

Engineering Materials

Syed Shahabuddin
Adarsh Kumar Pandey
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Advances in Hybrid Conducting Polymer Technology



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Engineering Materials

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Advances in Hybrid Conducting Polymer Technology

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Preface

This is an advanced text, compiled and designed to apprise postgraduate and undergraduate researchers, students and research industries with the basic theory and advanced applications of conductive polymers and its nanocomposites. The authors of this book also believe that the content of this book would serve as introductory literature for those researchers and students who are not acquainted with the background of the subject.

The research of electrically conductive, conjugated and electroactive polymers has progressed in due course of time and continues to thrive. There has been a significant advance in the understanding of fundamentals and advanced applications in the field of conductive polymers and its nanocomposites. Almost 40 years has been passed since the discovery of conducting polymers. Still, this field of research continues to flourish with the development of wide variety of applications being explored and reported. The importance of conducting polymers can be visualised by the fact the Nobel Prize was awarded to Alan Heeger, Alan MacDiarmid and Hideki Shirakawa in the year 2000 for the discovery of conductivity in polyacetylene. With the advent of nanotechnology and development of nanomaterials, conducting polymers have been tailored into unique nanocomposites which has enhanced the properties and developed unique characteristics. This field of research is still growing steadily, and there is a need of complete understanding of the concept of conducting polymers and how they can address the modern-day issues faced by humanity.

The properties of conducting polymers such as conductivity, optical properties and various physical properties along with the advance applications such as photocatalysis, energy storage devices, nanoelectronics devices, energy harvesting devices, heat transfer applications, waste water treatment, EMI shielding, tissue engineering, antimicrobial properties and dye-sensitised solar cells were discussed throughout the book.

We hope this book will be useful and will serve as a guide for universities and industrial institutions, postgraduate and Ph.D. scholars, researchers working in the area of chemistry, biology, physics, polymer sciences, material sciences, nanoscience and so on.

Lastly, this book has been the final product of the outstanding work of many experts, distinguished researchers and renowned scientists. They have provided their expertise and efforts in compilation of the state-of-the-art chapters. We appreciate the valuable time, hard work and efforts of all the contributing authors.

As a matter of fact, perfection is an assumption. The authors and the editors can never be satisfied with their final efforts. Albeit the book chapters and final draft have been comprehensively reviewed by authors, reviewers and editors, there is always a window to enhance and modify various sections of the chapters, providing an opportunity for improvement in the quality and quantity of the contents. Therefore, the readers of this book are welcome to recommend the errors, omissions and lack of inclusion of some important information. The recommendations from students, researchers, scientists and academicians will be highly appreciated.

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Introduction to Conducting Polymers



Syed Shahabuddin, Nurul Aqilla Mazlan, Siti Nor Atika Baharin,
and Kavirajaa Pandian Sambasevam

Abstract In recent years, the research about Conducting Polymers (CPs) have seen exponential growth due to their versatile applications. The widespread attention on CPs is due to its extraordinary properties such as simple preparation step, low cost of monomers, environmentally benign, and most importantly the high conducting properties like metals. In addition, lightweight of CPs and non-corrosive nature, have made it one of the versatile polymers in the materials group. These remarkable properties of CPs have made it to be easily integrated with the latest applications on photocatalyst, sensors, and actuators, solar cells, energy devices, and batteries. However, many have not realised the historical background of these versatile CPs. Hence, this chapter is an attempt to address the forgotten history of CPs with respect to certain selected well-known CPs.

Keywords Conducting polymers · Polyaniline · Polypyrrole · Polythiophene · History of conducting polymers

1 Introduction

Over the years, the concept of conducting polymers (CPs) continues to fascinate the scientific community as several research papers regarding this material have been annually increased. CP is an organic macromolecule that integrates both conventional polymers and metal properties into one system. This “synthetic metal” was

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formerly discovered by a group of Nobel laureates named Hideki Shirakawa, Alan MacDiarmid, and Alan Heeger with the recognition of new phenomena; “dawn of the new plastic age” [1]. Here, these scientists reported a dramatic increase in electrical conductivity of polyacetylene (PA) when doped with controlled amounts of arsenic pentafluoride (AsF_5) together with halogen group elements [2]. Subsequently, a series of CPs such as polyaniline (PANI), polypyrrole (Ppy) and polythiophene (PTh) have been widely developed (Fig. 1). Since the 1980, CPs have been used as the key principle in numerous potential applications such as electronics devices [1–4], energy storage devices [4–6], corrosion inhibitors [7, 8], degradation of pollutants [11–10] electromagnetic shielding materials [11] and sensors [12, 13]. Besides tough mechanical strength and remarkable rheological properties [14], this material possesses high magnetic properties, unique optical features, and good electrochemical reactions [18–14]. CPs also own an excellent light absorption ability where it acts as transporting material in visible-light excitation state, improving photovoltaic efficiency [11, 16].

Furthermore, CPs also show high conductive ability similar to those metals and semiconductors although originally, the polymer was classified as an insulator as for their dominant insulating properties. Figure 2 represents the comparison of conductivity between CPs with other materials. The conduction of electricity in these types of polymers is due to two factors; the conjugation of the double bonds in the polymeric chains and the doping process [17]. The conjugated π electron together with dopant ions allows the mobility of electrons in CPs to acts as charge carriers and to delocalise into the conduction band, thus increasing the metallic behavior of the polymer [17].

