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Synthesis of polythiophene and their application

[1]Susheel Kumar Singh, [2]RK Shukla, [3]CK Dixit
[1]Assistant Professor, Department of Physics (Applied Sciences), Institute of Technology and Management, Lucknow, Uttar Pradesh, India
[2]Professor, Department of Physics, University of Lucknow, Lucknow, Uttar Pradesh, India
[3]Professor, DSMNR University, Govt. of UP, Lucknow, Uttar Pradesh, India

Abstract

The identification and characterization of π-conjugated conducting polymers have had a significant influence on the field of organic electronics. These polymers' ability to switch between conducting and semiconducting states, as well as their ability to change mechanical properties through chemical modification, controlled doping, and stacking or composite creation with other materials, make them highly promising for integration into future optical and electronic devices. Polythiophene and its variants are π-conjugated polymers that have been examined extensively. They are being explored both computationally and experimentally for their potential application in electrical devices, including light-emitting diodes, water purification devices, hydrogen storage, and biosensors. Numerous theoretical modelling studies of polythiophene have been conducted to investigate a range of electrical and structural aspects of these polymers. These studies range from an oligothiophene approach to infinite chain lengths (periodic boundary conditions). We go over the most recent developments in our understanding of pure polythiophene and its derivatives in this review, including everything from basic viewpoints to device applications.

Keywords: Polythiophene, conducting polymers, application, synthesis

Introduction

Due to its superior thermal stability, low band gap energy, and good environmental stability, polythiophene polymer has drawn a lot of interest from researchers and industry. Furthermore, the polythiophene composites received a lot of attention because of their intriguing properties, which included semiconducting, electrical, and optical activities, as well as their superior mechanical qualities and ease of processing (Majid and Najar, 2015) [13]. They are commonly utilised in solar cells because of their increased contact with metal electrodes and stability under environmental conditions. Since n-type semiconducting particles can transport holes more effectively than polythiophene matrix, combining the two to create a novel hybrid variety with superior electrical properties was possible. Additionally, polythiophene's transparency confers noteworthy optical features. Furthermore, polythiophene (Fig. 1), which has conjugated double bonds in its backbone, is a great intrinsic conducting polymer. Similar to this, polarons and bipolarons can be produced in the backbone of various conducting polymers by either oxidation or reduction, so altering the polythiophene matrix to a more conducting one. They are therefore frequently utilised in solar cells, electrochromic devices, and polymer batteries by taking advantage of these properties (Namsheer and Rout, 2021) [20]. Furthermore, polythiophene is less significant for other conducting polymers due to its simple polymerization and airborne stability (Verdejo *et al*., 2017) [4].

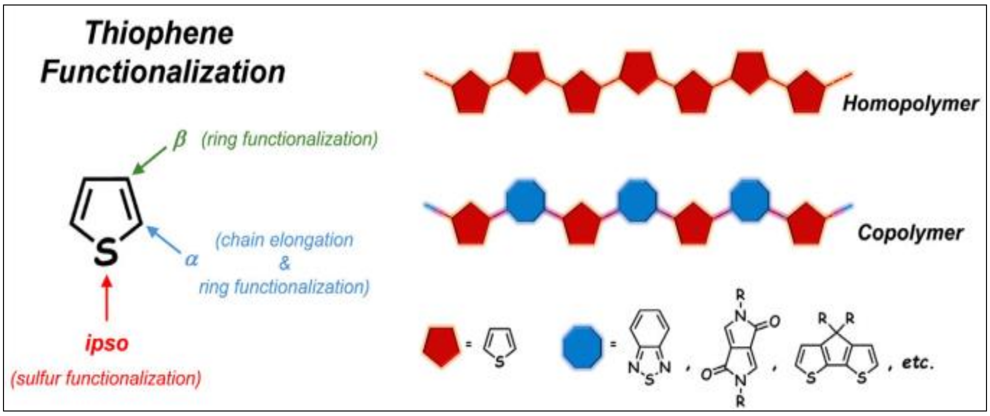

Fig 1: Thiophene ring functionalization (left) and TpM homopolymer and copolymer general structures (right)

