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**REVIEW ARTICLE**

# Reaction mechanism and kinetics of in-situ polymerization of pyrrole onto textiles: A review

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## ABSTRACT

Research into electro-conductive textiles based on conductive polymers like polypyrrole has increased in recent years due to their high potential applications in various fields. Conductive polymers behave like insulators in their neutral states, with typical electrical conductivity in the range $10^{-10}$ to $10^{-25}$ $Scm^{-1}$. These neutral polymers can be converted into semi-conductive or conductive states with conductivities ranging from 1 $Scm^{-1}$ to $10^{-4}$ $Scm^{-1}$ through chemical or electro-chemical redox reactions. By applying these polymers to a textile surface, we can obtain novel composites that are strong, flexible, lightweight, and highly electroconductive. These textile composites are suitable for applications such as heating pads, sensors, corrosion-protecting materials, actuators, electrochromic devices, EMI shielding, etc. The methods of application of conductive polymers onto the textile surface, such as in-situ chemical, in-situ electrochemical, in-situ vapor phase, in-situ polymerization in a supercritical fluid, and solution coating processes, are described here briefly. The merits and demerits of these methods are mentioned here. The reaction mechanisms of chemical and electrochemical polymerization proposed by the different researchers are described. Different factors affecting the kinetics of chemical and electrochemical polymerization are accounted for. The influence of textile materials on the kinetics of chemical polymerization is reviewed and reported.

***Keywords:*** electro-conductive textiles; polypyrrole; conductive polymers; in-situ chemical polymerization; in-situ electro-chemical polymerization

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## 1. Introduction

Research in the field of electro-conductive textiles based on conductive polymers has recently attracted considerable attention. Although conductive polymers have remarkable electroconductivity, they have limited real-world applications due to their lack of processability[1–3]. The lack of processability results from their inherent conjugated structure. A high degree of conjugation along their polymer chain imparts stiffness to the chain, which leads to its unprocessability to form film or fiber[4]. Conjugated structures are characterized by repeating units in which atomic valence is not satisfied by covalent bonds. The valence electrons of adjacent carbon heteroatoms (atoms other than carbon and hydrogen) significantly overlap and form double bonds that give rise to π-bonds. The π-electrons are delocalized over large segments of the polymer chain, which are responsible for the electronic properties of the conjugated polymers[4]. The chemical structures of some of the commonly known conducting polymers are shown in **Figure 1**. Among the conductive polymers, polypyrrole (PPy) has drawn considerable interest because of its availability, good environmental stability, and satisfactory electrical conductivity in doped condition[5–8]. PPy and other conductive polymers have been considered the key material for many potential applications such as electromagnetic shielding materials[9–14], strain sensor[15–19], gas sensor[20–24], transistors[25–28], corrosion-protecting materials[29], actuators[30,31], electrochromic devices[32,33], heating pads[21,34–39], gas separation[40], antibacterial efficacy[41], etc. The heteroaromatic and extended *p*-conjugated backbone structure of PPy provides chemical stability and electrical conductivity. However, the *p*-conjugated backbone structure is not sufficient to produce appreciable conductivity on its own. Partial charge extraction from the PPy chain is also required, which is achieved by a chemical or electro-chemical oxidation process referred to as doping[4,42]. The conductivity of the neutral PPy is remarkably changed from an insulating regime ($10^{-10}$ to $10^{-25}$ $Scm^{-1}$) to a metallic regime (1 $Scm^{-1}$ to $10^{-4}$ $Scm^{-1}$) by doping[43]. This is a very worthwhile feature for applications of the polymer in which the electrical conductivity of a material must be controlled.

