Chapter 10

Phenylenevinylene Systems: The Oligomer Approach

Juan C. Cárdenas, Cristian Ochoa-Puentes and
Cesar A. Sierra

Additional information is available at the end of the chapter

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Abstract

Among conducting polymers, poly-*p*-phenylenevinylenes (PPVs) have attained a special place in polymer electronics. The optoelectronic properties initially exposed by PPVs in organic light-emitting diodes (OLEDs) turned these organic electronic conjugated systems from the solo academic interest into a technologically very promising area. The easiness of the tuning of their optoelectronic properties through synthetic modifications make PPVs an outstanding and suitable compound for technological applications and fundamental science development. Unfortunately, the synthesis and structural optoelectronic characterization of novel PPVs is a long and difficult task that sometimes yields unclear results. However, phenylenevinylene oligomers (oPV) can be synthesized and characterized in a very straightforward manner, and their performance in novel applications can be directly related to their structural analogue polymer, methodology designated as the oligomer approach. Herein, we describe the oligomer approach using the Mizoroki-Heck reaction as a synthetic route for oPVs and PPVs, and the importance of an extensive characterization for novel applications, such as photocatalysis and matrix-assisted laser desorption/ionization (MALDI) matrices, where these electronic conjugated systems have very promising applications.

Keywords: phenylenevinylene, oligomer approach, optoelectronic polymers, Mizoroki-Heck reaction, conjugated systems applications

1. Summary

This chapter describes the physicochemical characteristics of conjugated polymers and the growing importance of the polymer electronics in our actual and future day life, followed by

advantages and disadvantages of the most common synthetic routes reported to get any imaginable electronic conjugated chemical structure.

As a result of the explanation and development of the oligomer approach in this chapter, applied to the synthesis of phenylenevinylene oligomers (oPV) and polymers by the Mizoroki-Heck reaction and the usefulness of this methodology to define precise chemical structure as target compound in a specific application, the reader will have a perspective of the convenience of working with oligomers instead of polymers as a previous and relevant condition, in terms of time, economy and simplicity, before a target poly-*p*-phenylenevinylene (PPV) system is designed for a specific application. Furthermore, since the most important methods of oPV synthesis are described and discussed, the reader can also select the methodology of his or her convenience according to the oPV structure and application of interest. Finally, taking into account that the optoelectronic properties of several oPVs will be exposed, the reader may develop a preview of the influence of some substituent groups over the main chain of the oPV.

2. Introduction to optoelectronic active polymers

Polymers are organic or inorganic macromolecules of natural, industrial and technological importance because of the wide range of physicochemical and mechanical attributes that they possess. Since the early twentieth century, due to their insulating properties, polymers were widely used as packaging and protecting materials, but the discovery in recent decades of their electrical conduction capability led them to become "active" materials within highly attractive applications such as light-emitting diodes, photovoltaic cells, chemical sensors, among others, to which it is known as polymer electronics. Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa were awarded with the Nobel Prize in chemistry in 2000 for the discovery and development of polymer electronics [1]. There are many advantages in using these materials over conventional electronic devices that are based on inorganic semiconductors. These polymer devices can be designed with large areas, they are mechanically flexible and very light, their operation requires less energy and their production is economically profitable.

Active polymers have a common structural feature—presence of an extensive electronic conjugation. In this conjugation, the alternation of single and double bonds creates the overlapping of electrons in *p* orbitals (unhybridized) over the entire polymer backbone, generating an electronic delocalization along the polymer structure. This delocalization provides the route to the mobility of charges along the polymer (**Figure 1**).

For interpreting the physical chemistry of conducting polymers, the use of the band theory is widespread. In this, induced or not induced "defects" lead to the formation of an energy difference between the HOMO (valence band) and the LUMO (conduction band) orbitals of the polymer, what is referred to as "band gap". Because of this, conducting polymers are considered as semiconductors and since the band gap depends on the molecular structure of the electronically conjugated repeating unit, there is a great challenge, and also a possibility, of controlling this energy difference by designing at the molecular level through the imple-

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mentation of various synthetic methodologies. Therefore, optoelectronic properties of the polymer can be finely adjusted according to the needs of any technological application.

