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SUMMARY

1. PURPOSE. To provide security and policy review on the document at Tab 1 prior to release to the public.

2. BACKGROUND.
Authors: Kiah I. A. Hicks, Kirsten M. Farquhar, Gary J. Balaich, Timm A. Knoerzer, and Scott T. Iacono

Title: An Integrated Laboratory Approach towards the Preparation of Conducting Polymers

Circle one: Abstract Tech Report Journal Article Speech [✓ Paper] Presentation Poster Thesis/Dissertation Book Other: ________

Description: As polymeric materials chemistry becomes more prevalent in the undergraduate curriculum, very few reports in the primary literature are suited for a structured laboratory course. This report details the preparation of a conjugated, conducting polymer suited for an undergraduate organic chemistry laboratory course and/or a polymer chemistry course should there be such a course offering at an institution.

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4. VIEWS OF OTHERS. N/A

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1 Tab
Manuscript

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An Integrated Laboratory Approach towards the Preparation of Conducting Polymers

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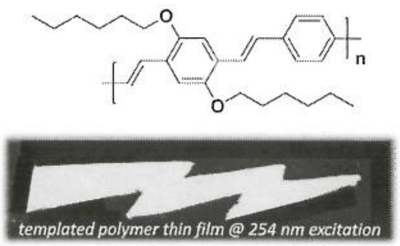
ABSTRACT

Poly(phenylene vinylene) (PPV) represents an important class of conjugated, conducting polymers that have been readily exploited in the preparation of organic electronic materials. In this experiment, students prepare a PPV polymer via a facile multi-step synthetic sequence with robust spectroscopic evaluation of synthetic intermediates and the final product. The synthetic sequence could be applied by university instructors as a capstone project for an undergraduate organic chemistry laboratory or as a centerpiece project for either a polymer or integrated laboratory course. The individual steps could be segmented and used as a modular piece in the traditional sophomore-level organic chemistry laboratory. The resultant PPV polymer is analyzed by UV-Vis and fluorescence spectroscopy to determine the quantum yield which promotes enhanced student understanding of the photophysical properties of the material. In addition, GPC analysis is completed to reveal the molecular weight and polydispersity of the polymer. Students completing this experiment gain valuable experience in organic/polymer synthesis and structural characterization utilizing GCMS, GPC, NMR, UV-Vis, and fluorescence spectroscopy, as well as in the mechanistic aspects and practical application of some of the classic transformations in organic chemistry including the S_N2 reaction, nucleophilic acyl substitution, organometallic chemistry, and Wittig reaction.

KEYWORDS: Upper-Division Undergraduate, Polymer Chemistry, Organic Chemistry, Laboratory Instruction

GRAPHICAL ABSTRACT:

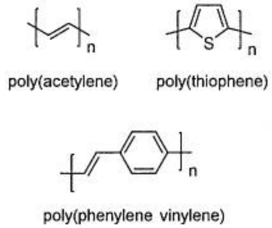


INTRODUCTION

Polymers with extended conjugation possess the intrinsic ability to delocalize electrons. The purposeful excitation by means of chemical, light, or electrical energy promotes electrical conduction, ultimately producing an emission of light. Such systems possessing these 'molecular wires' are a part of a vastly emerging field of conducting polymers for preparing organic electronics. The discovery of the first electrically conducting polyacetylene[1] has led to a renaissance in the utilization of light emissive organic conjugated polymers for the commercial preparation of highly efficient light emitting devices, magnetic storage media, photovoltaics, electro-optics, and chemical sensors.[2] As such, the 2000 Nobel Prize in Chemistry was duly awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa "for the discovery and development of conductive polymers".[3]

Organic polymers are inherently good insulators, whereby metals are exceptional conductors. By intentional manipulation of organic polymer structure, the HOMO–LUMO band gap can be narrowed allowing access to the conduction band. Classes of reasonably conducting polymers include, but are not limited to poly(acetylene) (PA), poly(thiophene) (PT), and poly(phenylene vinylene) (PPV), which serve in the broad field of organic electronics (Figure 1).

