The Molecular Structures and Modification Methods of Conducting Polymers

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Abstract. Extensive studies have been done in conducting polymers (CPs) in the past decades. To better design and produce CPs, the physiochemistry principles and mechanisms behind the conductivity should be deeply understood. Here in this passage, it is tried to describe the main determining factors of conducting electrons in CPs. Four factors are found to be interesting and important, which are the backbone structure, functional pendant group attached to the backbone, doping degree and grafting. The energy gap theory is applied to describe the phenomenon. The author studied, analyzed and summed up the existing pieces of literature, comparing the conductivity and structure of typical CPs in different conditions, whether they are doped, grafted, etc. The author suggested that the conducting polymers can be classified by the elements in the backbones. For a type of CPs, different kinds of modifications will affect the properties. To evaluate the properties of CPs, two main parameters are discussed.

Keywords: polymers, conductivity, influencing factors.

1. Introduction

In the past decades, using reproducible energy like green electricity has become a trend in the world. Related applications and devices have been paid attention in a large degree. To meet the need for environmentally friendly standards, new materials should be developed. Conducting polymers (CPs) have aroused growing interest because of their multiple advantages, including improved environment durability, low cost of manufacturing, fantastic mechanical and optical potential and exhibition of similar electrical properties to conventional inorganic materials [1]. While great progress has been made since conducting polymers were developed, many challenges and issues still troubled scholars in different application fields [1-3].

In order to design and produce higher-performance polymers, the principles that how conducting polymers work need to be understood. The interval appears of single and double bones, building a highly conjugated system, are the key to conducting electrons [4]. The electrons in the highly polarized and electron-dense π bonds hop among the molecules in a certain direction, generating current and conducting electricity. At the same time, in real engineering cases, some scholars pointed out that the fillers mixed into the polymer also contribute to the property of the composite material [5]. In addition, doping halogen atoms also enhance the conductivity of polymers in a large degree, suggesting that the structure of the material will change.

Examples of typical CPs include polyacetylene (PA), polypyrrole (PPy), polythiophene, poly (p-phynylene vinylene) and poly(p-phenylene) [4]. Observing the structure of those polymers, it is found that the backbone structure of them is partly polyacetylene, as shown in Figure 1, while others can be viewed as copolymer of ethyne and organics.