Generally, CPs can be doped via two methods widely known methods such as addition (n-doping) or reduction (p-doping) of an electron by using a different type of dopant as shown in Fig. 3. Though CPs own many promising characteristics, there are still few questionable issues that arise such as difficulties in the process, low

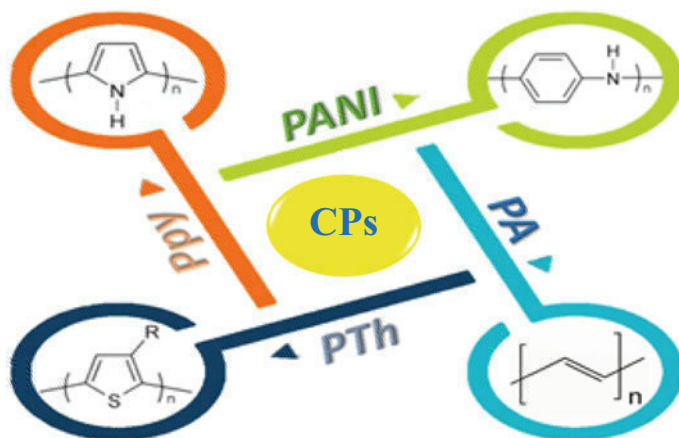


Fig. 1 Molecular structure of most studied CPs

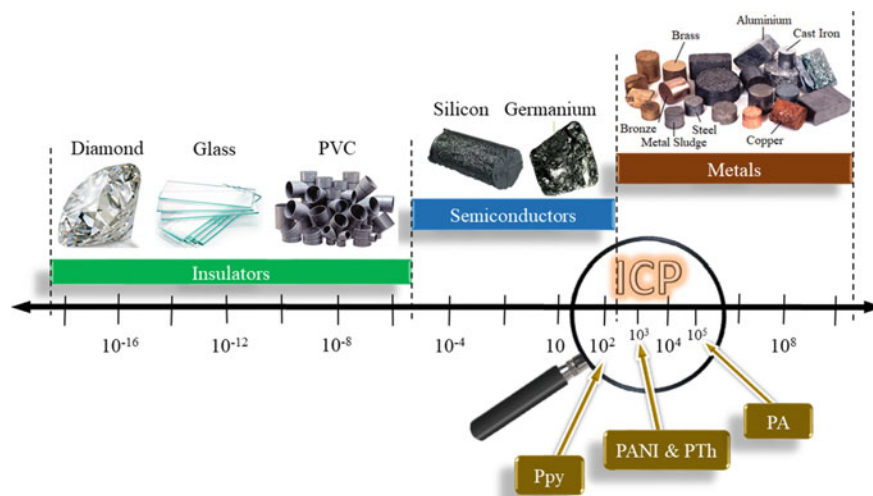


Fig. 2 The comparison of conductivity between CP and other material

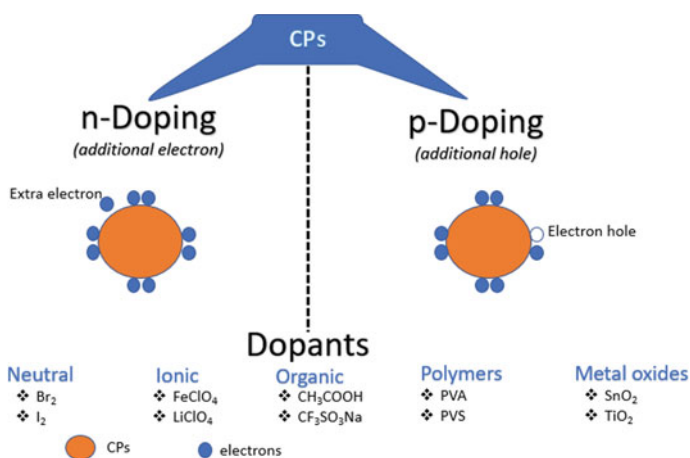


Fig. 3 Types of dopants used in n-doping and p-doping of CP materials

stability, and insolubility issues. Nevertheless, various modifications to the structure and functional group can be done to overcome those flaws in terms of blending, co-polymer, or hybrid composition.

1.1 Historical Background of the Development of Conducting Polymers

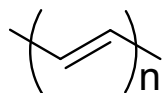
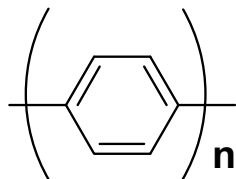
The initial work on conducting polymers have begun since the nineteenth century by Prof Dr Letheby [18]. In 1862, he attempted to investigate the properties of conducting polymers, and a study on electropolymerisation of aniline sulfate was published in the Journal of the Chemical Society [19]. However, the scientists of that time were still not clear about the chemistry behind the materials that they were investigating. Even though the research about CPs emerged 60 years ago, the possibility of producing those polymers was not recognised. A key discovery that changed the perspective was the findings of inorganic polymer polysulfur nitride $(\text{SN})_x$ which was highly conducting in 1973 [20] by Macdiarmid and Heeger partnership. The researchers also reported that the conductivity of $(\text{SN})_x$ was in the order of 10^3 S/cm which was close to the conductivity of copper ($\sim 10^5$ S/cm). This discovery convinced the entire scientific community to produce more polymeric conductors.

Polyacetylene was first synthesised by Natta and co-workers which showed a range of conductivity between 10^{-11} and 10^{-3} S/cm in 1958. The conductivity of this polymer could be manipulated by the synthesis process. However, this polymer also did not get widespread attention, until a co-worker of Prof Dr Hideki Shirakawa accidentally added an excess of Ziegler–Natta catalyst which resulted in a silvery polyacetylene thin film in 1967. This film exhibited a higher conductivity than the graphite powder. Then after some time, MacDiarmid who was a visiting professor at Tokyo Institute of Technology, Japan gave a talk on $(\text{SN})_x$ conducting properties where it brought together MacDiarmid and Shirakawa to sit down for a cup of green tea while sharing their fascination for conducting materials. Soon after, MacDiarmid invited Shirakawa to the University of Pennsylvania to work on the CPs with Alan Heeger. In 1976, the group of trios—Alan Heeger, Alan Macdiarmid, and Hideki Shirakawa announced the discovery of novel conducting polymers which triggered the interests of many scientific communities around the world to venture into the field of conducting polymers. The trios received Nobel Prize for conducting polymers in 2000 [21].

