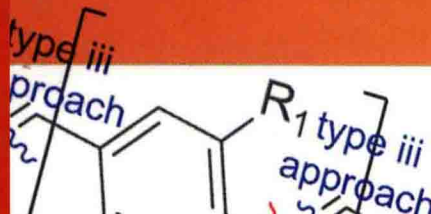
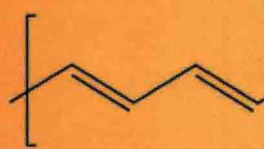
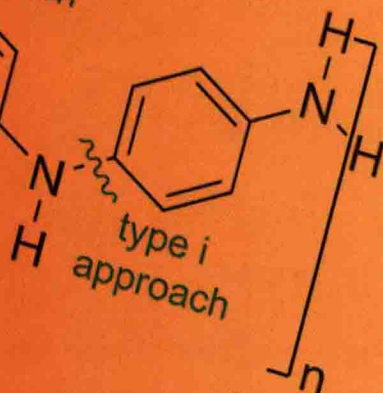
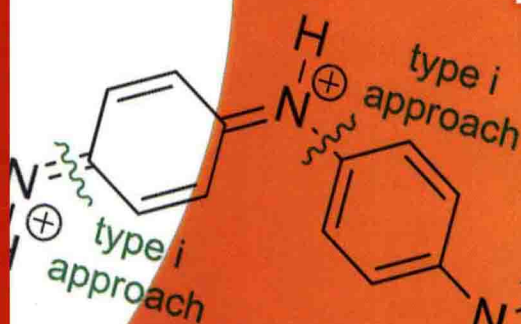


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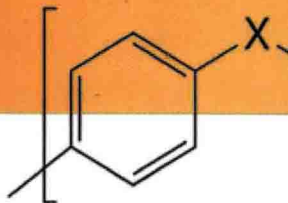
Polymer Science and Technology

Conducting Polymers

Synthesis,
Properties and
Applications



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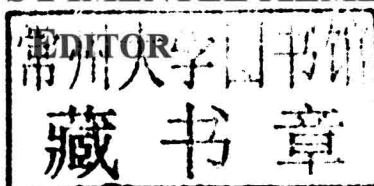
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POLYMER SCIENCE AND TECHNOLOGY

CONDUCTING POLYMERS

SYNTHESIS, PROPERTIES AND APPLICATIONS

LUIZ CARLOS PIMENTEL ALMEIDA



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POLYMER SCIENCE AND TECHNOLOGY

CONDUCTING POLYMERS
SYNTHESIS, PROPERTIES
AND APPLICATIONS

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PREFACE

Conducting polymer field date back to the late 1970s when Alan G. MacDiarmid, Hideki Shirakawa and Alan J. Heeger discovered the high electrical conductivity in doped polyacetylene. Achieving electrical conductivity in polyacetylene as high as that of copper metal inspired the development of new conducting polymers such as polyacetylene, polythiophene, polypyrrole, poly(p-phenylene), poly(p-phenylene sulphide) and polyaniline and a large number of their derivatives and copolymers. It has consequently spawned new interdisciplinary research activities which collectively contributed to the success of conducting polymers as molecular semiconductor materials enabling the development of new technologies in electronic and optoelectronic field.

This book, written by leading experts of the international scientific community, is divided in 10 chapters and gives a comprehensive coverage of important aspects of the conducting polymers. Synthetic methodologies of these polymers and their nanocomposites along with their electrical and electrochemical properties are highlighted herein. Application of the conducting polymers for sensors, solar cells and lithium batteries are also presented.

The subjects quoted above are important topics in the field of the conducting polymers and make this book a very useful scientific support to a large audience of readers, from students to senior researchers in the academic community and from engineer to business people in different industrial sectors.

I cannot finish this book without expressing my gratitude to our distinguished authors who have dedicated their valuable time and effort to write high-quality chapters.

Finally, my special thanks go to Nova Science for the opportunity of organizing this book.