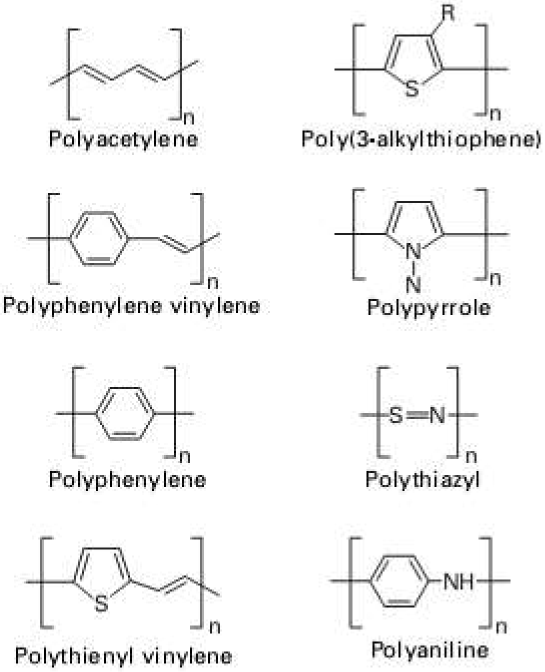

**Figure 1.** Chemical structure of some conductive polymers.

The π-bonding scheme of conjugated polymers decreases the gap between occupied (HOMO) and unoccupied (LUMO) states. The band gap of these polymers tends to lie between 1.5 eV and 3 eV, in the same range as that of inorganic semiconductors[44,45]. Doping not only increases the electrical conductivity, but it also improves the processability, catalytic properties, optical properties, and spectroscopic properties of the polymer[28]. After doping, when an electron is added to or withdrawn from a conducting polymer, a chain deformation takes place around the charge, which costs elastic energy and puts the charge in a lower electronic state. The competition between elastic energy and electronic energy determines the size of the lattice deformation, which can be of the order of 20 polymer units long. As a result, the volume of the polymer changes. The localized charged particle, along with the chain deformation, is known as a polaron. The hopping of polarons governs the charge transport in conducting polymers. Sometimes the charge transport is described by bipolarons. Bipolarons are similar to polarons but have a double charge. Instead of the single charge that distorts the chain, there are two charges that are bound together by the same chain deformations. However, owing to Coulomb repulsion, these charges repel each other, but they remain bound because of common chain deformations[4,42]. The most widely used oxidants for redox reactions are ammonium persulfate, ferric chloride, hydrogen peroxide, potassium dichromate, cerium sulfate, etc. The level of conductivity is determined by the extent of dopant incorporation. Conductivity also strongly depends on the crystallinity of the polymer. Amorphous polymers are highly conductive, favoring the ease of doping, while the crystalline forms are insulator[7,46].

## 2. Methods of application to textile substrate

A key requirement of methods of application of conducting polymers onto textiles is that the conjugated nature of the polymer should be conserved during the synthesis process. Due to strong interaction within polymer chain, they are insoluble and do not melt. Hence, they are difficult to spin into filaments or fibers. Again, lack of thermal stability makes them unsuitable for the hot molding process. So, they are very difficult to apply to textiles. in-situ polymerization methods are found most suitable techniques in this regards. Electro-conductive textiles can be prepared by using in-situ chemical, in-situ electro-chemical, in-situ vapor phase polymerization, in-situ polymerization in supercritical fluid and solution coating processes[47–54].

### 2.1. In-situ chemical polymerization

The in-situ chemical polymerization is very simple. One of the key requirements in this process is that the monomer should be soluble. For chemical polymerization, solutions of the monomer and a suitable oxidant (e.g., $FeCl_3$) are mixed together and subjected to constant stirring for prolonged durations. Coating of different textile materials with conducting polymers is possible by means of in-situ chemical polymerization[1,55–58]. The in-situ chemical polymerization can be performed in a single bath or a double bath process. For single bath process monomer and oxidant solutions are mixed in a single beaker and the simultaneously textile substrate is immersed into it. For double bath process the textile substrate is treated with monomer solution first and then monomer enriched substrate is immersed in oxidant solution. As polymerization starts some polymers deposit on a textile substrate due to adsorption and some form in the solution in bulk. The color of the substrate and solution changes to greenish black which is the color of the polymer as shown in **Figure 2**[15,52,59–62]. This is the simples process and suitable for mass production.

**Figure 2.** In-situ chemical polymerization by single bath process[59].

### 2.2. In-situ electro-chemical polymerization

Electrochemical polymerizations are usually performed in a one-compartment cell where two electrodes such as anode and cathode are connected to external power supply. The cell is provided with monomer solution with suitable electrolyte and dopant as shown in **Figure 3**. Most of the cases electrolyte act as dopant also. Electro-chemical oxidation of monomer results in polymer films deposited on anode surfaces. If anode surface is covered by a textile substrate then polymers will deposit on the surface of the textile substrate[44]. The polymerization rate, polymer yield, thickness, and morphology depends upon the material of the electrode, types of solvent, electrolyte, supply voltage, temperature, time etc.[5,12,63–65]. Different electrolysis techniques can be used such as potentiostatic (constant potential), galvanostatic (constant current) and potentiodynamic (potential scanning, i.e., cyclic voltammetry) methods[66–69]. Potentiostatic (constant potential) and galvanostatic (constant current) methods are particularly suitable for mechanistic investigation (nucleation and the macroscopic growth) of polymers. Potentiodynamic techniques, such as cyclic voltammetry, correspond to a repetitive triangular potential waveform applied at the surface of the electrode. This method has been mainly used to obtain information about the redox processes involved in the early stages of the polymerization reaction, and to examine the electrochemical behavior of the polymeric film after deposition[70]. Even coating can be obtained by this process and thickness of the coating can be controlled easily by changing voltage and its application time. But the limitation is the sample size which is the size of the electrode.

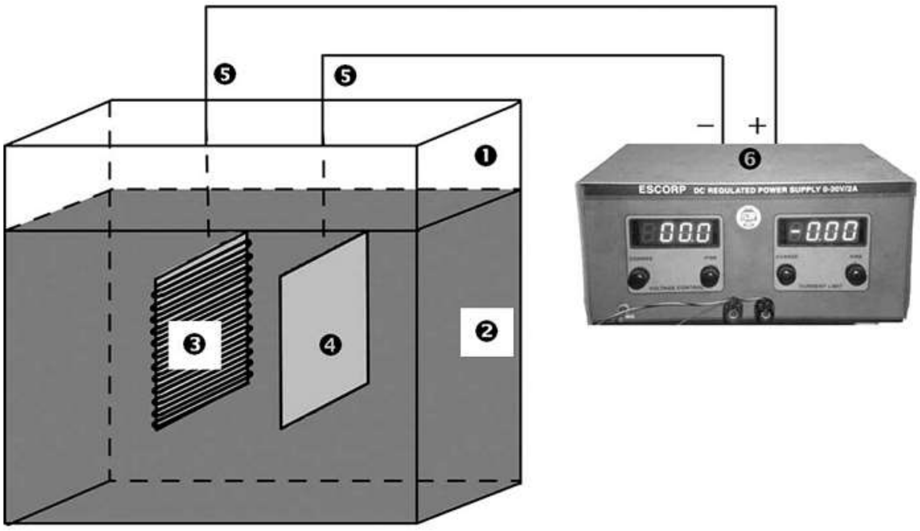

**Figure 3.** Schematic diagram of experimental set-up for electro-chemical polymerization: (1) polymerization bath, (2) electrolyte solution, (3) anode, (4) cathode, (5) electrical wire, (6) power supply[70].