1.2 Types of Conducting Polymers and Their Properties

1.2.1 Polyacetylene

One of the well-known conducting polymers is polyacetylene. The structure contains C-H units that constructed C_2H_2 . The conjugating of single and double bond C–C bond makes polyacetylene special with a stagnant carbon backbone with mobilised electron clouds around the structure as shown in Fig. 4. The structure of polyacetylene depended on the synthesis condition, with normal polymerisation condition cis polyacetylene predominates to trans polyacetylene [22].

Fig. 4 Polyacetylene**Fig. 5** Polyparaphenylene

The conductivity of polyacetylene was known to be increased as the polymer chain increased. Doping action with a halogen such as bromine and iodine have greatly increased the conductivity than undoped polyacetylene (10^3 – 1.7×10^5 S/cm). Polyacetylene was found to be crystalline with x-ray diffraction of powder samples, which were found to be ~ 90–95% crystalline, with a small amount of amorphous content [23]. Insolubility, high thermal stability, sensitivity towards air become some of the drawbacks of polyacetylene which leads to low processability and conducting performance [24, 25].

1.2.2 Polyparaphenylene

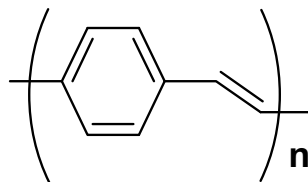
Another significant class of conducting polymer is polyparaphenylene (PPP). The polymer chain linked through conjugated aromatic rings as illustrated in Fig. 5. PPP is known to have a tremendous thermal property which can go up to 600 °C. However, PPP shows some issues in terms of solubility, due to the polymeric chains made up by mainly benzene rings [26].

PPV can be processed into a crystalline film by vacuum deposition which in turn shown interesting electronic and optical properties when doped (10^2 – 10^3 S/cm). The main application of PPV is electroluminescence specifically in organic light-emitting diodes (OLED). Delayed fluorescent and fluorescent are normal behavior of PPP which is mainly contributed by electrons mobilisation in the conjugated chains [27].

1.2.3 Polyparaphenylene Vinylene

High crystallinity rigid-rod structure is a property for polypara-phenylene vinylene (PPV). The polymeric chain is connected via alternating of benzene and vinyl group; Fig. 6 Similar to other conducting polymers, PPV tends to have unusual electrical properties upon doping (3 – 5×10^4 S/cm) and can be tailored by the functionalisation inclusion. PPV can be processed with a greatly ordered crystalline thin film.

Fig. 6 Polyparaphenylene vinylene



Dopants such as H_2SO_4 increase the conductivity of PPV with good metallic transport property. However, the H_2SO_4 -PPV dopant was revealed to have low stability in the presence of moisture [28].

Moreover, many approaches have been done in incorporating PPV with either organic or inorganic materials to enhance or tune the conducting properties of PPV. PPV was made in light emitting diode applications such as polysilicon-PPV [29], polyparaphenylene-PPV [30] and poly(2,5-dimethyl-para-phenylene vinylene)-PPV [31]. Another, interesting application of PPV, is solar cell device, for example blend of the poly 2,5-dimethoxy-1,4-phenylenevinylene-2-methoxy-5-(2-ethylhexyloxy-1,4-phenylenevinylene) (M3EH-PPV) and polyoxa-1,4-phenylene-1,2-(1-cyano-ethylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano-ethylene-1,4-phenylene) (CN-ether-PPV) [32] and TiO_2 -PPV bilayer [33].

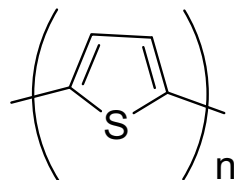
1.2.4 Polypyrrole

Pyrrole is a 5-membered ring that contains nitrogen (N) heteroatom. The conducting properties of polypyrrole (PPy) is a result of π electrons and a positive charge along the backbone [34]. PPy was first synthesised by using a common oxidative route with pyrrole monomer and hydrogen peroxide as the oxidising agent in 1916 [34]. The synthesis yielded a compound which was known as 'pyrrole black' and was not recognised as CPs. Then, in 1968 Dall'Olio and co-workers prepared PPy via an electrochemical route on a platinum electrode which has given the recognition for PPy as CPs [35]. This discovery has led to explosive research that revolves around the synthesis and application of PPy materials [30–25].

PPy possessed enormous advantages such as large surface area due to its fibrous structure and it is a high capacity electrode material. PPy can be easily synthesised via chemical or electrochemical route, high stability in aqueous and air medium makes it a promising candidate interfacial material [37]. Therefore, it made PPy one of the extensively applied and investigated materials in the current state of the art.

1.2.5 Polythiophene

Owing to the interesting properties; stable towards environment perturbation, thermal, conductivity, ease of synthesis, and variety of application standpoint, polythiophene (PTh) becomes one of the most studied conducting polymers for the last

Fig. 7 Polythiophene

twenty years with relative conductivity range of $10\text{--}10^3$ S/cm [38]. PTh belongs to a class of heterocyclic compounds containing a five-membered ring made up of one sulfur as heteroatom with the formula $\text{C}_4\text{H}_4\text{S}$. Thiophene and its derivatives isolated from petroleum or coal. Owing to their efficient light harvesting, structural versatility, and intrinsic charge transport behavior, thiophene-based π -conjugated systems have attracted much attention in developing high performance conducting cells. Figure 7 demonstrates the structure of thiophene repeating units PTh.