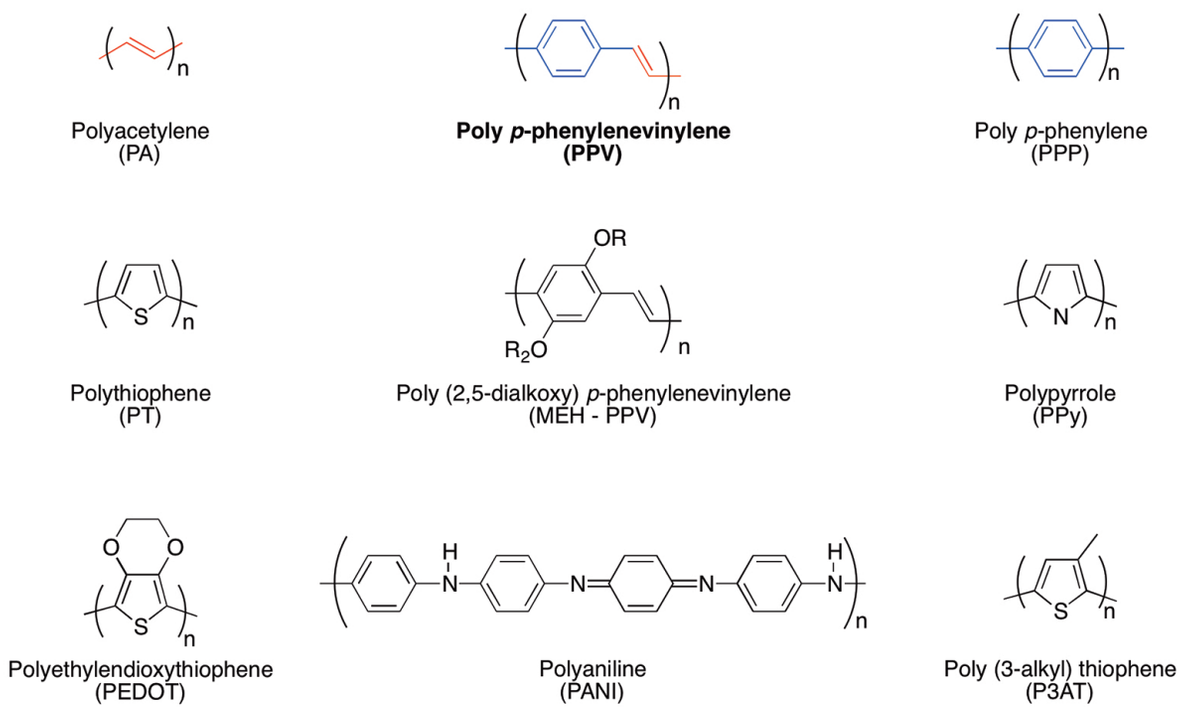


Figure 1. Chemical structures of some conducting polymers.

Among conducting polymers, PPVs (**Figure 1**) have a distinctive place in polymer electronics, which is confirmed by the large amount of scientific literature dedicated to this polymer over the last years. The impressive electroluminescence exhibited by this polymer in a diode with a very simple architecture [Al/PPV/ITO, where aluminium (Al) and indium tin oxide (ITO) act as electrodes] turned polymer electronics from an area of pure academic interest to a very promising technological area [2]. A few years later, the first solar cell based on MEH-PPV and C61-phenyl butyric acid methyl ester (PCBM) was reported [3–5]. Also in the 1990s, the first conjugated polyelectrolyte based on a sulfonated PPV was developed and it proved to be a highly sensitive fluorescent sensor [6].

Chemically, PPVs can be considered as a copolymer that combines the repeating units of polyacetylene (PA) and poly *p*-phenylene (PPP). In this way, their properties are located in the middle of these two polymers; thus, they are more chemically stable than the PA, while are not as robust as the PPP. Furthermore, while the PA is black and has a smaller band gap (E_g = 1.4 eV), PPV films without substituents are yellow due to absorption around 420 nm and with a band gap significantly higher ($E_g \geq 1.9$ eV) [3–5]. Additionally, the optical properties of PPVs can be influenced by conformational factors. This can be observed by the solvatochromism, wherein the length of the effective electronic conjugation can be modified according to the chemical nature of the solvent. This situation is exploited in the process of spin-casting, leading to the modulation of the device properties [7]. Another way of modulating the optoelectronic

properties in conducting polymers is by the chemical nature of the substituents present on the electronically conjugated structure, which will be explained in detail in the following sections.

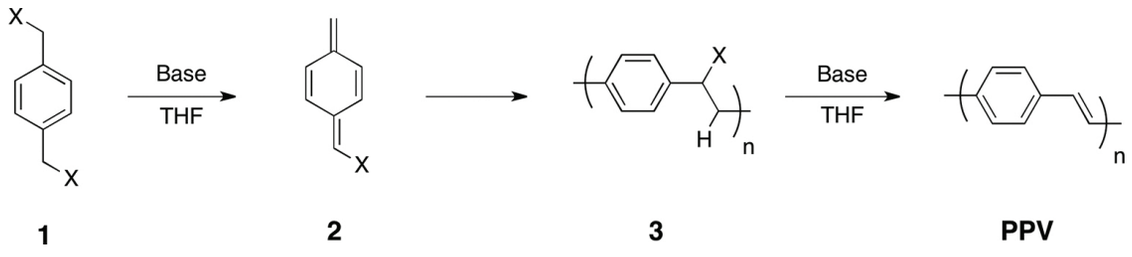
All these physicochemical attributes belonging to the polymer electronics have been successfully exploited by the industry through the generation of novel technological applications that generally seek to make concrete contributions in order to improve the living standards of humanity without forgetting the growing global preoccupation for the conservation and improvement of our environment. Just to mention a couple of examples, recently LG chem, the electronic giant company, developed a house lamp based on organic light-emitting diodes (OLEDs) with a brightness comparable to conventional LED lights and with a lifetime of 40,000 hours [8]; also, the Swager group at MIT developed a chemical sensor based on conjugated polymers that efficiently determines the ripeness of fruits at very low cost, which can be used as regular plastic bags in supermarkets [9].

3. Synthetic routes for obtaining PPVs

Although there have been several synthetic methods reported for the preparation of PPVs, we discuss only those that are notable for their easy implementation and good results in terms of molecular weight and stereochemistry control of the products, since these features will govern the solubility, crystallinity, processability and optoelectronic properties of the PPVs obtained. It is noteworthy that when designing a PPV for a given application, the need to add substituents to the PPV backbone should be taken into account, since this is necessary to produce a soluble and processable material.

3.1. Gilch polymerization

The Gilch reaction (**Scheme 1**) is an economic synthetic methodology that facilitates obtaining PPVs with very high molecular weight. This method, first developed in 1965, employs an α,α'-dichloro-*p*-xylene **1** as precursor. This, by treatment with a strong base such as potassium tert-butoxide, undergoes elimination of HCl to form α-chloro-*p*-quinodimethane **2**, which polymerizes via radicals to produce the intermediate **3**. This poly (α-chloro-*p*-xylene), in the presence of excess base, yields a high molecular weight PPV through E2 elimination [10–13].



Scheme 1. Gilch synthetic route.