The advantages of utilizing organic polymers as reasonable electrical conductors offer access to lightweight, synthetically tailorable, low-temperature processable materials which are not feasible for metals. As polymeric materials chemistry becomes more prevalent in the undergraduate curriculum, very few reports in the primary literature are suited for a structured laboratory course. This experiment details the preparation of a conjugated, conducting polymer suited for an undergraduate organic chemistry laboratory course and/or a polymer chemistry course should there be such a course offering at an institution.


poly(acetylene) poly(thiophene)

poly(phenylene vinylene)

Figure 1. Representative Examples of Conducting Polymers

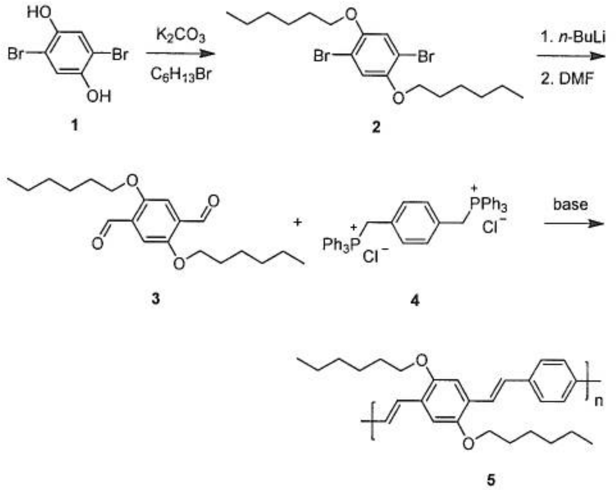
EXPERIMENT OVERVIEW

The goal of this integrated laboratory is to prepare a PPV-conjugated polymer, poly[2,5-di(*n*-hexyloxy)-1,4-phenylene(vinylene)-co-1,4-phenylene] **5**, utilizing step-growth Wittig polymerization from monomers **3** and **4**. The procedural details for the student and instructor notes are provided in the Supporting Information. This laboratory can be split into two separate laboratory experiments: (1) the synthesis of monomer **3** in an organic chemistry laboratory course and (2) the preparation of polymer **5** for a polymer (or materials) chemistry course or advanced synthesis course. Alternatively, the entire synthetic process can be undertaken as a project for an appropriately themed advanced laboratory course.

The synthesis, purification, and characterization of monomers **3** and **4** can be easily accomplished over the course of 3 × 3 h laboratory meetings. Either monomer **3** or **4** can be purchased through commercial sources if the instructor chooses to focuses on just the synthesis of one over the other. The preparation and characterization of polymer **5** requires 2 × 3 h laboratory meetings. The first session involves the synthesis, purification, and drying in preparation of the second session which is exclusively devoted to structural characterization (NMR, GPC, spectroscopy).

All laboratory manipulations, consumables, equipment, and glassware are typical of a standard organic laboratory. Each synthetic step produces products with acceptable student yields and reasonable purity with no major side products. This experiment is amenable to scale-up and can readily accommodate sections of 10−15 students either as individual experiments or by work in pairs.

Scheme 1. Monomer Synthesis and Polymerization to Conjugated PPV Polymer



HAZARDS

All organic solvents in this report include flammable liquids that are toxic by inhalation. Prudent use of personal protective equipment is recommended and all manipulations described here were carried out in a standard operating fume hood. Always consult the materials safety data sheet (MSDS) for chemicals before executing this laboratory. Specific emphasis is placed on the conversion of compound **2** to **3** which employs metal halogen exchange via use of *n*-butyl lithium. Use of protective gloves and lowered hood sash are highly recommended during the addition step. It is recommended that *n*-butyl lithium should be transferred using disposable plastic syringes with a luer lock (e.g., NORM-JECT®) and not glass syringes. This reagent that is used for the preparation of **3** and **5** is a strong base and very hydroscopic, thus reacting violently with water. Therefore, scrupulous drying of glassware and use of anhydrous reaction conditions are recommended. Disposal of the needle and syringe requires flushing with hexanes and dispensing contents into *tert*-butanol. Students should avoid chemical contact by wearing gloves and working in an adequate fume hood environment.