## 2.3. In-situ vapor phase polymerization

In this method, the substrate is treated first with oxidant solution and dried. After that, the dried oxidant enriched substrate is exposed to monomer vapor under ambient condition for predetermining times[40,49,71–77]. As result polymers are being formed inside and the surface of the textile substrate. The polymer add-on depends upon the amount of absorbed oxidant, time of exposure of monomer vapor and ambient conditions[40]. The vapor-phase method is much quicker than the solution polymerization and results in a thinner and even coating. However, both solution and vapor-phase polymerization, when applied on to loosely wound yarns in a batch process, resulting in a patchy, non-uniform coating since only the surface exposed to the monomer vapor is coated. Uniform coating of yarns can only be achieved by a continuous coating process, where the entire yarn surface is exposed to the monomer vapor[78–80].

## 2.4. In-situ polymerization in supercritical fluid

Non-conductive fiber materials can successfully be covered by thin films of conducting polymer. The use of such coated fibers in textile products that require washing is still problematic because the coating is worn out quite soon. Improved washing resistivity has been achieved using in-situ polymerization of polyaniline and polypyrrole in supercritical $CO_2$ onto polyester and polyamide fibers. The main advantage of using this technology is that the environment of super critical fluid during polymerization which helps the substrate polymer to expands so that pyrrole monomer can be able to penetrate into it. As a result, a much durable electro-conductive textile can be prepared[49,81].

### 2.5. Solution coating process

Conducting polymers such as PPy is insoluble in most of the solvent available. Synthesis of soluble polymers can be possible in the form of alkyl PPy[49,82,83]. Solubility increases with the increase of the length of the alkyl chain attached to the pyrrole ring without significantly affecting the conductivity. These soluble alkyl pyrroles can be pre-packaged in aerosol cans or as commercially available paints and applied directly to any surface in any desired pattern for intelligent textile applications. The main advantage of soluble conducting polymers is that they can be directly applied to any substrate, which avoids exposure of the surfaces to damaging oxidizing agents and fulfill the requirements for controlled laboratory conditions[49]. Homogeneous composite films of polyurethane/PPy are obtained by solution casting method[84].

## 3. Mechanism of chemical polymerization

Concerning the in-situ oxidative chemical polymerization of pyrrole, there are no detailed mechanisms is reported as those reported for the electrochemical polymerization[5]. It is generally accepted that the first step of the polymerization consists of the formation of the dimeric species of the monomer. Then the dimers are quickly oxidized by an electrophilic aromatic substitution, followed by further oxidation and deprotonation to afford the trimers. This process is repeated, leading eventually to the formation of the polymer[85].

Other researchers proposed an iron-catalyzed polymerization of pyrrole by two mechanisms when $FeCl_3$ used as oxidant[5]. These are, (1) catalytic oxidative polymerization via complex formation, and (2) catalytic oxidative polymerization without the intermediate complex. The reaction schemes for both mechanisms are shown in **Figures 4** and **5** below:

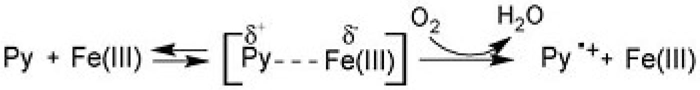

**Figure 4.** Catalytic oxidative polymerization via complex formation.

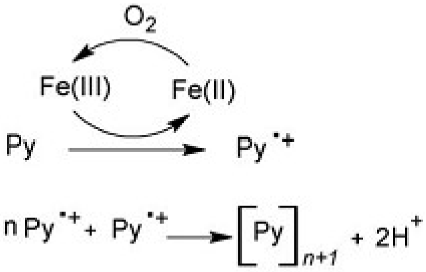

**Figure 5.** Catalytic oxidative polymerization without complex formation.

In the mechanism 1, $FeCl_3$ assists the oxidation of pyrrole with molecular oxygen by forming the complex[$Py^{\partial+}$---$FeCl_3^{\partial-}$]. In mechanism 2, pyrrole is oxidized by $FeCl_3$, and the produced $FeCl_2$ is oxidized by molecular oxygen[5]. The most widely accepted polymerization mechanism of PPy is the coupling between radical cations without complex formation as described in **Figure 6**[86–88]. In the initiation step, the oxidation of a pyrrole monomer yields a radical cation. Coupling of the two generated radical cations and deprotonation produces a bipyrrole. The bipyrrole is oxidized again and couples with another oxidized segment. In the propagation step, reoxidation, coupling, and deprotonation continue to form oligomers and finally PPy. The radical coupling between oligomeric pyrrole species is favored since the oxidation potential of oligomeric or polymeric pyrrole species is lower than that of the monomer. Once the chain length of the oligomers exceeds the solubility limit of the solvent, precipitation of PPy occurs. The termination step has not been fully elucidated by literature[5,86,87].

