Novel Dopant for Conductive Polymers: Spherical Polyelectrolyte Brushes

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Abstract. Conductive polymers with special structure and excellent physical and chemical properties, have become a research focus in materials science since the first discovery in 1977. While a growing body of work in recent years has concentrated on the improvement of the electrical conductivity of conductive polymers by using doping technique. The spherical polyelectrolyte brushes (SPB) consisting of polyelectrolyte chains grafted densely to the surface of the core particles, have shown great promise of novel dopant for conductive polymers due to its spherical structure, high charge density and high grafting density. After summarizing the researches of the general dopant for conductive polymers, this review mainly emphasizes on the preparation, doping mechanism and advance prospect of conductive polymers doped with spherical polyelectrolyte brushes.

Keywords. Spherical polyelectrolyte brushes, polypyrrole, polyaniline, dopants.

1. Introduction

Organic polymer, which contain no free electrons or holes, has always been regarded as insulators. This viewpoint remained until in 1977, when researches on p-doped polyacetylene by Shirakawa H et al. [1] showed electrical conductivity comparable to that of metal. Since then, a series of conductive polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PT) and their derivatives have been extensively explored. Organic conductive polymers have been widely used in high-tech fields and emerging industries in recent years due to their light weight, easy synthesis, good flexibility, and controllable electrical conductivity [2-4].

Long-range linear molecule chains of π-conjugated structure are present in conductive polymers, which provides migration conditions for delocalized electron [5]. The electrical conductivity of conductive polymers depends on band gap (\(E_g\)), which decreases with the increase of conjugated length of conductive polymers. At room temperature, thermal excitation can produce carriers under the condition of \(E_g \leq kT = 0.025\) eV, which needs high degree of polymerization. Therefore, the electrical conductivity of conductive polymers with π-conjugated structure is only at \(10^{12} \sim 10^4\) S/cm. Furthermore, the solubility in common organic solvents and mechanical property of conductive polymers are poor due to the rigidity of its molecular chains. These disadvantages limit the practical applications of conductive polymers on a large scale. Studies have shown that “doping” not only increases the electrical conductivity of conductive polymers, but also improves their solubility,
thermal stability, and processability [6-7]. More importantly, the overall performance of conductive polymer is greatly enhanced with the decrease of cost. Accordingly, studies on novel dopants to improve the comprehensive properties of conductive polymers in practical applications are undoubtedly the hot topic of conductive polymers.

Spherical polyelectrolyte brushes (SPB) with spherical structure and charged chains are expected to be novel and efficient dopants for conductive polymers by the selection of sphere cores and brush polymer with certain functional groups. In this review, recent progress of research and development in dopants of conductive polymer is firstly described. Taking polypyrrole and polyaniline as examples, SPB doped with polypyrrole, SPB doped with polyaniline, and SPB doped with Poly (pyrrole-co-aniline) are then discussed. Furthermore, the doping mechanism of SPB is explored, which provides a theoretical basis for SPB as novel dopant for conductive polymers.

2. Dopants for Conductive Polymers

Currently, the conventional dopants, (i.e., dodecylbenzenesulfonic acid (DBSA) [8], p-toluene sulfonic acid (TsOH) [9], and sodium p-toluenesulfonate (TsONa) [10] are widely utilized. Studies by Lee et al. [11] in 1995 indicated that pyrrole (Py) solvation was achieved by DBSA as surfactant in an aqueous solution of ammonium persulfate (APS). Based on this research, other large sulfonic acid compounds were further to be explored [12-14]. In addition, the mechanical properties and processing properties of conductive polymers were essential for practical applications. Researches have shown that the electrical conductivity and mechanical properties of conductive polymers are improved by polymerization, or blending, or interpolymer complexation with polystyrene (PS) [15], polymethyl methacrylate (PMMA) [16] in the process of synthesis or post-processing. Fabrication of conductive polymers/modified inorganic nanoparticles composites show good processability, such as PPy/Fe₃O₄ [17], PPy/SiO₂ [18, 19], etc.

Recently, the techniques based on polyelectrolytes dopants for conductive polymers have attracted considerable interest [20]. Wu et al. [21] designed different concentrations of polystyrene sulfonate (PSS) as dopants to improve the electrical conductivity of PPy. The increased electrical conductivity may be due to the high molecular weight of polyelectrolyte chains, which makes it difficult to dedoped process for the doped ions in the macromolecular chains. Meanwhile, the propagation of PPy may be hindered effectively by polyelectrolyte chains, leading to the dissolution of PPy.

3. Conductive Polymers Doped with SPB

3.1. Spherical Polyelectrolyte Brushes

Polymer brushes refer to assemblies of polymer chains which are densely grafted by one end to surface or interface. To form a “brush” conformation, the graft chains need to be extended in a direction perpendicular to the grafting surface. Therefore, the distance between adjacent graft chains is required to be less than a critical value. Three possible conformations of surface graft polymers are shown in figure 1 [22].