DISCUSSION

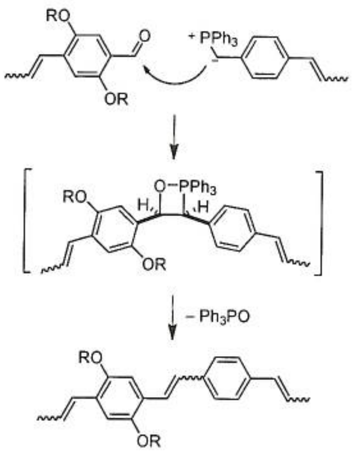
Monomer synthesis of **3** commences with the Williamson ether synthesis of 2,5-dihexyloxy-1,4-dibromobenzene (**2**) by reaction of the bisphenol (**1**) with 1-bromohexane in the presence of K_2CO_3 in DMF (Scheme 1). Typically, the reaction is left to reflux overnight, but we have also tested the reaction with as little as 1 h reflux. The shorter reaction times generally resulted in lower yields (40% compared with 60–80%), but the truncated time does not appear to compromise the ability to isolate a reasonable amount of pure product. The work-up involves addition of water which affords facile isolation of **2** via precipitation. The product can be further purified by recrystallization leading to an off-white to pale purple solid that is of high purity according to GCMS and ^1H NMR (Figures S1–S5). Special attention is paid at this point to the fragmentation pattern in the GCMS. First of all, the M^+, M^{+2}, M^{+4} pattern for the incorporation of two Br atoms in the molecule is noted based upon isotopic abundances. Secondly, the two primary fragment ions (at 350, 352, 354 *m/z* and 266, 268, 270 *m/z*) provide a clear example of a McLafferty-type rearrangement and an excellent opportunity to engage students in a discussion of this important mass spectral fragmentation mechanism. In this process, the molecule loses 1-hexene in an iterative fashion ultimately generating the corresponding hydroquinone of **2**. The product can be further characterized by IR, ^{13}C NMR, ^{13}C DEPT NMR, and 2D NMR techniques depending upon the instrumental infrastructure of the institution. As an alternative to recrystallization, the product may be purified by silica gel column chromatography. This alternative approach can be employed if the instructor would like to utilize the opportunity for students to learn purification by column chromatography. We found that 5 g of silica gel is a reasonable quantity to employ for the scale of reaction with gradient eluent concentrations from 100% hexanes to 90:10 hexanes:EtOAc. In either case, ample product is yielded to allow full characterization and for continuation of the polymer synthesis. In addition, this particular reaction provides an opportunity to discuss the mechanistic aspects of the Williamson ether synthesis (S_N2 reaction), an important reaction in organic chemistry, which aligns nicely with the sequence in our corresponding lecture course.

Once in hand, monomer **2** can be readily converted to the dialdehyde **3** by iterative lithium-halogen exchange and nucleophilic substitution with DMF. The initial step here involves the use of 2.5 M *n*BuLi in hexanes. Optimally, the reaction conditions should be sufficiently dilute to avoid any aggregation that is apt to happen when using this reagent. The lithium–halogen exchange is readily observed by a distinct change in color of the solution from clear amber to off-white and cloudy (likely due to the formation of lithium salts). Upon subsequent addition of DMF, the solution proceeds to a milky white appearance that will resolve to a clear, yellow solution upon addition of dilute aqueous HCl during the work-up. The product was effectively purified by recrystallization from absolute EtOH yielding a yellow solid in high purity. A standard ensemble of spectroscopic techniques is employed to characterize the product. In particular, students are prompted to consider how the spectroscopic profile changes for the conversion of aryl bromide to the corresponding aldehyde. Most notably, students recognize the disappearance of the C–Br stretch in the IR and the appearance of the aldehyde hydrogen at 10.52 ppm in the ^{1}H NMR. Students also note the chemical shift alteration for the *C*–Br vs. *C*–CHO aromatic carbon in the ^{13}C NMR. There is also minor chemical shift difference for the hexyl side chains as a result of the functional group interconversion from **2** to **3**. In addition, monomer **3** still retains the hexyloxy side chains which afford the same type of McLafferty rearrangement possibilities as observed for the previous monomer **2** (*vida supra*).

This particular transformation from **2** to **3** is attractive as the reaction sequence reinforces fundamental organometallic chemistry as well as nucleophilic substitutions involving carbonyl-containing molecules. The novelty here resides in the identification of the leaving group for the nucleophilic acyl substitution reaction. Students in organic chemistry often struggle with leaving group effects and the concomitant application of acid-base principles. Indeed, this particular example provides an interesting opportunity to consider leaving group capacity of the $(CH_3)_2NH$ group from DMF. Normally, students would not identify this functionality as a viable leaving group. However, the relativistic basicity of the amine versus the nucleophilic organometallic species leads to a useful discussion point regarding this reaction, reinforcing key organic chemical principles.

Polymer **5** is prepared via a step-growth chain extension through Wittig coupling of the bifunctional aldehyde monomer **3** with the phophonium chloride monomer **4**. This choice for studying polymer **5** was out of coincidence as the monomer precursor **2** was prepared as part of the experimental sequence in our undergraduate organic laboratory. This exemplar synthesis compliments a similar iterative synthesis for the preparation of oligomeric **5** as a subunit.[4] Initially, base is required for the *in situ* generation of the phosphonium ylide which produces a bright red solution. The choice of base is important to promoting effective polymerization. The use of *n*-BuLi (2.1 equiv) provided the most efficient production of the desired phosphonium ylide. Upon addition of monomer **3**, the oxaphosphatane intermediate was formed ultimately expelling triphenylphosphine oxide (Ph_3PO), which generated a visible precipitate in solution (Scheme 2). The resulting polymeric material was characterized by an intensely orange colored solid that was readily precipitated from methanol at room temperature; Ph_3PO is soluble in methanol, therefore, the side product can be readily separated from the polymer. This solid could be easily filtered and then dried in a vacuum oven to provide a sample of acceptable purity for structural characterization. GPC analysis revealed number-average molecular weight (M_n) of 4000 (versus polystyrene standards in THF) and a polydispersity index (PDI) of 1.9. Given the repeat unit molecular weight (434 g/mol), this result indicates approximately 9 repeat units presumably comprised of discreetly-sized oligomers. However, the brightly yellow colored material (in solution) was capable of forming clear films using either spin- or drop casting onto microscope slides from a concentration solution of THF (see Graphical Abstract figure as an example of a drop cast film onto a template glass slide). ^1H NMR in $CDCl_3$ can also be employed in order to confirm the polymeric unit structure with clear evidence of aromatic and vinyl functionalities in addition to the aliphatic ether side chain (Figure S9). Furthermore, ^1H NMR evidence suggests predominance of the *E* configuration for the vinyl groups as evidenced by 13.0 Hz coupling constants (see NMR results in the Supporting Information) in the vicinity of 6.5–6.75 ppm.