Luiz Carlos Pimentel Almeida
Serra-ES, Brazil

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Chapter 1

CURRENT SYNTHETIC METHODOLOGIES FOR SEMICONDUCTING POLYMERS

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ABSTRACT

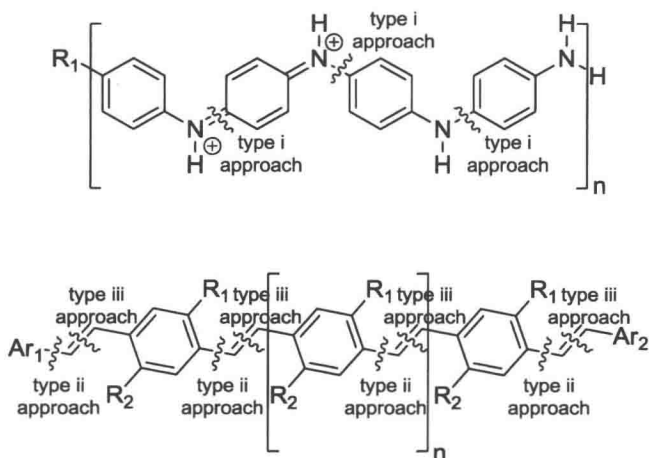
Since the publication of pioneering work in the 1970's, which described and evaluated conducting polymers, the preparation of precisely substituted polymers for the purpose of obtaining materials with tuned electrical and mechanical properties has seized great attention from the scientific community. The arsenal of synthetic methodologies available to access archetypal or tailored polymer structures can be either wide or limited depending upon the nature of the desired monomer. These type of materials include polyacetylene itself or its related poly(hetero)arylenevinylenes analogues and the major synthetic approaches towards polymer synthesis comprise Ullmann, Heck or Wittig type reactions, olefin metathesis, aldol condensation and, of course, electrochemical polymerizations. The regio- and chemoselectivity of these methodologies will be discussed here with special emphasis covering synthetic approaches to homopolymer preparation, although some of these reactions can be effectively used to prepare different types of copolymers.

INTRODUCTION

Semiconducting polymers typically have an extended conjugated double bond framework and we will therefore focus on just some of the numerous synthetic methodologies that are employed to construct these bonds with high selectivity and yields. Commonly used

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approaches usually involve three different strategies (Scheme 1): i) carbon-heteroatom single bond construction followed by oxidation, such as in the case of Ullmann-Goldberg type reaction or electrochemical reactions; ii) carbon-carbon single bond formation, such as in the case of cross-coupling reactions; or iii) carbon-carbon double bonds construction, such as in the case of addition-elimination or metathesis reactions. Given the fact that Ullmann-Goldberg type reactions just create a carbon-heteroatom single bond, this step of course must be followed by a mild oxidation step to provide the semiconducting π -conjugated system.



Scheme 1. Different synthetic approaches to polymeric semiconductor frameworks.

ULLMANN-GOLDBERG TYPE REACTIONS

Ullmann-Goldberg type reactions are amongst the most commonly used methodologies for nucleophilic substitution of aryl halides. Aryl halides are relatively inert to the halogen atom substitution unless it is activated by the presence of electron withdrawing groups (e.g. a nitro, sulfonyl or carbonyl group and aryl pyridines) [1]. However, metals and metallic complexes may facilitate substitution of deactivated aryl halides by several mechanistic pathways [2]. In the case of Ullmann-Goldberg type reactions, the suggested mechanism for nucleophilic substitution facilitated by the transition metal involves oxidative addition/reductive elimination [3], single electron transfer, and halogen atom transfer [4].

