

Conductive Polymers and Their Properties for Flexible Devices

Subjects: Polymer Science

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Flexible sensing devices have attracted significant attention for various applications, such as medical devices, environmental monitoring, and healthcare. Numerous materials have been used to fabricate flexible sensing devices and improve their sensing performance in terms of their electrical and mechanical properties. Among the studied materials, conductive polymers are promising candidates for next-generation flexible, stretchable, and wearable electronic devices because of their outstanding characteristics, such as flexibility, light weight, and non-toxicity.

Keywords: conductive polymers ; flexible sensors ; printing techniques ; flexible devices

1. Polyacetylene (PA)

PA, a linear polyene chain $[-(\text{HC}=\text{CH})_n-]$, is an archetypal conjugated polymer exhibiting multifaceted properties and possessing many interesting features for developing electronic devices. These include good electrical conductivity, photoconductivity, gas permeability, supramolecular assembly formation, chiral recognition, helical graphitic nanofiber formation, and liquid crystallization ^{[1][2]}. PA has the simplest structure of organic polymers that can exhibit metal-like conductivity ^[3]. Owing to the repeated units of two hydrogen atoms in the chemical structure of PA, the chain can be easily decorated with pendant groups by replacing these hydrogen atoms with foreign molecules to form monosubstituted or disubstituted PAs ^[4]. The electrical conductivity of non-doped PAs depends strongly on their conformation, with values of $10^{-9} \text{ S}\cdot\text{cm}^{-1}$ and $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ for cis- and trans-PA, respectively ^[4]. In contrast, PAs can achieve an almost metallic conductive level (10^4 – $10^5 \text{ S}\cdot\text{cm}^{-1}$) via p- or n-doping ^{[5][6][7]}. Although PA has promising conductive ability, its high instability, even at room temperature, and the difficulties in its processing have considerably limited its practical applications ^{[8][9]}. Compared to other CPs with lower electrical conductivity but better stability and processability, PA has rarely been used in designing and developing flexible devices.

Methods including catalytic and non-catalytic polymerization and precursor-assisted synthesis are used to prepare PA ^[10]. Of these, catalytic polymerization techniques, Ziegler–Natta or Luttinger catalysis, are commonly used to polymerize acetylene and other monomers to produce PA and oligomers such as cyclooctatetraene and vinyl acetylene ^[11]. The catalysts must have high solubility in organic solvents and high selectivity, such as Ziegler–Natta catalysts, which are a combination of $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$ and $(\text{C}_2\text{H}_5)_3\text{Al}_1$, to produce highly crystalline PA films ^[12]. Furthermore, these techniques allow the monitoring and observation of the structures of the final PA products with variations in the temperature and catalyst content. PA can also be synthesized by radiation polymerization approaches, such as glow discharge, ultraviolet, and γ -radiation ^[13]. Compared with polymerization catalysis, radiation polymerization methods can avoid using catalysts and solvents; thus, they are very promising techniques for the future development of PA. In the design and development of flexible devices, PA is often hybridized or doped with different materials, such as dihexadecyl hydrogen phosphate ^[13], quaternized cellulose NPs ^[14], and Au NPs ^[15], to improve their conductivity. PAs are also known as acetylene black or PA black, depending on the preparation method, and they are usually applied in electrochemical biosensors and bioelectrodes.

2. Polyaniline (PANI)

PANI is one of the most promising conjugated CPs, owing to its excellent environmental stability, high processability, high and tunable electrical conductivity, and optical properties ^[16]. The conductivity of PANI is highly dependent on the dopant concentration and pH; it can show metal-like conductivity at $\text{pH} < 3$ ^[17]. PANI occurs in the three different forms of leucoemeraldine $[(\text{C}_6\text{H}_4\text{NH})_n]$, emeraldine $[(\text{C}_6\text{H}_4\text{NH})_2(\text{C}_6\text{H}_4\text{N})_2]_n$, and pernigraniline $[(\text{C}_6\text{H}_4\text{N})_n]$, based on the idealized oxidation states during the polymerization of the aniline monomers ^[18]. The pernigraniline base (blue/violet) is fully oxidized PANI, while the leucoemeraldine base (white/clear) is completely reduced, and emeraldine (salt-green/base-blue)