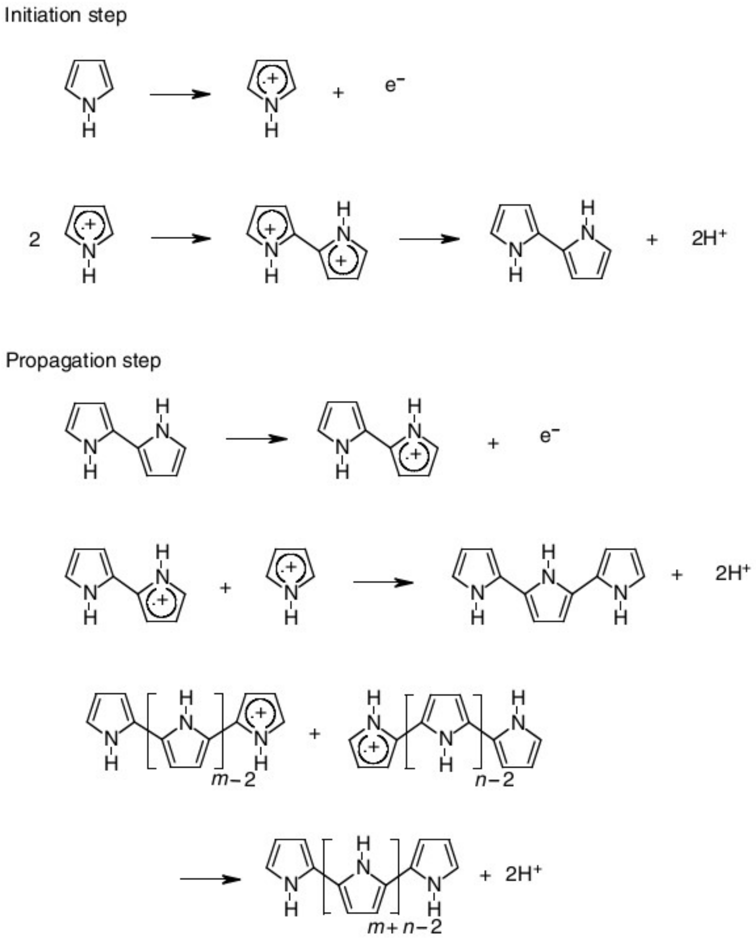

**Figure 6.** Polymerization mechanism of pyrrole[86,87].

## 4. Mechanism of electro-chemical polymerization

The electrochemical formation of conducting polymers, i.e., PPy, involves two stages such as initiation and propagation[89]. These are described in **Figure 7**:

Initiation

$$2\mathrm{Py}_{(ac)} \rightleftarrows 2\mathrm{Py}^{\bullet+}_{(ac)} + 2e^-$$

$$2\mathrm{Py}^{\cdot+}_{(ac)} \rightleftarrows \mathrm{Py}^{2+}_{2(ac)}$$

$$\mathrm{Py}^{2+}_{2(ac)} \rightleftarrows \mathrm{Py}_{2(ac)} + 2H^+$$

Propagation

$$\mathrm{Py}_{n(ac)} \rightleftarrows \mathrm{Py}^{\cdot+}_{n(ac)} + e^-$$

$$\mathrm{Py}_{j(ac)} \rightleftarrows \mathrm{Py}^{\cdot+}_{j(ac)} + e^-$$

$$\mathrm{Py}^{\cdot+}_{n(ac)} + \mathrm{Py}^{\cdot+}_{j(ac)} \rightleftarrows \mathrm{Py}^{2+}_{j+n(ac)}$$

$$\mathrm{Py}^{2+}_{j+n(ac)} \rightleftarrows \mathrm{Py}_{j+n_{(s)}} + 2H^+$$

**Figure 7.** The electrochemical formation of conducting polymers.

Alternative mechanisms, where only heterogeneous reactions at the electrode solution interface are considered, have also been proposed as shown in **Figure 8**[90].

Initiation

$$\mathrm{Py}_{(ad)} \rightleftarrows \mathrm{Py}^{\cdot+}_{(ad)} + e^-$$

$$\mathrm{Py}^{\cdot+}_{(ad)} + \mathrm{Py}_{(ad)} \rightleftarrows \mathrm{Py}_{2(ad)} + e^- + 2\mathrm{H}^+_{(ac)}$$

Propagation

$$\mathrm{Py}_{n(ad)} \rightleftarrows \mathrm{Py}^{\cdot+}_{n(ad)} + e^-$$

$$\mathrm{Py}^{\cdot+}_{n(ad)} + \mathrm{Py}_{(ad)} \rightleftarrows \mathrm{Py}_{n+1(s)} + e^- + 2\mathrm{H}^+_{(ac)}$$

$$\mathrm{Py}_{m(s)} + \mathrm{Py}_{(ac)} \rightleftarrows \mathrm{Py}_{m+1(s)} + 2e^- + 2\mathrm{H}^+$$

**Figure 8.** Alternative mechanisms.

$Py_{(ad)}$ represents the monomer species adsorbed, $Py^{\bullet+}_{(ad)}$ an adsorbed radical cation formed by the oxidation of the monomer $Py_{(ad)}$. $Py_{2(ad)}$ is an adsorbed dimer. This dimer can also be formed through adsorption of monomers at the electrode surface followed by coupling of the formed radical cations. $Py_{n(ad)}$ is an adsorbed oligomer. $Py_{n(ad)}^{\bullet+}$ is an adsorbed radical cation oligomer formed by the oxidation of the oligomer $Py_{n(ad)}$. $Py_{m(s)}$ is an insoluble oligomer. The last reaction involves the growth of the polymer film formed by either of the aforesaid mechanisms through direct incorporation of the monomers in solution[90]. The mechanism of electrochemical potentiostatic formation of polypyrrole involves three main processes, such as, one due to pyrrole oxidation, other related with bidimensional nucleation of the oligomeric form of pyrrole, that saturated the solution near the electrode surface, and finally a contribution due to the oxidation of pyrrole or its oligomers onto the surface of the polypyrrole film deposited during the 2D nucleation. This last contribution can be related to the three-dimensional growth of polypyrrole through direct incorporation of the monomer to the polymeric film or a similar process described by the first two stages[89–91].