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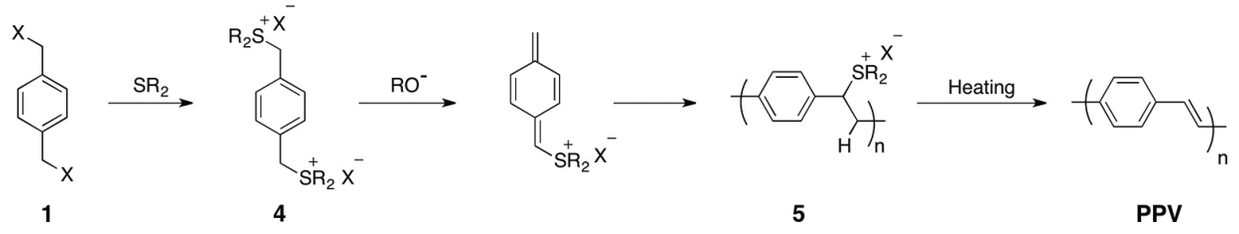
The polymerization process occurs rapidly with few defects and low dispersity, but it must be carried out at temperatures as low as -78°C, which is considered an experimental and economical difficulty. The rapid polymerization also leads to a *cis*/*trans* ratio large enough to produce a loss in the photoluminescent properties of the PPV yielding blue-shifted spectra, simultaneously making the obtained polymer not attractive for some technological applications [14].

3.2. Wessling polymerization

This method, implemented in 1966, utilizes a pre-monomer in which the two chlorine atoms over the α,α'-dichloro-*p*-xylene **1** are replaced by sulfonium groups to get compound **4**. Base-catalyzed polymerization of compound **4** (**Scheme 2**) leads to a poly-*p*-xylene precursor functionalized with sulfonium groups **5**, which is soluble in water and alcohols. Heating of compound **5** leads to the elimination of HCl to yield the target PPV [15].



Scheme 2. Wessling polymerization route.

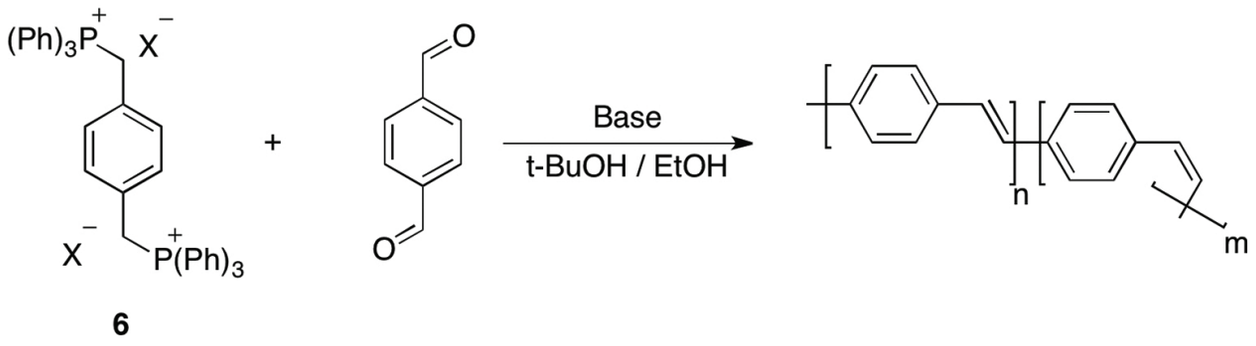
However, it is important to highlight that despite the good yields of this reaction, the production of HCl in the process might damage the substrates [(e.g., (ITO)] during the in situ polymerization for the construction of a device like OLEDs, thus demanding a more complex design for device production.

3.3. Wittig polycondensation

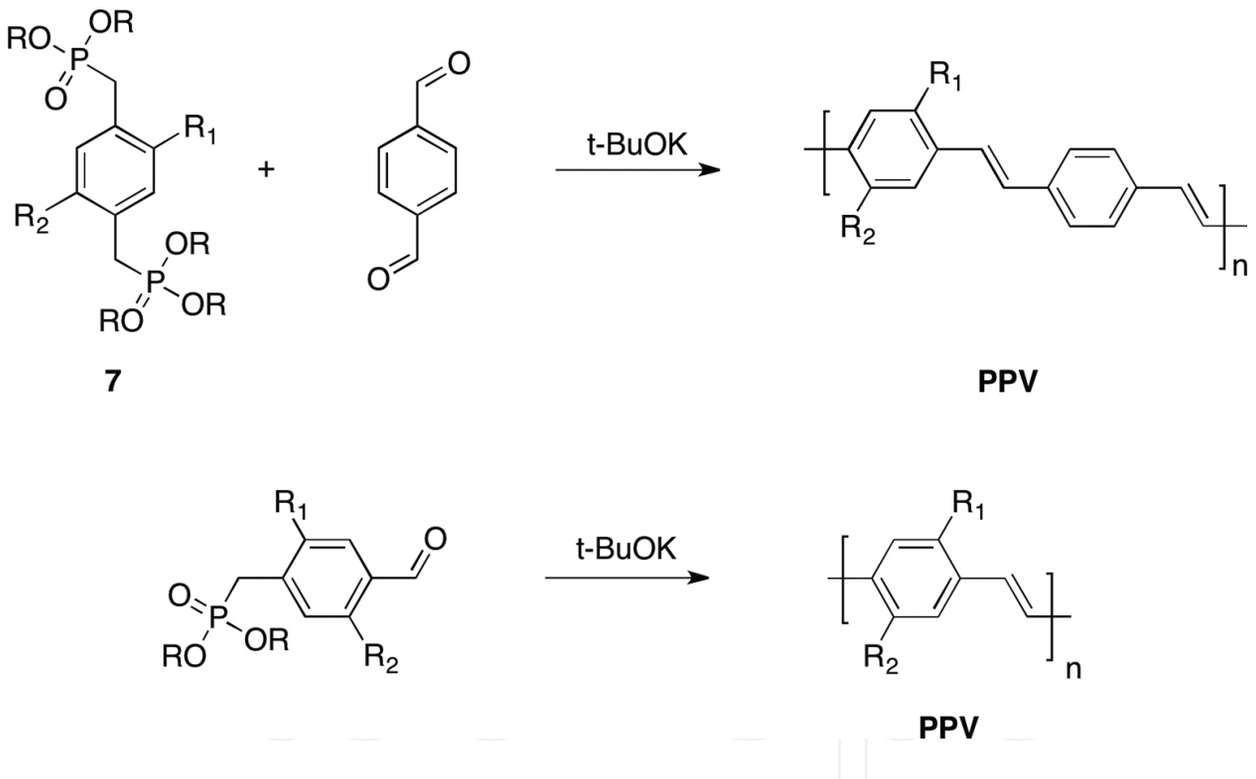
Perhaps the most simple, direct and widespread methodology to produce completely conjugated PPVs and derivatives is the Wittig polycondensation reaction (**Scheme 3**). However, although this represents a very favorable approach to get PPVs with or without substituents, the Wittig reaction generally produces only low molecular weight materials, with a mixture of *cis* and *trans* vinyl bonds. This mixture of *cis* and *trans* segments is very inconvenient to achieve homogeneous optoelectronic properties that are required in some polymer electronic applications [16, 17].

