ACS Macro Letters
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Direct (Hetero)arylation Polymerization: An Effective Route to 3,4-Propylenedioxythiophene-Based Polymers with Low Residual Metal Content

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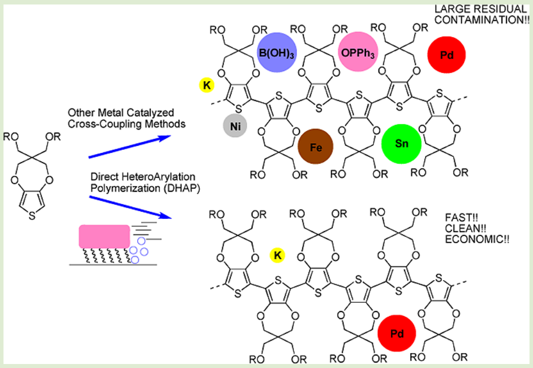
Supporting Information

ABSTRACT: We report the use of direct (hetero)arylation polymerizations (DHAP) as a means of obtaining 3,4-propylenedioxythiophene-based conjugated polymers for use in electrochromics. This method offers a rapid route to achieving polymers in high yields with simplified purification procedures and low residual metal content, as determined by inductive coupled plasma-mass spectrometry (ICP-MS). The studied polymers possess comparable electrochromic properties to those previously reported by our group, implying that their switching ability from a colored to a transmissive state is independent of the residual metallic impurities.



The organic electronics community has benefited tremendously from the development of palladium-catalyzed, cross-coupling reactions,[1] which offer facile access to a wide range of chemical structures that would otherwise be challenging to achieve.[2] This capability has enabled structure−property relationship studies that provide design parameters for useful organic materials. The unique processability of organic materials renders these attractive because the replacement of inorganic semiconductors with organic surrogates helps to decrease device fabrication costs.[3]

Furthermore, considerable research efforts have been devoted to the simplification of these reactions. The success of Heck protocols[4] for the coupling of vinyl termini to halogenated arenes has generated a large amount of effort that, building upon the work of Ullmann[5] and Goldberg,[6] led to the discovery of "activated" C(sp^2)−H bonds in aromatic systems that react in similar fashion.[7] The Pd-catalyzed direct arylation of (pseudo)halides has been rapidly developing through the years to the point where minute amounts of undesired side products are generated upon coupling completion. While the mechanistic details of the Pd insertion to the activated C−H bond are not fully understood,[8] successful protocols have been developed for the coupling of thienyl-based molecules to a wide variety of organic halides.[9,10] Once it was reported that this dehydrogenative cross-coupling takes place at fast rates under phosphine-free conditions,[11] many groups[12] successfully transposed this improved methodology for the synthesis of thiophene-based conjugated polymers; hence, its name direct (hetero)arylation polymerization (DHAP).

Compared to the standard Suzuki and Stille polymerizations, DHAP simplifies the purification procedures for the conjugated polymers obtained thus reducing overall costs.[13] Furthermore, the absence of phosphine in the reaction mixture avoids its incorporation into the polymer backbone,[14] which is often the reason why residual phosphorus is hard to remove from the polymer during the purification stage. The residual contaminants left in conjugated polymers are often associated with poor performances when these are utilized as active components for electronic devices.[15] Such impurities (Sn-, Pd-, and Br-based) can act as charge trapping sites, thus, hampering efficient charge transport. Therefore, it is important to understand the type and quantity of residual impurities of various polymerization protocols due to the potential high impact that these may have in their final application.

As an attempt to understand this, we have applied DHAP for the synthesis of 3,4-propylenedioxythiophene-based electrochromic polymers (ECPs). We have found that the DHAP is appealing for the preparation of polymers with low residual metal content (10−100 ppm) given the simplified purification process. Additionally, these polymers display vibrant colors and

Received: July 24, 2013
Accepted: September 9, 2013
Published: September 17, 2013

