Continuous Synthesis of Device-Grade Semiconducting Polymers in Droplet-Based Microreactors

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A method is reported for the controlled synthesis of device-grade semiconducting polymers, utilizing a droplet-based microfluidic reactor. Using poly(3-hexylthiophene) (P3HT) as a test material, the reactor is shown to provide a controlled and stable environment for polymer synthesis, enabling control of molecular weight via tuning of flow conditions, reagent composition or temperature. Molecular weights of up to 92 000 Da are readily attainable, without leakage or reactor fouling. The method avoids the usual deterioration in materials quality that occurs when conventional batch syntheses are scaled from the sub-gram level to higher quantities, with a prototype five-channel reactor producing material of consistent molecular weight distribution and high regioregularity (>98%) at a rate of ≈60 g/day. The droplet-synthesized P3HT compares favorably with commercial material in terms of absorption spectrum, polydispersity, regioregularity, and crystallinity, yielding power conversion efficiencies of up to 4% in bulk heterojunction solar cells with [6,6]-phenyl-C61-butyric acid methyl ester.

1. Introduction

Semiconducting polymers (SPs) are attracting widespread interest due to their potential applications in lighting, displays, and solar cells,[1,2] and for their compatibility with high volume manufacturing on flexible plastic substrates.[3,4] However, several significant obstacles to commercialization remain. Key challenges include: increasing device efficiencies and operating lifetimes to application-viable levels;[1,5,6] developing improved processing methods for high-yield, large-area fabrication under ambient conditions;[4] and reducing the bill of materials (BOM) for cost-competitiveness with alternative technologies.[7]

Owing to their specialized nature, semiconducting polymers account for a large part of the total BOM,[7] and significant efforts have been devoted to developing new lower cost SPs that can be readily obtained from inexpensive, easily accessible starting materials in a minimum of synthetic steps.[8] Whilst progress in this regard has been substantial, a key challenge is the development of quality-assured production methods for semiconducting polymers that provide reliable batch-to-batch reproducibility and can be readily scaled to high volumes. Factors such as molecular weight distributions, chemical defects in the conjugated backbone, end groups and impurity levels can change significantly between individual batches,[9] leading to substantial variations in rheology, processability and optoelectronic performance for nominally the same material. This is a particular issue when attempting to increase production from the small sub-gram quantities used in research and development to the kilogram-scale batches needed for industrial application.[10] Increased reaction volumes typically lead to diminished mixing efficiencies and poorer heat management,[11] causing spatial variations in both chemical composition and temperature that affect reaction kinetics and lead to the emergence of unwanted side reaction pathways that can detrimentally influence the final product. Intensive optimization of reaction conditions is required for each reactor scale, and even then unavoidable reductions in materials quality or yield frequently occur.[12]

Here, we propose a new strategy for the large-scale production of high quality semiconducting polymers based on the use of droplet microfluidics.[13] In brief, by injecting monomer feedstock into a fast-flowing stream of immiscible carrier fluid, a series of near-identical sub-microliter droplets is generated, each of which acts as a self-contained micrometer-scale reaction vessel. The small droplet size ensures rapid equilibration of composition and temperature,[14] and so provides a highly uniform environment for polymerization. Importantly, since materials throughput can be raised independently of droplet volume (by ramping up the rate of droplet generation while keeping the droplet size fixed), production levels can in principle be scaled-up indefinitely without detriment to product quality. The use of droplet reactors to synthesize, at the kg/day level, high quality semiconducting polymers from inexpensive starting materials offers a viable route to lowering production costs and thereby reducing the BOM for plastic electronic devices.