Consequently, the use of phosphorous ylides (**7**, **Scheme 4**) instead of phosphonium ylides (**6**, **Scheme 3**), modification of the Witting polycondensation mechanism and known as the Wittig-Horner reaction (**Scheme 4**), not only increased the amount of *trans* bonds in PPVs, but also increased the molecular weights to exceed 10 KDa. These features as well as the versatility in the selection of monomer have led to the wide use of Wittig-Horner reaction for the preparation of PPVs. However, despite the higher molecular weights obtained with this modification, the

stereoselectivity of the reaction remains insufficient to obtain configurationally pure *trans* PPV systems [18].



Scheme 3. Classical Wittig polymerization.



Scheme 4. Wittig–Horner polymerization.

3.4. Knoevenagel polycondensation

This reaction is especially useful for producing electronically deficient PPVs by exploiting the characteristic acidity of the benzylic hydrogens derived from *p*-xylene with strong electron-withdrawing groups in the α position. The formation of the respective carbanion over compound **8** in the presence of a strong base allows the condensation with terephthaldehyde derivatives **9** to produce PPVs of low to high molecular weights depending on the easiness of

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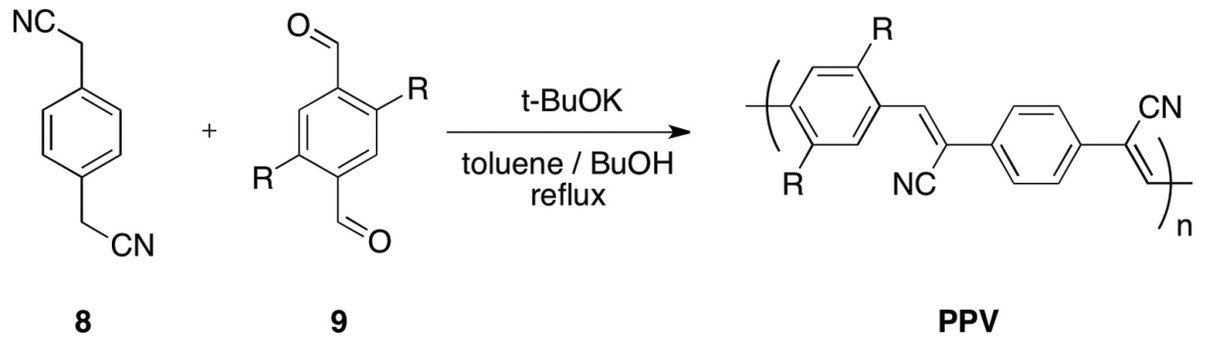
the activation of the carbonyl group due to the substituents on the aromatic ring **9** (**Scheme 5**). To perform this reaction in a straightforward manner, it is important to handle the synthesis conditions carefully, avoiding the competitive Michael addition of the propagator nucleophile to a cyanovinyl unit of another polymeric chain [19–21].



Scheme 5. Knoevenagel polymerization.

3.5. The Mizoroki-Heck reaction

This cross-coupling reaction, catalyzed by palladium, uses olefin derivatives **10** and unsaturated halides **11** (**Scheme 6**) as precursors for the formation of C-C bonds. Unlike the methods described earlier, the Mizoroki-Heck reaction employs mild bases, and although the traditional reaction conditions use refluxing dimethylformamide (DMF), novel catalytic systems allow the reaction to take place at room temperature in a variety of solvents [22]. Unfortunately, though the reaction conditions are usually simple and there are no specific structural limitations for the precursors, most of the literature reported for the synthesis of PPVs with this methodology produced polymers with very low molecular weights [23, 24]. However, many advances in the development of catalytic systems have been employed to improve the degree of polymerization under this protocol [25–28]. Notably, the most important feature of this reaction is that it allows obtaining configurationally pure *trans* PPVs.

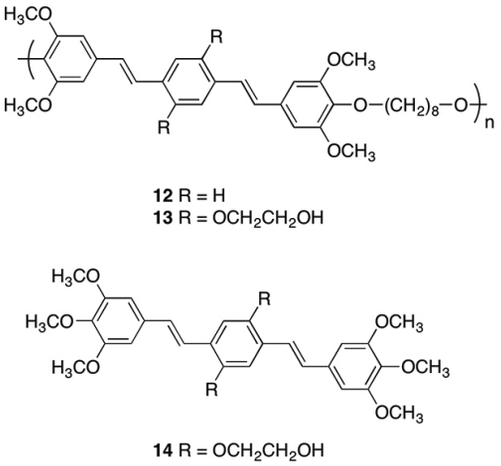
Scheme 6. The Mizoroki–Heck cross-coupling reaction polymerization.

