Recent advances in the green, sustainable synthesis of semiconducting polymers

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Abstract

There is a significant need for economic and environmentally sustainable chemistry in both academia and industry. The field of organic electronics is also rapidly growing due to substantial interest in semiconducting polymers. A major limitation associated with semiconducting polymers is their synthesis, which often requires many synthetic steps and relies on stoichiometric amounts of toxic metallic reagents. For a technology to be sustainable, both the economic and environmental costs must be feasible. Recently, significant effort has been expended towards synthesizing semiconducting polymers with greener biomass-derived solvents, more sustainable catalysts, and under energy-efficient reaction conditions. This review highlights key efforts in synthesizing environmentally benign, scalable, and high performing semiconducting polymers.

Keywords: Semiconducting polymers; Green chemistry; Solvent; Catalyst; π-conjugated polymers

The importance of sustainable semiconducting polymers

A significant number of electronic technologies (e.g., phone, laptops, and solar cells) employ semiconducting materials for light-emitting diodes, transistors, and photovoltaic cells. Traditionally, these are based inorganic materials such as silicon. However, a new generation of organic electronics employing organic semiconductors has grown rapidly primarily due to the rich optical and electrical properties of semiconducting polymers. Semiconducting polymers are now used in a variety of applications such as organic photovoltaics [1-4], organic light-emitting diodes [5-6], organic field effect transistors [7], and stretchable electronic devices [8-11]. Interest in semiconducting polymers originates from the influential work on the conductivity of polyacetylene conducted by Heeger, MacDiarmid, and Shirakawa in the 1970s [12]. Although polyacetylene in particular has not found success as an applied semiconductor, since then, the scope of semiconducting polymers (with increasingly complex structures, properties, and syntheses) has grown tremendously. A major advantage of semiconducting polymers over inorganic semiconductors stems from polymer compatibility with solution processability and synthesis from inexpensive resources. Polymer solutions can be used as electrically conducting ink and printed as plastic electronics with roll-to-roll or inkjet printers for large-area and flexible solar panels. The current record for power conversion efficiency in organic photovoltaics is 17.3% [13]. However, the efficiency of organic photovoltaics still lags in comparison to inorganic photovoltaics using silicon [14-15]. Despite exhibiting lower efficiencies, organic photovoltaics are competitive with inorganic photovoltaics because of several advantages including inexpensive solution processability, flexible mechanical properties, lightweight, and significant range in optoelectronic tunability.

For semiconducting polymers to be successfully incorporated into devices, careful design is needed for critical properties such as solvent solubility, charge mobility, film morphology, and molecular packing. Considerable attention has been expended towards developing high performing semiconducting polymers from the first polyacetylene, to the synthetically accessible poly(3-hexylthiophene) (P3HT), and to current highly complex and high performing donor-

acceptor polymers. The more desirable structures for semiconducting polymers today are donor-acceptor-type polymers with perfectly alternating units. Box 1 provides background information on the principles of semiconducting polymers. Figure 1 lists several examples of semiconducting polymers along with details of their synthesis, highlighting the evolution of molecular complexity in recent years. Despite the clear advantages of current semiconducting polymers, a severe limitation is that their synthesis often requires many steps and relies on stoichiometric amounts of toxic metallic reagents. The most common methods to synthesize semiconducting polymers are through Heck, Suzuki, Kumada, Negishi, or Stille couplings (Figure 1). These current methods require arene pre-functionalization but are compatible with a wide range of functionalities. However, pre-functionalization of highly complex monomers can extend the number of synthetic steps, require stoichiometric amounts of reagents, and produce toxic metallic byproducts. A key challenge standing between high performing semiconducting polymers and commercial mass-production of organic electronics lies in the long synthetic processes that generate large amounts of waste. In this review, we focus on the most recent advances in synthesizing semiconducting polymers in a greener, more sustainable way with an emphasis on solvent and catalyst choice, and energy efficiency.

The worldwide demand for energy and high performing electronic devices, along with the increasing need for economical and environmentally sustainable chemistry, requires semiconducting polymers that are both scalable and sustainable (i.e., both economically and environmentally feasible). The concern with waste generation and use of toxic/hazardous chemicals has already shaped many operations in chemical and manufacturing industries. In the past, emphasis has been placed on the treatment of waste generated during production. However, waste prevention at the source is necessary for developing cleaner processes and products. Green chemistry is a refocusing of chemical strategy from chemical waste treatment to prevention.