Property tailoring to match an explicit electronic application is likely by integrating electronic groups along with the conjugated framework in addition to copolymerising with other heterocyclic monomers. Copolymerisation and homopolymerisation of PTh are commonly prepared either electrochemically or via chemical polymerisation [39]. have been the focus of many applications due to its outstanding optoelectrical properties including field-effect transducers (OFET), light-emitting diodes (OLED), photovoltaics (OVD), and nonlinear optical devices (NLO) [40, 41]. Moreover, PTh also has been applied as materials for the electrochromic device in which by principle the material owns the capacity to transform the color by tuning the redox state; for example, polyalkyl thiophene can appear blue color in oxidised and red in the reduced state [42].

1.2.6 Polyaniline

Among the CPs, polyaniline (PANI) has attracted widespread attention around the world due to its versatile properties such as ease of synthesis by both chemical and electrochemical route, thermal stability up to 250°C [43], unique acid–base chemistry and tunable electrical conductivity [44]. These extraordinary properties opened a wider window of application for PANI in solar cells [45], corrosion inhibitors [46], organic light-emitting diodes [47], electromagnetic interfering devices [11] and bio/chemical sensors [48]. These widespread applications of PANI have made it one of the versatile CP in its group.

Historically, PANI was prepared and used centuries ago, before it was realised that it could be functionalised as a semiconductor. The research on PANI was started by Runge (1834) and was extensively continued by Prof Dr Letheby [49]. Between 1907 and 1911 a Nobel Laureate Richard Willstatter characterised the PANI derivatives via his methodic way of research. Then, in the 1960 a group of researchers from

Czechoslovak developed an iodine doped PANI which produced a 1 S/cm conductivity for the PANI-iodine complexes. However, at that time, the whole global attention was diverted to the discovery of polyacetylene by the Nobel Prize trios. Then, the conducting properties of PANI were reaffirmed by another study conducted in parallel with PPy research. Interestingly, the study reported a higher conductivity for PANI ranging from 5–30 S/cm.

Then, the research of Willstatter was continued and more oxidation states of PANI were revealed. Figure 8 shows the chemical structure PANI in various oxidation states. PANI possessed different colors in the acid–base environment [50] and reversible protonation-deprotonation which made it an exclusive CP compare to other CPs in the group [51].

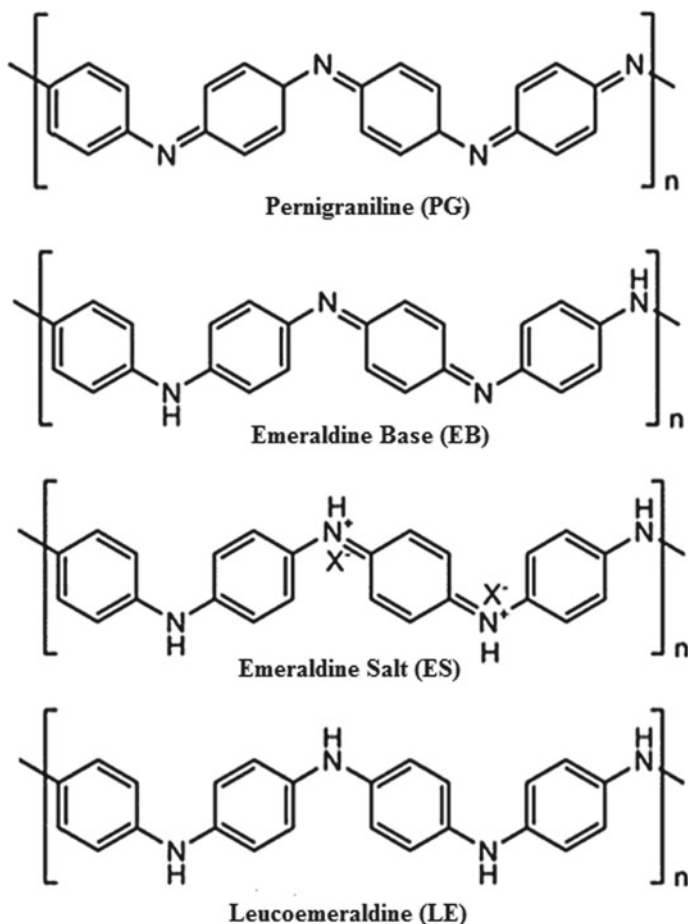


Fig. 8 Various oxidations states of PANI [52]

2 Synthesis Pathways and Polymerisation Mechanism

2.1 Synthesis Method for Conducting Polymers (CPs)

Polymerisation is a process where the monomer undergoes chemical reaction to form a polymeric chain. Theoretically, the monomer that has been oxidised will produce radical cation, which will be reacted with another monomer, resulting in the formation of an oligomer [53]. In general, three methods that commonly used to synthesise CPs are (i) chemical polymerisation, (ii) electrochemical polymerisation, and (iii) photochemical polymerisation. Each of the synthesis methods possesses its advantages and disadvantages.

2.1.1 Chemical Synthesis

In general, this method uses dopant ions such as ammonium persulfate or potassium nitrate to react with the targeted monomer through the oxidation process [23, 24]. Chemical synthesis can be divided into two main classes which are condensation polymerisation with step-growth mechanism and addition polymerisation with chain-growth mechanism (Fig. 9).