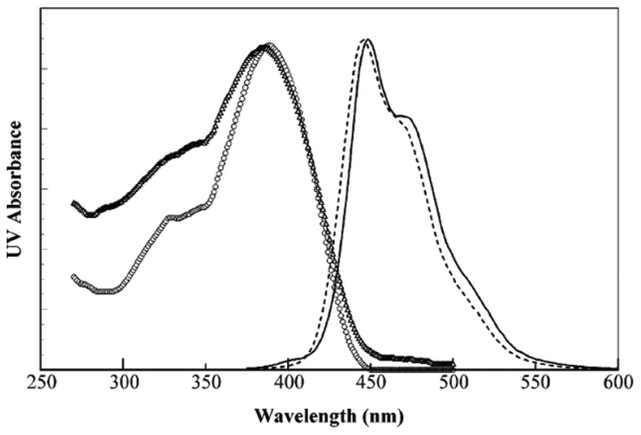
Among the improvements to the reaction conditions, the use of palladium (0) sources as well as the utilization of phosphite ligands instead of phosphines, are the most important changes for the reaction optimization. Additionally, solvothermal conditions have been explored with excellent increase in the product yield and enhancing the easiness through the purification process.

However, it can be inferred that the synthesis and characterization of small molecules is much simpler than that for polymers; therefore, to make significant and rapid progresses for obtaining high molecular weight PPVs, it will be easier if this is done initially with oligomers, and subsequently with these optimized synthetic conditions, which will lead to the formation of structurally analogous polymer. In a similar way, to explore the optoelectronic properties in PPVs for a targeted application, it is easier to start with the study of the properties of oligomers, and then synthesize only one or few polymers with the chemical structure that resembles the structure for the oligomers with the best performance for the application in question. These and other favorable aspects of the oligomer approach will be discussed in detail in the next section using only the Heck methodology as synthetic route for PPVs or oPVs, since this methodology has proven to be the right choice to get conjugated electronic systems with high stereochemical control.

4. The oligomer approach

Whichever is the chosen methodology for the synthesis of conjugated polymers, synthetic and characterization processes are challenging and this sometimes causes the scaling of production not to occur at the speed demanded by industry or at the pace required for impacting basic research on time. Therefore, different strategies have been designed to solve these issues, the most reported being “the oligomer approach".





Electronic spectra for **13** and **14**, 10^{-6}M in chloroform at room temperature, arbitrarily scaled to a similar ordinate. UV - Vis for **13** (Δ), UV - Vis for **14** (O), FL for **13** (-) and FL for **14** (---). FL spectra shown for excitation wavelength of 365nm.

Figure 2. Segmented PPV and analogue oPV structures (taken from reference 29).

Of course, the synthesis and characterization of oligomers is usually much easier and more efficient than the synthesis of their respective analogue polymers, which leads to faster and cheaper results in terms of the design of a polymer with particular applications. Analysis of the optoelectronic properties of synthesized oligomers helps us determine which electronically conjugated structure is the most appropriate for the intended application, and thus, only few

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polymers structurally analogous to the oligomer will be synthetized. These analogous polymers, according to several reports, demonstrated to maintain the same optoelectronic properties of the oligomer previously synthetized. This homogeneity of the properties between oligomer and its polymer analogue is more evident when the target polymer is a segmented structure (**Figure 2**) instead of a fully conjugated polymer (e.g., MEH-PPV in **Figure 1**) [4, 15, 29], since the optoelectronically active segment in the segmented polymer can be truly reproduced in the oligomer (**Figure 2**). In segmented conjugated polymers, the chain tensions that cause torsions on the polymer backbone are suffered and assumed by the flexible aliphatic segments. Therefore, the conjugated segment responsible for the optoelectronic properties in the polymer conserves an unaltered chemical structure, closely similar or equal to the oligomer analogue.

Another advantage of working with segmented polymers is that it is possible to make theoretical studies regarding the relationship between the structure and the optoelectronic properties. The computational cost of working with oligomers is much more reachable than that for working with polymers. Furthermore, in the electronically conjugated polymers, the segmented part and its properties can be easily modelled in computer and these data can be validated by the experimental results obtained with the previously synthesized structurally analogous oligomers, which can often include even the crystal structure (**Figure 3**) [30]. In applications like OLEDs, the optical and electrical behavior comes from the polymer in solid state; unfortunately, getting the solid-state structure of a polymer is not an easy task. Then, it is more accurate to get the conformation and packing properties from the crystal structure of oligomers, as can be seen in **Figure 3** for an oPV, and use this information to make more precise assumptions, observations, conclusions and structure-property relationships to the structurally analogous polymer.