The green synthesis of semiconducting polymers

Quantifying "green"

Green chemistry is a strategy to maximize efficiency and minimize hazardous impacts on the environment and human health. In 1991, the “12 principles of green chemistry” were developed to help guide scientists in achieving the goals of preventing environmental contamination and protecting human health [25]. Figure 2 (Key Figure) summarizes the 12 principles of green chemistry (circled icons) and general descriptions of each. The two oldest and most commonly used metrics to quantify green chemistry are mass-based metrics: atom economy and environmental factor [26]. Atom economy is defined as the percentage of the total product molecular weight over the total reactant molecular weight. The higher the atom economy, the greener the reaction is considered. The environmental (E) factor is defined as the total waste mass over the product mass. Thus, a higher E factor indicates increased waste production and a potentially more negative environmental impact. Some wastes are more hazardous to the environment than others, but as of current there are few assessments of the level of greenness of different wastes. As of now, solvents are the only chemicals that have been widely ranked in level of greenness.

The 12 principles of green chemistry applied to semiconducting polymers

The generation of chemical waste poses significant issues with the scalability and long-term sustainability of semiconducting polymers in organic electronics. Each additional synthetic step will result in an increased economic cost and generation of chemical waste. It is estimated that even for the synthesis of P3HT, one of the most synthetically accessible semiconducting polymers which require only three steps, the production of 1 kg of P3HT would generate about 430 kg of waste, some of which contain toxic metallic byproducts [17]. Following the generation of chemical wastes, industries and academic laboratories have their wastes disposed of properly by the rules and regulations implemented by the environmental health and safety. Historically, hazardous wastes were allocated to regular landfills and resulted in the leaching of hazardous materials into the ground and water sources. Current hazardous wastes are destroyed in an incinerator, neutralized, and then placed in a landfill. Incineration is considered one of the best ways for waste management and disposal. In 2016, a new incinerator developed by Clean Harbor was built in El Dorado, Arkansas, USA, and is held to the most rigorous standards to reduce the

emission of hazardous air pollutants into the environment such as NO_x [27]. However, to maintain those stringent standards, scientists must do their part in reducing the wastes that require incineration.

Although green chemistry is well known and practiced in chemical and industrial manufacturing, until recently, academia has put less emphasis on environmentally benign methods in favor of obtaining specific target compounds. Specific target compounds may lead to desired functionality and improve human well-being, such as more efficient photovoltaics, but the consequences of such endeavors result in the disruption of global climate and challenges the morality of our chemical creations [28]. Despite our good intentions, we must face and examine the potential deleterious impacts of our work. Concerns about atom economy, E factor, and overall greener chemistry have gained more attention from academic researchers studying more sustainable semiconducting polymer synthesis in efforts to reduce costs and synthetic complexities of designer semiconducting polymers [29]. Figure 2 also summarizes major the principles applied to semiconducting polymer synthesis along with recommended and ideal reaction parameters (boxed) in terms of atom economy, safer solvents and auxiliaries, catalysts, and energy efficiency that are discussed in this review.

Emerging green strategies for semiconducting polymer synthesis

Greener Solvents

In 2005, a green solvent selection guide was produced by the ACS pharmaceutical panel to integrate green chemistry and engineering in pharmaceutical companies [27]. The rankings of green solvents are based on the level of toxicity to humans and the environment (refer to Figure 2, under safer solvents and auxiliaries) [30]. The overarching goal was to achieve business and environmental sustainability. For typical laboratory chemical waste, hazardous organic solvent wastes comprise of more than 80% of the chemical waste produced [31,32]. Chemical purification is usually a major source of solvent waste, leading to many attempts to bypass excess waste through one-pot syntheses requiring minimal purification steps. However, purification via column chromatography is occasionally unavoidable when synthesizing monomers required for

polymerizations; achieving a greener chemical synthesis using less hazardous organic solvents is imperative. A strategy to minimize the use of organic solvents resulted in the usage of alternative greener solvents primarily as the polymerization solvent. Below, we explore several recent studies of semiconducting polymer synthesis in greener solvents.

