reliant on productive mass exchange to reach the catalytic site within the organic micelles. Conversely, Suzuki polymerization allows the use of organic bases such as Et₃N, which promote the reactivity of the polymerization more efficiently within the lipophilic pocket.³²

The impact of adopting such emulsion conditions on the sustainability of DArP is significant as only 0.16 mL of organic solvent (toluene) is used to produce 164 mg of conjugated polymer, compared to 0.75 mL of organic solvent required for the preparation of 78 mg of P1 in conventional DArP methods, resulting in a 10-fold improvement of the E-factor.²³ Previously, we disclosed p-cymene as a naturally-sourced, sustainable alternative to toluene offering superior solubilizing ability for conjugated polymer synthesis via DArP.²³ Therefore, we envisioned that by replacing the small amount (10 vol%) of toluene in the emulsion medium with p-cymene, a true “green” condition for DArP could be realized. By mixing H₂O/p-cymene 9:1 (v:v) with 2 wt% of K-EL, a stable emulsion was obtained

with an identical physical appearance compared to the H₂O/toluene 9:1 (v:v) emulsion solution previously employed (see Figure S1 in the SI). This reaction medium resulted in an improvement of the M_n for P1 to 10.3 kg/mol and the yield to 63.3% (Table 1, entry 3) (see Figure S2 for the visualization of DArP in emulsion). Due to an observed premature precipitation of P1 by the end of the polymerization, the monomer concentration in the emulsion medium was decreased from 0.25 M to 0.05 M. Such a strategy has been employed in Suzuki polymerization to afford fluorene-based conjugated polymers with good M_n under mini-emulsion conditions albeit with a sacrifice of sustainability.³⁶ However, only oligomeric product of P1 was obtained when this strategy was applied to DArP (entry 4), indicating the effectiveness of DArP in emulsion conditions relies on the presence of highly-concentrated colloids.

Small-molecule direct arylation studies in emulsion conditions performed by Beverina et al. demonstrated that an increased reaction temperature of 130 °C and the use of NaO^tBu as the base afforded the desired coupling product with optimal yields.³³ Inspired by this study, we were able to further improve the M_n of P1 to 11.9 kg/mol and the yield to 75.4% by increasing the reaction temperature from 110 °C to 130 °C (Table 1, entry 5). However, changing the base from Cs₂CO₃ to NaO^tBu led to a suppression of the polymerization (Table 1, entry 6), in contrast to the small-molecule study. On the other hand, replacing Cs₂CO₃ with K₂CO₃ provided P1 with the optimal M_n of 13.6 kg/mol and yield of 79.2% (entry 7). Significantly, consistent with the Suzuki polymerization counterpart, these emulsion-DArP reactions were carried out under aerobic conditions, which is highly attractive relative to conventional DArP conditions that require inert atmosphere and stringent Schlenk-techniques.^{21,37} As a control experiment, we attempted the synthesis of P1 via DArP with emulsion conditions under N₂ atmosphere (entry 8), which did not result in an improvement of M_n or yield (12.9 kg/mol, 76.3%, respectively). ¹H NMR analysis reveals identical structures of P1 synthesized via emulsion-DArP under aerobic and N₂



Scheme 3. Synthesis of PPDTBT via DArP using the optimal emulsion conditions listed in Table 1, entry 7.

atmosphere (Table 1, entry 7 and 8), which will be discussed below.

Leclerc et al. reported that a saturated K_2CO_3 (40 equiv.) aqueous solution provided the optimal results for DArP in biphasic conditions.²¹ However, this strategy cannot be applied to emulsion conditions because a high equivalence of K_2CO_3 drastically increases the density of the aqueous solution, resulting in the breakage of the emulsion and the separation of the 10 vol% of organic solvent (p-cymene) from water (see Figure S3 for visualization). With this approach, we found that the emulsion was turned into two separate layers, which is against the intention of this study and therefore this polymerization was not attempted (Table 1, entry 9). Interestingly, while Beverina et al. showcased that the addition of Aliquat 336 as a phase transfer agent improved the yields of small-molecule direct arylation couplings in emulsion conditions, such an approach was detrimental to the DArP conditions developed in this study as no polymer product was obtained (Table 1, entry 10).³³ Strategies that have been found to improve the performance of biphasic-DArP protocols such as the addition of tetrabutylammonium bromide (TBAB) or the use of a lower catalyst loading (1 mol%) did not enhance the outcome of DArP in the emulsion medium (Table 1, entry 11 and 12).²¹

