Conducting Polymers: Methods for Enhancing the Electric Conductivity

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Abstract. Driven by the immeasurable prospect of the applications in the reality on the organic semiconductors, scientists had devoted a lot of effort into exploring the properties and their influence factors of these new materials that differ the conducting polymers from the conventional polymers. To maximize the electrical performance of the conducting polymers for practical usage, specific methods of altering both the physical and chemical properties by adjustments of material structures were sorted out. This paper will summarise three different types of changes that can be made to tune the properties for our real needs in two divided perspectives – structural modifications within and out of the molecules of the conducting materials, which are increasing the conjugation length, reducing the band gap, and doping respectively. Among which, the reduction of the band gap can be realized in six different more specific aspects: bond-length alternation, esonance energy, planarity of the conjugated structure, substituents effects, intermolecular interactions, donor-acceptor structure.

Keywords: Conducting polymer; Conductivity; Conjugation; Bang gap; Doping.

1. Introduction

Traditional polymers, which are long chain molecules consisting of monomers that are linked to each other by covalent bonds, were previously thought to be non-conductive. However, since the mid-twenties' centuries, scientists started to find out that some of the polymers, with their special chain structures (especially for those who have conjugation systems), process interesting electrical properties. The conceptual shift finally turned up when it was demonstrated by Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, that one of the simplest linear conjugated polymers, Polyacetylene [Poly(vinylene), -$(CH=CH)_n$-] (PA), successfully polymerized by Job and Champetier, doped with iodine, could conduct electricity [1-4], which verified the existence of conductive polymers (CPs) in the reality.

Since the great potential in extensive applications as in high-mobility OFETs [5], in organic photovoltaics [6,7], or in localised drug delivery, [8] etc. that are originated from CPs' striking merits, including lightweight, resistance to corrosion, structural flexibility, chemical diversity, tunability of their opacities, optical properties, and electrical properties, the investigations on the new organic conductive materials have received a great deal of attention in the past few years. The process of discovering new CPs is very fast. Among all existing CPs, the most used are Polythiophene (PT), Polypyrrole (PPy), Poly (3,4-ethylene dioxythiophene): poly (styrene sulfonic acid) (PEDOT: PSS), etc.

The CPs are subdivided into more elaborated categories according to the relationships between the compositions and the conducting mechanisms of the polymer materials. Intrinsic conducting polymer is a branch of conjugated polymers, which has electrically conductivity in their pure form that arises from the conjugated double bonds that can be further improved by reducing the band gap. While conjugated polymers themselves, in comparison, feature alternating double and single bonds, may requires doping to bring their abilities to conduct electricity up to a level where they can be used for practical applications.

2. The Effect of Molecular Inner Structure in Electrical Conductivity

2.1. Increasing the conjugation length

The alternating single and double bonds in the polymer backbones are basic components of conjugation system. Either a single bond or a double bond has a localised σ-bond, while localised π-bond only exists on each double bond. Consecutive transfer of π-bonds along the conjugative organic backbones provides a path for the electric flow composed of continuous overlapped π-bonds where delocalized π electrons can be transported freely, [9] enables the conductive polymers (CPs) to conduct electricity [10].

The mean length of conjugation in the polymer directly affects the electric conductivity of the CPs as the extended conjugation usually brings a higher efficiency of charge transportation [11] and the electroactivity of polymers in two ways – augmenting the charge delocalisation and/or inter chain molecular interaction. Interchain effects are restrained in the systems when the molecular ordering is decreasing. The spacial distance between polymer chains can be increased by the enornous side chains or steric hindrance, which reduces the interaction between the polymer chains [12].

For example, when the increasing the number of thiophene units in the ligands polymers (poly-1-3), a greater linearity the current will arises t- vs -scan rate curve, showing the electroactivity and conductivity of the polymer film increases with the extending conjugation length of the organic backbone, as shown in figure 1 [13].