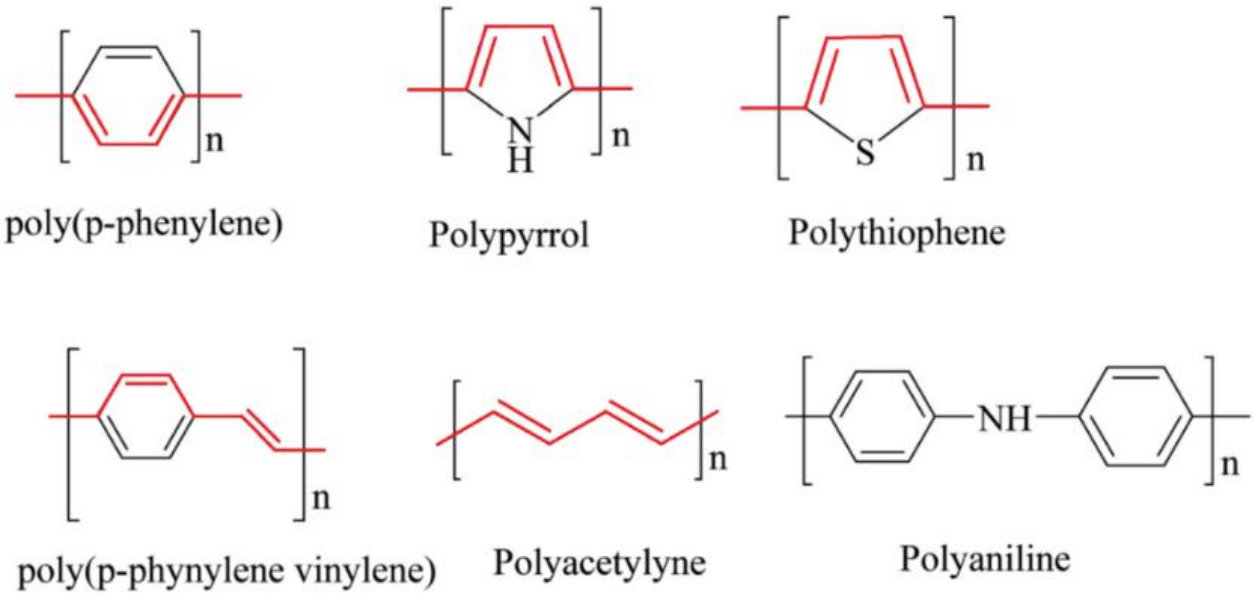

Fig. 1 Six typical conducting polymers and the structures that can be viewed as polyacetylene are marked in red [4]

2. Bone Structure

The bone structure of a conducting polymer is the base of conducting charges, suggesting the importance of classifying and studying them. As shown in figure 1, in the CPs, the backbone might have several ways to determine, especially for those that have ring structures. In this article, it is manually defined that the backbone of a polymer is the longest chain can be found in the polymer, possessing as many carbon-carbon bonds as possible, to simplify the study.

Among those examples of polymers, some of the polymers only have carbon-carbon bonds in the bone structure, while others include other elements in the bone. Thus, the bone structure can be divided into two types, which are pure carbon chain and multi-elements chain. It should be noted in particular that the principle of choosing a molecular backbone should strictly follow the way mentioned in this passage, because the grafting technique and crosslink technic are used in some polymerization, changing the real backbone of the polymer, resulting in changing the performance greatly [6,7].

2.1. Pure Carbon Chain

The type of pure carbon chain CPs is the most common one. This kind of polymer is called a derivative of Polyacetylene. Examples include polythiophene, which is the sharing of two adjacent carbon atoms with one sulfur atom, poly (p-phynylene vinylene), which a single vinyl group is substituted on two carbon atoms alternatively. In these two polymers, the vinyl and sulfur atoms should be viewed as substitutions. Of course, polyacetylene belongs to this category.

Generally speaking, pure carbon chain polymers have good chemical stability and thermo-stability due to the high energy of the carbon-carbon bond, which is 347 KJ/mol. These CPs are adorned with notable flexibility and great optical properties [8]. They can be used to manufacture solar cells, bionic sensors, brain-computer interfaces, etc. However, it is worth pointing out that some of the pure carbon chain polymers fail to reach versatility status, making the shaping process complicated, even if the synthesis process is quite easy and economically feasible. Poly (p-phenylene vinylene) (PPV) is a good example of it.

In the typical cases mentioned in this passage, pure carbon chain CPs do better in conducting electrons. Different from the multi-element chain, the polarity of the pure carbon chain is lower, influencing the conductivity of CPs. The electrons will not bump into the high charge density region in these polymers, so they can move more fluently. However, this character does not significantly

change the ionic conducting ability, indicating that what kind of material to choose depends on the type of charge: electrons or ions. Also, choosing what kind of material depends on the mechanical property, cost, environmental conditions, etc [7].

2.2. Multi-element Chain

Since the atoms of non-carbon elements in the bone structure might have rather large affection on the electron cloud, indicating the modification of properties, so this type of CPs should be discussed individually. Polyphenylene oxide (PPO) and polyaniline (PANI) are good examples of this category. The nitrogen atoms or oxygen atoms interrupt the normal carbon chain into small fragments; hence it is called a multi-element chain in this passage.

PANI is a hot research goal in this category, which is attracting to scholars due to superior conductivity, environment stability and oxidation process. One of the unique applications of PANI is a bionic sensor used in BCI and other vital signs detection instruments [9,10]. If the temperature and humidity of the condition are controlled suitably, the sensors will detect precise signals. In addition, PANI is a good base to produce composites. Research about structuring PANI composites with graphene, oxidated graphene, carbon nanotubes (CNTs), Fe_3O_4, other carbon composites and metal nanoparticles has been done worldwide, contributing to fascinating properties [9]. Application scenarios have also been widely expanded.