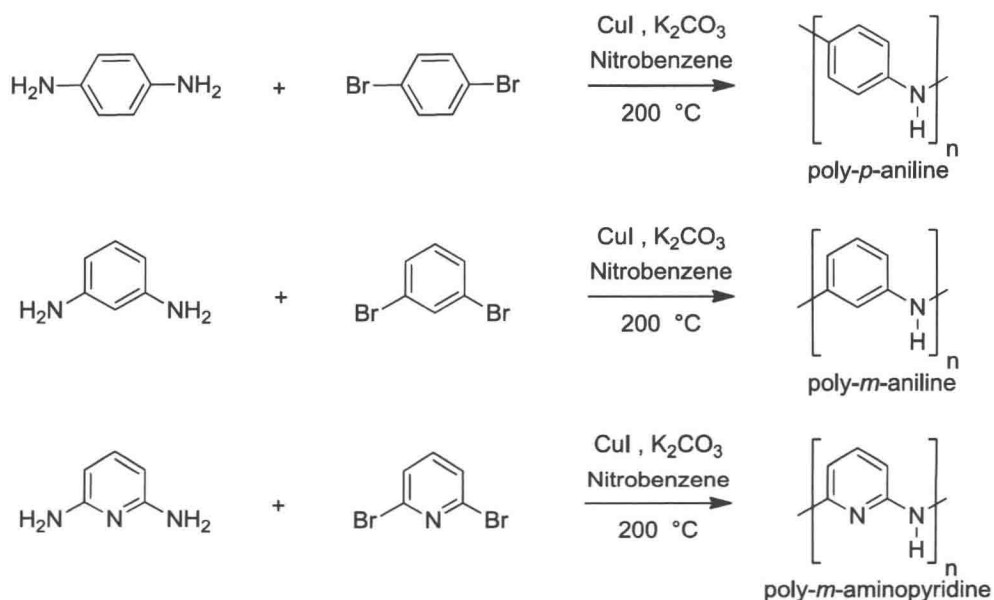
At the beginning of last century, the pioneering work of Ullmann and Goldberg on copper catalyzed coupling reactions led to new ways to form C-N and C-O bonds [5]. These studies are considered to be the basis for all subsequent work on Cu-promoted nucleophilic substitution of aryl halides, and the importance of their results is demonstrated by the wide application of these methodologies in various fields of Chemistry, particularly, in the conjugated polymers synthesis. Since the discovery of Shirakawa, MacDiarmid, and Heeger in the 1970s that electrically insulating polyacetylene can be made highly conducting by chemical or electrochemical doping [6,7], efforts have been devoted to developing conjugated materials. In this context, there are many examples in the literature that describe

polycondensation methods based on the catalytic action of copper and its salts in coupling reactions.

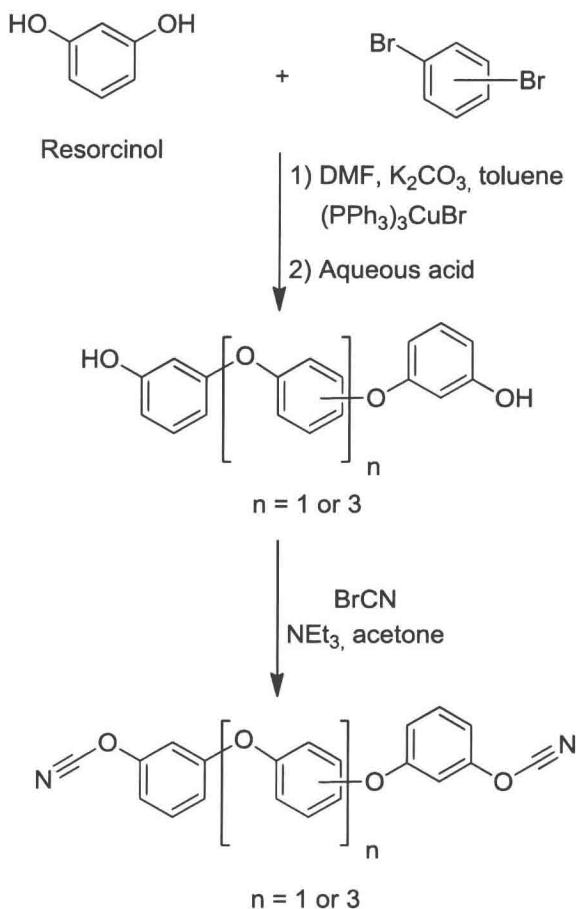
Goto and coworkers reported the synthesis of polyanilines by the polycoupling reaction of dibromobenzene with diaminobenzene or polyaminopyridines and by coupling of dibromopyridine with diaminopyridine (Scheme 2). Copper(I) iodide was used as catalyst and nitrobenzene as solvent [8]. In this case, the regioregulation of the polymer structures was not evaluated and the possibility of crosslinking reactions occurring during the polymerization of monomers could not be ruled out or discarded.

Despite the several applications of these Cu-promoted nucleophilic coupling reactions, up until 2000, the full potential of these methodologies has far from been completely exploited. As shown in the above examples, these methods usually require harsh reaction conditions (strong bases, high temperatures, and stoichiometric amounts of copper or copper salts, long reaction times) to effect these transformations, which restrict the scope of suitable substrates [9].

