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Brief Review On Various Polymerization Methods Of Polyindole

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Abstract: Polyindole (PIND) in current times is one of the chiefly studied conductive material and is being used in numerous electrical and electrochemical field. However the conductivity of any conducting polymer chiefly affected by its polymerization technique. Various polymerization techniques viz. Chemical oxidative polymerization, Electrochemical polymerization, Interfacial/Emulsion polymerization, etc. are employed for the same. Each technique used by researcher do have its own pros and cons which further depends upon the chemical (solvent, oxidants, surfactants, concentration etc.) and physical (temperature, pressure, etc.) condition to be implied.
Keywords: Polyindole, oxidants, surfactants, conducting polymers, polymerization.

Introduction:

Polyindole (PIND, benzopyrrole) had been designated as one of the most common studied conducting polymer. Various researchers had presented numerous methods of synthesis of PIND, the several synthetic procedure are able to generated nano and micro sized PIND particles which had been earlier employed for their several applications in diverse areas. *Phasuksom, and Sirivat et al. 2016,* describes that the 2^{nd} and 3^{rd} position of 5 member ring (Pyrrole) in PIND are the real sites of polymerization while nitrogen (N) and phenyl ring does not take part in the process of polymerization [1]. It had been observed that the site of substitution and the solvent being used for the process of polymerization do had a significant effect on the monomer's polymerization [2, 3]. Various solvents had been used by researchers as to fabricate PIND from monomer, *Soylu et al 2011*, describes the effect of solvents like BF_3 and $HClO_4$ on the polymerization of the conducting polymer, it was suggested that BF_3 (being an electrophile) fastens to N atom and it does not have any affect over the polymer chain conjugation whereas H^+ of $HClO_4$ adds to 3^{rd} carbon of the monomer (Indole) and discontinue the conjugation.

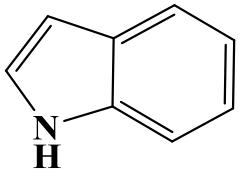

Fig. 1: Benzopyrrole (Polyindole))

As discussed PIND can be generated via numerous ways viz. Chemical oxidative polymerization, Electrochemical polymerization, Interfacial/Emulsion polymerization, etc. This document is a brief attempt to put forward these various method of polymerization of PIND.

Electrochemical polymerization method: This method is significant and comparably newer, firm, and rapid way of synthesizing polymer. Electrochemical polymerization method is supported with excellent thermal stability, high redox behavior, and slow degradation kinetics

of conductive material. For this method three-electrode system are of prime importance where a conjugation between galvanostatic, potentiodynamic or potentiostatic is required. As the method is electrochemical hence involvement of ionic solution (electrolytes) viz. ethanol, $HClO_4$, BF_3, ionic liquids etc. is there. The electrochemically fabricated π-conjugated backbone of polymers in respective electrolytic solutions demonstrate some more improved and rapid cycle with minimum loss of polymeric material.

It had been observed by various researchers that various substitutions present on PIND effect the electrochemical polymerization and onset oxidation potential [2]. For three different aminoindoles (viz, 4-substituted, 5- substituted, and 6- substituted) in 0.5 M H_2SO_4 the onset oxidation potential was found to be ranged from 0.4 to 0.54 V against standard calomel electrode [3-6]. A cyclic voltammetry (CV) method was employed by *Sarac and Ozkara, 2004* for effective polymerization of indole over the surface of Platimum in $NaClO_4$ (0.1 M) [7]. BF_3-diethyl etherate-was used as an electrolyte for electrosynthetic polymerization of indole and its derivatives over stainless steel surface [8]. Stable and homogenous PIND thinfilms were made to appear over Platinum and mild steel/Nickel electrodes in containing Acrylonitrile–Lithium chlorate electrolytic medium [9-13].

The method of electrochemical polymerization is blowed by certain disadvantages such as hydrolysis of polymeric chains and over-oxidation that can bring down significant electroactivity and conductance of the synthesized polymer [14].

Chemical oxidative polymerization: For fabrication of polymer via chemical oxidative method there is requirement of monomer along with a suitable oxidsing and doping agent. Though various studies suggest the use of various oxidants but $FeC1_3$, H_2O_2, APS, $CuCl_2$ etc are the most commonly used one. Also use of certain solvents viz. ethanol, methanol, ethanol-water, water, phenol etc. are used as to make the effective medium of monomer, oxidant, surfactant (SDS, CTAB, SLS, TW-80 etc.) and dopant (most commonly acidic). The nature oxidants, used solvent, applied temperature, concentration of reagents strongly affects the polymerization [2].

Indole along with citric acid (dopant) was sonicated in methanol and then added with oxidant ($CuCl_2$); to produce green-black polymeric product [15]. Similarly $FeCl_3$ was used as an oxidant for polymerization of Indole on DNA template by [16]. $FeCl_3$ (as an oxidant) and Indole were allowed to heat at 15 °C in 1:5 concentration with continuous stirring to produce PIND as to be used as cathode for Li-ion [17, 18].

However, this polymerization method is limited with certain drawbacks viz. difficult to fabricate regular polymer, tough to limit the molecular weight (hence degree of polymerization) or dispersity, polymer end group can't be regulated, along with this the purification of final finished product is not easy.

Interfacial polymerization method: In this mode of polymerization oxidative polymerization takes place at the interface of organic monomer and aqueous solvent (containing oxidant) biphase [2], due to this monomer get self-assemble at the monomer-solvent interface. It is a rapid method of polymerization where polymer of low dispersivty with high molecular mass can be fabricated and can be extracted without any problem due to its minimum viscosity [14]. Varity of oxidants and surfactants are require which can further effect the electrical properties of the as synthesized material [14].