Synthesis of polythiophene

A number of reasons, including its exceptional optical quality relative to other conducting polymers and its thermal and environmental resilience, polythiophene and its derivatives are the subject of substantial research. Polythiophenes are frequently utilised in energy storage devices, photochromic modules, polymer LEDs, non-linear optical systems, and anti-corrosion coatings. Chemical or doping engineering alterations can be used to modify the electrical and optical characteristics of polythiophenes. Depending on the side chain and dopant used, polythiophenes have a band gap ranging from 3 to 1 eV (Kaloni *et al*., 2017) [18]. An important polythiophene derivative, poly (3, 4-ethylenedioxythiophene) (PEDOT) has been extensively explored due to its strong electrical and electro-optical characteristics. The PEDOT derivative's insolubility non water is the primary issue. A polyelectrolyte similar to polysulfonates (PSS) was successfully added to the PEDOT matrix to get around this. Through a mechanism of charge balance, PSS function as both a stabiliser and a dopant. According to McCullough (1998) [3], the PEDOT: PSS derivative possesses excellent mechanical flexibility, high conductivity, and long-term thermal stability. By treating the polythiophene and its derivatives in a solvent, adding a surfactant, and adjusting the PSS concentration, one can improve their electrical characteristics. Another class of polythiophene compounds is poly (3-hexylthiophene) (P3HT), with a primary focus on opto-electronic and electronic applications. P3HT is widely available, inexpensive, has a well-known morphology, and is simple to process, which contribute to its popularity. The backbone of P3HT, a semi-crystalline polymer, is composed of linear side chains and isolated rings. The freedom to explore conformational space is made possible by this structural arrangement. P3HT has a high tensile modulus ranging from 200 MPa to 1 GPa, which varies depending on the synthesis technique and sample purity. Its glass transition temperature is observed at 12 °C (Dubal *et al*., 2012) [5]. The Yamamoto and Lin-Dudek techniques were used to chemically synthesise polythiophene in the early 1980s (Figs. 2 and 3).

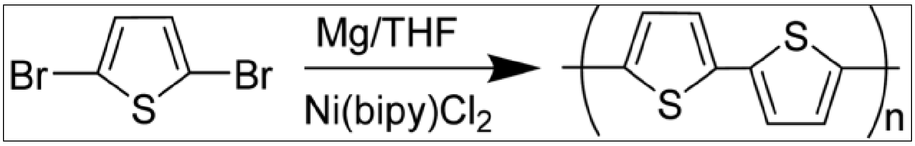

Fig 2: Synthesis of polythiophenes by the Yomomoto route.

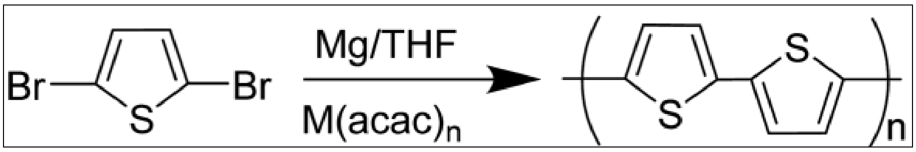

Fig 3: Synthesis of polythiophenes by the Lin–Dudek route.

Other sophisticated methods have been thoroughly investigated, including template-assisted synthesis, direct sol-gel, oxidative synthesis (Faisal *et al*., 2020) [14], electropolymerization, organometallic coupling reaction (Babudri *et al*., 2004) [8], hydrothermal and solvothermal methods, and electropolymerization (Mccullough, 1998) [3]. A variety of methods, such as electropolymerization, green synthesis, synthesis in microfluid systems, and other unique techniques, were used to synthesise polythiophene derivatives such as PEDOT, PEDOT: PSS, and P3TH. (Kiari *et al*., 2020; Kim *et al*., 2021) [15, 19].

Applications of Polythiophene

Nanocomposites based on polythiophene have found numerous uses because of their unique chemical, mechanical, optical, and electrical characteristics. Conjugated polymers have a wide range of applications due to their semiconductor qualities, including chemical sensors, photovoltaic cells, field-effect transistors (FETs), LEDs, electrochromic devices (EDCs), and rechargeable batteries.

1. Sensors

The sensitivity tests of PTh / SnO_2 composites, namely PTh (1%) / SnO_2, PTh (5%) / SnO_2, PTh (10%) / SnO_2, PTh (20%) / SnO_2, and PTh (30%) / SnO_2, were conducted by Kong *et al*. (2008) at room temperature, 50 °C, 70 °C, and 90 °C. SnO_2 exhibited n-type behaviour and polythiophene p-type behaviour in semiconductor behaviour. As a result, the composites have p-n junction characteristics. In a different study, Zhang *et al*. (2010) [12] found that compared to a sensor based on pure PTh, the gas sensor based on SnO_2 hollow spheres/PTh demonstrated a stronger gas response, good response, and quicker recovery time for detecting NO_2 of ppm levels at low temperature. Additionally, found that at room temperature, PTh/SnO_2 hybrid sensors exhibited great sensitivity in detecting liquefied petroleum gas (LPG). According to Yavuza *et al*. (2009) [2], PTh/SiO_2 nanocomposites can be utilised to create cutting-edge glucose biosensors with quick response times. Al_2O_3/polythiophene nanocomposites were successfully synthesised by Tripathi *et al*. (2015) [1] using the chemical oxidation polymerization process. At room temperature, they examined the sensing characteristics of both pure and Al_2O_3/PTh nanocomposites. According to the current work, pellets of Al_2O_3-doped polythiophene nanocomposites that have the right amount of dopant can be employed as ammonia sensors. Guo *et al*. (2016) [11]