![Figure 1. The conformation diagram of polymer brushes.](image-url)
When the graft density is low, which means the distance between two adjacent graft chains is greater than their rotational radius ($R_g$), no interaction occurs. If the polymer chains are insoluble in solvent, they will be tiled on the interface, showing a “flat” conformation. On the contrary, if the polymer chains are dissolved in solvent, a “mushroom” structure is formed, which is unstable. When the grafting density increases, the polymer chains extend because of steric effect. A brush-like structure is formed when the critical graft density ($\bar{\eta}_c$) is $1/(4\pi R_g^2)$.

In addition, the curvature of grafted surface has an important effect on the brush conformation [23]. From the perspective of colloidal particle radius, a planar brush forms when the radius of the colloidal particles is much greater than the thickness of the grafted brush layer. While the colloidal particle size is much less than the thickness of the grafted brush layer, the formation of star-polymer brush is observed, as shown in figure 2. If a charged polyelectrolyte chain is attached to a spherical surface, spherical polyelectrolyte brushes (SPB) result.

![Figure 2. The structure diagram of polymer brush on different grafting surface.](image)

Since the first study by Pincus [24] and Borisov [25] in 1991, Polyelectrolyte Brushes have attracted extensive attention not only to theoretical models [26-28] but also to its systematic study. Because of its spherical symmetry or quasi-symmetrical structure, high graft density and high charge density, spherical polyelectrolyte brushes have been widely used in many fields such as colloidal stability [29], nanocatalysis [30, 31], biomedical materials [32, 33] and so on.

3.2. Polypyrrole Doped by SPB

PPy is one of the most commonly used conductive polymers due to its easy synthesis, high electrical conductivity, and environmental friendliness.

A conjugated structure is composed of alternating C−C and C=C in PPy chains. C=C consists of $\sigma$ and $\pi$ electrons. The $\sigma$ electron is fixed on carbon atom by covalent bond. While no fixed $\pi$ electron in the conjugated double bonds moves to the entire molecular chains, as shown in figure 3 under external electric field, Polypyrrole exhibits an electron conductivity by fast-moving $\pi$ electron in the molecular chains [34].

![Figure 3. The $\sigma$ band and $\pi$ band in PPy chains.](image)
However, the electrical conductivity of pristine PPy is poor (10^{-8} S/cm), which is mainly because high degree of polymerization is required for activated carrier at room temperatures. “Doping” may cause defects in its conjugated structure, thus improving its electrical conductivity. As shown in figure 4, the doping of PPy is performed by either redox doping or protonic doping.

![Figure 4. Two doping structure of PPy.](image)

The redox doping of PPy means that the electrons are removed (oxidized) or added (reduced) from polymer chains in a certain way, and this process is reversible. The doping process of protonic acid of PPy is as follows: the β carbon of pyrrole is firstly protonated, the positively charged protons are then transferred to the PPy chains, and the negatively charged anion is doped with the polymer chains [35].

Wang et al. [36] studied the composites of PPy doped with anionic spherical electrolyte brushes (ASPB) in organic electronic devices. A two-step process for the preparation of the ASPB was as followed. The core with vinyl groups of ASPB was firstly synthetized by the copolymerization of styrene and divinylbenzene. After adding sodium styrene sulfonate (SSS), polymerization reaction was initiated by azodiisobutyronitrile (AIBN). The study found that ASPB acted as the carrier of PPy, which provided the conducive ink good film-forming performance. With the increasing content of PPy, the electrical conductivity of composites increased. Furthermore, the leakage current of PPy doped with ASPB was lower than that of PEDOT/PSS, providing favorable conditions for its application in the field of electrochemistry. The reaction scheme of PPy doped with ASPB was shown in figure 5.

![Figure 5. Schematic representations of reaction process of PPy doped with ASPB.](image)

Mpoukouvalas et al. [37] thoroughly investigated on the nanoparticles of polypyrrole-polystyrene sulfonate PPy/PSSx (x = H\textsuperscript{+}, Li\textsuperscript{+}, Na\textsuperscript{+}, Cs\textsuperscript{+}). The results revealed that at the same PPy concentration, the effects of different cations on PPy/PSS nanoparticles were rather different. When the temperature was above 400 K, significant difference of the chemical behaviors of cations (H\textsuperscript{+}, Na\textsuperscript{+}, Li\textsuperscript{+}, Cs\textsuperscript{+}) was observed, which may be due to the influence of ionic conductivity. Moreover, the constant temperature DC conductivity of PPy/PSSx nanoparticles decreased with the increase of the atomic radius of counter ion (except for Lithium). This work helped to the selection of dopants.
3.3. Polyaniline Doped by SPB
Polyaniline has become one of the most promising conductive polymers with its readily available, diverse structures, and good environmental stability. Contrary to the doping mechanism of most conductive polymers, valence changes of dopant have not occurred in the doping process of Polyaniline. Based on the doping mechanism of protonic acid, the positive charges carried by the proton can be spread throughout the conjugated chains, leading to the change of charge distribution in polymer chains (see figure 6). It is thus clear evident that the protons of dopant are only attached to the carbon atoms of polymer chains, so no charge transfer takes place between polymer chains and dopants. This doping mechanism, however, is not suitable for every proton acid. The doping mechanism of strong oxidizing proton acids needs further research.