This type of polymers has other elements in the backbone chain, which alter the electron morphology and polarize the backbone. In the region near the electron-attracting atoms like oxygen and nitrogen, the charge density is higher, weakening the delocalization degree. So, the conductivity is relatively lower. Although this type of material has differences in terms of electrical conductivity, compared to pure carbon chain polymer discussed in this passage, it has great advantages in biological affinity. That is because the non-carbon atoms polarize the molecular, resulting in better hydrophily.

3. Pendent Group of Polyacetylene

3.1. Polyacetylene

Polyacetylene is the simplest CPs in structure. Natta et al. [11] were the first to report the synthesis of conducting polymers, created the rush in studying them. With the increasing length of the molecule, double and single bond lengths become narrowing into almost the same. π-electrons move among the nearby atoms, contributing to the merge of electron bands. The electron behaves similarly to those in the metal, where valence electrons can move freely in the crystal.

In the previous research, two aspects have been found to determine the conducting ability, which are a narrow $\Delta\pi$-π^* energy band (the gap between HOMO and LUMO state) and a relative plan molecular stereo structure [12,13]. In the molecular that are relatively more plan, π-electron is easier to delocalize and the electron cloud is greater overlapped.

π-electron orbit in polyacetylene without a branch chain has a relatively low contact ratio because of the existence of -trans and -cis models. Even if in the strict synthesis condition, two different models still exist, reducing the conducting ability [11,14]. In addition, polyacetylene has the highest Potential energy band, suggesting that the stability is lower than that of other polymers shown in Fig 2. In this figure, the orange line is the potential energy of a certain derivation in the HOMO condition, while the blue line means the potential energy in the LUMO condition. It is worth noting that all the polyacetylene derivatives are doped with Na in the doublet state.