Cross-coupling reactions are often carried out in aprotic solvents (e.g., dimethylformamide (DMF), chloroform, dimethylacetamide (DMA), and tetrahydrofuran (THF)) because these solvents readily solubilize many monomers, carrying out a wide range of reactions [32]. Currently, most semiconducting polymers are synthesized and processed in halogenated solvents. These solvents pose the greatest risk towards human health and environmental sustainability because of their volatility and high toxicity. In recent years, the use of alternative greener solvents has been encouraged [33]. However, a major challenge in solvent selection for polymerizations lies with polymer solubility. The current strategy to enhance polymer solubility in a given solvent is to attach side chains or other solubilizing groups on the repeat units. Although there has been progress in using greener solvents for processing organic electronics (e.g., organic photovoltaics [34-36]), there are fewer studies exploring semiconducting polymer synthesis in greener solvent reaction mediums. This is often because of low polymer solubility, as well as degradation of active species for polymerizations and catalysts in alternative solvents.

Complicating the matter further, more than one principle of green chemistry is often relevant at a given time when synthesizing a semiconducting polymer. For example, prioritizing biocompatibility and usage of renewable resources (Figure 2), Strappaveccia and colleagues developed a bio-mass derived solvent medium (i.e., γ-valerolactone; GVL) to replace DMF or N-methyl-2-pyrrolidone (NMP) and carry out cleaner Heck coupling reactions (Figure 3a) [32]. Here, GVL provided a suitable reaction medium for synthesis of poly(p-phenylene vinylene) (PPV) derivatives in high yields and purity with a low palladium content of 0.1 mol%. Special attention was also given to palladium leaching into the final product. Compared to NMP, GVL was superior in controlling palladium impurities in the final PPV polymer. Other noteworthy achievements with bio-derived solvents were achieved by Bannock and colleagues using 2-MeTHF to perform

flow-chemistry synthesis of P3HT using Grignard metathesis polymerization (Figure 3b) [33]. Derived from inedible bio-mass, 2-MeTHF is one of the most popular green solvents used as an alternative to THF, which poses difficulties in large-scale manufacturing because of its energy intensive recycling practices and non-renewable nature [37,38]. This work represents a significant improvement towards the scalability of P3HT (and other GRIM-type polymerizations) in greener solvents.

C-H bond functionalization offers tremendous potential for atom-efficient synthetic methodologies (Figure 2) [39]. In polymerizations, significant synthetic effort is expended on creating the monomers. Much of C-H functionalization focuses on small molecule couplings, and therefore, provides an advantage for synthesizing complex monomers. However, there are still considerable shortcomings when applying C-H bond functionalization to polymerization [40]. The current challenge for C-H functionalization applied to polymer synthesis stems from poor selectivity and lower molecular weights compared to the Stille-synthesized counterparts. Thus far, direct arylation polymerization (DArP) has been the most prominent C-H functionalization method for synthesizing semiconducting polymers. DArP requires only one monomer to be pre-functionalized and avoids producing toxic metallic byproducts from the more traditional synthetic methods (Figure 1). However, achieving the desired sequence with certain monomers, for example, is challenging due to possible activation of multiple C-H bonds. The activation of multiple C-H bonds can introduce defects (e.g., homocoupling or branching) into the polymer backbone, generate undesired byproducts, and/or result in cross-linked polymer chains. These outcomes often result in non-uniform chains, lower molecular weights, and lower performance in devices. Additionally, each monomer requires reaction-condition optimization (e.g., additives, ligands, catalysts, and reaction time and temperature). To date, there is no general DArP condition that is applicable to all monomer types; the quest to find robust DArP conditions is of utmost interest to many research groups.