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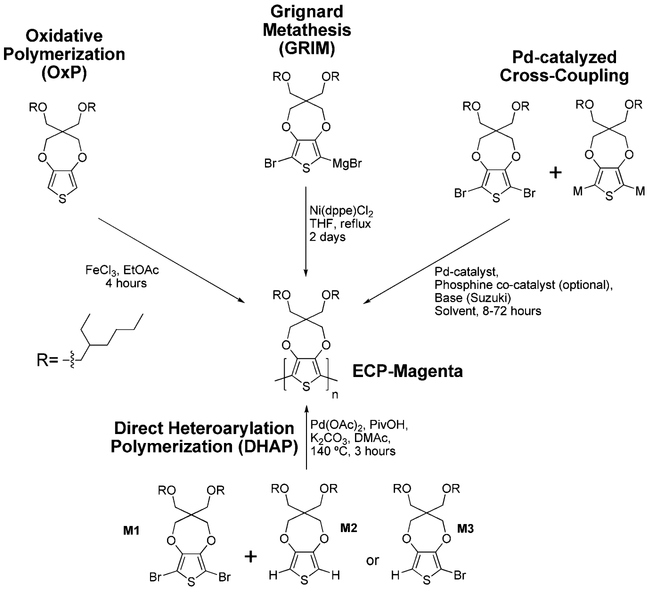
electrochromic properties comparable to those previously reported by us using other transition-metal-based procedures.[16]

We investigated the impact of residual impurities in the color purity and transparency upon oxidation of our ECPs with the intent to reduce fabrication costs and increase performance. For this, the synthesis of the homopolymer ECP-Magenta served as an initial standard to examine the residual metal content generated from common routes, illustrated in Scheme 1, such as oxidative polymerization (OxP),[17] Grignard metathesis (GRIM),[18] or Pd-catalyzed cross couplings (e.g. Suzuki, Stille, etc.). OxP yields ECP-Magenta with molecular weights (M_n) of 30 kDa on average, yet large amounts of $FeCl_3$ (≥4 equiv) are necessary to achieve these weights.[17] This approach creates difficulties during the purification stage through the disposal of large amounts of residual Fe/Fe(II) composites. In comparison, GRIM polymerization also provides polymers with high molecular weights (M_n = 10−48 kDa), although the removal of impurities via Soxhlet extraction requires multiple days.

Scheme 1. Synthetic Routes Studied for the Generation of ECP-Magenta



We have noticed after using slightly modified conditions to those reported by Kanbara,[12a] illustrated in Scheme 1 as direct (hetero)arylation polymerization (DHAP), that there is a compromise between processing time and atom economy for the synthesis and purification of ECP-Magenta which is completed in less than one day. We have found that the role of the temperature is important; the reaction is slower within the 80−100 °C range than at 140 °C where the transformations occur at fast rates without any noticeable decomposition. Our observations are in line with previous reports of Yu et al.[12e] where almost identical substrates fail to react in DMAc at 100 °C (in their case, R = n-C_6H_{13}). The initial characterization analysis was performed after precipitating the polymer in a 1:1 MeOH/1 N aqueous HCl solution with vigorous stirring, followed by filtration and washing with a copious amount of water (until the AgCl test is negative) and then MeOH. The utilization of this procedure resulted in high yielding (80−90%) polymers with $M_n \geq$ 10 kDa against polystyrene standards and relatively small dispersities ($Đ_M \sim 1.6$)[19] in reasonably short times (3−15 h). Initially, negligible differences were observed in aliquots analyzed after 3 and 15 h of reaction time (M_n = 10.0 kDa, $Đ_M$ = 1.59 after 3 h; and M_n = 10.6 kDa, $Đ_M$ = 1.64 after 15 h). Other polar aprotic solvents such as NMP and HMPA were also tested and the results compared with those from DMAc. These results are summarized in Table 1, where it is clear that both solvents have a good influence on the resulting M_n values.

Table 1. Influence of Solvent on the Preparation of ECP-Magenta via DHAP

solvent	ε[a]	time (h)	yield (%)	M_n (kDa)	$Đ_M$
DMAc	38	15	87	10.0	1.64
NMP	32	24	82	23.0	1.74
HMPA	31	24	80	26.3	2.52

[a] ε = dielectric constant.

Next, we decided to evaluate the evolution of molecular weights, and monomer consumption of the DHAP with time (case A). Small aliquots (∼1−2 mL) of the reaction mixture were precipitated in a 1:1 concd HCl/MeOH mixture, extracted with DCM, and concentrated. The resulting polymers were analyzed by GPC and ^{1}H NMR. The plot of M_n and $Đ_M$ versus polymerization time of each aliquot can be seen in Figure 1A. These data suggest that the polymer chains grow to a size that tends to remain constant with polymerization time; coupled with the relatively small $Đ_M$ values, a chain-growth polymerization mechanism could be initially considered.[20] However, the GPC traces shown in Figure S1 (Supporting Information) highlight polymer formation at short time scales (∼2 min) as well as the formation of shorter chains, which disappear from the mixture after 24 h.