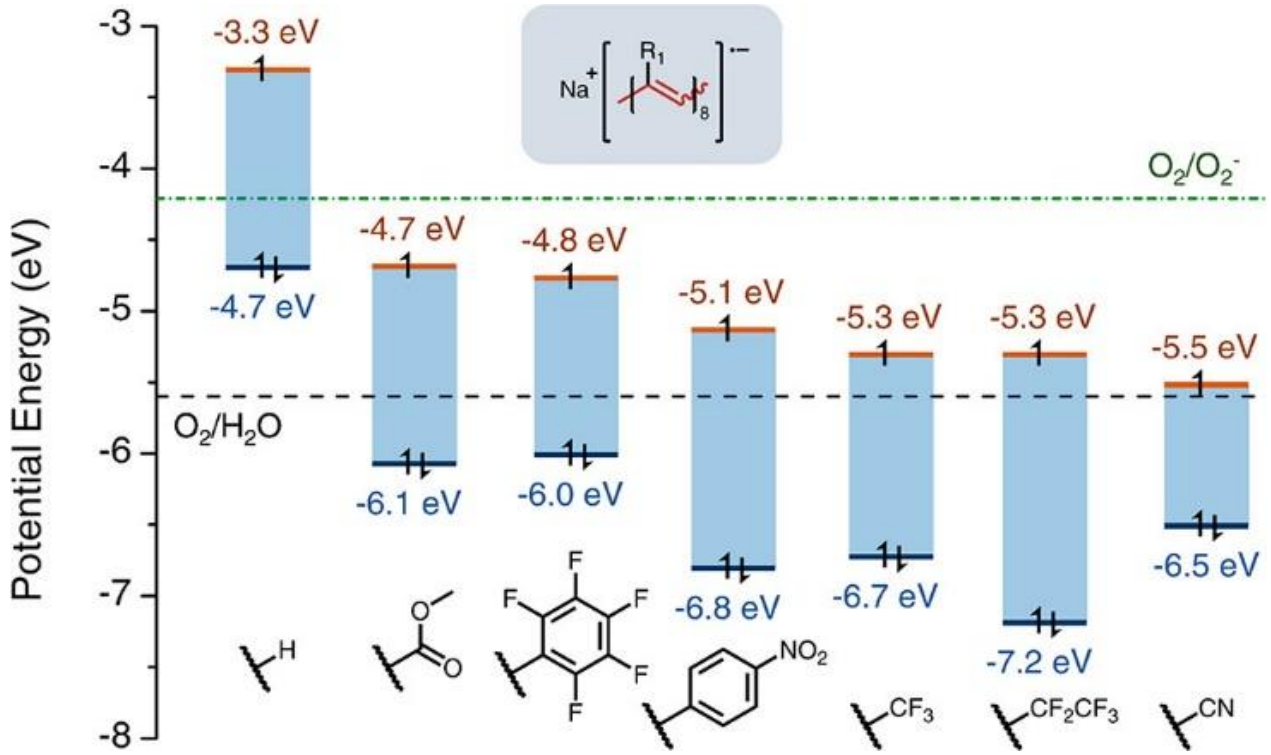

Fig. 2 Potential energy sketch of monosubstituted polyacetylene derivatives [12]

3.2. Polyacetylene with Single-junction Pendant Group

Liam's team made a comparation of the properties of polyacetylene with the pendant group, finding that the potential energy and Δπ-π* energy bands of them vary when the pendant group changes (Table 1) [12]. In the table, Δπ–π* is the energy difference between the π and π* orbitals. Viewing the figure, comparing the reduction potential of oxygen and the polymers, it is found that introducing the pendant group into the polymer will decrease the potential significantly to less than the degree of oxygen. Hence, the anti-decay ability of those improved polymers is much better than polyacetylene because the redox reaction will happen in the opposite direction when the potential of the cathode is higher than the anode.

Side chains that have certain volume and electron attraction affect the synthesis process and finally enhance the two key properties the author has mentioned. Analyzing the electron-withdrawing of the pendant group, the higher attraction of electrons results in a smaller π–π* molecular orbital energy difference, indicating more full electron delocalization, suggesting better-conducting ability. However, comparing the -CF_3 substitution and the -CF_2CF_3 substitution and taking notice of the same π* potential and the different wideness of the energy band, it is assumed that additional electron-withdrawing only makes a limited contribution π* stabilization while distorting the backbone and increasing Δπ–π*.

Table 1. Pendant group and the potential energy [12]

R_1	R_2	π^*(eV)	$\triangle\pi$-π^*(eV)
—H	—H	-3.3	1.4
—CO_2CH_3	—H	-4.7	1.4
—C_6F_5	—H	-4.8	1.2
—$C_6H_4NO_2$	—H	-5.1	1.7
—CF_3	—H	-5.3	1.4
—CF_3	—CF_3	-5.3	3.2
—CF_2CF_3	—H	-5.3	1.9
—CN	—H	-5.5	1.0
—CN	—CN	-7.0	1.5

3.3. Polyacetylene with Double-junction Pendant Group

In the world of conducting polymer, there are two general forms, depending on the junction point number to the backbone. All the pendant groups mentioned before only have one junction point. However, typical CPs include polypyrrole (PPy), polythiophene (PTH), poly(para-phenylene) (PPP), poly(phenylenevinylene) (PPV), and polyfuran (PF) do not belong to single-junction pendant group. The pendant group of them have two junction points on the backbone, forming a ring structure. The structure of them determined the energy band, and then decided the electrical and electronic properties.

Polythiophene typically has a five-member ring with Sulphur at one position. Sulfur in the polymer has additional unbonded electrons, which can delocalize easily. The delocalization of the hetero-atom results in higher conductivity values. One electron-withdrawing atom in the molecular induces little change in the stereo structure while providing notable electron withdrawing. Sarang's research revealed that electron-withdrawing groups attached to the backbone help improve density and capacitive performance [15]. The band gap is about 2.7eV in the doped condition [16]. Another unique advantage of polythiophene is that this polymer is easy to attach additional functional groups including alkyl, alkoxy, phenyl, etc. The additional functional groups may improve the performance further. For example, PEDOT has fascinating electrical performance. It is the special properties that make the polythiophene family a good material to produce photocatalysis, batteries, supercapacitors and sensors [17].