Despite the above limitations, DArP has been successfully employed to produce high molecular weight polymers. Focusing on solvent development, Matsidik and colleagues combine the use of

2-MeTHF with DArP to synthesize a high electron mobility polymer, PNDIT2 [41]. Dudnik and colleagues then used 2-MeTHF for the development of high photovoltaic efficiency conjugated polymers reaching power conversion efficiencies of >8% [42]. With this method, the authors showed that the polymers were comparable, and sometimes superior, to the Stille-derived polymers. Pappenfus and colleagues were also able to scale batch synthesis of P3HT via DArP in 2-MeTHF to 10 g [18]. Further development of DArP in greener solvents by Grenier and colleagues demonstrated biphasic DArP using equal parts of toluene and water, and the addition of a phase-transfer agent (Figure 3c) [43]. Impressively, these biphasic conditions were able to produce polymers in reasonable yields and molecular weights while in the presence of oxygen. Pankow and colleagues also explored DArP in cyclopentyl methyl ether and successfully synthesized a PPDTBT semiconducting polymer [44]. When comparing polymers synthesized in THF and under hazardous high-pressure conditions, the polymer made with the cyclopentyl methyl ether showed high yields, higher molecular weights, higher regioregularity, and no β-defects.

Less Costly Catalysts

Current catalysts used for synthesizing semiconducting polymers rely heavily on precious metals (e.g., ruthenium, rhodium, iridium, and palladium). Not only are these metals toxic, but their low natural abundancies lead to volatile market prices and increased cost of semiconducting polymers. One strategy to mitigate the costs and environmental impact of precious metal catalysts is to use low catalyst loadings (ppm amounts). Many polymerizations still rely on palladium or tin as catalysts, for example, in Stille couplings. Current synthetic methods must minimize the need and heavy reliance on toxic metal catalysts. Figure 2 provides some more information on more ideal catalyst selections for semiconducting polymer synthesis. Some promising work conducted by Handa and colleagues employed ppm levels of palladium catalysts (sourced from iron impurities) in coupling reactions [45]. Additionally, several polymerizations have successfully carried out with <1% catalyst loadings [42,43]. However, significantly fewer reports have achieved ppm levels of catalysts in polymerizations. In 2015, Rudenko and colleagues performed DArP with ppm amounts of palladium to synthesize P3HT [46]. Interestingly, their reagent lowering strategies resulted in the increase of polymer regioregularity

from 94.6% to 96.5%. Other recent advancements moving away from toxic metal catalysts are developing more environmentally benign catalysts involving first-row transition metals.

First-row transition-metal catalysts: Novel catalysts based on first-row transition metals (e.g., nickel, copper, cobalt, and iron) have attracted major interest due to their high natural abundancies and biocompatibility. With the design of new ligands, first-row transition-metal catalysts (TMCs) have emerged as attractive alternatives to precious metal chemistry. Past studies have demonstrated the use of first-row TMCs for the synthesis of small molecules and in bi-aryl cross-couplings. Recently, studies have demonstrated the synthesis conjugated semiconducting polymers with first-row TMCs based on nickel and copper. However, there are very few recent investigations that explore the use of other abundant metals, especially iron.
Despite the environmental concerns of organotin wastes, current methods for synthesizing semiconducting polymers still rely primarily on Stille coupling reactions because resulting polymers are produced in superior yields, high molecular weights, and low dispersity. In 2018, an improved Stille polymerization protocol with chlorobenzene as the solvent and Pd(0)/Cu(I) as the co-catalyst was developed to produce high number-average molecular weight electron-deficient semiconducting polymers composed of naphthalenediimide and benzothiadiazole derivatives to produce n-type semiconducting polymers (Figure 4a) [47]. Compared to p-type polymers, n-type semiconducting polymers are more difficult to synthesize. It was found that the Cu(I) salts reacted with the organostannes to produce a more reactive organocopper intermediate. These organocopper intermediates in turn lead to quicker transmetalation in the catalytic cycle for coupling.

Nickel catalysts have potential use for inexpensive Stille and Suzuki couplings, partly due to facile oxidative addition with a range of pseudohalides and halides [48]. Nickel catalysts have been successful in synthesizing polythiophene in Negishi-type catalyst-transfer polycondensation to produce regioregular P3HT with low dispersity [49]. Nickel catalysts have also been used in Suzuki reactions affording ester-functionalized conjugated polymers (Figure 4b) [50]. Currently, nickel is predominately used to synthesize monomers prior to polymerization [51], whereas palladium is

used primarily for polymerizations due to higher functional-group tolerance and superior performance [52].