Chemical synthesis is the most widely used technique for CPs due to mass production, small expenditure, processability and it offers various routes in accordance with the type of CPs used [54, 24, 25]. However, chemical synthesis can only produce thick film and have a problem of large activation barriers in its reaction, making it inconvenient for certain application [53].

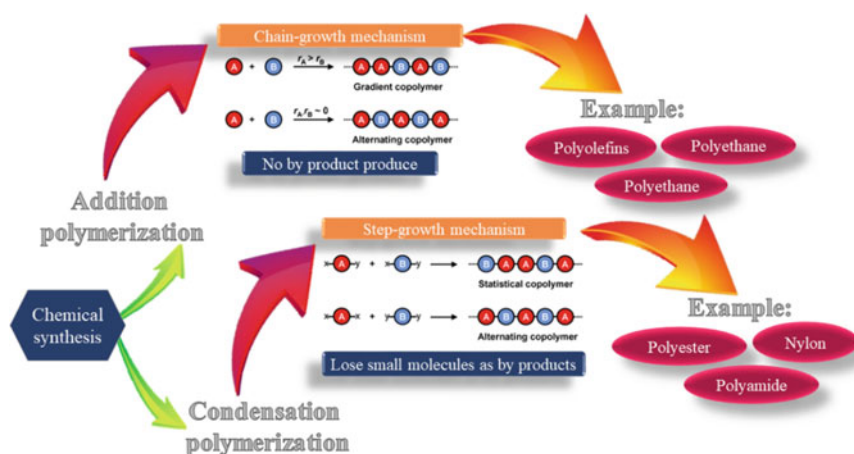


Fig. 9 Classification of chemical synthesis in CPs' polymerization

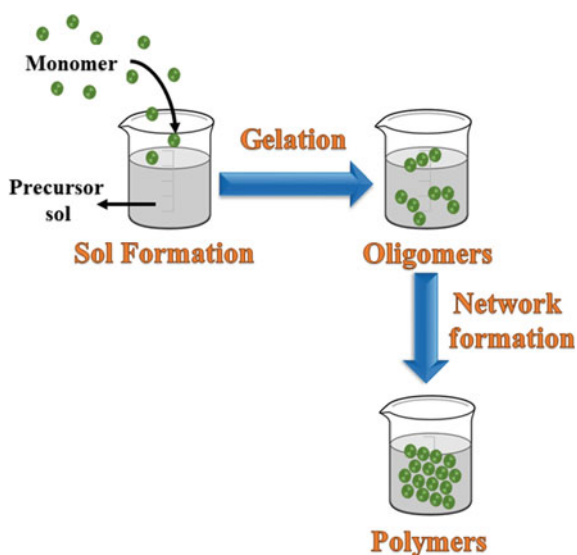
Another chemical technique commonly used in this chemical synthesis are sol–gel polymerisation and emulsion polymerisation. Sol–gel polymerisation (Fig. 10) is a colloidal precipitation process of dispersing polymeric molecules into a solid–liquid state [55]. This technique offers several advantages such as it occurs at relatively low temperature, has high homogeneity of organic moieties into the inorganic materials and it is an effortless fabricating process [56].

Despite that, sol–gel polymerisation often faces problems in porosity and weak intermolecular bonding [56]. On the other hand, emulsion polymerisation (Fig. 11) is a hetero-phase process involving initiator, monomer, and surfactant where it is instantaneously added to the solvent (water), resulting in the formation of micelles [16]. The monomers get polymerised within the micelles and lead to the formation of stable colloidal dispersions [55]. This polymerisation technique lowers the viscosity of the reaction making good reaction kinetics between the hybrid materials [55]. Moreover, this technique produces non-toxic and inflammable product [55], thus making it an environmentally friendly approach, however, the usage of surfactants limit its usage in other applications [57].

Besides, the selection of an appropriate oxidising agent is crucial to yield CPs with desired properties. Besides that, the use of oxidising agents in solution polymerisation is feasible, less time consuming, common, and economic method for the synthesis of CPs. Various oxidising agents have been utilised by the researchers in the synthesis art of CPs such as ammonium peroxydisulfate [48], hydrogen peroxide [58], ferric chloride [59] and ceric nitrate and sulfate [60] to obtain certain desired properties in CPs.

The use of chemical polymerisation has been widely reported by many authors. In a study by Peng et al. [61] polythiophene grafted poly(methacrylate) (PTh-g-PMA)

Fig. 10 Basic mechanism of sol gel polymerization



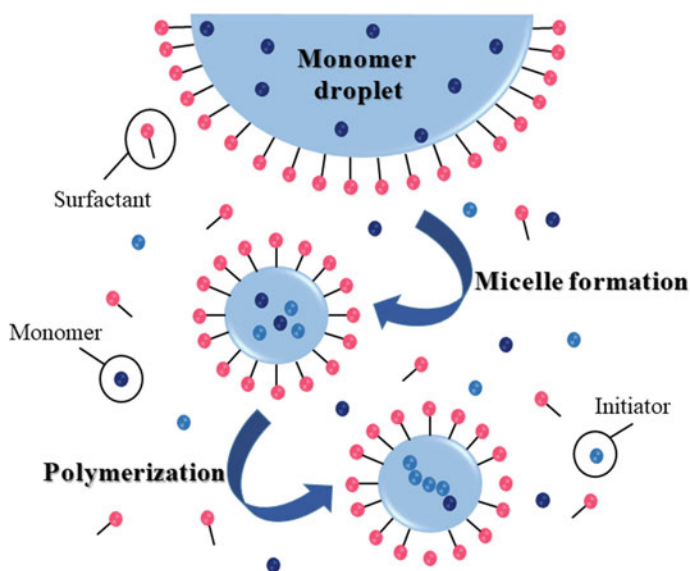


Fig. 11 Basic mechanism of emulsion polymerization

was synthesised using in-situ chemical polymerisation to investigate the optical properties of this material. This material has a great photon efficiency whereby it can reduce 85% of photoluminescence, making it suitable for photovoltaic applications. Similarly, Kwon et al. [62] have also investigated PPy composite by sol-gel technique as suitable photovoltaic materials.