created a nanocomposite of polythiophene (PTh) and reduced graphene oxide (RGO) modified by ethylenediamine using in-situ chemical polymerization that took place at room temperature for two hours. They looked into how nanocomposites responded to NO_2 gas in terms of sensing. In addition to its excellent sensitivity and selectivity to NO_2, the sensor's flexible, low-cost, and simple features will enable the development of wearable and portable electronic devices that can detect harmful chemicals in the surrounding air.

2. Photocatalysis

PTh/TiO_2 nanocomposite was created by Yi *et al*. (2011) in order to photocatalytically degrade methyl orange (MO) dye when exposed to UV light. For the catalytic process, they employed a self-designed UV irradiation apparatus equipped with 10W germicidal lamps that had a maximum wavelength of 253.7 nm. This implies that solar light may be able to stimulate the PTh/TiO_2 nanocomposite. In a different finding, Xu *et al*. (2010) observed that the PTh/TiO_2 composites' ability to adsorb MO rises as the PTh concentration increases from 0% to 2%. Zetapotential analyses revealed that the PTh/TiO_2 composites' surface is positively charged in the dispersion, whereas the TiO_2 surface is negatively charged. As a result of Coulombic repulsion, MO is hardly adsorbed on the TiO_2 surface. However, the PTh/TiO_2 composites' positively charged surface has a considerable ability to adsorb MO, which helps to explain the high photodegradation efficiency because of effective interfacial charge transfer. The PTh/TiO_2-Cu composite made using a sol-gel method demonstrated a robust connection between the PTh and TiO_2-Cu interface, according to Chandra *et al*. (2015) [16]. The experiment also demonstrated that increasing the photocatalytic activity was significantly influenced by the PTh content in TiO_2-Cu. The adsorption and desorption of the dyes on the catalyst surface are impacted by the pH shift, which also modifies the catalyst's charge. The photocatalytic rate for PTh/TiO_2-Cu rose when pH rose as well.

3. Secondary Batteries

Ag/poly(3,4-ethylenedioxythiophene) (PEDOT) nanocomposites were synthesised, as reported by Jung and Lee (2011) [10], by polymerizing 3,4-ethylenedioxythiophene (EDOT) and reducing Ag(I) acetate into neutral Ag in a simultaneous one-pot process. Ag/PEDOT nanocomposites were found to develop as a core-shell structure with excellent surface area and electrical conductivity, retaining well-dispersed Ag nanoparticles in the PEDOT polymer. Ag particles are kept from clumping together, their dispersion is enhanced, and their stability is increased by the addition of PEDOT, a suitable buffering agent.

4. Supercapacitors

According to Verdejo *et al*. (2017) [4], composites of graphene (GR) and polythiophene (PTh) with varying mass proportions were investigated for use as supercapacitors. They used cyclic voltammetry to assess the electrochemical behaviour of these composites, and the results allowed them to create specific capacitance curves. When combined in specific ratios between GR and conducting PTh, the mixture may make it possible to create high-performance, inexpensive electrode materials for use in supercapacitors.

5. EMI Shielding

Using the photo adduct of sodium pentacyanonitrosylferrate (II) dehydrate and hexamine, Majid and Najar (2015) [13] effectively created a polythiophene (PTh) nanocomposite through in situ polymerization. According to their research, dielectric measurements revealed that the nanocomposite had an AC conductivity of 10^{10} Scm-1 and a dielectric constant of order 2×10^4 at 10^4 Hz. The nanocomposite exhibits strong dielectric constant and AC conductivity, making it a valuable tool for electromagnetic interference shielding applications.

Conclusions

When compared to pure PTH, the electrical, mechanical, optical, thermal, and other properties of PTh nanocomposites are superior. Nevertheless, the secondary component frequently tends to lessen its electrical conductivity as well. The methods used to prepare PTh nanocomposites and fabricate devices for possible uses such as chemical sensors, optical sensors, LEDs, display devices, photovoltaics/solar cells, transistors, rechargeable batteries, super capacitors, EMI shielding, etc. have all been compiled in this review. PTh nanocomposites' multi functionality has been widely used in a variety of applications with outstanding outcomes. These materials are especially appealing as gas sensing elements because of the beneficial interactions among the constituents. In order to expand the possible sectors of use for PTh nanocomposites, efforts are being made to comprehend their functioning mechanism.

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