Copper is another commonly used first-row TMC for aryl-aryl cross-couplings. Only recently have copper catalysts been studied for the synthesis of semiconducting polymers. In 2018, Pankow and colleagues reported the first copper-catalyzed DArP conditions to synthesize perfectly alternating donor-acceptor polymers [53]. Soon after, the catalyst loading was decreased from 50% to 5% for copper-catalyzed DArP of a fluorinated conjugated polymer (Figure 4c) [54]. The authors are currently working to expand the scope of copper-catalyzed DArP.

Micellar catalysts: In an effort to combine greener solvents and catalysts, micellar catalysts can be used to synthesize novel and conventional materials in aqueous media without the use of organic solvents. To our knowledge, the earliest evidence of micellar catalysts or phase-transfer catalysts for the synthesis of semiconducting polymers is the generation of polypyrrole with soybean catalysts [55, 56] and hematin [57]. Very recently, Suzuki-Miyaura reactions have been carried out using Kolliphor EL, a non-ionic oil-in-water emulsifier synthesized from reacting castor oil with ethylene oxide, as a phase-transfer catalyst for coupling reactions [58]. Although this study involves small molecule couplings, the authors state that promising results have been achieved with polymerizations. Although micellar catalysts have not yet been formally applied to synthesize semiconducting polymers, this potential class of catalysts holds promise [31, 45, 59].

Energy efficient and aerobic reaction conditions

Most semiconducting-polymer syntheses require input of energy, such as heat. High reaction temperatures are often the source of byproducts in reactions and contribute to the costs of synthesis. Scalability is a significant issue when reactions require enormous energy inputs for synthesis and fabrication. Although more difficult to achieve, synthesis at mild or room temperatures is ideal to maintain energy efficiencies for polymerization (Figure 2). Additionally, aerobic conditions can be beneficial to reactions so that long purges to achieve air-free environments are no longer required. To date, few polymerizations of semiconducting polymers

have been successfully performed under aerobic conditions. Those that have been successful have primarily utilized C-H functionalization, as discussed below.

Energy efficient synthesis: Energy efficient syntheses have employed less conventional polycondensation reactions and methods to produce semiconducting polymers. In 2018, room temperature synthesis of iridium-containing polymers was achieved with copper through reversible deactivation radical polymerization [60]. Another polymer synthesis at room temperature was performed under high pressures with a diamond anvil without the use of catalyst or solvents [61]. Additionally, poly(*o*-anthranilic acid) emeraldine salt (PANA-ES) as a conjugated polymer was also synthesized at room temperature through an oxidative polymerization route [62].

Oxygen as an oxidant: Reactions that can tolerate aerobic conditions may bypass the need for energy intensive deoxygenation, especially at larger scales. There are few reactions that are able to withstand the radical effects of oxygen and the majority of reactions that are able to undergo aerobic conditions are direct arylation polycondensation reactions. In 2018, Kanbara and colleagues synthesized thienopyrroledione-based π-conjugated polymers via DArP under aerobic conditions using a palladium catalyst in toluene [63]. By refluxing the reaction mixture, they were able to degas oxygen and, owing to the high vapor density of toluene, prevent oxygen resolubilization. Additionally, Kanabara and colleagues synthesized bithiazole-based semiconducting polymers via DArP under aerobic conditions using a copper catalyst [64].

Concluding remarks

Achieving environmentally benign synthesis for semiconducting polymers is a multifaceted problem that requires investigations from the multiple facets of the Principles of Green Chemistry. This review focuses on recent advances and trends in greener synthesis of semiconducting polymers specifically in regard to greener solvents, sustainable catalysts, and aerobic and benign conditions. Solvents account for a substantial amount of chemical waste produced. Recent successful polymerizations with greener biomass-derived solvents

demonstrate the potential to move away from halogenated solvents and that 2-MeTHF is the most commonly used green solvent. Another approach to greener polymerizations investigates alternative catalysts to current precious metal catalysts, such as palladium. Among these alternatives, the most popular first-row transition metal catalyst is copper. Additionally, a significant amount of work has been put forth to synthesize polymers through C-H functionalization to reduce the number of synthetic steps. Although direct arylation polycondensations have ushered the wave of cleaner and more efficient synthetic methodologies, their selectivity and ability to produce high molecular weight and defect-free polymers still require further improvements.