The previous results prompted us to look at the evolution of monomer concentration in solution. The polymerization was carried out again in the presence of dodecane as internal standard, where aliquots from the reaction mixture were subjected to GC-MS. The results, shown in Figure 1B, show that the starting monomers are consumed within 2−3 min. This information correlates well with the ^{1}H NMRs of the aliquots taken from solutions without dodecane, shown in the inset for comparison (Figure S2 offers the ^{1}H NMR traces of the individual components). Thus, it is clear the monomers are totally consumed prior to the weight evolution of the polymer and that the relationship between monomer conversion and M_n of the polymer is nonlinear.

The DHAP of the monobrominated adduct (**M3**), instead of the nonbrominated (**M1**)/dibrominated (**M2**) mixture, was also evaluated (case B). Figure S3 shows a similar behavior for the consumption of the starting materials for both cases at $t < 3$ min, where it is evident that the **M1**/**M2** reaction (case A) proceeds faster. Additionally, the reaction kinetics of the DHAP of **M3** is analogous to that reported by Ozawa et al. on the DHAP of 2-bromo-3- hexylthiophene (2B3HT) using Pd(*o*-tolyl)$_3$ and a phosphine cocatalyst.[21] Figure S4 shows the progression of the concentration of **M3** for $t < 3$ min. We have found that our conditions render a faster reaction, however: the stage obeying first-order kinetics with respect to the concentration of **M3** presents in our case a $k_{obs} = (8 \pm 1) \times 10^{-3}$ s^{-1}, which is two orders of magnitude larger than that observed for Ozawa for the synthesis of P3HT from 2B3HT.[21]

The polymer, freshly prepared as mentioned above, was subjected then to a more thorough cleansing procedure: it was redissolved in chlorobenzene at 50 °C and treated with a Pd-

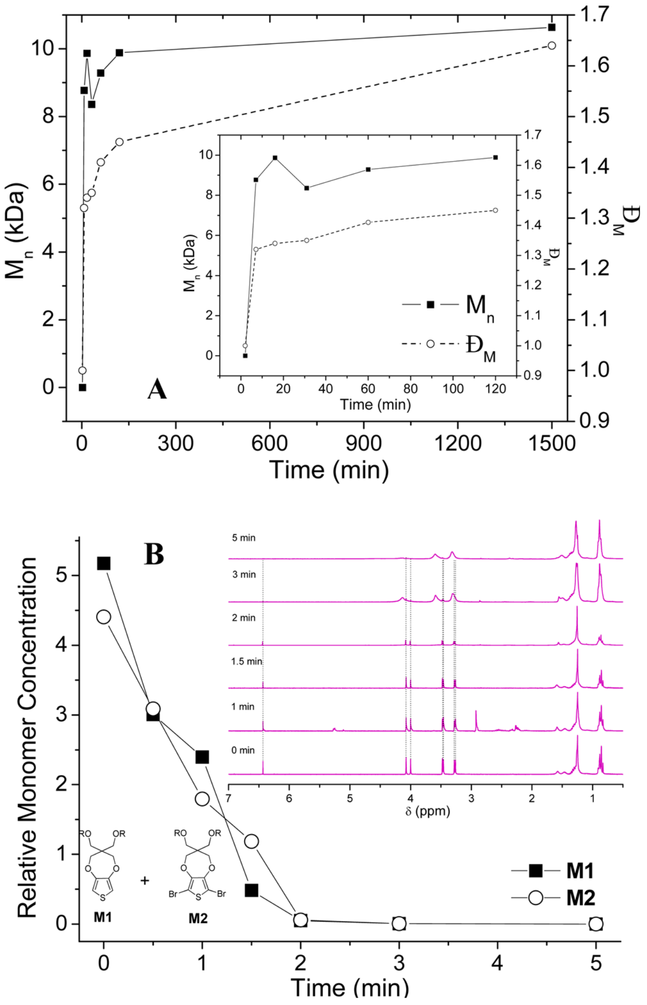


Figure 1. (A) M_n (filled rectangles) and $Đ_M$ (open circles) as a function of time for the synthesis of ECP-Magenta via DHAP in DMAc. (B) Change in relative concentration of monomers **M1** and **M2** with respect to dodecane (internal standard) as judged by GCMS. Inset: ^{1}H NMR signal evolution of the different aliquots taken from this polymerization.