is half of the oxidized PANI. PANI is conductive and more stable in the emeraldine state at room temperature. The pernigraniline and leucoemeraldine forms have poor conductivity even with doping. PANI conductivity depends significantly on the preparation method, and it can be modulated by submerging the emeraldine base in an aqueous acidic solution [19]. However, the emeraldine base state is poorly soluble owing to the stiff polymer backbone and the hydrogen bonding interactions between adjacent chains; thus, it is difficult to process. Moreover, it exhibits instability at the melt-processing temperature, which limits its practical applications. Therefore, functionalized PANI and alternative PANI derivatives are often used to develop flexible devices [20][21]. Owing to its low cost, good environmental stability, excellent optical and electrical properties, and good anticorrosion and mechanical properties, PANI has attracted much attention in the design and development of commercial technologies, especially flexible electronic devices, in various fields such as organic electronics [22], biosensors [23], chemical sensors [24][25], corrosion devices [26], photovoltaic cells [27], solar cells [28], organic light emitting diodes [29], and electrorheological materials [30]. Furthermore, PANI-based nanocomposites have undergone tremendous development via the regulation of electrical properties by protonation or charge-transfer doping. Owing to the controllability of the electrical, magnetic, mechanical, and thermal properties of CP–inorganic nanocomposites [31], PANI-based composites are considered one of the most important nanocomposite materials.

For PANI synthesis, the chemical oxidation method is the most common and straightforward; this uses a doping acid and a mixture of an oxidizing agent and a monomer precursor, in which the color change of the obtained solution to green confirms PANI formation [32][33]. Although the process is simple, such conventional methods have shown significant problems regarding the use of strong acids and oxidants, such as ammonium peroxydisulfate [34][35][36]. Moreover, this conventional technique only yields irregularly shaped PANI products. In order to obtain PANI nanostructures with diameters of <100 nm, different functional molecules have been introduced during the chemical polymerization, including surfactants, liquid crystals, polyelectrolytes, nanowire seeds, aniline oligomers, or organic dopants [37]. Such agents may work as templates to promote the self-assembly of ordered “soft templates” for forming PANI nanostructures. Moreover, a side-by-side electrospinning technique can prepare PANI nanofibers with enhanced mechanical and electrical properties [38].

3. Poly [3,4-(ethylenedioxy)thiophene] (PEDOT)

PEDOT is one of the most popular CPs because of its high conductivity, good air stability, optical transparency, and simple processing [39]. PEDOT crystals have monoclinic lamellar structures consisting of inclined π -stacks, in which the electrons are lighter than the holes [40]. The PEDOT structural model has a pseudo-orthorhombic unit cell with four monomers and one tosylate ion per cell; the lattice parameters a , b , and c are 14.0, 6.8, and 7.8 Å, respectively [41]. Owing to its advantageous properties, PEDOT has been broadly applied in the design of various flexible devices in bioelectronics and energy conversion and sensors [42][43]. Because PEDOT is hydrophobic, hydrophilic surfactant additives (i.e., poly(styrenesulfonate) (PSS)) must be used to improve its aqueous processability as a thin film [44]. Consequently, PEDOT:PSS, a water-soluble CP, can be obtained by incorporating positively charged conductive conjugated PEDOT with negatively charged insulating PSS [45]. In particular, the water-soluble long molecular chains of PSS interact with the insoluble short chains of PEDOT by Coulombic forces to form grains, which induces good water dispersion of PEDOT. Nano-sized PEDOT:PSS grains (30–50 nm) are composed of tangles containing several PEDOT segments and a single PSS chain. To improve the electrical conductivity of PEDOT:PSS, many processing methods and doping agents have been employed to remove excess PSS and induce phase separation or morphological rearrangement [46]. In these processes, polar solvents such as dimethyl sulfoxide (DMSO), ethylene glycol, and co-solvents [47] or acids such as chloroplatinic acid, sulfonic acid, and mineral acids [48][49][50] have been used to increase the conductivity of PEDOT:PSS films. Moreover, electrospinning has recently offered the possibility of producing flexible 1D PEDOT:PSS nanofibers with high conductivity [51].