With the optimal emulsion conditions for DArP in hand (entry 7), we explored the compatibility of this novel, sustainable DArP method for the synthesis of poly[[2,5-bis(2-hexyldecyloxy)phenylene]-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole) (PPDTBT), a polymer that can be easily prepared and is promising for large-area, roll-to-roll processed solar-cell devices with good power conversion efficiency (PCE).¹⁴ By applying the best conditions for the synthesis of P1 using a H_2O/p -cymene 9:1 (v:v) emulsion, PPDTBT was synthesized in air with M_n of 14.5 kg/mol and yield of 75.6%. Compared to PPDTBT prepared by conventional DArP protocol using the unsustainable solvent THF, emulsion-DArP conditions afforded the polymer with a similar M_n (14.5

kg/mol vs. 15 kg/mol) and yield (75.6% vs. 78%).³⁸ This indicates that the new emulsion-DArP method is applicable for the preparation of conjugated polymers that are suitable for large-area OPV devices and rivals the performance of traditional DArP methods using toxic reaction media.

In regard to polymer structural analysis, 1H NMR spectroscopy and UV-vis absorbance spectroscopy were performed for P1 and PPDTBT and compared to samples previously prepared using conventional DArP methods. For P1, analysis was performed for those with satisfactory M_n values (exceeding 10 kg/mol). Specifically, 1H NMR and UV-vis spectra of P1 in Table 1, entry 3, 5, 7, 8, were collected and included in the SI. Figure 1 shows a comparison of the 1H NMR spectra of P1 synthesized using the H_2O/p -cymene 9:1 (v:v) emulsion in air and under N_2 atmosphere (Table 1, entry 7 and 8, respectively), illustrating identical major resonances (A-D') without donor-donor (δ) or acceptor-acceptor (α) homocoupling defects being detected.²³ End-group assignments were performed based on literature reports (7.25, 7.12 ppm).^{23,35} Structures of potential defects and end-groups are shown in Figure S9. Importantly, resonances corresponding to the β -protons of the 2,2'-bithiophene moiety (D,D') were unaffected and integrated to the correct values (see Figure S4-S7), which indicates a likely exclusion of β -defects when using the novel emulsion conditions for DArP.^{23,35} When emulsion polymerization is used for Suzuki methods under aerobic conditions, OH-termination signals of the fluorene unit (~6.95 ppm) were identified as a result of oxidative deborylation events in the presence of oxygen in the reaction medium.²⁷ As expected, such termination events did not occur when air was introduced to the emulsion-DArP conditions (Figure 1, top), which demonstrates another advantage of the C-H activation methodologies over the Suzuki counterpart by alleviating the use of unstable organoboranes under aerobic reaction conditions. UV-vis spectra of P1 samples (Figure S10) show similar absorption profiles compared to those reported with the same λ_{max} of 451 nm.^{23,35} It should be noted that P1