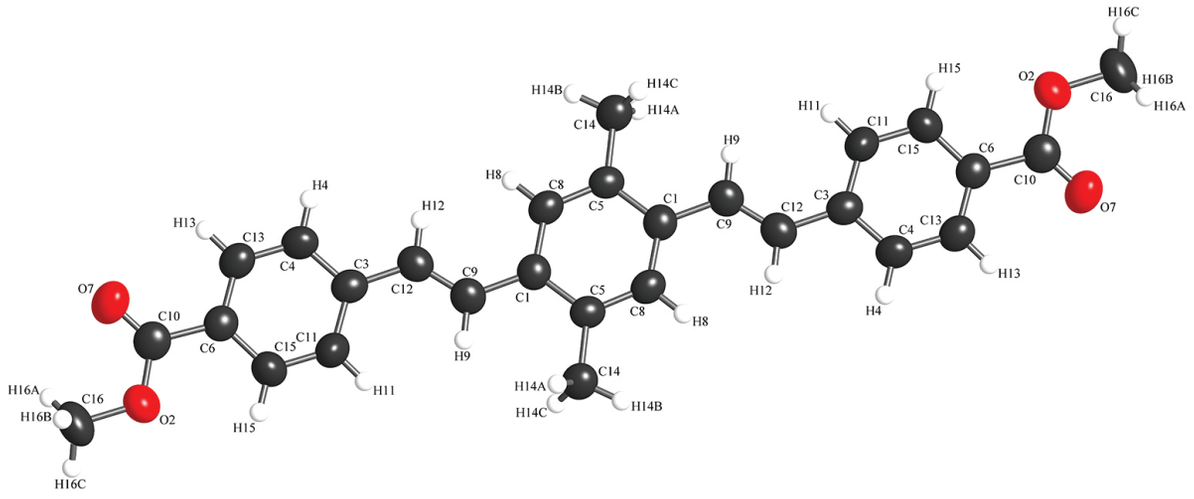

Figure 3. Crystal (top) and supramolecular structures (bottom) of compound **22** in **Table 1**.

As an example of the development of the oligomer approach, in order to solve the problem of low molecular weights obtained in the polymerization of PPVs through the Heck reaction reported by many research groups around the world [22], recent investigations showed that

the use of a catalytic system composed of triphenylphosphite and $Pd(dba)_2$ in the presence of ionic liquids, significantly increases the reaction yields during the synthesis of oPVs and shows the catalyst reusability throughout several cycles [25]. Thus, these reaction conditions were applied to synthesize several oPVs [26–28] and according to the results obtained regarding the reaction yields as well as the optoelectronic properties, a segmented PPV with a degree of polymerization close to 20 (twice superior the size obtained previously with conventional Heck conditions) was obtained [27]. The molecular weight obtained for this PPV following the oligomer approach methodology yielded polymer films of sufficient quality to fabricate OLEDs. This improved synthetic route has also been used for the synthesis of several series of oPVs with a clear enhancement on the reaction yields and incorporating substituents that are very difficult to use as part of the precursors by other synthetic methodologies [31].

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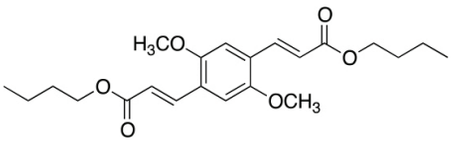
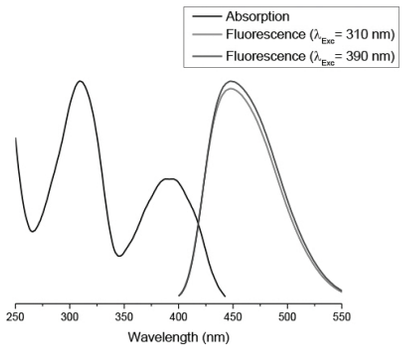
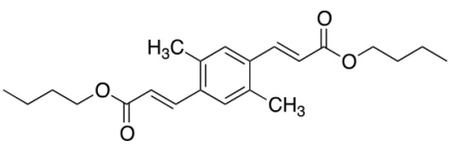
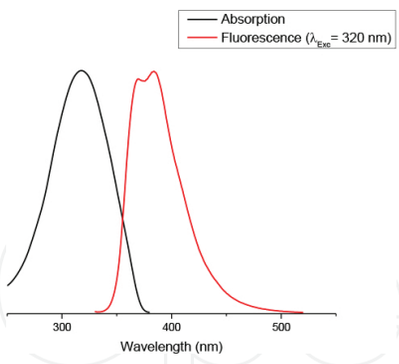
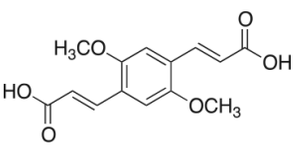
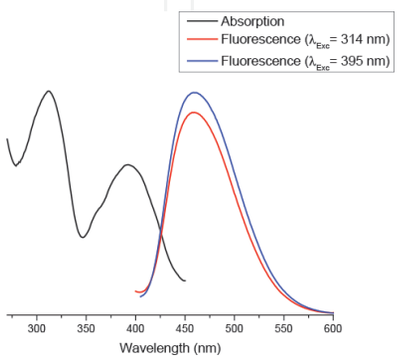
 **15**	
 **16**	
 **17**	