In general, pristine PEDOT:PSS films show an inherent direct-current electrical conductivity (less than $1.0 \text{ S}\cdot\text{cm}^{-1}$) [52][53], while the modified films can show substantial improvements in conductivity of 2–3 orders of magnitude, reaching $4000 \text{ S}\cdot\text{cm}^{-1}$ owing to doping. In addition, PEDOT:PSS films possess a typical work function of 4.8–5.4 eV and are thus usually implemented as a p-type contact layer with fast charge transfer and injection, favored for optoelectronic use devices. Moreover, doped PEDOT:PSS films exhibit higher flexibility and stretchability than undoped films [54][55]. Such films are robust against mechanical shear, impact, bending, folding, twisting, and large tensile strains of over 100% [56][57]. In conclusion, PEDOT:PSS films with morphological evolution and structural rearrangement show high conductivity, flexibility, and stretchability [45].

4. Polypyrrole (PPy)

PPy is a heterocyclic positively charged CP containing N atoms in its oxidized form; however, its conductivity can be completely lost due to overoxidation [58]. In addition, PPy is more electroactive in organic electrolytes and aqueous solutions [59]. PPy is particularly interesting among the various CPs because its monomer (pyrrole) is easily oxidized, water-soluble, commercially available, lightweight, low-cost, and bio-compatible [60]. It also exhibits good environmental stability, high conductivity, and good redox properties [61]. Therefore, PPy has been considered in numerous applications ranging from biochemical to electrochemical energy devices [62][63][64]. Furthermore, PPy presents greater flexibility than most other CPs [64], and it can be combined with other nanostructured materials such as graphene or other carbon materials to form nanocomposites, which can show significantly enhanced properties owing to their improved ion diffusion rates and increased contact surface areas [65][66]. These outstanding features make PPy a promising candidate to meet the requirement of portable and flexible electronic devices [67][68].

PPy may be conductive because of its structure of alternating single and double bonds, which create some delocalization of electron density in the molecule [69]. However, pristine PPy is an insulator with a large bandgap energy (3.16 eV) [70]. To enhance PPy conductivity, chemical and electrochemical doping methods have been employed [71][72]. In these doping processes, PPy oxidation can remove a π -electron from the neutral polymer chain, causing its structure to change from benzenoid (aromatic) to quinoid [70][73]. Consequently, doping can convert PPy into an ionic complex comprising cations and incorporated counterions. Chemical and electrochemical polymerization methods are commonly used for PPy synthesis [67]. Recently, other advanced polymerization techniques, such as ultrasonic irradiation, vapor-phase polymerization, electrospinning, microemulsion, mechanochemical polymerization, and photopolymerization, have attracted interest in the preparation of highly conductive PPy [74][75].

5. Polythiophene (PT)

PT is an important CP owing to its simple structure, high stability, and various optoelectronic properties. PT and its derivatives in both undoped and doped states have gained great attention in sensing device applications due to the structural modification and solution processability [76]. Moreover, it also exhibits a selective barrier effect to specific molecules and high adsorption affinity on the electrode surface. The overall electronic properties can be tuned using side-chain groups or dopants with a band gap from 3 to 1 eV [77]. However, the polymerization and deposition of PT on large insulating substrates have remained a big challenge because of the high oxidation potential. Several methods have been widely used for the preparation of polymeric thin films from thiophene monomers, including chemical oxidation in solution, electrochemical oxidation, and oxidative chemical vapor deposition [78]. Among them, electrochemical oxidation polymerization is the most common technique due to the easy control of the polymerization degree [79]. Moreover, PT nanofiber structures can be obtained using electrospinning [80].

Poly(3-alkylthiophene)s (P3ATs) are one of the most important types of PTs because they present high electrical and thermal conductivity, processability, and environmental stability [81]. However, P3AT has a high price; thus, its practical applications are limited [82]. Within the P3AT family, regioregular poly(3-hexylthiophene) (P3HT), poly(3-pentylthiophene) (P3PT), and poly(3-butylthiophene) (P3BT) are well-known CPs that have been widely used in organic electronic sensing applications owing to a good balance between the solubility and electric properties. With the increase of alkyl chains, the degree of phase separation is gradually improved and a balanced hole/electron transport enables to be achieved [76][83][84][85].