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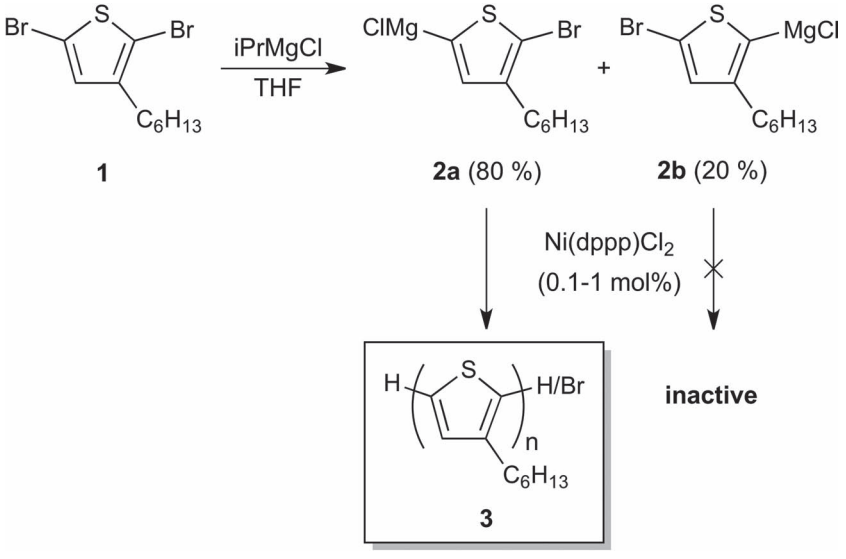
There are only a few reports of droplet-based polymerization reactions in the literature,[15–17] and these have largely focused on the production of micrometer-sized polymer particles, e.g., for drug delivery applications. McQuade et al. for instance have reported the preparation of oil-filled polyamide microcapsules,[15] and several groups have described the production of polymeric beads via photo-initiated polymerization of monomer-containing droplets.[16,17] These studies were principally concerned with tuning the size and shape of the particles or with improving the speed and fidelity of particle formation. Until now few if any attempts have been made to control and optimize polymer growth using droplet reactors. Furthermore, whilst there have been several reports of polymer synthesis in single phase reactors (including one relating specifically to semiconducting polymers),[18] such reactors are typically affected by problems of excessive back pressure due to polymer viscosity[19] and/or reactor fouling,[18,20] and do not yet offer the degree of control and reliability needed for industrial application.

In this manuscript we report the droplet-based synthesis of poly(3-hexylthiophene) (P3HT)—one of the most widely studied of all semiconducting polymers. We find that synthesis in droplets provides exceptional control over polymer properties, allowing for the sustained production of device-grade polymer equal in performance to the best commercially available material. The P3HT reported here was prepared via the Kumada cross-coupling route,[21,22] using a microfluidic adaptation of the batch synthesis route of McCullough et al. (see **Scheme 1**).[23] In short, the method involves a two-step process of monomer activation followed by catalyst-mediated cross-coupling polymerization. The initial step involves the metallation of 2,5-dibromo-3-hexylthiophene (**1**) by isopropyl-magnesium chloride in tetrahydrofuran (THF), yielding an 80:20 mix of active 2-bromo-5-chloromagnesio-3-hexylthiophene (**2a**) and inactive 2-chloromagnesio-5-bromo-3-hexylthiophene (**2b**). The polymerization step is then induced by addition of 1,3-bis[diphenylphosphinopropane]nickel(II) chloride (Ni(dppp)Cl_2) catalyst.



Scheme 1. Synthesis of regioregular poly(3-hexylthiophene) [P3HT] (**3**) following McCullough et al.[23]

Our droplet reactor comprises a single length of polytetrafluoroethylene (PTFE) tubing of inner diameter 1 mm, into which a syringe injects a continuous stream of viscous perfluorinated polyether (PFPE) carrier fluid loaded with a uniform dispersion of Ni(dppp)Cl_2 (see **Figure 1**a). A second syringe delivers a pre-prepared 80:20 mixture of the two monomers (**2a**+**2b**) in THF to the main capillary via a glass auxiliary capillary that pierces the PTFE from one side. A growing bead of the monomer solution forms at the tip of the auxiliary capillary, and eventually buds off as a discrete droplet that is carried downstream by the PFPE, leaving a new droplet to form at the tip (see Figure 1b). Importantly, since PFPE wets preferentially to PTFE, the THF droplets are kept beneficially isolated from the channel walls and so cannot cause fouling of the reactor—the principal failure mode for conventional (single phase) flow reactors. Polymerization begins at the point of droplet creation, with the growth rate increasing rapidly when the PTFE passes into a heated oil bath.

2. Results and Discussion

Initial runs were carried out at an oil bath temperature of 55 °C using monomer (**2a**+**2b**) and catalyst solutions of concentration 0.29 M and 0.2 mg/mL (0.37 μmol/mL), injected from their respective syringes at rates of 72 and 360 μL/min (equivalent to a catalyst loading of 0.64 mol%). The distance of the droplet generator from the oil bath entrance and the distance of the oil bath exit to the end of the PTFE were both fixed at 5 cm. The intervening section of PTFE was arranged in a loose horizontal spiral of length 1.1 m, implying a heating time of 2 min for the selected injection rates. The effluent was quenched in excess methanol, with the THF/methanol mixture forming a discrete layer above the PFPE that could be removed by simple decantation. The polymer was dried by gravity filtration, and then purified by successive Soxhlet extractions in methanol for 24 h and chloroform for 72 h to first remove catalyst and salt by-products from the polymer and then extract the polymer itself from residual contaminants.[24]

Under the chosen reaction conditions, the THF formed stable droplets of volume ≈0.5 μL that moved uniformly along the PTFE tubing at a common speed of 0.92 cm/s without coalescence (see Figure 1c and the video file in the Supporting Information). The polymerization proceeded rapidly, with the color of the droplets changing progressively from a pale yellow/orange to pink/red as they spiraled their way through the oil bath. Importantly, the product and reactants remained fully compartmentalized within the THF droplets, with no deposition occurring on the PTFE wall at any point. Operating the reactor for a period of 16.6 h yielded a final (purified) solid product of 0.9 g, corresponding to a yield of 44% (compared with a theoretical maximum of 80%) and a conversion efficiency of 55%. (The modest conversion efficiency is consistent with the short residence time in the reactor as discussed below).

