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Poly (P-phenylene) S: Synthesis and applications

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Abstract

PPP stands for poly (para-phenylene), a linear, stiff-rod polymer made up of p-phenylene units that repeat. PPP's outstanding mechanical, chemical, and thermal qualities make it a great option for a range of high-performance, lightweight applications in the semiconductor, aerospace, and medical sectors. When doped with p and n, it demonstrates electrical conductivity, making it suitable for energy storage. PPP has also been employed as an electroluminescent material while acting as a blue-light emitter ($\lambda_{\text{max}} = 459 \text{ nm}$). PPP synthesis and application, however, continue to be extremely difficult despite these encouraging qualities and uses.

Keywords: Poly (P-phenylene) s; synthesis, applications

Introduction

PPP is the starting point for a conducting polymer of the rigid-rod polymer host family, which is created by repeating p-phenylene units and then doped or oxidised to become conducting. To achieve conductivity similar to PA, PPP was doped in 1980 (Ballard *et al.*, 1998) [8]. This is the first instance of a nonacetylenic hydrocarbon polymer having conducting characteristics due to doping with either an electron donor or an electron acceptor. Using benzene as a transformation substrate by homo polymerization, Ballard *et al.* synthesised PPP by deriving cis-dihydrocatechol from bacterial fermentation (Kumar and Sharma, 1998) [9]. Moreover, extremely high crystalline PPP films have been produced *via* electrochemical oxidation of a 96% H_2SO_4 /benzene solution.

Synthesis of poly (P-Phenylene) S

A macromolecule known as poly (p-phenylene) is composed of benzoid aromatic nuclei that are directly connected by C-C bonds. Due to their excellent air and temperature stability, ease of doping, adjustable conductivity, and good optical qualities, poly (p-phenylene)s are of great interest. A promising development in the realm of nonlinear optics is the combination of conjugation and the mechanical stiffness of the polymer backbone. The solubility of poly (p-phenylene)s is restricted, but it progressively rises with the attachment of flexible side chains to the backbone. When doped with appropriate dopants, poly (p-phenylene) will increase in conductivity 14 times and allow both p-type and n-type doping. As the dopant exposure period increases, the conductivity rises (Shacklette *et al.*, 1980) [1]. Because poly (p-phenylene)s have better optical properties and emit blue light when compared to other conjugated systems, they are essential to the creation of organic LEDs. Temperature affects the structural characteristics of poly (p-phenylene); at higher temperatures, the material has a planar structure; at lower temperatures, the material exhibits a phase transition and a distorted planar structure. The optical band gap of poly (p-phenylene) can be adjusted, and side chains or appropriate dopants can be added to alter the structure of the material (Ambrosch-Draxl *et al.*, 1995) [2]. Comparing poly (p-phenylene) to engineering polymers, it demonstrates significantly greater tensile and mechanical properties. When compared to thermosetting polyimide (PI) or polyetheretherketone (PEEK), it exhibits a modulus and strength that are two times higher. Within the 140 °C temperature range, polyparaphenylene finds usage in a variety of mechanical applications (Friedrich *et al.*, 2010) [3].

The production of poly (p-phenylene)s is a common application of direct oxidation of benzene molecules. Carbon-carbon bonds are created in this process by the dehydro coupling of benzene nuclei with an oxidative catalyst. Reagents comprising of a binary or single system are used to carry out the polymerization reaction (Figs. 1 and 2).

The binary system is made up of an oxidant and a Lewis acid system. In the instance of the single reagent system (FeCl_3), the system functions as both an oxidative and a Lewis acid system on its own. One example of a binary reagent system is a mixture of AuCl_3 and CuCl_2 , where AuCl_3 functions as a Lewis acid and CuCl_2 as an oxidant. The temperatures at which reactions take place are 36-37 °C.

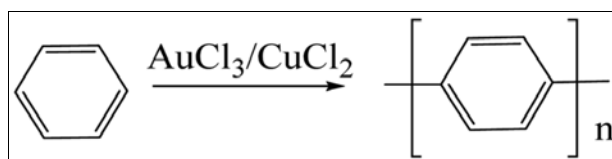


Fig 1: Synthesis of poly(p-phenylene)s using a binary system (both a Lewis acid and an oxidant system) (DOI: 10.1039/d0ra07800j, RSC Advances).

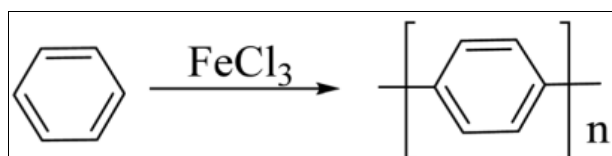


Fig 2: Synthesis of poly(p-phenylene)s using single system (oxidant system) (DOI: 10.1039/d0ra07800j, RSC Advances).