## 5. Kinetics of polymerization

Kinetics is a subject which deals with the study of reaction rates of the chemicals and their mechanisms. Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered. The factors such as concentration, temperature, pressure, and catalyst affect the rate of a reaction. At the macroscopic level, we are interested in amounts reacted or formed and the rates of their consumption or formation. At the molecular level, the reaction mechanisms involve orientation and energy of molecules undergoing collisions.

### 5.1. Kinetics of electro-chemical polymerization

The synthesis of electro-conductive polymers by electro-chemical method requires two major reactants such as monomer and electrolyte. Study of reaction kinetics can be conducted by two methods such as microgravimetric method and voltammetric method. In the microgravimetric method, the increment of deposited polymer weight on the electrode with time is measured corresponding to change of reactant concentration. And in case of voltammetric method, the electrical charge consumed during polymerization with time is measured. The empirical kinetics of the electro-synthesis of the PPy can be written in Equation (1).

$$R_p = \frac{dQ}{dt} = \frac{dW}{dt} = k[monomer]^{\alpha}[electrolyte]^{\beta} \tag{1}$$

where $Rp$ is the reaction rate or polymerization rate. It can be defined as electrical charge consumed during the polymerization per unit of polymerization time ($\frac{dQ}{dt}$) or change in weight of the deposited PPy on electrode per unit of polymerization time ($\frac{dW}{dt}$). $\alpha$ and $\beta$ are reaction orders and $k$ is kinetic constant. Taking the logarithms of Equation (1), we have Equation (2):

$$logR_p = log\frac{dQ}{dt} = logk + \alpha \log[monomer] + \beta\log[electrolyte] \tag{2}$$

Equation (2) shows that a plot of $log\frac{dQ}{dt}$ or $log\frac{dW}{dt}$ against $\log[[monomer]]$ or $\log[electrolyte]$ gives a straight line, the slope of which represents the order of reaction related to the monomer concentration ($\alpha$) or electrolyte concentration ($\beta$). Indeed, the double logarithmic plot of the experimental data gives a straight line. This straight line plot allows us to obtain the kinetic order of reaction. Literature has some studies related to find out the reaction rate and reaction order as **Figures 9** and **10**[92]. In **Figure 9** charge consumed with time has been shown for different monomer concentrations. It can be seen that if monomer concentration increases consumption of charge also increases. If a double logarithmic plot of slope versus monomer concentration can be constructed as **Figure 10** then we can get Equation (4) from Equation (3). From Equation (4) reaction rate and reaction order can be found out empirically.

$$log\frac{dQ}{dt} = logR_p = -3.84 + 0.20[monomer] \tag{3}$$

$$R_p \propto [monomer]^{0.20} \tag{4}$$

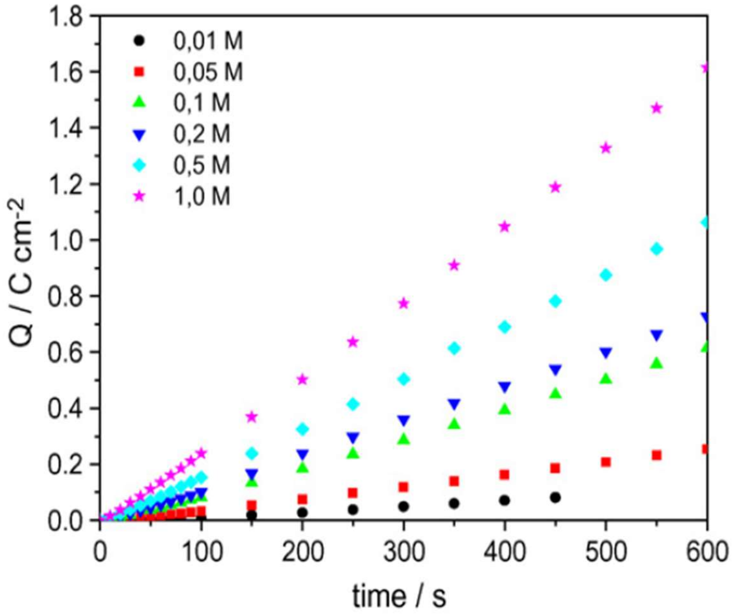

**Figure 9.** Charge versus polymerization time for at different monomer concentration[92].

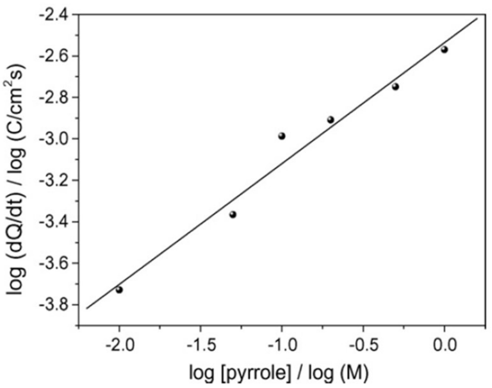

**Figure 10.** Double logarithm plot of charge and monomer concentration[92].

Here, reaction order $\alpha = 0.20$ is found related to pyrrole monomer for formation of PPy–$ClO_4$ nano-composite using ITO electrode. Whereas reaction order in case of $LiClO_4$ salt has been reported 0.46 and 0.56 for PPy nano-composites and film respectively[92]. The effect of heparin sodium salt as electrolytes in nano-structures template form in the synthesis of polypyrrole by using ITO electrodes is studied. The order of reaction for this electrode is reported 0.77[92]. In another study with platinum electrode, a higher order of reaction $\alpha = 0.86$ is observed in case of pyrrole monomer[93]. In other studies carboxymethylcellulose (CMC), polystyrenesulphonate (PSS), polyacrylate (PAA), sulphate ($SO_4^-$) are used as electrolytes[94–97]. Electrodes used are platinum, graphite felt or carbon. The reported kinetic rates are as follows.