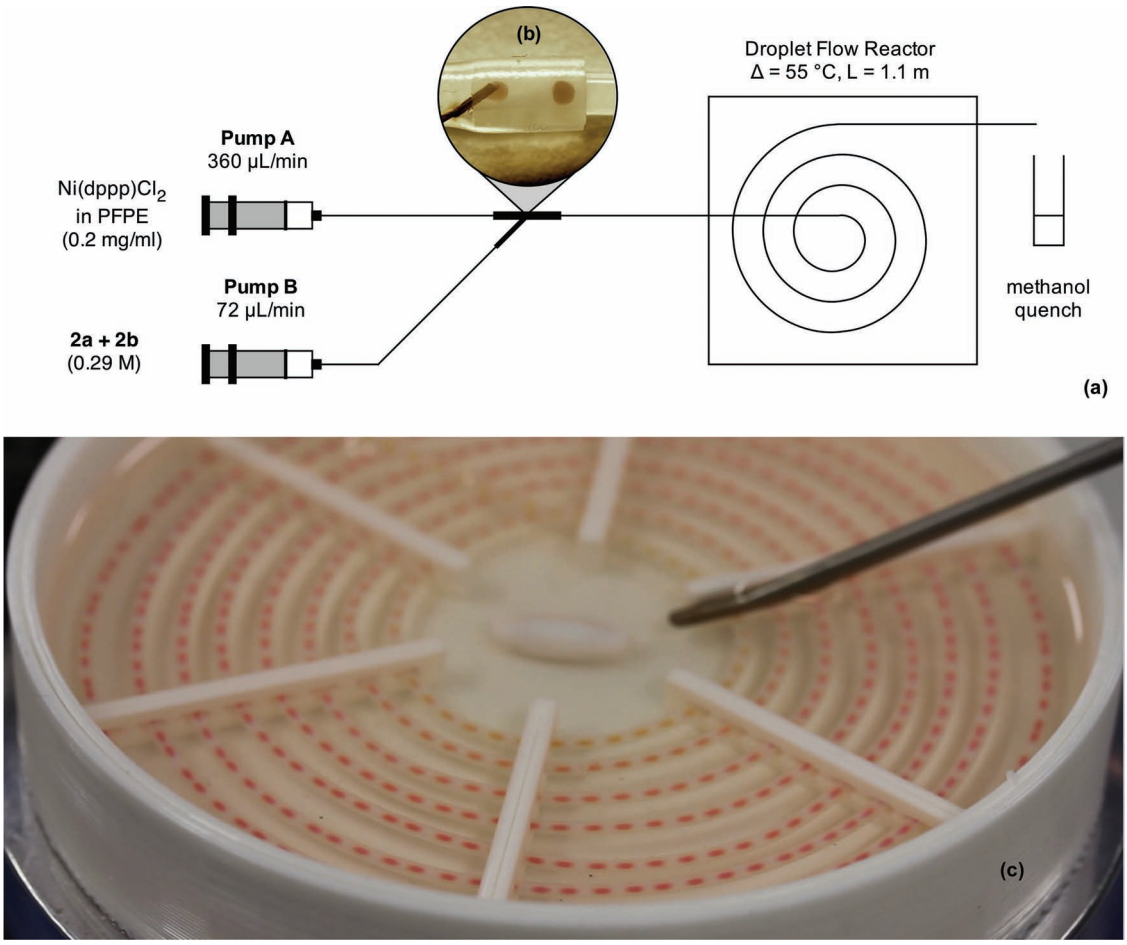


Figure 1. a) Schematic of droplet reactor, comprising a droplet generator and coiled PTFE tubing in a temperature-stabilised oil-bath; b) close-up of the droplet generator; note, the droplet phase has been dyed with colored ink for clarity; c) photograph showing droplet flow through coiled PTFE tubing as the polymerization proceeds. The stated flow conditions correspond to a 2 min residence time in the oil-bath.