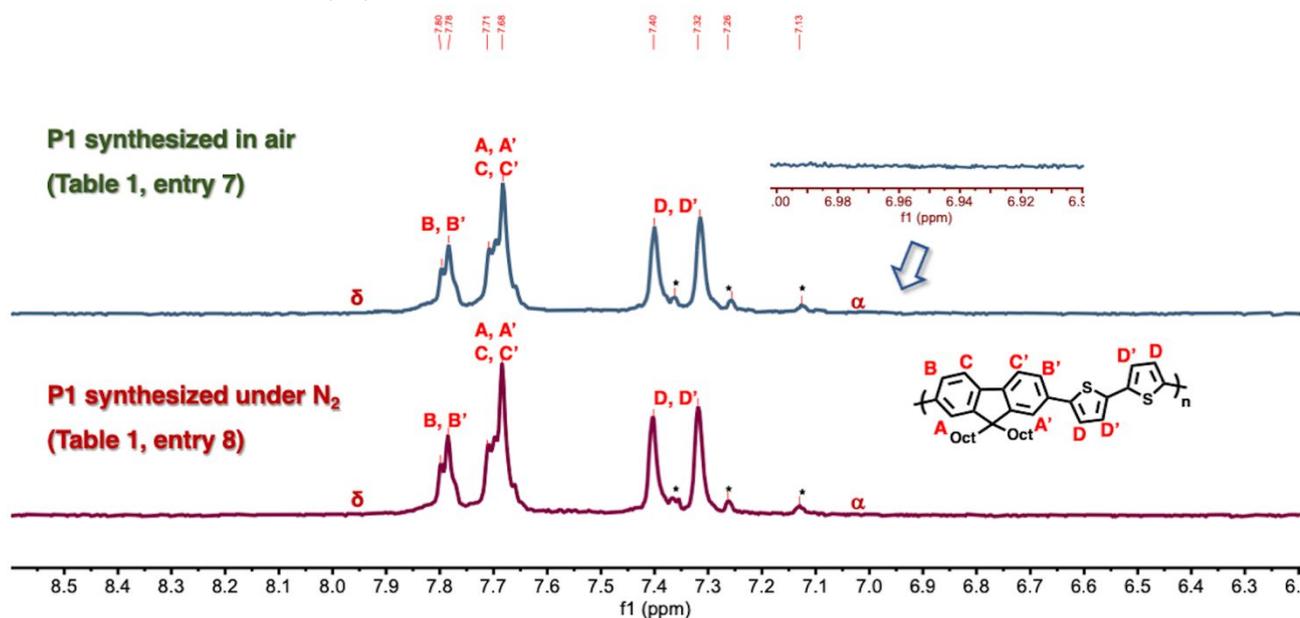


Figure 1. 1H NMR analyses of P1 synthesized using H_2O/p -cymene 9:1 (v:v) emulsion in air and under N_2 atmosphere (Table 1, entry 7 and 8, respectively). Major resonances (A-D'), potential resonances for end groups (*) and potential defects (δ , α) are denoted. Collected in $C_2D_2Cl_4$ at 100 °C and 600 MHz. The inset in the top spectrum shows the intensified region in which oxidative end-capping event might appear (~6.95 ppm).

synthesized using the conditions from Table 1, entry 5 displayed a vibronic shoulder with a slightly higher intensity compared to the other polymer samples of P1, although the reason for this result is unclear. The ^1H NMR spectrum of PPDTBT (Figure S8) synthesized using the emulsion-DArP protocol matched previous reports without observable deviation.^{22,38} The UV-vis spectrum of PPDTBT (Figure S11) is similar to samples synthesized using conventional methods with $\lambda_{\text{max}} = 655$ nm, and an apparent vibronic shoulder in the absorption profile suggesting a minimization, if not exclusion, of β -defects of the synthesized polymer.^{22,38}

Conclusions

In summary, we presented a novel, sustainable method for DArP using a $\text{H}_2\text{O}/p\text{-cymene}$ 9:1 (v:v) emulsion medium under aerobic conditions. With only 10 vol% of organic solvent present in these emulsions, we were able to significantly decrease the amount of organic waste generated per kg of conjugated polymer synthesized (E-factor) by 10 times compared to conventional DArP methods. As a model study for the optimization of emulsion-DArP conditions, P1 was synthesized with M_n up to 13.6 kg/mol and yields up to 79.2% without detectable structural defects. This sustainable DArP method is also compatible with the preparation of a conjugated polymer suitable for roll-to-roll processed OPV, PPDTBT, resulting in an M_n of 14.5 kg/mol and yield of 75.6%. With a growing demand of large-scale preparation of semiconducting materials and roll-to-roll printed organic electronic devices, we believe the “in-water” strategy for DArP under ambient conditions presented in this study marks an important step towards enhancing the sustainability of industrial-scale conjugated polymer synthesis. Future studies will focus on the further optimization of reaction conditions to improve M_n and yield with the emulsion-DArP protocol, such as utilizing organic bases that are more soluble in the organic micelles, potentially enhancing reactivity under emulsion conditions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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