Polymerization rate $=[\text{pyrrole}] \times [\text{CMC}]^{0.6}$ (Microgravimetry method)[94]

Polymerization rate $=[\text{pyrrole}] \times [\text{CMC}]$. (Voltametric method)[94]

Polymerization rate $=k[\text{pyrrole}]^{0.35} \times [\text{PSS}^-]^{0.7}$ (Microgravimetry method)[95]

Polymerization rate $= k[\text{Pyrrole}]^{0.51} \times [ClO_4^-]^{0.55}$ (Microgravimetry method)[96]

Polymerization rate $= k[\text{Pyrrole}]^{0.50} \times [ClO_4^-]^{0.44}$ (Voltammetric method)[96]

It can be seen that for all cases electrolyte has the higher reaction order than that of monomer. The reason behind the high reaction order of electrolytes for all cases is attributed to an addition of three factors such as oxide generation, the doping process, and electrolyte discharge. The rate of reaction depends on the types of electrolytes and electrodes. The process depends on chemical nature of the electrode and faradaic processes occurring through the electrode/electrolyte solution[98]. As well established, different results in microgravimetric and voltammetric kinetic studies are due to the morphology and the electrochemical properties of conducting polymer which is strongly affected by the nature of the anions used during the electro-synthesis. Even solvents such as water or acetonitrile have significant influence in polymerization rate due to the difference in solvent-polymer interaction[99]. pH of the solvent and applied potential also affect the kinetics of polymerization[100].

## 5.2. Kinetics of chemical polymerization

The textile processes, such as dyeing and finishing, are usually conducted in aqueous solutions. We are interested to see how the polymerization of water-soluble monomer such as pyrrole would proceed in the presence of textiles. It is observed that monomer forms the conductive polymer in the form of a smooth, coherent film on the surface of the textile material, under certain conditions, irrespective of the type of fiber used. But it is well understood that a uniform coating of polymer is not possible unless there is adsorption of monomer through the fiber surface to some extent. So the adsorption mechanism of monomer through fiber surface has great importance for uniform deposition of polymer. We may also produce an ordered or crystalline deposition of polymer onto fiber surface which leads to better conductivity and stability. Few kinetic studies have been done by the chemical polymerization process. As mentioned earlier chemical polymerization process is much easier and cheaper process than electro-chemical process. The control of process parameter is very essential to obtain an optimum yield of polymerization. It is found that the rate of polymerization is not only dependent on the concentration of the monomers but also depends on the type of oxidizing agents used. The polymerization of pyrrole, is much faster with ammonium persulfate than with ferric chloride[101]. The rate of reaction can be influenced by changing the pH conditions[102–104]. The polymerization of pyrrole with ferric chloride is much faster in the presence of an acid, such as hydrochloric or sulfuric acid. The presence of doping agents can also influence the polymerization rates[28,105–109]. Decreases in rates have also been observed, with certain surface active agents, particularly nonionic surfactants[82,110–115].

## 6. Methodology used for Kinetic study of chemical polymerization

To study the reaction kinetics of pyrrole polymerization, the monomer exhaustion with pyrrole or oxidant such as $FeCl_3$ can be studied using a gas chromatographic method or High-Performance Liquid Chromatography (HPLC) method. The polymerization reaction can be quenched using a solution of sodium dithionite ($Na_2S_2O_4$) to reduce the Fe(III) to Fe(II) thus preventing further oxidation of the pyrrole and subsequent polymerization. It is reported that this quenching reaction occurs very quickly and a constant pyrrole monomer concentration is obtained if an aliquot of the reaction mixture is withdrawn and added to the dithionite solution[101]. The chemical synthesis of polypyrrole in water, with $FeCl_3$ as the oxidant, is investigated by High-Performance Liquid Chromatography (HPLC) method[116]. It is reported that the polymerization is first order with respect to the pyrrole and second order with respect to the $FeCl_3$ as shown in Equation (5). It is explained that an intermediate $FeCl_3$–pyrrole complex is formed in the first step of polymerization kinetics and afterward oxidation of pyrrole occurs as the second step which is the rate determining the reaction[116].

$$\frac{d[Py]}{dt} = \beta[Py] \times [Fe]^2 \tag{5}$$

The yield of polypyrrole is stabilized and attained at a constant value after 4 h of polymerization time. This similar experimental observation is made by other researchers where no polypyrrole is formed within reaction solution after 4 h in the presence of the textiles[57]. Faster rate of increase of polypyrrole thickness on the textile surface at lower pyrrole concentrations (**Figure 11**) suggests a faster reaction rate. Pyrrole concentration of about 0.4 mg/mL indicates a critical point for transportation and consumption of pyrrole on the surface of textile[57].