Using refractive index size exclusion chromatography (RI-SEC) with chlorobenzene as the eluent, the dominant product was found to have a M_w of 62 000 Da and a favorably low polydispersity index (PDI) of 1.56 versus polystyrene standards (see **Figure 2**a); also present at <1.5 wt% was a ≈5 kDa oligomeric side product that if required could be removed by a further Soxhlet extraction in hexane. Thin films of the droplet synthesized P3HT showed strong well-structured absorption spectra (Figure 2b), with clear peaks at 524, 545, and 610 nm, and a long-wavelength tail up to and beyond 650 nm—beneficial for efficient light harvesting in solar applications. These characteristics are typical of ordered chains with long conjugation lengths, with the intense peak at 610 nm arising from strong interchain interactions that favour efficient (high mobility) charge transport.[25] The principal defects in P3HT are unwanted head-to-head or tail-to-tail couplings that induce a twist in the thiophene rings and disrupt conjugation. 1H NMR analysis showed the polymer to be of a high regioregularity >97%, consistent with a strong preference for head-to-tail coupling during chain growth (see Supporting Information Figure S1).

The above properties are favorable for device applications in terms of absorption spectrum, molecular weight distribution and regioregularity. (For reference device-grade material from Rieke Metals Inc. had an M_w of 63 000 Da, a PDI of 2.3, and a regioregularity of 91%, see Supporting Information Figure S2 and Figure S3). To assess the electronic performance of the material, bulk heterojunction organic solar cells were fabricated by successively coating indium tin oxide (ITO) coated glass with: a 50 nm layer of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS); a 250 nm (equal weight composition) layer of P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM); a 30 nm Ca cathode; and a 150 nm Ag capping layer (see the Supporting Information). Figure 2c shows the current-voltage characteristics of thirteen 0.15 cm^2 pixels under 100 mW/cm^2 simulated solar illumination. The droplet-synthesized P3HT yielded consistently high short-circuit current densities, open-circuit voltages and fill-factors of 10.9 ± 0.1 mA/cm^2, 0.55 ± 0.01 V and 66.7 ± 0.4%, resulting in high overall power conversion efficiencies of 4.0 ± 0.1% (comparable to efficiencies for P3HT:PCBM devices reported elsewhere in the literature).[26] Importantly, the high short-circuit currents and fill-factors indicate good charge generation and transport characteristics even at low internal field strengths, implying a low density of trap-states, and recombination centres in the active layer.

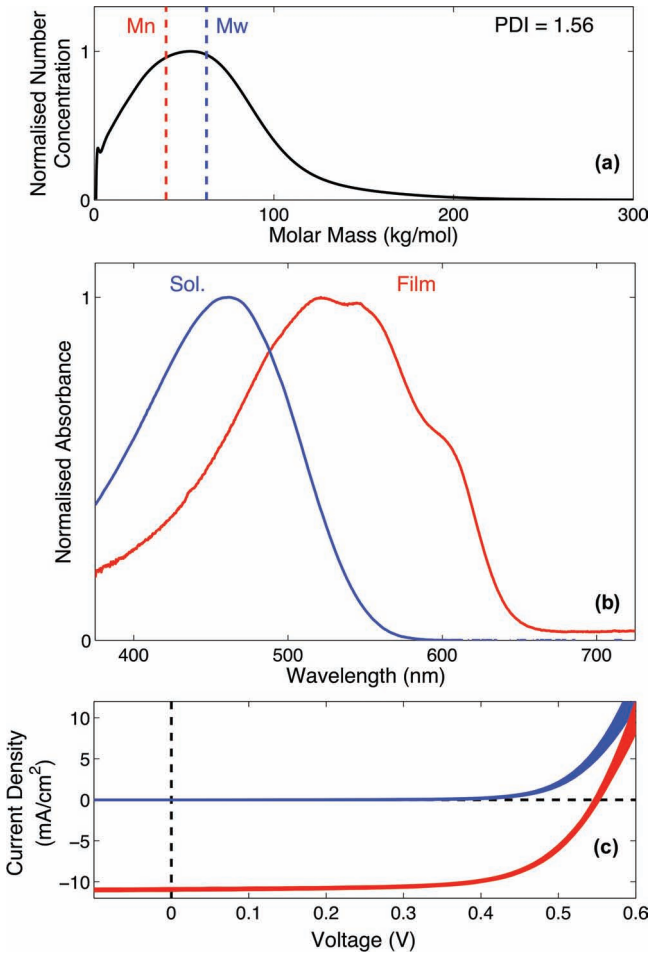


Figure 2. a) RI-SEC chromatogram for P3HT, synthesized in the droplet reactor under the conditions stated in Figure 1; M_n and M_w values were ≈40 and ≈62 kDa relative to polystyrene standards; b) absorption spectra (in chlorobenzene and thin film) of the droplet synthesized P3HT; c) current–voltage characteristics of ITO/PEDOT:PSS/P3HT:PCBM/Al/Ag solar cells under 100 mW/cm^2 simulated solar illumination. Data is shown for 13 pixels of area 0.15 cm^2 (average efficiency: 4%, highest efficiency: 4.1%). P3HT was synthesized in the droplet reactor under the conditions stated in Figure 1.