However, in the 1990's, improvements to those aforementioned procedures were developed for the Ullmann-Goldberg coupling reactions based on the utilization of some bidentate ligands such as 1,10-phenanthroline [10, 11]. These modified methods made it possible for a catalytic amount of the copper complex to be used at lower reaction temperatures, thus broadening the applicability of the reaction to a wider variety of functional groups. In recent years, other combinations with different copper sources and ligands were used in the synthesis of many classes of molecules [5, 9, 12].



Scheme 2. Goto route to polyanilines and polyaminopyridines.

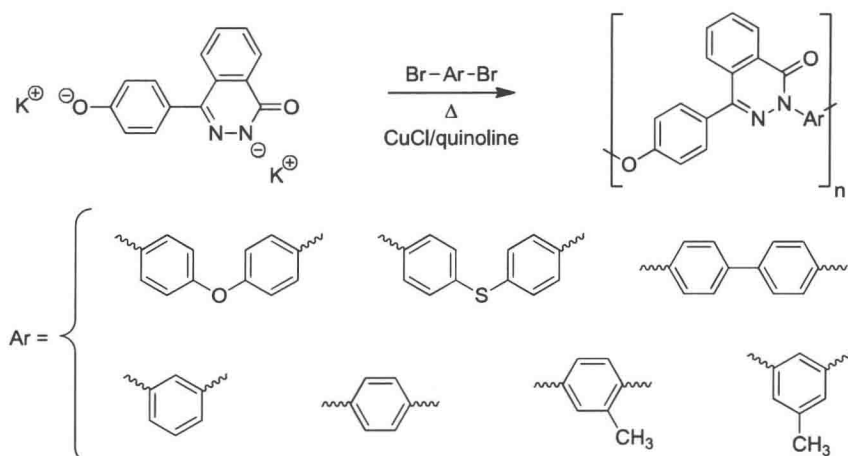


Scheme 3. Laskoski route to cyano ester resin systems.

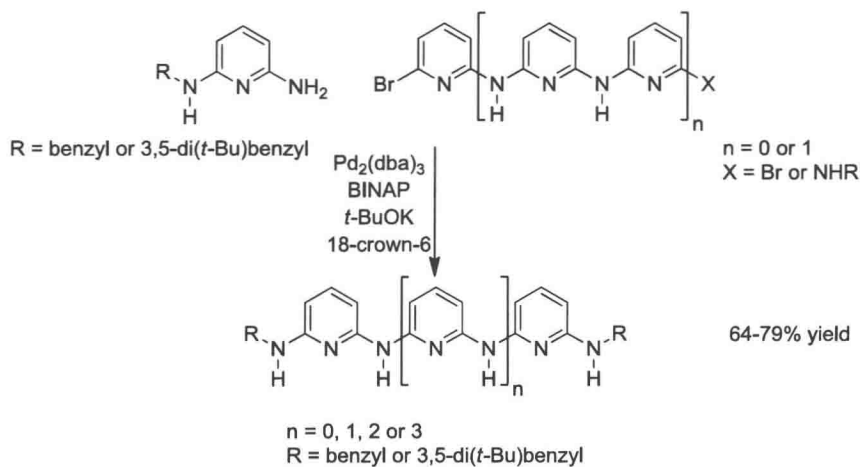
Some examples on the use of catalyzed coupling reactions by Cu/ligand systems in conjugated polymers synthesis have already reported in the literature. Laskoski and coworkers prepared bifunctional aryl ether oligomers by a reaction between resorcinol and 1,3- or 1,4-dibromobenzene in the presence of K_2CO_3 and catalytic amount of $(PPh_3)_3CuBr$, Scheme 3. These aryl ether oligomers were converted into novel cyano ester resins that have innumerable potential applications, such as printed circuit boards, and radomes [13].

In 2008, Wang and coworkers reported the synthesis of a new class of poly-(phthalazinone ether)s from modified Ullmann-Goldberg coupling between a potassium salt of 1,2-dihydro-4-(4-hydroxyphenyl)-1-(2H)-phthalazinone and aromatic dibromide compounds, Scheme 4. $CuCl$ was used as the copper source and quinoline as ligand making it possible to obtain materials with molecular weights up to 20,000 [14]. The inherent properties of these materials potentiate its use in optical systems [14].