scavenger and 18-crown-6 to remove the residual Pd and K metals (see details in section S2.2, Supporting Information). After the polymer was precipitated in acidic MeOH, it was filtered and washed with MeOH, then hexanes. Finally, the polymer was dried under vacuum overnight. This purification procedure showed little differences in the M_n values (+2–3%) signifying losses of only lower molecular weight material as expected. Further, no observable differences were detected in the ^{1}H NMR spectra (Figure S5). The residual content of representative elements was determined by ICP-MS from polymer samples subjected to similar purifications procedures but created from different polymerization methods. This is illustrated in Figure 2, where it is shown that the metal content displayed by the polymers made via DHAP is less than 20 ppm for all cases. For example, the OxP utilizes more than 4 equiv of $FeCl_3$, which results in a high content of elemental Fe (>1000 ppm). All other selected elements were low in content. GRIM polymerization displayed elevated contents of Mg and Ni (>900 ppm), as judged by the use of these metals in the polymerization. While the presence of phosphorus is relatively larger than the other two polymerization procedures, these are not significantly large (less than 1 order of magnitude). While the potassium content is an important consideration, technical limitations of our ICP instrument hampered its study. The relative values were unresolved due to the large K background signal. Figure S6 provides the residual content for selected elements, as measured by ICP-MS from ECP-Magenta samples synthesized in DMAc, NMP, and HMPA before and after purification. Interestingly, the sample synthesized from HMPA displayed the highest content of Pd before and after purification (~30–50 times those of DMAc/NMP samples). The higher number of residual phosphorus implies the presence of HMPA in the polymer (i.e., it is the only source of phosphorus), which makes us consider that HMPA could be binding Pd.

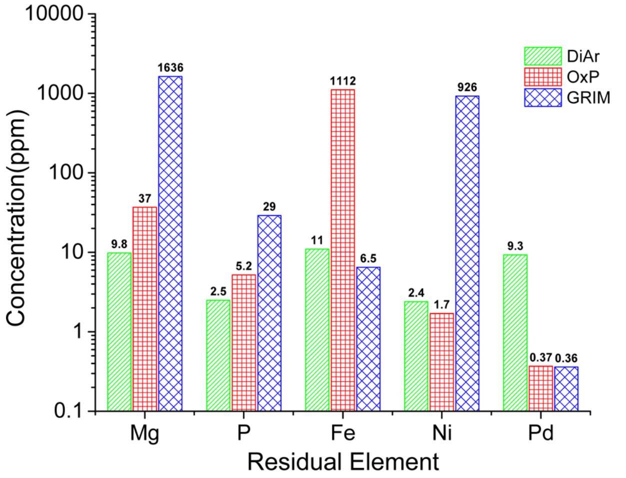


Figure 2. Residual content of selected elements for polymers obtained via DHAP, OxP, and GRIM.

Figure S7 provides the UV–vis absorption and emission spectra of the toluene solutions of polymers synthesized by different methods. Their absorption was identical, except in the low energy maximum localized at 595 nm, which is more intense in the case of the GRIM and DHAP generated polymers (DMAc). These solutions follow Lambert–Beer law at the 1–10 mg/mL concentration regime Figure S8). However, the solution fluorescence differs more noticeably; the OxP and DHAP polymer before purification presented the reddest shifted spectra and the other two polymers, GRIM and DHAP after purification, presented almost identical spectra. Figure S9 illustrates that samples with O.D. ≤ 0.1 show linear behavior in their fluorescence intensity; also, the fluorescence gradients from these polymers presented in Figure S10 are comparable. The lower fluorescence yield of the DHAP sample before purification illustrates the effect of residual Pd content in promoting nonradiative decay paths, presumably via intersystem crossing through external heavy atom effect.[22] Technical restrictions precluded the acquisition of the emission lifetimes, as these are shorter than the pulses of our nanoLED source (~1.2–1.4 ns).