The authors found that the higher the PPy concentration, the higher the photoelectric power conversion. This is due to the uniform chain interpretation, which intensifies the charge transfer and thus resulting in increased power conversion. Another study conducted by Dai et al. [63] have reported the synthesis of PEDOT using a high concentration of poly[2-(3thienyl)- ethoxy-4-butylsulfonate] (PTEB) has boosted the thermal stability, crystallinity and electrical conductivity of the hybrid material. Clement et al., have reported that PTh hybrid silica nanomaterial synthesised via chemical oxidative method [64] has an excellent performance in terms of optical and thermal features whereby it could be the primary material for LED, photoactive and conducive materials.

2.1.2 Electrochemical Synthesis

Electrochemical synthesis is a process using a three-electrode system that allows manipulation of molecular oxidation states and capable of generating high reactive species [65]. The principle of electrochemical synthesis includes a system where it makes use of working, counter, and reference electrodes in the presence of monomer, suitable electrolyte, and proper additives in the system [53]. The polymerisation can

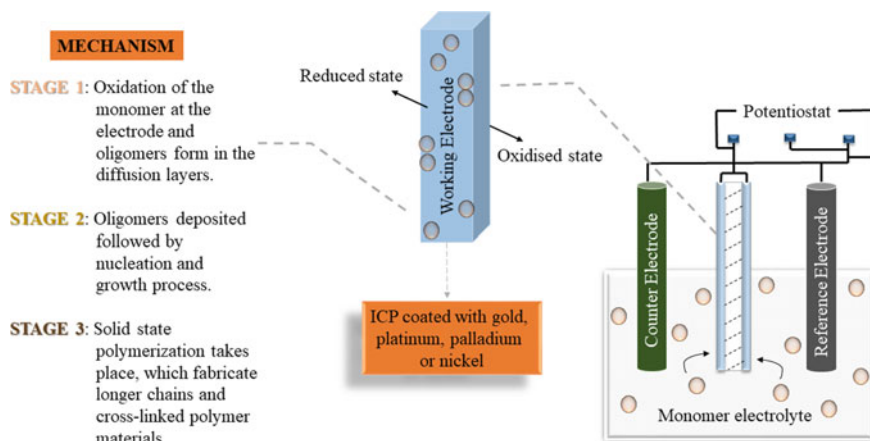


Fig. 12 Electrochemical polymerization cell setup and its basic mechanism

be done in three different techniques; with constant current (galvanostatic), constant applied potential (potentiostatic) or potential scanning or sweeping method [66]. Figure 12 shows the basic mechanism in electrochemical synthesis. This technique is a simple and reproducible method for CPs polymerisation. Additionally, electrochemical synthesis with sufficient electrical potential allows the film to have a good control in the film thickness.

Electrochemical synthesis can produce high-quality films with a desired thickness, which makes this route is much preferable to compare to chemical synthesis polymerisation in producing a thin film of CPs. Besides, the electrochemical route has been proven to offer a better polymerisation mechanism for CPs, which easily controls the initiation and termination steps during polymerisation. Moreover, electrochemical polymerisation provides a cleaner and cheaper route because it does not require the addition of oxidants, surfactants, and so on. Hence, it makes this method one of the facile and environmentally benign procedures [67].

However, this method has complications in terms of producing bulk sample as it is difficult to discharge the film that has been deposited on the electrode surface [53]. The use of gold and platinum as an electrode in electrochemical synthesis also becomes a conflict as the material is expensive. Moreover, this method is also restricted to the only monomer that can undergo oxidation through applied potential [65].

Despite its drawback, many authors have reported that electrochemical synthesis brings out an excellent electrocatalytic and conductive activity of the hybrid material whether in acid, alkali, or neutral medium, which makes them a suitable candidate for various applications such as sensors, catalysis, and energy conversion devices [55]. Wang et al. [68] reported PANI that has been synthesised via electrochemical polymerisation with constant potential (0.75 V) possesses excellent gravimetric and volumetric capacitance to compare to the existing carbon-based electrode, which

enables it to become a suitable electrode in supercapacitors. Another study conducted by Liu et al. [69] also observed an increased conductivity of PPy when synthesised using electrochemical polymerisation. This is because of the surface morphology of this hybrid material is denser and more compact, which is responsible for enhancing conductivity. This hybrid material was synthesised using electrochemical polymerisation under UV irradiation constant applied potential of 0.85 V. Cai et al. showed a similar result, [70] where synthesised PANI via solvothermal and electrochemical polymerisation exhibit unique nanotubules structure, which leads to high electrical conductivity. PEDOT synthesised by electrochemical polymerisation also showed good electrochemical ability with maximum faradaic interaction [71].