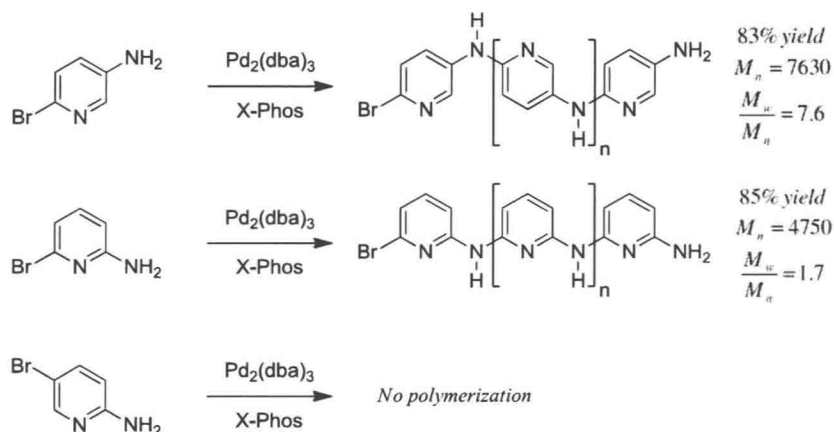
Metals other than copper can be used in Ullmann-Goldberg type aryl aminations such as palladium. In 2002, Chou and coworkers disclosed the synthesis of aminopyridine oligomers in moderate yields using $Pd_2(dba)_3$ as catalyst [15]. Such oligomers showed a highly complex hydrogen bond network and thus reducing their solubility in common organic solvents (Scheme 5).



Scheme 4. Wang route to poly(phthalazinone) ethers.



Scheme 5. Chou route to oligo(aminopyridines).



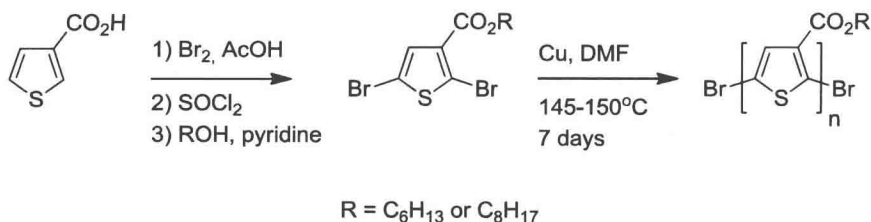
Scheme 6. Kanbara route to polyaminopyridines.

This work was one of the first examples of heteroatom-arylation cross coupling reactions to produce π -conjugated extended systems. A few years later, in 2009, Kanbara and coworkers in a similar approach showed that the polymerization of two bromoaminopyridine isomers could be accomplished when using $\text{Pd}_2(\text{dba})_3$ as catalyst (Scheme 6). The yield, molecular mass and weight dispersion of polymers depend strongly on the isomer structure [16].

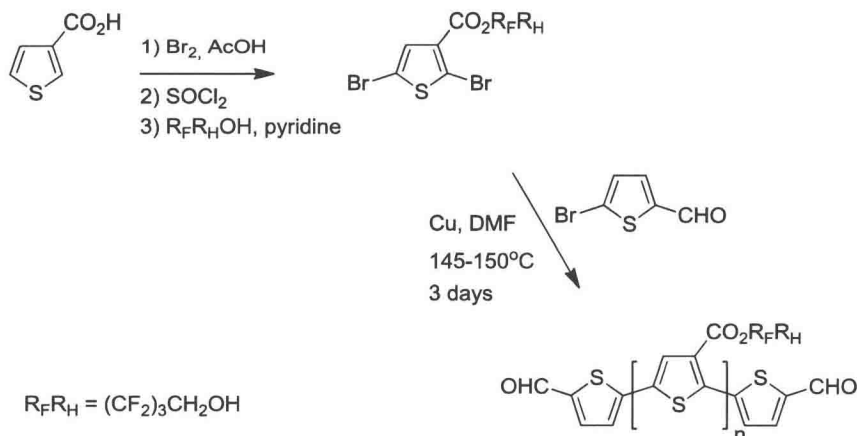
CROSS-COUPLING REACTIONS

The classical reductive coupling called “Ullmann Reaction” was first reported in 1901 [17] and employs metallic copper or salts of this metal to make $\text{C}_{sp^2} - \text{C}_{sp^2}$ single bond between two aromatic nuclei. Normally, two equivalents of aryl halide are reacted with stoichiometric amounts of copper at high temperature (above 200 °C) to form a biaryl and a copper halide [18]. For these catalyzed reactions, the ease of halogen substitution from the aromatic ring follows the order $\text{I} > \text{Br} > \text{Cl} > \text{F}$ [2].