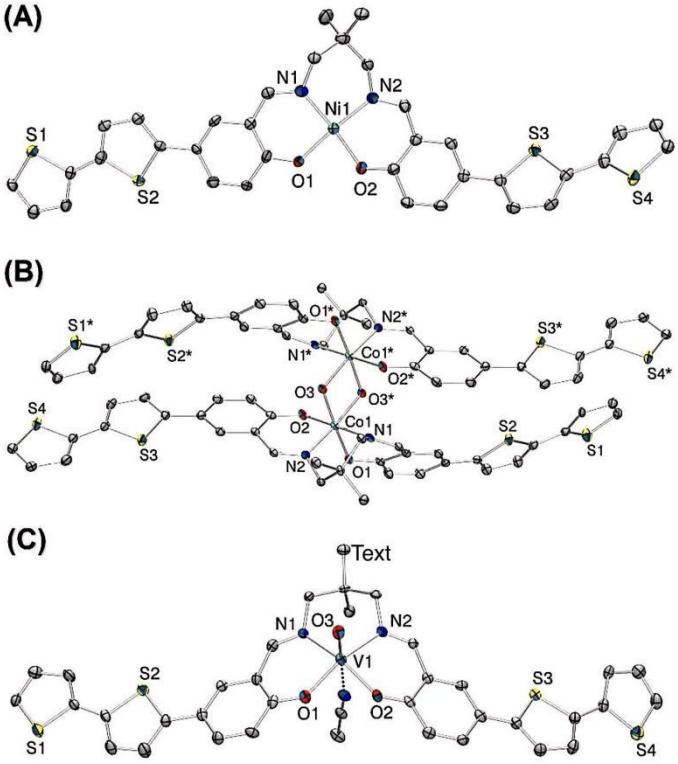

Fig. 1 ORTEP diagrams of 11(A), (8)2 •2H_2O(B), and 5•MeCN(C), drawn with the thermal ellipsoids at the 50% probability level. Hydrogen atoms and other solvent molecules have been omitted for clarity [13]

2.2. Reducing the band gap

Band gap, the position of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) compared with vacuum, is another essential factor that can tune the electric properties of the CP materials without inducing any extra exterior components into the organic backbones of the polymers. The conductivity of the organic semiconductors could be tuned depending on the actual needs through molecular chemical design, modification of the position of HOMO and LUMO levels. Comparing to the inorganic semi-conductors, the small modification in

the chemical structure will results in great difference in the electric properties of the polymeric polymers. Several factors were confirmed to be influential to the band gap of the conjugated polymer materials:

2.1.1 Bond-length alternation

Alternation of bond length can stabilize the structure, which will leads to the localization of π-electrons and semiconductor-like band structure. Synthetic method that modifies the structure will result in a reduced bond length alternation and hence can be expected to generate polymers with a lower band gap.

2.1.2 Resonance energy

The aromatic form often has a more stable energy state, while the quinoid form is always accompanied by a higher energy whereas a low energy gap[14]. Energy required to switch the form from the aromatic type to the quoid type is determined by the aromatic stabilization resonance. The aromaric ring sets a limit to the π-electrons and hence the π-electrons cannot delocalise along the conjugated backbone of the CPs. The bandgap is increased, therefore.

2.1.3 Planarity of the conjugated structure

The disorder in the rotation along the conjugated long chain molecules will influences the band gap of the material. Larger the angles between each two adjacent units are, greater the limitation of the delocalization of π-electrons along the conjugated organic backbone and thus increases the band gap.

2.1.4 Substituents effects

The import of electron-density donating or withdrawing substituents is the most effective way to modify the HOMO and LUMO levels of a conjugated polymer material, as the electron withdrawing group will gets the HOMO further away from the vacuum level and the electron donating group will brings the HOMO closer to the vacuum.

2.1.5 Intermolecular interactions

The intermolecular interaction might occur through the stacking of individual molecules in the solid state films, which can leads to the greater electron delocalization between polymer chains or exciton coupling and can give rise to an alternation of the band gap [15].

2.1.6 Donor-acceptor structure

Donor- acceptor approach is characterised in the alternating electron rich donor units (D) and electron pool acceptor units (A) along the conjugated molecule chains [16]. And the hybridization of the corresponding frontier orbitals of the donor and acceptor units resolves the position of the HOMO and LUMO levels and the band gap. Nevertheless, merely rearrange the HOMO and LUMO positions is insufficient. Appropriate side groups and substitutions are necessary when tuning the interaction between the individual polymer chains as well as between the electron donor and electron acceptor finely. For instance, perpendicular attachment oof PTB7-Th addition thiophene rings further extends the conjugation and reduces the band gap [12].