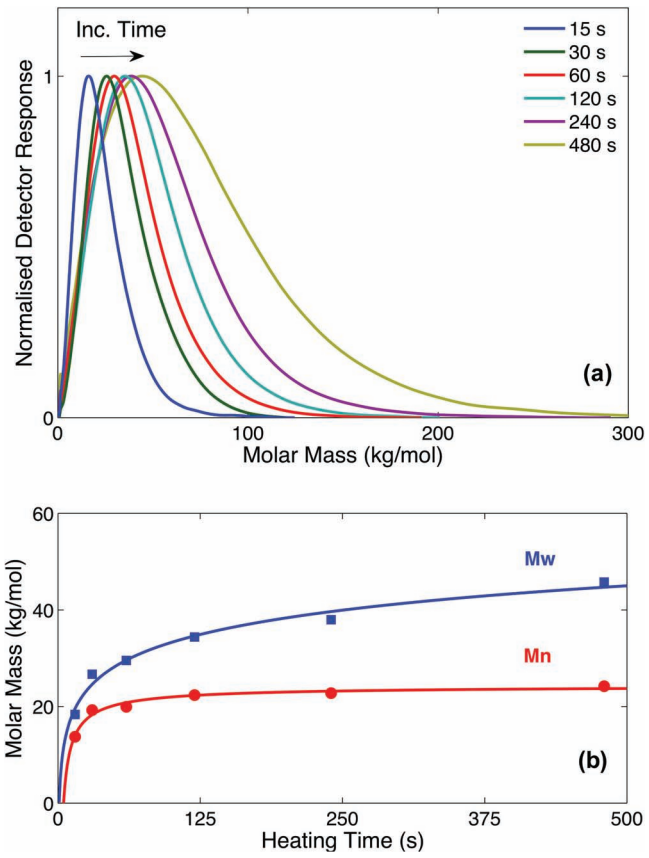


Figure 3. a) Series of RI-SEC chromatograms for heating times in the range 15 to 480 s, obtained by varying the total flow rate from 3.5 to 0.1 mL/min and holding all other reaction conditions at the values stated in Figure 1, except total monomer concentration which was fixed at 0.21 M; b) M_n and M_w versus reaction time, using data from chromatograms.

As with standard batch synthesis, varying the reaction time provides an effective means of controlling the molecular weight distribution, with longer heating times yielding higher molecular weights. A key advantage of the microfluidic approach, however, is the ability to control the reaction time with exceptional "dial-up" precision by simply adjusting the total flow rate of liquid through the channel (while holding the ratio of the carrier and monomer flow rates fixed to maintain droplet size and reaction stoichiometry). **Figure 3**a shows a series of RI-SEC chromatograms for heating times in the range 15 to 480 s, obtained by varying the total flow rate from 3.5 to 0.1 mL/min. As expected the plots reveal a steady increase in average molecular weight with time due to increasing monomer conversion. The controlled nature of the growth process is evident in Figure 3b which shows the smooth progression of M_n and M_w with reaction time.

The molecular weight may be controlled in many other ways, e.g., by varying the catalyst loading or monomer concentration as shown in **Figure 4**a,b for a fixed reaction time of 4 min. The plots are broadly consistent with the quasi-living polymerization model,[27] in which each catalyst molecule is predominantly—although not exclusively[28]—associated with a single polymer chain. In this model an increase in the catalyst loading (holding the monomer concentration fixed) results in a larger number of shorter chains, while an increase in monomer concentration (holding the catalyst loading fixed) results in broadly the same number of chains but a higher average chain length. The initial linear increase in M_n and M_w with monomer concentration is consistent with living polymerization at a fixed conversion rate, while the subsequent plateauing at M_n = 27 000 Da, M_w = 46 000 Da suggests there is a limiting chain length above which new chain formation is preferred over further chain growth (as previously suggested by Achord and Rawlins).[28] PDIs were lowest at low monomer concentrations (high catalyst-to-monomer ratios), increasing from 1.3 at 0.08 mol/dm^3 (M_n = 10 000 Da) to 1.7 at >0.32 mol/dm^3 (M_n = 27 000 Da). Figure 4c implies increased monomer conversion at higher temperatures, resulting in longer chains for a given composition of the reaction mixture. In all cases, the growth kinetics are complicated