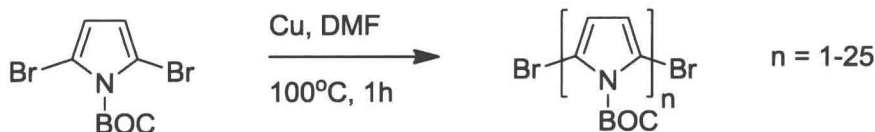
Among the numerous families of conjugated polymers, poly(thiophene)s (PTs) have been one of the most studied. PT have been considered as a model for the study of charge transport in conjugated heteroaromatic polymers with a nondegenerate ground state, or in other words, polymers with quinoid and aromatic structures that are not energetically equivalent [19].



Scheme 7. Pomerantz route to 3-substituted polythiophenes.



Scheme 8. Thomas route to n-type polythiophenes.



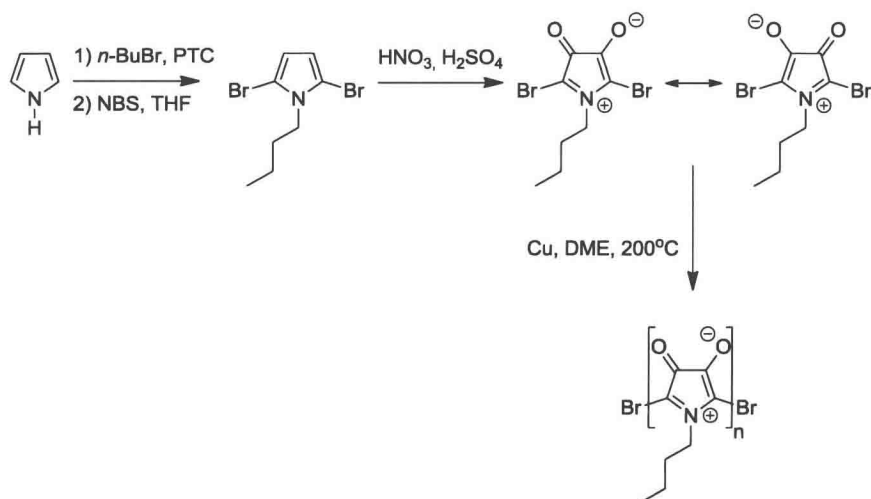
Scheme 9. Groenendaal route to oligo(pyrrole-2,5-diyl).

In addition, the high environmental stability of both its doped and undoped states together with its structural versatility, have allowed PT to be applied in electrochromic and electric devices [20]. The preparation of these polymers by metal catalyzed polycondensation is the method of choice for obtaining materials with high structural quality. Pomerantz and coworkers were the first to report poly(thiophene) synthesis by Cu-catalyzed polycondensation of substituted thiophene rings at the 3-position (Scheme 7) [21]. The authors employed metallic copper in DMF and they obtained polymers with low polydispersity and a low degree of polymerization (DP): in between 14-17. These PTs were soluble in common organic solvents such as CHCl_3 , THF, DMF, CH_2Cl_2 , benzene, toluene and xylene.

More recently, employing a similar methodology to that described by Pomerantz, Thomas and collaborators prepared a new terminal-functionalized and side-chain-fluorinated acceptor-type (n-Type) PT with a molecular weight up to $15,000 \text{ g}\cdot\text{mol}^{-1}$ (Scheme 8) [22]. The presence of fluorine groups in the polymer backbone may improve some material characteristics such as thermal stability, chemical resistance, and a high tendency for phase separation with hydrocarbon segments. Moreover, electron-withdrawing groups such as fluorine, provide an acceptor character to the polymer, which highlights the potential use of this type PT in light-harvesting applications [23].