Similarly, polypyrrole has a nitrogen atom in the five-number ring at one position. The nitrogen atom has two electron layers, one layer less than Sulphur. Although the delocalizing ability of nitrogen is lower than Sulphur, the electron-withdrawing is higher. The polypyrrole in a pristine state has a band gap of 4eV and the band gap will be less than 2.5eV after doping [18].

4. Modifications

4.1. Doping

Doping plays an important role in modifying the performance of the CPs. Yang Lu et al. developed a high-performance doping technology that the conductivity can be as high as 14 S/cm [19]. Doping iodine or bromine into polyacetylene (PA) can enhance the conductivity up to 10,000 S/cm. Doping dodecyl benzene sulfonic acid (DBSA) into PANI can enhance the conductivity up to 300S/cm, which is much higher than undoped polymer [20].

In general, there are two kinds of doping, named p-doping and n-doping. The former refers to adding oxidant into the material, creating electron holes in the polymer, while the latter refers to bringing anions into the polymer, resulting in a rich electronic system. Molecules tend to be electric neutral, indicating that electrons are difficult to move around. In the case of doping, extra charge is added manually, so the electron is much easier to move around, approximately in 2 orders. If an external electric field is applied to the material, the current will be viewed [15]. In order to better describe the conducting properties of the CPs, several models have been constructed including the Mott model and the Schaefer–Siebert–Roth model [21,22].

Usually, the CPs are used as an interface conducting catalyst applied on the metal. According to the simulation, the final conducting effect is also relevant to the relation between doping and metal-polymer coupling. When the coupling is relatively so low that the orbits of the polymer layer do not hybridize well, the electrons in the dopants may be injected into the proper channel arising from the localized states. Hence, a great contribution will be made to the transport mechanism. Although doping plays a good role in most cases, it brings no benefit when the coupling is high [22].

4.2. Grafting

Grafting is connecting the polymer with another organic composite, which can be viewed as the highest degree of mixing. Generally, grafting technology includes conventional covalent grafting and non-covalent approach. Grafting impacts the processability, morphology, stability, solubility and

durability a lot, integrating the properties from the grafted organics. Since the nature of the side chain affects the polarity of the backbone, grafting also tunes the conductivity. However, in most cases, the grafting material does not conduct electrons, which might scarify the conducting properties severely [23].

Jenny Malmström et al. reported a grafting of poly (acrylic acid) Brushes from poly(3,4-ethylenedioxythiophene) backbone. They concluded that the material fit in the organic condition better because it is electroactive in aqueous solutions. Also, the conductivity changes with a lower potential at 1.1 V than at 1.2V [24].

5. Conclusion

Till now, there have been a lot of studies done on how conducting polymers work and the mechanics of conducting electrons. The main aim of this passage is to discuss the influencing factors of conductivity. The mechanism of how these factors affect conductivity is also discussed. It is found that decisive factors lay in the backbone structure, functional pendant group attached to the backbone, doping and grafting. Among them, the backbone and pendant group determine the level of conducting performance in the final product, while the doping degree and grafting determine how much conductivity the material has. Pure carbon chain exhibits better conductivity, compared with the multi-element chain. However, the better biocompatibility of multi-element chain makes it difficult to substitute them with pure carbon chain. The pendant groups make a great contribution to the performance of CPs by altering the potential energy. Generally speaking, more electron-attractive pendant groups result in a narrower potential gap between the HOMO and LUMO states, suggesting better conductivity. If the pendant group makes the polymer closer to a plane, it is a beneficial group. In addition, if the pendant group enhances the delocalization of electrons, it will enhance the conductivity. Doping is a fantastic process that extremely reduces the electric resistance by creating extra electrons or electron holes. Thus, doping is an essential step for producing CPs products. Although grafting also affects conductivity, in the practical application case, this technique is usually used to improve non-conducting properties like processability, morphology, stability, solubility and durability. The main difficulty in the CPs field is still how to improve conductivity, which is far from the theoretical limit. Studying CPs based on the polyacetylene backbone will be the research emphasis. The core of CPs design will be around the four main factors: backbone, pendant group, doping and grafting.

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