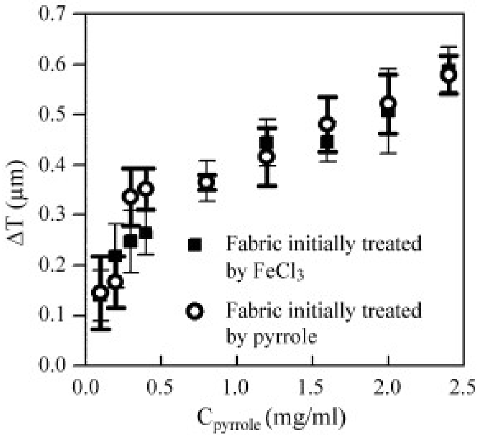

**Figure 11.** Change in thickness of polypyrrole coating on textile fabric with pyrrole concentration.

In another approach[116] of the kinetic study of PPy formation by aqueous method by mixing a solution of pyrrole with the solution of $FeCl_3$, it is proposed that the rate of polypyrrole polymerization can be determined by the rate of the initial electron-transfer reaction. The mechanism and kinetics of the formation of polypyrrole (PPy) films are studied by UV-VIS and IR spectroscopy. It is reported that the anion is linked with the links of a polymer chain with a charge transfer. After addition of the $FeCl_3$ solution to pyrrole the intensity of the new bands increases with time, while that of the pyrrole vibrations simultaneously decreases as shown in **Figure 12**. The full width at half maximum and the mutual arrangement of these bands suggest that they refer to deformation vibrations of the pyrrole ring in a pyrrole complex. The UV-VIS absorption diffuse-reflectance spectra are typical spectra for PPy a constant and progressive increase of the pyrrole bands is observed due to the radical polymerization, associated with the character of the chemical bond between pyrrole rings in polymer chains and the chlorine anions from $FeCl_3$ as shown in **Figure 13**. It is proposed that the formation of a polypyrrole involves very reactive intermediate species. Their interaction between themselves and the solution components my lead to deviation from ideal stoichiometry$[(C_4H_5N)_xCl)]_n$[116].