Another important family of conjugated polymers that can be prepared by Cu-catalyzed polycondensations are the poly(pyrrole)s. These polymers are characterized by high conductivity and good stability of their doped forms. Groenendaal and coworkers prepared well-defined oligo(pyrrole-2,5-diyl) by coupling of *N-t*-BOC-2,5-dibromopyrrole using Cu-bronze in DMF (Scheme 9). In their protocol, oligomers with up to 25 pyrrole repeating units were obtained [24]. The isolated oligomers were used to study their optical and electrical properties as a function of chain length. The results showed a linear relationship between the band gap energy and the degree of polymerization, confirming that the electronic and optical properties of conjugated polymers are largely dependent on the extent of conjugation.

Tour and coworkers described the synthesis of low-band gap (1.1 eV) zwitterionic pyrrole-derived polymer by Ullmann coupling (Scheme 10), however, the use of common solvents in this reaction (DMF, quinoline, pyridine) did not allow for polymerization to occur. The effective coupling was only achieved through the use of 1,2-dimethoxyethane as solvent and copper-bronze as catalyst after 18 h at high temperature [25]. The obtained polymer presented molecular weights of approximately 4,000 Da and polydispersity between 1.15-1.25. This compound can be reversibly converted to a linear or a planar conjugated polymer and its absorption spectral ranges from the UV to the near-IR spectral region. It also possesses an enormous pH and solvent dependences which expands the potential for optical and electrical material applications. During the first 70 years after the discovery of the Ullmann reaction, copper was almost the only metal employed to catalyze C-C bond formation among two C_{sp^2} fragments.



Scheme 10. Tour's route to zwitterionic conjugated pyrrole-derived polymers.

In this period, numerous modifications in relation to the classical Ullmann and Goldberg methods resulted in the increasing of the scope of Cu-catalyzed reactions, however, the major advance was achieved in the replacement of copper by nickel as the catalyst in coupling reactions. Despite the use of terms such as "Ullmann reaction" and "Ullmann condensation" which relate to the use of copper and its derivatives in coupling reactions, from a broader perspective of "Ullmann Chemistry", the similarity of the initial procedures which utilize Ni(0) with those employing copper, and the fact that in both cases the product of reaction is a result of reductive elimination step and thus these nickel methods fall within the class of an "Ullmann type reaction".

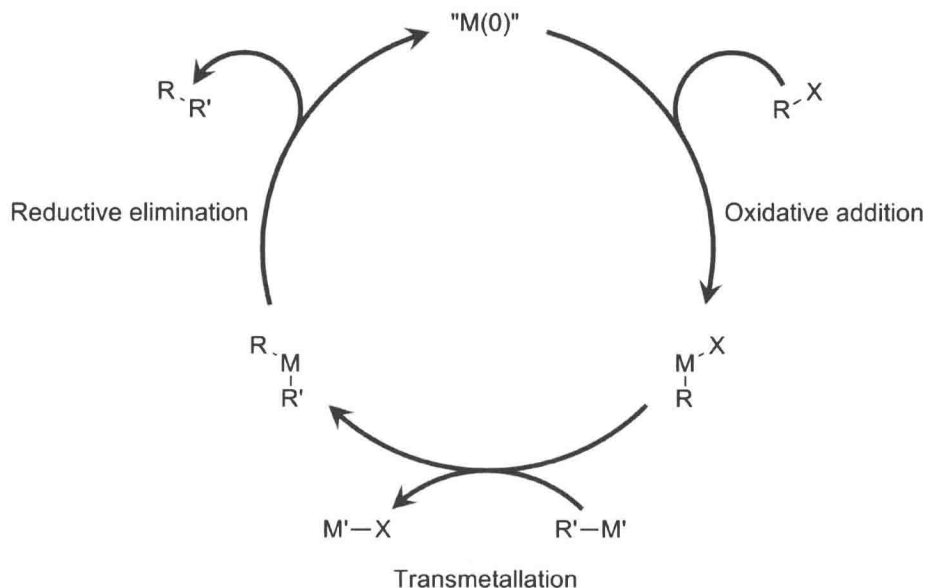


Figure 1. Simplified metal(0)-catalyzed coupling catalytic cycle.