6. Poly(o-phenylenediamine) (PoPDA)

PoPDA is recently considered a low-cost electroactive organic material and an attractive CP widely used in sensors, energy-conversion devices, and biomedical fields [86]. It exhibits good solubility, processability, high electroactivity, and thermal stability [87]. PoPDA has a ladder-type CP with a phenazine-like structure, in which an o-phenylenediamine, an aniline derivative with an amino group at its ortho position, is polymerized in an aqueous hydrochloric acid medium (pH < 1) [88]. The molecular properties of PoPDA are remarkably different from PANI, which contains a 2,3-diaminophenazine repeat unit in a ladder-like fashion or an open PANI-like structure [89]. To enhance spectral, morphological, and photo physical properties, PoPDA can be doped by luminol to form luminol-doped PoPDA.

PoPDA can be prepared by similar methods to PANI, including (i) using an oxidizer to polymerize o-phenylenediamine at room temperature [90]; (ii) using a reprecipitation approach to prepare nano/micro-structured PoPDA by transferring the o-phenylenediamine from a “good” solvent to a “bad” solvent where the o-phenylenediamine precipitate due to its lower solubility. For the chemical oxidation method, using high redox potential reagents, i.e., FeCl_3 , AgNO_3 , HAuCl_4 , and

(NH₄)₂S₂O₈, is required to form PoPDA structures. In the reprecipitation procedure, the formation of 1D structures is facilitated when transferring o-phenylenediamine from N-methyl pyrrolidone to water [91]. For the preparation of PoPDA nanofibers, direct electrospinning has been reported as a potential process [92]. **Table 1** summarizes the structures, synthesis methods, properties, and applications of several common π -CPs.

Table 1. Summarized structures, properties, synthesis methods, and applications of CPs for flexible devices.

CPs	Structures	Synthesis methods	Properties	Refs
PA	-Linear polyene chain and multifaceted properties.	Ziegler–Natta catalysis, non-catalytic polymerization, and precursor-assisted synthesis.	Good electrical conductivity, photoconductivity, gas permeability, supra-molecular assembly formation, chiral recognition, helical graphitic nanofiber formation, and liquid crystallization capability.	[1][2] [10][13] [14]
PANI	Three different forms: leucoemeraldine, emeraldine, and pernigraniline.	Chemical oxidation method, interfacial polymerization, and electrospinning.	Leucoemeraldine (insulator), pernigraniline (insulator), and emeraldine salt (10^{-2} – 10^0 S/cm)	[16][18] [38][93]
PEDOT	A monoclinic lamellar structure consisting of inclined π -stacks.	Chemical polymerization, electrochemical polymerization, and electrospinning.	-The highest conductivity of 6259 S.cm ⁻¹ for thin films and 8797 S.cm ⁻¹ for single crystals. -Ultra-low thermal conductivity, processability, non-toxicity and unique flexibility, water insolubility.	[39][40] [42][45]
PEDOT:PSS	PEDOT: PSS grains with a nano-size (30–50 nm).	Chemical polymerization, electrochemical polymerization, and electrospinning.	High conductivity, air stability, transparency, flexibility and intrinsic stretchability, and water insolubility.	[47][49] [50][51] [54]
PPy	A heterocyclic and positively charged CP.	Electro-polymerization, vapor-phase polymerization, electrospinning, microemulsion polymerization.	Good environmental stability, high conductivity, and good redox properties.	[62][63] [64][94]
PT	Four different oligomeric structures (2-ring, 4-ring, 6-ring, and 8-ring).	Chemical oxidation, electrochemical oxidation, oxidative chemical vapor deposition, and electrospinning.	High stability, structural modification, and solution processability.	[77][78] [80][95]
PoPDA	A ladder polymer possessing a phenazine-like structure.	Chemical oxidation, electrochemical polymerization, electrospinning, and reprecipitation.	Good solubility, processability, high electroactivity, and thermal stability.	[87][90] [91][92]

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