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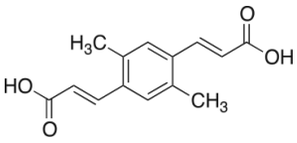
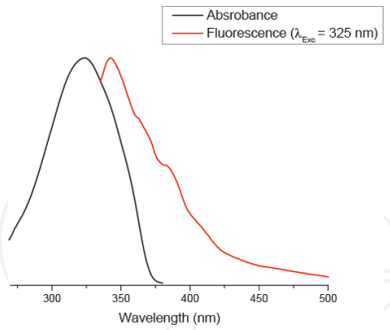
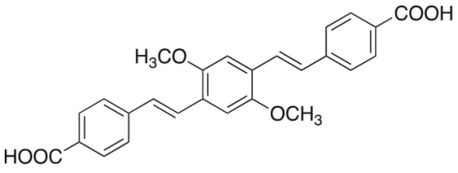
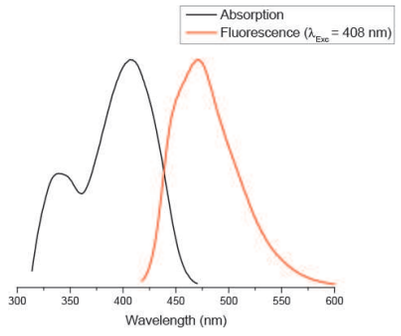
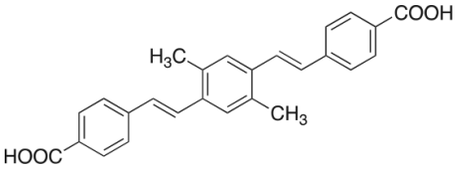
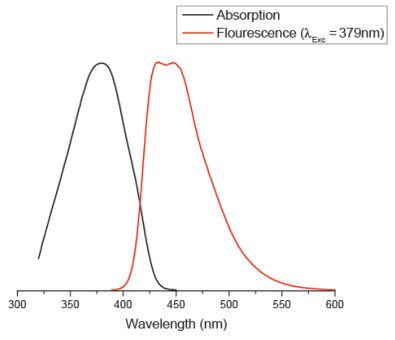
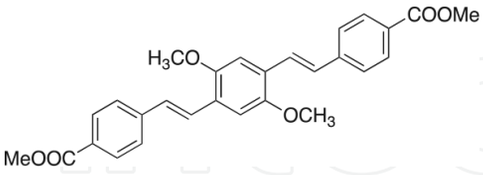
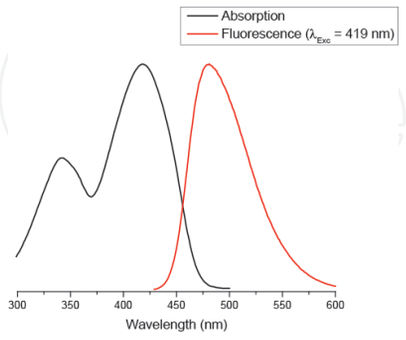
 **18**	
 **19**	
 **20**	
 **21**	

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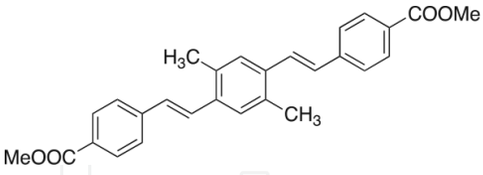
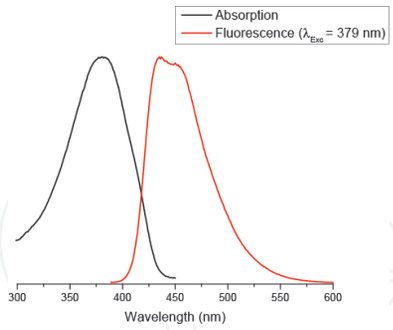
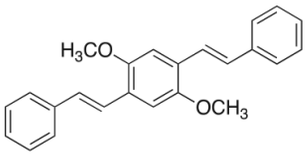
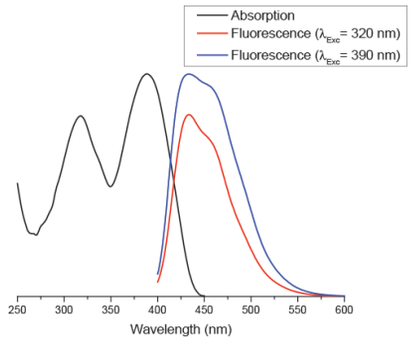
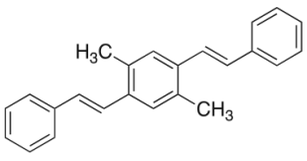
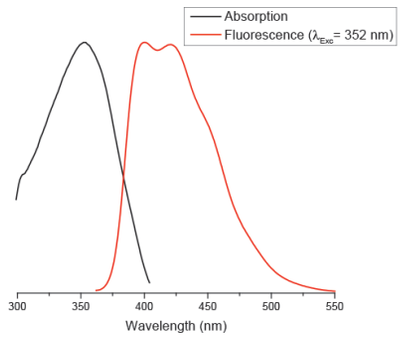
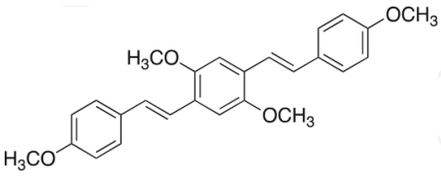
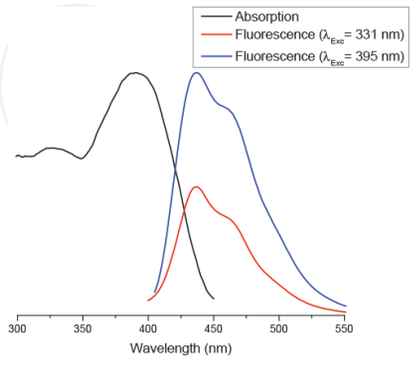
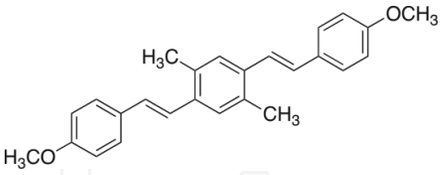
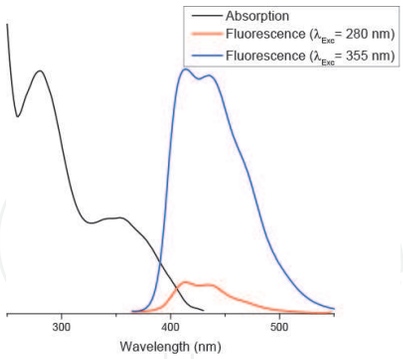
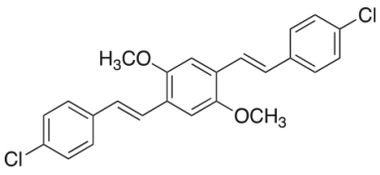
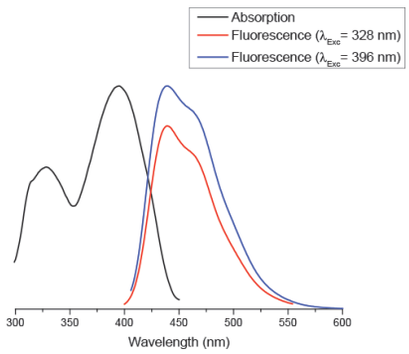
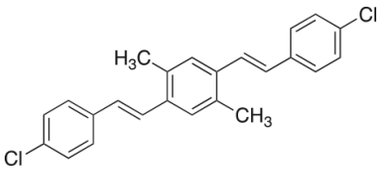
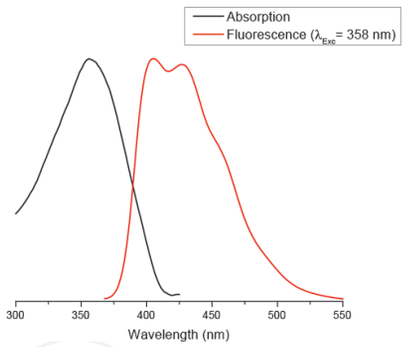
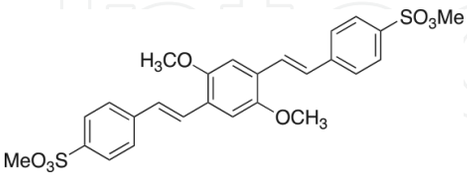
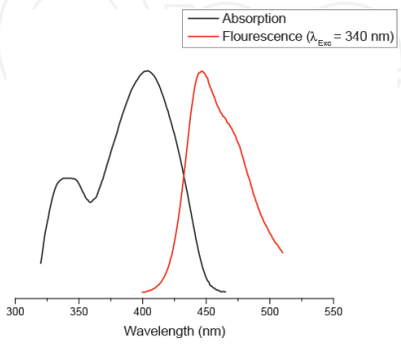
 **22**	
 **23**	
 **24**	
 **25**	