Scheme 2. Step-growth Polymerization via Wittig Coupling of the Aldehyde Monomer with the *in-situ* Generated Phosphonium Ylide



The optical properties of the PPV polymer **5** can be qualitatively observed from a dilute polymer solution in THF (ca. 5 mg/mL) and a solvent cast film which revealed a high degree of luminescence upon exposure to a UV lamp (350 nm) (see Supporting Information photo and Graphical Abstract). The spectral measurements of polymer **5** in solution (THF) and thin films obtained from UV-Vis and fluorescence (emission) spectroscopy is shown in Figure 2. Emission spectra are recorded with excitation at λ_{max} taken initially from absorption measurements. A single π–π absorption characteristic of phenylene-vinylene conjugation functionality is observed at λ-max excitation of 460 nm in THF. The thin film of PPV polymer **5** showed emission broadening compared with the dilute solution. Emission spectra from films displayed a ca. 33 nm red shift in λ_{em} from 513 nm to 546 nm, in addition to broadening of emission onset to near 600 nm. This result is typical due to the π–π stacking of the independent, rigid phenylene-vinlylene chains and facilitates intermolecular transitions ultimately lowering emission energy.

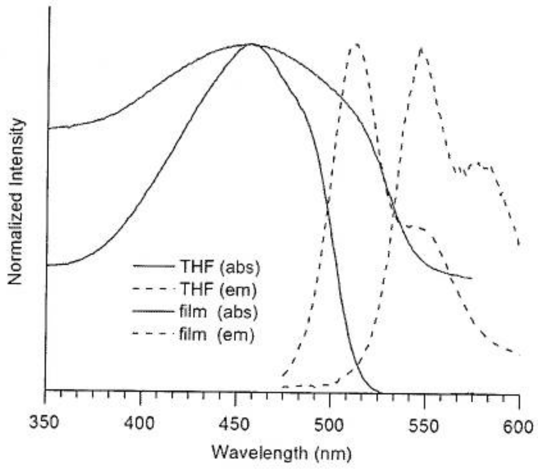


Figure 2. Solution and Film Absorption and Emission Spectroscopy of PPV polymer 5

The optical properties of the PPV polymer **5** can be further demonstrated by performing a quantum yield determination versus an appropriate fluorescence standard. In this case, coumarin 153 was chosen as the standard due to the fact that its absorption and emission profiles correspond nicely with spectroscopic characteristics of the PPV polymer. As shown in Table S1 (see Supporting Information), the absorbance and emission spectra for a dilution series was performed for both the coumarin 153 standard as well as the PPV polymer **5**. A graph of integrated fluorescence intensity versus absorbance produced a good linear relationship used to calculate the solution quantum yield (Φ) (Figure S10). A typical quantum yield for the PPV polymer **5** is 0.42 and is in agreement with published literature values.[5]

SUMMARY

The protocol for the preparation and characterization of a PPV-derived polymer provides undergraduate students the exposure to materials chemistry in organic-based photonics. This integrated laboratory provides appreciation for the synthesis involved in preparation for a functional material, in this case, a light-emissive polymer. The laboratory can be utilized in its entirety for an undergraduate organic laboratory course or compliment an advanced course such as polymer chemistry or advanced techniques. The methods described in this account have been successfully implemented in both organic and polymer chemistry courses encompassing over fifty students and optimized by two senior undergraduate researchers. Topics for discussion during the classroom or laboratory period can include mechanistic rationale of each monomer synthesis step, the step-growth polymerization, spectroscopic interpretation, structural elucidation, or photophysical properties of the polymer.

ASSOCIATED CONTENT

Instructions for students, spectral data, and notes for the instructor are available as supporting information via the internet at http://pubs.acs.org.

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