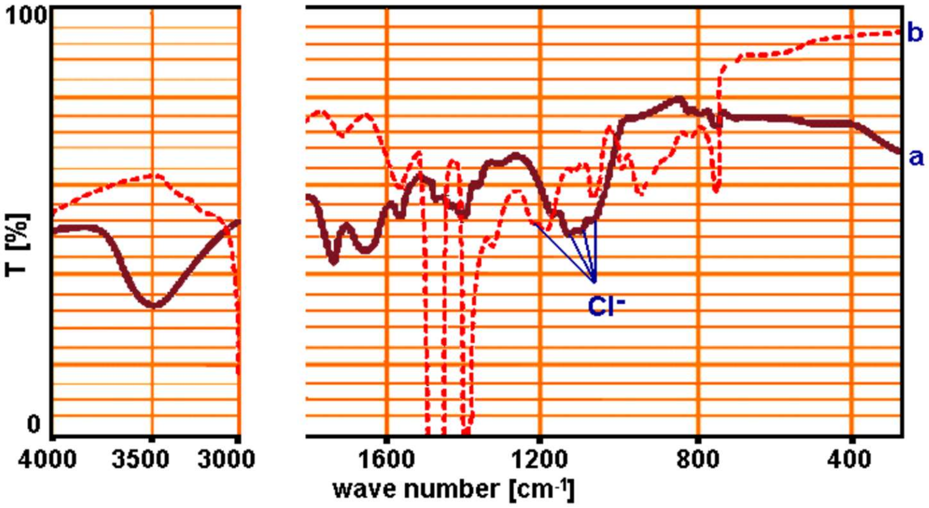

**Figure 12.** IR spectra of (a) Pyrrole and (b) PPy in ferric chloride solution[116].

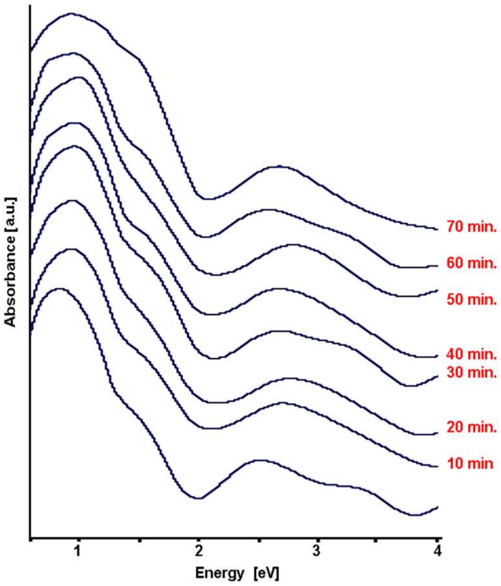

**Figure 13.** The UV-Vis spectra of PPy in the presence of $FeCl_3$[116].

## 7. Effect of textile substrate on kinetics

Nature of the textile substrate may influence the kinetics of in-situ deposition of PPy on its surface. But, no significant difference is found by the use of different fibers[106]. Polyester, nylon, rayon, acrylics, Kevlar, Nomex, wool, and cotton, all seem to perform very similarly[106]. Again, it another study, it is reported that the morphology and conductivity of PPy and polyaniline films differ greatly according to whether the films are deposited on hydrophilic or hydrophobic substrate surfaces. The conductivities of the films deposited on the hydrophilic surfaces are $\geq 10^4$ smaller than those deposited on hydrophobic surfaces[117]. PPy is electrochemically deposited onto cotton fabrics with the aid of a water-soluble adhesive. The mechanism for growth of the polymer appears to follow the template laid out by the yarns in the cotton fabric. This template growth is seen to be distinctly different from that of a freestanding film in which growth appears to progress through spherical nodes. Films prepared with an added adhesive show significantly better structural uniformity than those prepared without[118]. It is reported that the presence of textile material in the reaction chamber has no influence on the polymerization rate as shown in **Figure 14**[119]. It can be seen that the kinetic curves of with polyester textiles and without textiles are practically coincide. But in another study, it is reported that in presence of textile surface higher polymerization rate is observed than that of without the presence of textile surface[101]. A pseudo first-order rate constant $3.7\times10^{-4}$ $M^{-1}sec^{-1}$ is obtained in the presence of a textile surface at 25°C. In the absence of surface at same temperature, the reaction showed second order behavior and the rate is significantly slowed with a rate constant of $3.2 \times 10^{-4}$ $M^{-1}$ $sec^{-1}$ as shown in **Figure 15**[101].

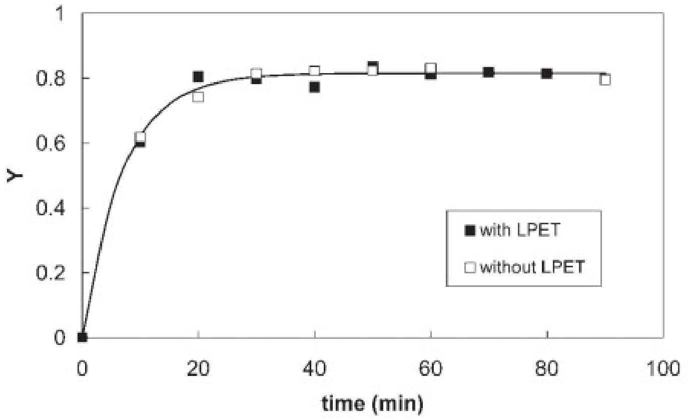

**Figure 14.** Pyrrole polymerization yield versus time at 25ºC (pyrrole 0.020M, APS 0.021M, Na2NDS 0.009M)[119].

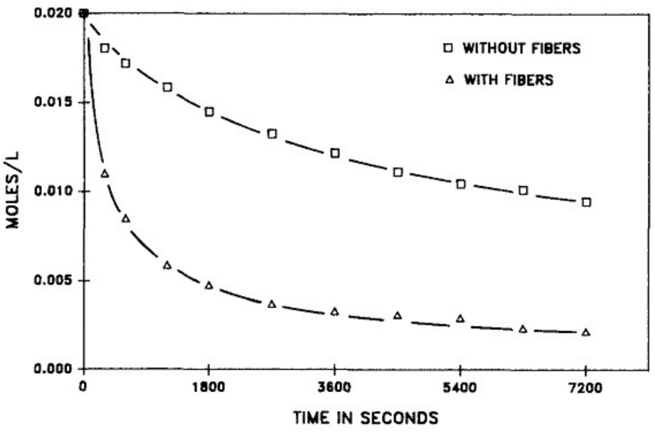

**Figure 15.** Pyrrole monomer depletion with polymerization time[101].

## 8. Conclusions

Research into electro-conductive textiles based on conductive polymers like polypyrrole has increased in recent years due to their high potential applications in various fields. By applying polypyrrole to textile materials, we can obtain the synergistic properties of both polypyrrole and textile materials in terms of a strong, flexible, lightweight, and highly electro-conductive composite that is suitable for potential applications such as heating pads, transistors, sensors, microwave attenuation, antimicrobial efficacy, EMI shielding, etc. PPy is remarkably changed from an insulating regime ($10^{-10}$ to $10^{-25}$ $Scm^{-1}$) to a metallic regime (1 $Scm^{-1}$ to $10^{-4}$ $Scm^{-1}$) by doping. These neutral polymers can be converted to semi-conductive or conductive states with a conductivity range of 1 $Scm^{-1}$ to $10^{-4}$ $Scm^{-1}$ through chemical or electro-chemical redox reaction*s*. In-situ polymerization methods are found to be the most suitable techniques for the application of polypyrrole to textiles. Electro-conductive textiles can be prepared by using in-situ chemical, electrochemical, and vapor-phase polymerization processes. In-situ chemical polymerization can be performed in a single bath or a double bath. In the case of in-situ electro-chemical polymerization, different electrolysis techniques can be used, such as potentiostatic (constant potential), galvanostatic (constant current), and potentiodynamic (potential scanning, i.e., cyclic voltammetry). The vapor-phase method is much quicker than solution polymerization and results in a thinner and even coating. A much more durable electro-conductive textile can be prepared by in-situ polymerization using a supercritical fluid as a solvent. Concerning the in-situ oxidative chemical polymerization of pyrrole, no detailed mechanisms are reported as those for electrochemical polymerization. The electrochemical formation of conducting polymers, i.e., PPy, involves two stages, such as initiation and propagation. The termination step has not been fully elucidated in the literature. The rate of reaction of electro-chemical polymerization depends on the types of electrolytes, electrodes, solvent, pH of the solvent, electrolysis techniques, etc. The rate of reaction in chemical polymerization depends on the oxidant and its concentration, the monomer concentration, the pH of the solvent, the dopant, etc. The nature of the textile substrate may influence the in-situ deposition of PPy on its surface.

## Conflict of interest

The author declares no conflict of interest.

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