2.1.3 Photochemical Synthesis

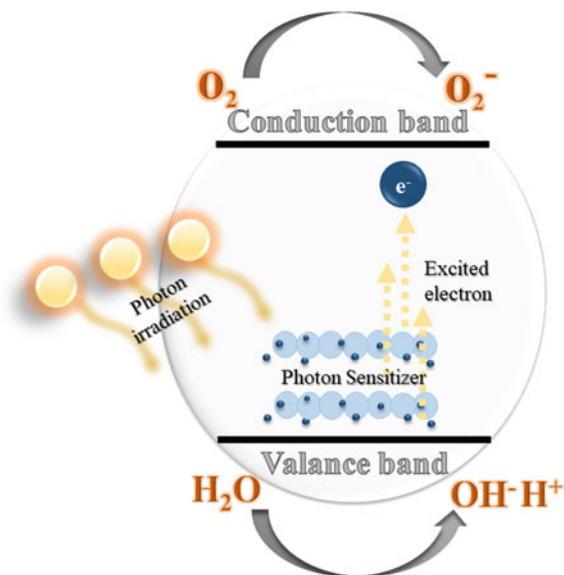
Photochemical synthesis is a process that utilised light sources such as ultraviolet (UV) light, visible light, or laser generating radicals as the initiator for monomer polymerisation [53]. This technique reduces the time consuming experimental procedures, economical method and it is not destructive to the surroundings [16]. Moreover, in comparison with chemical synthesis, photochemical polymerisation produces its radical via hydrogen abstraction by irradiation which gives higher efficiency rather than direct fragmentation via thermal reaction in the chemical polymerisation method.

Additionally, this method provides great control over the shape, size, and physical properties of the CPs. This is because in this method, many parameters, such as light intensity and temperature, can be easily controlled. For example, the initiation rate can be easily adjusted by turning the light source on or off [53]. The photochemical synthesis method also enhanced the electrical conductivity of nanomaterial as illumination of the semiconductor electrode embedded in this method employs band gap irradiation, which will help in increasing the conductivity via photoconductivity. The basic mechanism is illustrated in Fig. 13 below.

Photochemical synthesis can be divided into two which are direct polymerisation (where this method directly absorbs the photon energy to decompose the monomer to form radicals) and photosensitised polymerisation (where this method use dye-sensitised semiconductor (metal oxide or chalcogenides) as a photosensitiser to transfer the photon energy into the corresponding excited states. For CPs, it should be noted that it is impossible to use direct photochemical polymerisation. This is because direct polymerisation gives more positive oxidation peak potential compare to redox potential by photosensitiser in photosensitise polymerisation [72].

The working principle of photochemical polymerisation is as follows; when photosensitiser being hit with photon energy greater than the bandgap energy, it will make photosensitiser undergo electron excitation. The electron from the valence band jumps to the conduction band of the semiconductor, leaving a hole that is highly oxidising. The polymerisation takes place when the holes produced reacts with the monomer. A primary aspect of photochemical polymerisation is that the oxidation

Fig. 13 Basic mechanism of photochemical synthesis



step is guided by the difference between the potential of the valence band edge of the inorganic species and the oxidation potential of the monomer [53].

Lee and co-workers have carried out an extensive study of using the photochemical route to synthesise, [73] polythiophene (PTh) with self-assembled $RuL_2(NCS)_2/Di(3\text{-Aminopropyl})Viologen$ on Indium Thin Oxide (ITO) as working electrode using 10% thiophene in acetonitrile as the electrolyte medium and platinum as the counter electrode. Here, they reported that the PTh showed a thickness of ~ 360 nm, a dense surface, and possessed an optical gap of 2.38 eV. Zhang et al. [74] have conducted a photochemical synthesis of poly(3,4-ethylenedioxythiophene) as hole-transporting material in dye-sensitised solar cell (DSSC) application. The material showed a better dye regeneration along with the high charge recombination energy levels. Besides, it also showed excellent light absorption capability where it exhibits a high power conversion efficiency of 5.2%.

Another study in the same DSSC application also showed a similar result where the use of PEDOT as the hole transporting material enhanced proficient power conversion efficiency of 3.4%. The procedure of in-situ photochemical polymerisation involved the use of stainless steel as counter electrode and two electrolyte medium which are organic electrolyte (10 mM EDOT and 0.1 M $LiN(CF_3SO_2)_2$ in acetonitrile) and aqueous micellar electrolyte (10 mM EDOT in an aqueous solution containing 0.1 M $LiN(CF_3SO_2)_2$ and 50 mM TritonX-100 surfactant) [75]. The summary of each method presented in this section is listed in Table 1.

Table 1 Different polymerisation methods of CPs

Routes	Details	Technique	Advantages	Limitation
Chemical	A method that uses a dopant ion to react with targeted monomer through the oxidation process	Sol-gel polymerisation	Low cost Easy process	Large activation barriers Poor control of film thickness
		Emulsion polymerisation	Produce bulk quantity of sample	
Electrochemical	A method that uses a three-electrode system with the applied potential to generate high reactive species	Galvanostatic	Great control on film thickness Reproducible method	Difficult to discharge film deposited on the electrode Consume a lot of time
		Potentiostatic		
		Potential scanning/sweeping		
Photochemical	A method that utilised light intensity in generating radicals	Direct polymerisation	Great control of the morphology of the material Green process Fast reaction	Oxygen inhibition Need to use a high resolution of light intensity
		Photosensitiser		

3 Conclusion

CPs are a versatile group of macromolecules. Even though it was challenging to understand the polymerisation and the conducting properties of CPs back in the 1970, the current industrial revolution with sophisticated instrumentation techniques has opened the door for a better understanding of these macromolecules. Hence, it is always important to track the evolution of CPs in terms of its origin and synthetic route to tailor a better polymer engineering in the prospect. In conclusion, this chapter covered most of the notable CPs and its polymerisation pathway which would bridge the knowledge gap to enhance the design of new CPs.