PIND nanofibers were synthesized at the stationary interface of aqueous solvent containing $FeCl_3$ [17]. Interfacial polymerization was carried by *An et al, 2008*, synthesized PIND (100-200 nm) at the interface of $(NH_4)_2S_2O_8$ aqueous solution/indole chloroform solution. Nano PIND (60.3 ± 10.8 nm) were synthesized by *Phasuksom, and Sirivat 2016*, at room temperature with oxidising agent $FeCl_3$ and ammonium persulphate in acidic (HCl) condition [1]. PIND with greater surface area and number of pores was generated from its monomer by sonication of aqueous solution of Ethylene glycol dimethacrylate and TW-60.

The as prepared ppolymer was found to follow both Langmuir and Freundlich isotherm models [19].

Though the method is significant and rapid still it is affected with some of the limitations viz. the presence of emulsifier in finished material, cogulation in obtained polymer which can make it difficult to get the good yield a of polymer and also prove costly.

Conclusion: PIND is one of the chiefly studied conductive material to be used in numerous field of electrical and electrochemical field. However the conductivity of any conducting polymer chiefly affected by its polymerization technique. Each technique used by researcher do have its own pros and cons which further depends upon the chemical (solvent, oxidants, surfactants, concentration etc.) and physical (temperature, pressure, etc.) condition to be implied. Before using a particular method of polymerization one should make a thorough study to get a material to be used significantly in various filed of interest.

References:

[1] Phasuksom, K., and Sirivat, A. (2016). Synthesis of nano-sized polyindole via emulsion polymerization and doping. Synth. Met. 219, 142–153

[2] Zhou, W., and Xu, J. (2016). Progress in conjugated polyindoles: synthesis, polymerization mechanisms, properties, and applications. Polym. Rev. 57(2), 248–275

[3] Soylu, O., Uzun, S., and Can, M. (2011) The investigation of acid effect on chemical polymerization of indole. Colloid Polym. Sci. 289(8), 903–909

[4] Berkes, B. B.; Inzelt, G. and Vass, E. (2013). Electrochemical nanogravimetric study of the adsorption of 4-aminoindole and the surface layer formed by electrooxidation in aqueous acid media, Electrochim. Acta, 96, 51–60

[5] Broda, B.; Inzelt, G. (2014). Preparation and characterization of poly(5-aminoindole) by using electrochemical quartz crystal nanobalance technique, Acta Chim. Slov., 61, 357–365.

[6] Berkes, B. B.; Inzelt, G. (2014). Electrochemical nanogravimetric studies on the electropolymerization of indole and on polyindole, Electrochim. Acta, 122, 11–15.

[7] Sarac, A. S., and Ozkara, S. (2004) In-situ spectroelectrochemical investigation of indole polymerization. Int. J. Polym. Mater. Polym. Biomater. 53(7), 587–599 https://doi.org/10.1080/00914030490461702

[8] Xu, J., Hou, J., Zhou, W., Nie, G., Pu, S., Zhang, S. (2006). 1H NMR spectral studies on the polymerization mechanism of indole and its derivatives. Spectrochim. Acta Part A. 63, 723–728

[9] Cai, Z., and Yang, G. (2010). Synthesis of polyindole and its evaluation for Li-ion battery applications. Synth. Met. 160 (17–18), 1902–1905

[10] Mudila, H., Prasher, P., Kumar, M. Kumar, A. Kumar, M. G. H. Zaidi and A. Verma. (2019). Critical analysis of polyindole and its composites in supercapacitor application. Mater Renew Sustain Energy 8, 9

[11] Mukherjee, R., Lawes, G., & Nadgorny, B. (2014). Enhancement of high dielectric permittivity in CaCu3Ti4O12/RuO2 composites in the vicinity of the percolation threshold. Applied Physics Letters, *105*(7), 072901.

[12] Mukherjee, R., Huang, Z. F., & Nadgorny, B. (2014). Multiple percolation tunneling staircase in metal-semiconductor nanoparticle composites. Applied Physics Letters, *105*(17), 173104.

[13] Laha, S. S., Mukherjee, R., & Lawes, G. (2014). Interactions and magnetic relaxation in boron doped Mn3O4 nanoparticles. *Materials Research Express*, *1*(2), 025032.

[14] Chhattise, P., Handore, K., Horne, A., Mohite, K., Chaskar, A., Dallavalle, S., Chabukswar, V. (2016). Synthesis and characterization of polyindole and its catalytic performance study as a heterogeneous catalyst. J. Chem. Sci. 128(3), 467–475

[15] Mukherjee, R. (2020). Electrical, thermal and elastic properties of methylammonium lead bromide single crystal. Bulletin of Materials Science, *43*(1), 1-5.
[16] Hassanien, R., Al-Hinai, M., Al-Said, S.A.F., Little, R., Siller, L., Wright, N.G., Houlton, A., Horrocks, B.R. (2010) Preparation and characterization of conductive and photoluminescent DNA-templated polyindole nanowires. ACS Nano. 4(4), 2149–2159
[17] Zhijiang, C., and Guang, Y. (2010). Synthesis of polyindole and its evaluation for Li-ion battery applications. Synth. Met. 160, 1902–1905.
[18] Koiry, S. P.; Saxena, V.; Sutar, D.; Bhattacharya, S.; Aswal, D. K.; Gupta, S. K.; Yakhmi, J. V. (2007) Interfacial synthesis of long polyindole fibers, J. Appl. Polym. Sci. 103, 595–599.
[19] Wenming, Y., Yang, C., Xiaoling, X., Zhiping, Z., Lukuan, L., and Wanzhen, X. (2013). Preparation of indole surface molecularly imprinted polymer by atom transfer radical emulsion polymerization and its adsorption performance. J. Mater. Res. 28(19), 2666–2676.