Given the promising results obtained up to this stage, we decided to test the flexibility of the DHAP conditions for the preparation of alternating copolymers. As an initial example, copolymerization of 4,7-dibromo-2,1,3-benzo-thiadiazole with monomer **M1** in NMP afforded ECP-blue[23] in high yields with M_n = 9.4 kDa and $Đ_M$ = 1.54. From this success, we expanded this protocol to complete the full CMYK palette: cyan,[24] yellow,[25] and black.[26] The structures of all synthesized polymers are shown in section S2 in the Supporting Information. All attempts afforded us with polymers of high molecular weight in good yields, comparable to those previously reported except for ECP-blue.[21−24] The pertinent characterization data for all polymers are summarized in Table 2. In the case of ECP-cyan, the ^{1}H NMR data are identical to those of the reported sample synthesized via OxP.[24] We believe that the DHAP sample presents higher M_n values than the reported polymer since its insolubility in THF prevented the GPC characterization.

Table 2. Scope of DHAP for the Synthesis of ECPs

polymer	yield (%)	M_n (kDa)	$Đ_{\mathrm{M}}$	DP
ECP-magenta	82	23.0	1.74	52
ECP-yellow	76	27.5	1.19	53
ECP-blue	81	9.41	1.54	16
ECP-cyan[a]	89			
ECP-black	76	11.0	2.03	

[a] This polymer was not soluble in THF at the required concentrations for successful GPC analysis.

Toluene solutions of these polymers were sprayed on ITO slides and characterized by means of UV−vis spectrophotometry. As shown in Figure 3, the ECP-magenta film exhibits good color purity and excellent contrast ($\Delta\%T$ = 79% at 530 nm) comparable to the best performing polymers previously reported ($\Delta\%T$ = 80% at 609 nm).[18a] Interestingly, the contrast is steady in spite of the lower amounts of residual metal content from the DHAP samples. By comparing the spectroelectrochemical curves of these polymers with those reported in the literature,[21−24] we see no remarkable differences in performance from polymers that were synthesized through other Pd-catalyzed cross-coupling reactions (Figures S11 and S12), except for the case of ECP-blue, whose contrast was smaller than that reported by us for a polymer with higher M_n.[23] This implies that the contrast is a function that could be more dependent on the M_n of the polymer rather than the residual impurities. Given the atom economy, shorter times, and simpler purification procedures, we envision the DHAP methodology to reduce costs for the synthesis of ECPs that render the full color palette.

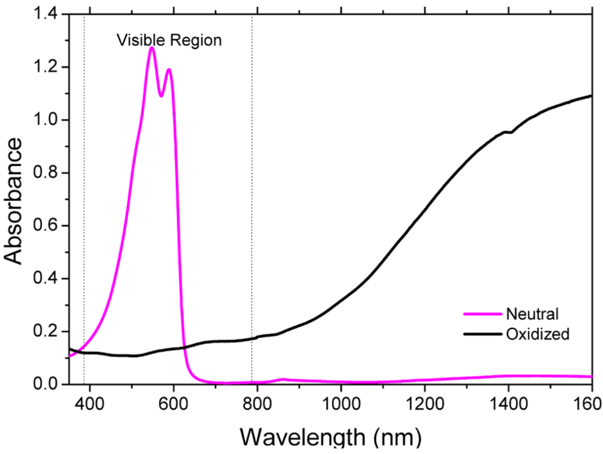


Figure 3. UV−vis spectra of ECP-magenta in neutral and oxidized forms (V = +0.8 V vs Ag|Ag$^+$).

■ ASSOCIATED CONTENT

Supporting Information

Synthetic procedures and characterization plus materials and instrumentation details; supporting figures; ^{1}H and ^{13}C NMR spectra of novel compounds and ^{1}H NMR spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Funding

We gratefully acknowledge the U.S. Air Force Research Laboratories UES Prime Contract FA8650-09-D-5037 and the AFOSR (FA9550-09-1-0320) for financial support.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to thank Dr. Michael C. Craig and Mr. Justin Kerszulis for the synthesis of ECP-magenta samples via GRIM and oxidative polymerization methods, respectively. Dr. Frank Arroyave is acknowledged for fruitful discussions. We also thank Ms. Brenda Calderon for help with preliminary spectroelectrochemistry studies of ECP-magenta.

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