Impact of factors 2.2.1 to 2.2.4 are demonstrated by Figure 2**.**

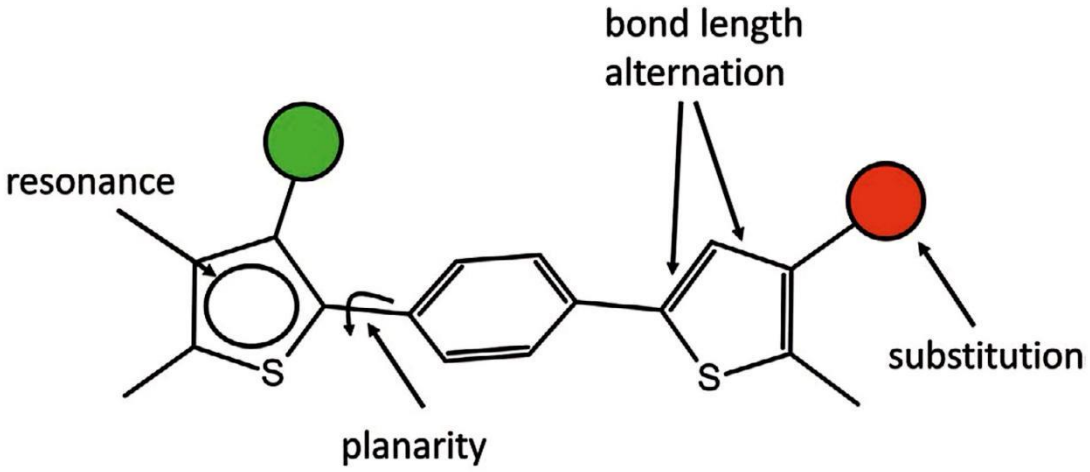

Fig. 2 Structural factors infuencing the band gap of linear-conjugated polymers [12][17]

3. The Effect of Molecular Exterior Structure in Electrical Conductivity

3.1. Doping

The electrical conductivity of the conjugated polymer can be greatly enhanced by doping from the level of semiconductors or even insulators to the scale of metals, either chemically or electrochemically (including 'p-doping'(oxidation) and 'n doping'(reduction of the conjugated backbones))[18]. Inducing the molecular dopants to the PCs introduces polarons by charge transfer, while ideal electrical conductivity desired is achieved by highly effective chanrge transfer[19,20].

To improve the efficiency of doping as to reach high electrical conductivity, conventional means often tends to increase the dopant concentration. While the high cost and the great structural defects prompts the innovations of new doping techniques, such as sequential doping, [21-26]ion-exchange doping [27], and hybrid doping [28].

Take Polyacetylene, $(CH)_n$, derived by the catalytic polymerization, as an example, since it is the most extensively studied conducting polymer concerning to the doping concept[29]. Both of cis- and trans- (CH)n can undergo 'p-dope'(partially oxidise) or 'n-dope' (partially reduce) with certain different types of 'dopants', which is oxidazing agent or reducing agent[30]. The similar conductivities are obtained by the p- or n-doping (CH)n without cosiderring the exact type of the polymer isomer is used since the isomerization happens randomly thoughout the doping process.

However, the doping of organic CPs is completely different from the notion of doping of classical semiconductors such as silicon. The complete p-doping process of an organic CPs, as a partial oxidation, for example, is demonstrated below:

$$(CH)_x \rightarrow [(CH)^{y+}]_x + (xy)e^- \quad (1)$$

To maintain the electrical neutrality, a counter-anion, A-, shall be induced into the system:

$$[(CH)^{y+}]_x + (xy)A^- \rightarrow [(CH)^{y+} A_y^-]_x \quad (2)$$

To date, all the counter-anions involved in the process shall be monovalent. Homoplastically, the complete n-doping process of an organic CPs, as a partial reduction, for example, is demonstrated below:

$$(CH)_x + (xy)e^- \rightarrow [(CH)^{y-}]_x \quad (3)$$

This time, to maintain the electrical neutrality, a counter-cation, M+, shall be induced into the system:

$$[(CH)^{y-}]_x + (xy)\, M^+ \rightarrow [M^{y+}\, (CH)^{y-}]_x \quad (4)$$

Similarly, all the counter- cations involved in the process shall be monovalent[18].

4. Conclusion

By reforming the structure of the CPs, lengthening the conjugation length as well as minimizing the band gap (shortening the bond length, restricting the delocalisation range of the π-electrons, ensuring the planarity of the conjugated system, introducing electron-density donating or withdrawing substituents, enhancing intermolecular interactions, and placingthe donor and acceptor units in the appropriate positions), intrinsic conducting polymers will experience a huge impact on their electroactivities and hence increases their electrical conductivities. Though adding extra composites(molecular dopants) into the conjugated molecule chain, doping, CPs materials will be possible to reach a high electrical conductivity that has never been achieved before by enhancing the efficiency of transferring of the electrons. Ways of modifying the structure mentioned in this paper are the most used and the most effective to No matter which perspective has targeted, whatever the past and future have researched into, there is still a tremendous space left for development in the various fundamental but interesting and challenging but fashionable topics concerning CPs.

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