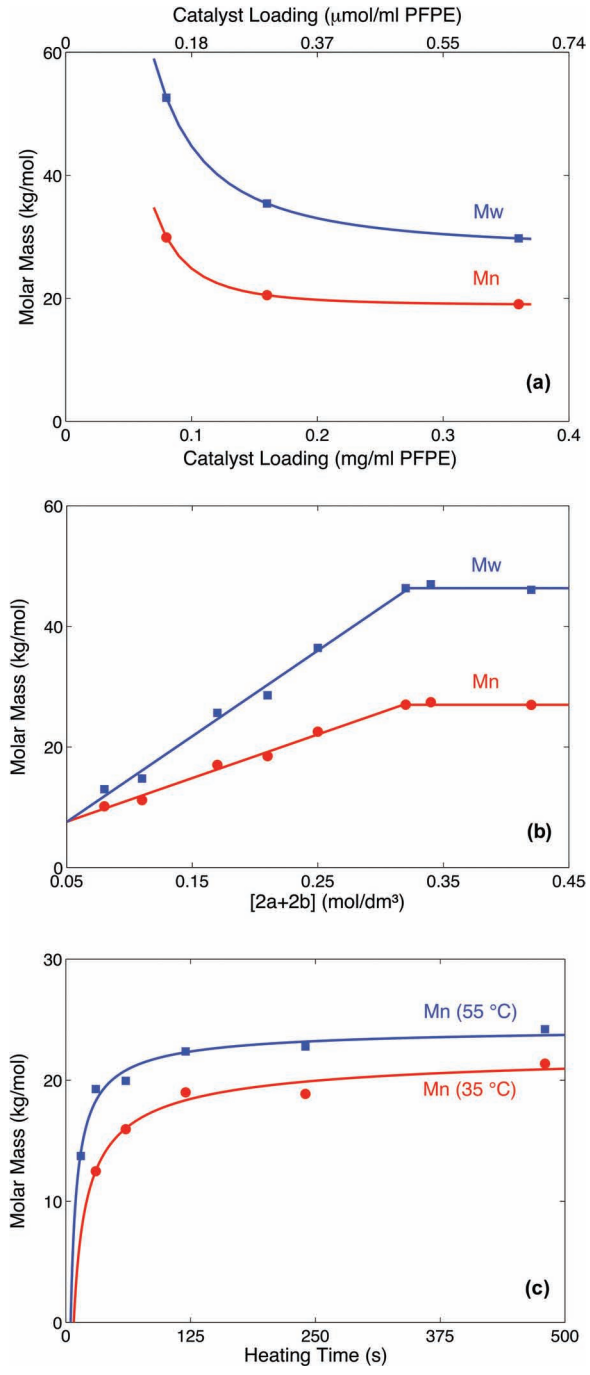


Figure 4. a,b) M_n and M_w versus catalyst loading and monomer concentration; flow-rates were halved relative to Figure 1 and all non-varying reaction conditions were held at the values stated in Figure 1, except total monomer concentration which was fixed at 0.21 M. c) M_n versus heating time at 55 and 35 °C, using reaction conditions stated in Figure 1.

by the slow diffusion of new catalyst from the carrier fluid to the droplet surface (enabling additional chain formation), and further investigation is underway to understand how this influences the final size distribution. (Note: if precise control of the catalyst concentration inside the droplet is required, the Ni(dppp)Cl_2 may instead be dissolved directly in THF alongside the other reagents, taking care to stabilize the complex against ligand dissociation so as to maintain catalytic activity.)

Irrespective of the detailed growth mechanisms, it is evident that droplet synthesis provides an effective means of controlling molecular weight distributions. For optimal control over the reaction—and to further streamline the production process—the microfluidic approach may be straightforwardly extended to include in-line preparation of the Grignard precursor **2a** (and **2b**). This is readily achieved by directly reacting 2,5-dibromo-3-hexylthiophene with isopropyl magnesium chloride (iPrMgCl) Grignard reagent—a process that yields no precipitates and hence may be implemented in a simple (single phase) continuous flow reactor without risk of reactor fouling. Three independent syringes were separately loaded with 2,5-dibromo-3-hexylthiophene, (as received) 2 M iPrMgCl in THF, and pure THF as a diluent, and their outlets merged using a simple three-way mixer. One end of a 2.25 m length of PTFE tubing was connected to the outlet of the mixer, and the other end was connected to the auxiliary capillary of the droplet reactor (see **Figure 5**a). 2 m of the intervening tubing was loosely coiled and immersed in an oil bath at 55 °C. As before the PFPE carrier fluid was doped with Ni(dppp)Cl_2 at a loading of 0.2 mg/mL (0.37 μmol/mL). Flow rates of 2.35, 5.33, 28.33, and 180 μL/min were selected for the 2,5-dibromo-3-hexylthiophene, iPrMgCl, THF and PFPE, implying a one-to-one equivalence of thiophene monomer and iPrMgCl, a five-to-one flow rate ratio between the PFPE and the droplet phase, and residence times in the first (continuous flow) and second (droplet flow) oil-baths of 44 and 4 min, respectively. The reaction times were selected to ensure near complete conversion at each stage.