A Wurtz–Fittig reaction, a metal coupling process, was used to create the first chemically synthesised poly (p-phenylene) (Fig. 3) (Brydson, 1995) ^[4]. Poly (p-phenylene)s are also prepared by the Ulman reaction, and the results are less structurally irregular and have a lower molecular weight (Fig. 4). However, Jones and P. Kovacic (1989) ^[5] found that this technique is helpful for preparing substituted phenyls such methyl and nitro groups.

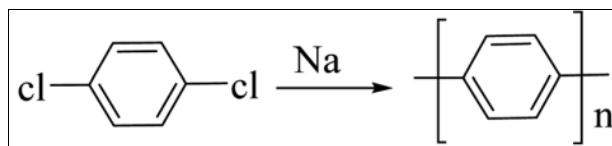


Fig 3: Synthesis of poly (p-phenylene)s using a Wurtz–Fittig reaction (DOI: 10.1039/d0ra07800j, RSC Advances).

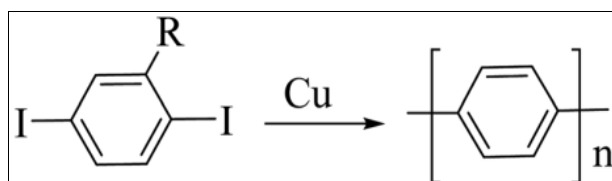


Fig 4: Synthesis of poly (p-phenylene)s using an Ulman reaction (DOI: 10.1039/d0ra07800j, RSC Advances).

Poly (p-phenylene) synthesis was also studied using the precursor technique. Since conducting polymers are insoluble by nature, producing the desired polymer from an insoluble precursor polymer makes for a fascinating study subject. The ICI precursor technique, Marvels, and Grubbs were well-known for producing poly (p-phenylene)s. According to Vogel and Marvel (1996) ^[6], the primary disadvantage of the Marvels approach is that the final product will have a low molecular weight and less stereo chemical control. Reductive polymerization and electrochemical synthesis have also been applied (Kiebooms *et al.*, 2001) ^[7].

Application of poly (P-phenylene)s

Although poly (p-phenylene)s and its derivatives are typically

used in the form of thin films functioning as active layers in light-emitting diodes (LEDs), photodetectors, other optoelectronic devices, and biomedical applications, poly(para-phenylene) (PPP) exhibits exceptional mechanical strength, stiffness, toughness, and chemical inertness. Orthopaedic biomaterial made of high-strength poly(para-phenylene) (Frick *et al.*, 2014) ^[11].

Semicrystalline thermoplastic polyphenylene sulphide, or PPS, has many industrial uses, including automotive, aerospace, electronic, and chemical container components. It also has good mechanical and rheological qualities, high thermal stability, excellent chemical and flame resistance, and high impact resistance. PPS's compressive strength is superior. When combined with additives to create a composite material for particular uses, PPS exhibits better mechanical properties (Yan, 2016) ^[12].

Cell targeting and drug carrier materials

Because polymers have so many inherent benefits, drug delivery systems are paying close attention to them. For the medication to have an impact, it must reach the intended location and be released. This study employed poly(p-phenylene)s with amino and poly(ethylene glycol) substituents (PPP-NH₂-g-PEG) as a vehicle for the anticancer medication doxorubicin (DOX) and the ligand that targets the sigma receptor, haloperidol. The expression levels of Sigma receptor 1 (SigmaR1) in two human cell lines, the human cervical adenocarcinoma cell line (HeLa) and the human keratinocyte cell line (HaCaT), were compared. SigmaR1 was discovered to be expressed twice as much in HeLa as in HaCaT cells. Research on cell imaging revealed that when haloperidol was used to target HeLa cells, DOX cell uptake increased (Guler *et al.*, 2016) ^[10].

Conclusion

Repeating p-phenylene units serve as the building block for a conducting polymer of the rigid-rod polymer family, which is what poly (p-phenylene) (PPP) is composed of. Polyphenylenes were of great interest because of their unique thermo-oxidative and thermal stabilities. When doped with electron donors or acceptors, the poly (p-phenylene) can change from an electrical insulator to an electrical conductor. Light emitting diodes (LEDs) use poly (para-phenylene) (PPP) and certain of its derivatives (ladder polymers) as the active layer. Both the electrode materials and the organic layer's band structure affect these devices' electrical properties. Their current biomedical application is quite noteworthy.

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