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Intrinsically Conducting Polymer Based Nanocomposite in Photocatalytic Study



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Abstract It is well noted that Intrinsically Conducting Polymer (ICP) have been the main focus for many researchers for many applications involving energy storage devices and system. It is due to its remarkable properties, simple preparation technique, environmentally stable and safe as well as low expenditure cost. Integrating ICP with nanocomposite have also widened its capabilities in venturing into other application such as photocatalysis process. The photocatalytic study is a photoreaction process involving the use of nanomaterials and sunlight. Using ICP nanocomposite (ICP) as the sole material in the photocatalysis process increases the performance for photocatalytic study in various applications, water remediation, and production of Hydrogen gas. This chapter is an attempt of combining the recent performance of ICP nanocomposites mainly in the photocatalytic study that involves the preparation routes, fundamentals, comparison on recent literature with prospects and recommendation.

Keywords Conducting polymer · Nanocomposite · Photocatalyst · Photocatalytic process · Polyaniline

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1 Introduction

In general, polymers that can conduct electricity almost like metal are known as conducting polymers. These conducting polymers can be further classified into three categories such as intrinsically conducting polymers (ICPs), extrinsically conducting polymers (ECPs) and co-ordination, or inorganic conducting polymers (CICPs). ECPs are prepared by simply adding conducting fillers or blending insulating polymers with conducting polymers either physically or chemically [1]. CICPs are prepared via the addition of charge transfer complexes such as metal atoms with polydentate ligands [2]. Interestingly, ICPs are designer polymers where one can architecture the modeling of the polymer via an appropriate synthetic route [3]. ICPs usually possess a solid backbone with extensive conjugation which results in its fascinating conductivity. Besides that, ICPs can be achieved via the doping process namely, p-doping or n-doping (refer to Chap. 1; Fig. 3).

Recently, ICP based nanocomposite (ICPn) has received great attention and become a prominent area of current research as well as development. ICPn is a hybrid material between polymer matrix and different types of nanofillers reinforced within it [4]. The nanofillers can be in one-dimensional (nanotubes and fibers), two-dimensional (layered materials like clay), or three-dimensional (spherical particles). ICPn have been recognized by various application where it: (i) fasten the electrolyte diffusion in supercapacitors, (ii) give effective excitation dissociation in solar cells (iii) enhancing the sensitivity of sensors and (iv) reduce responses time in electrochromic devices [5]. Other applications associated with ICPn is illustrated in Fig. 1.

Hybridizing ICP with nanoscale material contributes to many advantageous features including controlled morphology, film-forming ability, dimensional variability, and activated functionalities [6]. Moreover, ICPn gives a greater performance

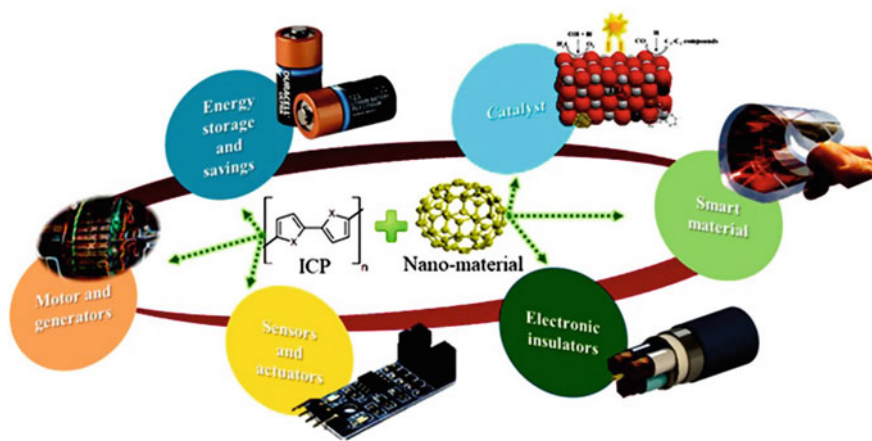


Fig. 1 Application of ICPn

in electrical conductivity, electrochemical, and mechanical properties in comparison with macro-scale materials [7, 8]. In comparison with micro filler composites like glass or carbon fibers, ICPn attributes substantial advantages due to the properties of the nanomaterial itself which are lightweight, provide large surface area, size confinement, dominance in interfacial phenomena and good quantum effects [9]. Although nanofiller composite shows remarkable features, the polymer matrix also plays a vital role in determining the whole performance of ICPn [10]. Typically, ICP has usually been combined with inorganic species such as quantum dots (semiconductors metal oxides and sulfide), carbonaceous material (nanotubes or nanowires), and chalcogenides [5]. Table 1 shows some examples of ICPn together with its highlighted properties.

This article is concentrating on the different types of ICP with nanocomposite for the photocatalytic process. Owing to low cost, facile methods of fabrication, and environmentally friendly nature, conducting polymer have believed to be the most promising material for many applications. Research regarding ICPn gives rise in interest towards many researchers. This can be related to the increasing number of publications of ICP doped nanomaterials that are illustrated in Fig. 2. This article is categorized into the following subsection which are the different synthesis pathways and polymerization mechanism of ICPn, fundamentals on photocatalysis with its principles, and the performance of the different types of ICPn for photocatalytic study. The review provides the reader with a systematic study about different kinds of blended ICP with their commercial impacts mainly as photocatalysts and problems related to its performance by recent literature examples.

2 Synthesis Method for ICPn

The properties of ICPn do not depend on the properties of individual components but also depends on the whole system. The most common feature of ICPn is the existence of phase border between matrix and filler material and the development of an interface layer between the two. The properties, composition, and microstructure at the interface vary across the interface region and are different from both matrix and filler. Most of the interphase properties depend on the bound surface and therefore the nanocomposite properties can be tailored by optimizing the interfacial bond between the nanofiller and polymer matrix. Thus, to modify its properties, ICPn can be fabricated through various methods available. In this review, ex-situ and in-situ polymerization, solution mixing, electrospinning, and some other method will be briefly introduced.