![Figure 6. The doping mechanism of proton acid.](image)

The chemical properties of polyaniline are closely related to its preparation conditions and pH value of electrolyte. Researches have shown that the doping of polyaniline occurs easily in the acidic system. While in the alkaline and neutral system, the de-doping process of polyaniline happens. The interaction principle of polyaniline and SPB is shown in figure 7.

![Figure 7. Schematic representations of reaction process of polyaniline doped with ASPB.](image)

Ke et al. [38] analyzed the suspensions of polyaniline-coated polystyrene microsphere by cyclic voltammetry test. Results showed that two oxidation peaks were appeared. The oxidation peak at 0.5 V might be attributed to the oxidation of polyaniline [36]. Furthermore, the oxidation peaks of current and potential of the microsphere suspension after centrifugation and purification were significantly different. In the synthesis process, consequential recurrence by cyclic voltammetry test was poor because of inconsistent chain length distribution and cross-linking degree of polyaniline on the microspheres, which brought difficulties to electrochemical study. Therefore, the synthesis of microspheres with active functional groups was crucial to explore the doping mechanism of conductive polymers.

Korovin et al. [39] synthesized ASPB-PANI composites in a 0.01 M hydrochloric acid with ASPB (PS core, PSS brush) as template and APS as oxidant. Results showed that the zeta potential of synthesized composites was ranging from -40 mV to -80 mV when the concentration of NaCl was $10^{-5}$ M ~ $10^{-1}$ M, proving its excellent colloidal stability. Moreover, under the same conditions, the
electrical conductivity of SPB-PANI composites was higher than that of PS-PANI composites, which indicated that the SPB was efficient dopant for conductive polymer.

3.4. Poly (aniline-co-pyrrole) Doped by SPB

Compared with a large number of reports of polypyrrole and polyaniline, studies on copolymers of aniline-pyrrole and its dopants are very inadequate. Copolymer is obtained by overcoming the disadvantage of a single π-electrons in the homopolymer [40], so it has gradually raised lots of concerns. So far, most research has focused on the synthesis of copolymers with nanostructures using various templates [41], such as synthesized poly (aniline-co-pyrrole) composites coated on carbon fibers by one-step electrochemical method [42] and poly (aniline-co-pyrrole) nanospheres prepared by chemical copolymerization [43].

Huang [44] et al. prepared poly (aniline-co-pyrrole)/ASPB composites by chemical oxidation polymerization method. The room temperature conductivity of the composites reached to 8.3 S/cm, which was higher than that of un-doped poly (aniline-co-pyrrole).

4. Doping Mechanism

The doping mechanism of ASPB can be explained by template theory. ASPB serve as a template, which is mainly based on its ability to capture and control the kind and number of ions in the brush layers through electrostatic interaction [45]. Figure 8 represents the charge distribution within ASPB. Due to the steric effect, densely grafted PSS chains provide a loop of density gradient. The effective concentration of the monomer of conductive polymers in the PSS chains increases by exchange of sodium ions, and its distribution follows the density gradient of PSS chains. Therefore, the high-concentration of the monomer of conductive polymers is located at the cores of the ASPB, where polymerization occurs with a priority. Based on the doping mechanism of protonic acid, polymerization of the monomer of conductive polymers leads to the formation of polymeric cations, which act as multivalent counter ions in the PSS brush layer. The complexation of conductive polymers and PSS is irreversible, so the polymerization is confined in the brush layers. In brief, ASPB play the role of template and dopant in the synthesis of composites.

5. Conclusion

Spherical polyelectrolyte brushes with high symmetrical or quasi-symmetric structure can not only improve the electrical conductivity of conductive polymers, but also enhance its mechanical and processing properties by controlling the structure parameters (graft density, molecular weight, charge density, etc.). In view of the diversity of conductive polymers and the complexity of SPB, researches at present are far from enough, especially its structure-activity relationship. In short, conductive polymers using SPB as novel dopants shows good performance, which needs further study in depth.

Figure 8. Schematic representations of doping mechanism of ASPB.
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