A combination of lower-catalyst loading, energy efficiency, and greener solvents will no doubt benefit the field of semiconducting polymer synthesis towards cheaper and greener optoelectronic devices. In order to achieve sustainable semiconducting polymers, current environmentally benign methodologies must be able to synthesize high performing semiconducting polymers as well as, or better than, traditional synthetic methods. Yet, this remains a challenge and until more environmentally benign methods that combine more principles of green chemistry more are viable. See Outstanding Questions Box on possible future challenges and questions. Until then, the economic and environmental cost of semiconducting polymers may remain high.

Highlights

1. Green and biomass-derived solvents are desirable and popular as alternative solvents in achieving greener polymerizations; the most popular solvent being 2-MeTHF (an alternative to THF).
2. Direct arylation polymerization is one of the more atom efficient methods developed but still have limitations in producing high performing semiconducting polymers; the greenest solvent conditions thus far use biphasic conditions of toluene and water.
3. Copper catalysts are emerging as a first-row transition metal catalyst for polymerizations, as an alternative to rare metal catalysts, and are sometimes compatible with polymerizations under aerobic conditions.

Outstanding Questions Box

1. What is the origin of the success of 2-MeTHF as a green solvent alternative in polymerizations? Is the solvent able to aid the polymerization mechanism in ways that other solvents cannot? This may help in understanding how to develop greener reaction conditions.
2. How can we combine efforts of first-row transition metal couplings in greener solvents for polymerizations?
3. What kind of catalysts can help achieve polymerizations under ambient temperatures? So far, only few polymerizations can be achieved under ambient temperatures.
4. What is the origin of the differences in catalyst efficiency between precious metals, such as palladium, and first-row transition metals, such as copper, for polymerizations?
5. How would various chemical wastes produced from polymerizations be ranked in level of greenness and recyclability? Some wastes are more recyclable than others and can help achieve closed-loop recycling (such that materials can be re-used to create the same products and minimize overall waste production), yet there are no overall rankings to understand the recyclability of chemical wastes. Such assessments may aid chemists in developing more sustainable chemical methods to close the loop on chemical processes.
6. What is the best route to increase the selectivity and increase higher molecular weight polymers with C-H Functionalization?

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Conflicts of interest

The authors declare no conflict of interest.

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Box 1. Principles of semiconducting polymers.

Semiconducting polymers are macromolecules that conduct electricity under specifically controlled conditions. Although there are different classes of semiconducting polymers, they are all typically described in terms of their energy bands from the bonding and anti-bonding energy levels associated with the σ- and orthogonal π-bonds between neighboring carbon atoms [16]. Structurally, semiconducting π-conjugated polymers are characterized with a backbone of

alternating single- and double- or triple-bonds; the delocalization of the π-electrons is primarily responsible for the unique optical and electronic properties of the polymer. The optoelectronic properties are modified by tuning the energy gap between the energy of the highest molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The energy band gaps in conjugated polymers can also be analogously considered as the energy difference between the conductive and valence bands in semiconductors. Photon absorptions lead to the excitation of electrons from the HOMO to the LUMO. Those electrons then move along the π-conjugated backbone of the semiconducting polymer to conduct electricity. Depending on the energy level difference, the photon energies required to excite the electrons range from ultraviolet to infrared, and therefore, determine the emission and energy thresholds for the polymer to conduct electricity.

The cost of semiconducting polymers increases linearly with each synthetic step, costing about $31 (USD) per gram per step [17]. Much of the development of these polymers occur in small-scaled batches in academic laboratory settings; however, for the commercial production of organic electronics these polymers must be able to be scaled from gram-scale to the thousands of kilograms [17]. Sustainable multi-ton synthesis of semiconducting polymers is a chemical challenge that will influence the types of materials that can be incorporated into large-area devices. Typically, semiconducting polymers are synthesized in small laboratory batches which is suitable for small scales of hundreds of milligrams. It has been shown that batch synthesis can result in high yields up to 10 g [18]. However, batch synthesis can result in large batch-to-batch variations in morphology, molecular weight, and dispersity. Ultimately leading to non-uniform device performance and poor-quality control. A strategy in producing uniform semiconducting polymers and in larger scales is through continuous flow chemistry [19].