http://dx.doi.org/10.5772/63394

Structure	UV and FL spectra
 **26**	
 **27**	
 **28**	
 **29**	

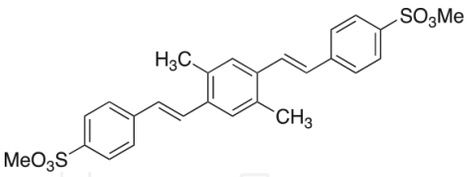
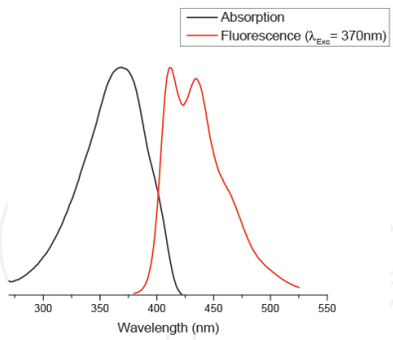
Structure	UV and FL spectra
 **30**	

Table 1. Ultraviolet and fluorescence emission spectra of some oPVs synthesized under solvothermal conditions.

Beyond this, novel protocols for the implementation of the Heck reaction have been developed, reaching the standardization of a very efficient green and economic solvothermal methodology that can be used in Heck polymerizations. In this protocol, minimal amounts of solvents are used, which helps to get very simple purification procedures that as a result gives reaction yields close to 100%, in over 40 oPVs systems synthesized. Thus, it is possible to explore the influence of any substituent over the physical and chemical properties in oPVs in order to obtain, for instance, a more precise description of the relationship between the structure and optoelectronic properties in this class of compounds, simplifying the chemical design of a target PPV with defined properties.

Some oPVs synthesized and their absorption and emission spectra are presented in **Table 1**, where it is seen how the optoelectronic properties of the oligomers change according to their structure and functional groups.

It is very important to highlight that the oligomer approach applied for the oPVs shown in **Table 1** allowed to predict that some of these systems can be used as MALDI matrices, [32–34], UV and visible photocatalyst and organic chromophores for chemosensors [35, 36]. Just as example, compound **27** in **Table 1** due to a very high molar absorptivity at 355 nm (wavelength for Nd:YAG laser in MALDI), low fluorescence quantum yield and crystallographic properties has been studied as matrix for MALDI, showing a very high efficiency at very low laser power, identifying more analytes than other conventional and commercially available matrices. As many authors have established, it is expected that the polymer analogue to compound **27** (currently under analysis) presents a much better behavior as matrix due to the amplification effect related to a greater population of conjugated structures in a close proximity [37], and additionally, a polymer matrix in MALDI might improve the analysis of small analytes, since the polymer matrix will have a very low volatility and fragmentation, leading to a few unwanted overlapping and ghost signals.

Here, employing only one single route, it has been shown that the oligomer approach has a vast scope for various areas like, for instance, chemical synthesis and materials science.

By the optimization of the synthetic conditions to yield small conjugated systems (oligomers) in which it is possible to track in a very easy way changes and effect of the catalyst source, solvent and ligand nature, among other synthetic factors, it is possible to get very efficient catalytic systems that can be used to improve the molecular weight of the analogue polymers. Also, the oligomer approach has shown to be very efficient in predicting exact polymer structures of conjugated systems to applications like matrices in MALDI and chemosensors. All these examples supported by a complete structural and optical characterization make over the oligomers that can be extrapolated to the analogue polymer.

Author details

Juan C. Cárdenas, Cristian Ochoa-Puentes and Cesar A. Sierra*

*Address all correspondence to: casierraa@unal.edu.co

Universidad Nacional de Colombia, Bogotá, D.C., Colombia

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