Once the flow had stabilized, the system was allowed to operate continuously for a period of 300 min, with small samples being taken at 30 min intervals for analysis by RI-SEC. In addition, for the purpose of determining the monomer conversion efficiency, a larger batch of material was collected between 155 and 177 min and then purified by successive Soxhlet extractions in methanol and chloroform as before. After filtering and purification 31.2 mg of material equivalent to 0.188 mol of repeat units was recovered, compared to 77 mg or 0.236 mol of consumed monomer over the 22 min collection period. Allowing for the 20% of 2,5-dibromo-3-hexylthiophene that remains inactive during the reaction, this corresponds to complete conversion of the active monomer. Supporting Information Figure S4 shows the RI-SEC chromatograms obtained at thirty minute intervals. The molecular weight distributions remained consistent throughout the run, with only small fluctuations (that are due in part to variability in the RI-SEC measurement itself). Figure 5b shows the calculated number- and weight-average molecular weights for the various samples: M_n = 29 000 ± 2500 g/mol and M_w = 50 000 ± 4500 g/mol, with PDIs consistently in the range 1.7–1.8. The ability to achieve stable high yield product from a fully integrated flow-based system, incorporating both Grignard precursor preparation and polymerization, significantly simplifies the overall synthesis procedure, allowing for the direct preparation of P3HT from off-the-shelf commercially available materials.

Finally, to evaluate the feasibility of higher volume production via droplet synthesis, we developed a five-channel

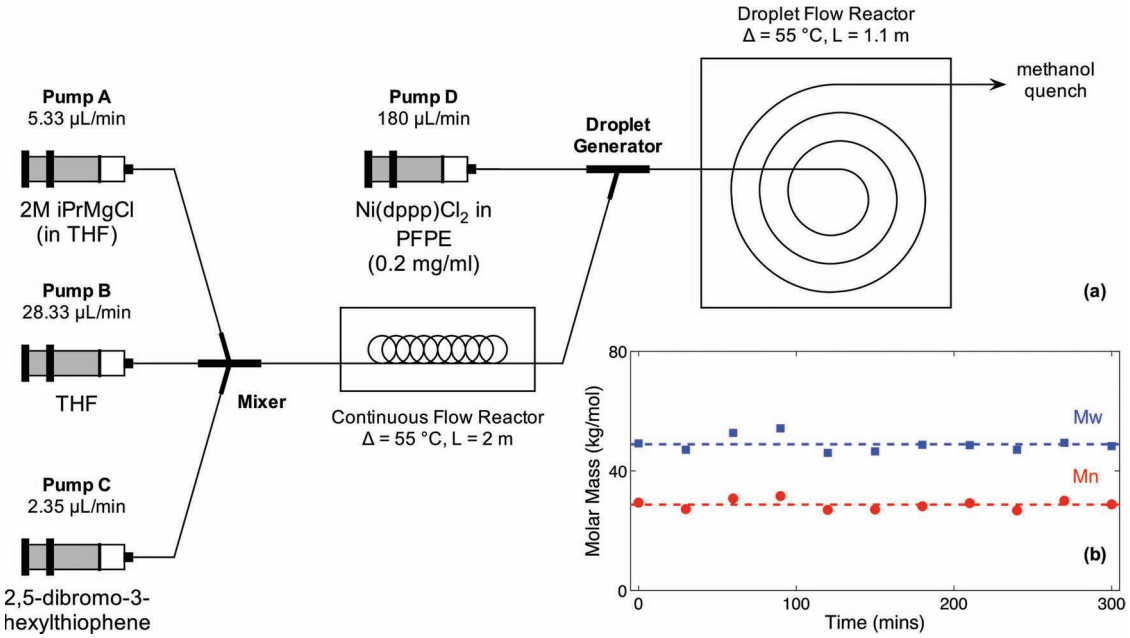


Figure 5. a) Schematic of fully integrated reactor, incorporating both Grignard preparation and polymer synthesis; b) M_n and M_w versus time under stable operating conditions. The stated flow conditions correspond to residence times of 44 and 4 min in the first and second oil-baths, respectively.

reactor (using pre-prepared Grignard precursors for ease of implementation). The precursor and carrier fluid were injected from their respective syringes into passive flow-dividers, creating five separate streams of each. Paired streams of precursor and carrier fluid were then individually combined in five parallel 4 m reaction channels to complete the reactor, see **Figure 6**a. The reaction was carried out at an oil bath temperature of 55 °C using monomer (**2a**+**2b**) and catalyst solutions of concentration 78 and 0.2 mg/mL (239.2 and 0.37 μmol/mL), injected from their respective syringes at an equal rate of 1.5 mL/min (0.12 mol%). With the carrier and reagent flows balanced, the reaction phase formed elongated segments inside the carrier fluid, with the carrier fluid continuing to wet the walls preferentially and so continuing to suppress any risk of reactor fouling. Collecting over a 6.25 h period (and following purification in methanol), 14.9 g of high quality P3HT was obtained in quantitative yield with Mw = 91 500, PDI = 1.7 and RR > 98%, see Figure 6b and Supporting Information Figure S5. The ability to attain an effective production rate of 57 g/day, while maintaining a low PDI and high regioregularity, indicates the inherent scalability of the droplet synthesis procedure. Indeed far higher (>10×) production rates should be readily achievable by using additional channels, increased reagent concentrations, and higher flow-rates. In this way we consider it will be possible to controllably and cost-effectively scale-up the production of P3HT (and other semiconducting polymers) to the kg/day levels required for industrial application.

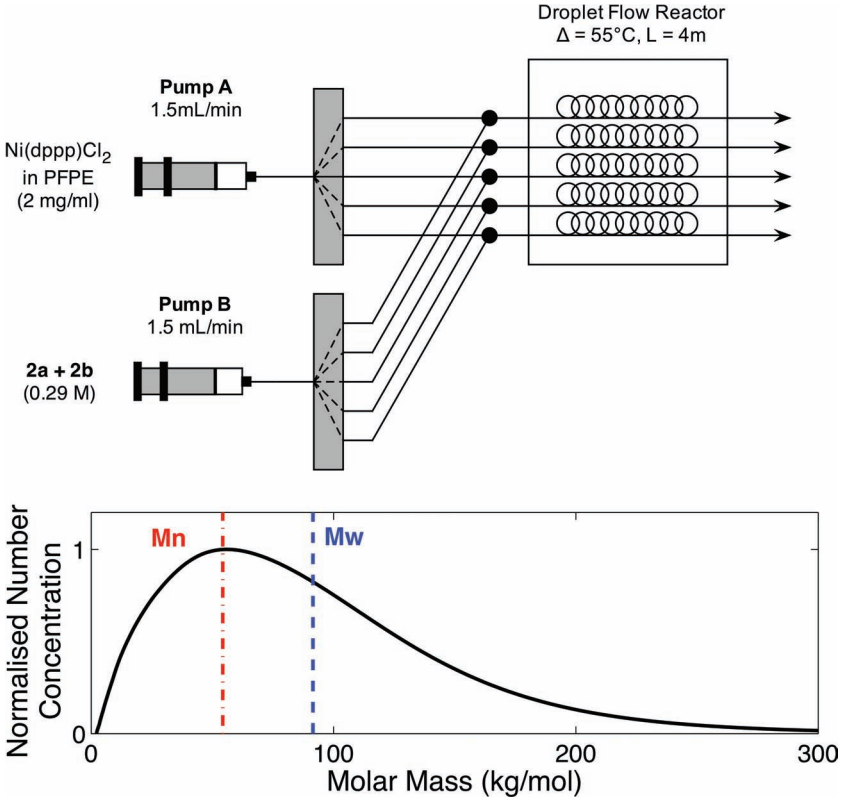


Figure 6. a) Schematic of parallel droplet reactor for higher volume synthesis of P3HT; b) RI-SEC chromatogram for the collected product. The stated flow conditions correspond to a 5 min residence time in the oil-bath.

3. Conclusions

In conclusion we have synthesized device-grade poly(3-hexylthiophene) of low PDI and high regioregularity in a droplet-based microfluidic reactor. The reactor provided a stable and highly controlled environment for polymer synthesis, enabling ready control of the average molecular weight via simple tuning of the flow conditions, reagent composition and/or temperature. Bulk heterojunction solar cells based on a 1:1 blend with $PC_{60}BM$ exhibited peak power conversion efficiencies of 4%.

The droplet-based approach was applied here to the gram-scale synthesis of P3HT by Grignard metathesis, but is readily applicable to other polymers prepared by the GRIM route, e.g., polyfluorenes and polypyrroles.[29] Preliminary trials have also shown it to be well suited to the GRIM synthesis of both statistical copolymers such as poly(3-hexylthiophene)-*ran*-poly(3-hexylselenophene) and block-copolymers such as poly(3-hexylthiophene)-*block*-poly(3-dodecylthiophene). Furthermore it should be straightforwardly adaptable to other commonly used coupling routes such as Suzuki and Stille methods. The ability to attain high production rates, while maintaining low PDI and high regioregularity, makes the droplet approach a highly attractive one for the scalable production of device grade semiconducting polymers. More broadly, flow methods have been gaining increasing traction in general organic synthesis due to the increased levels of reaction control they can provide and their ready applicability to multistep syntheses.[30] The application of droplet-based reactors to polymerization reactions is likely to prove especially beneficial in situations where (viscous) high molecular weight materials must be produced or where highly adhesive reaction products are formed–circumstances in which conventional single-phase reactors are prone to leakage or fouling.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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