

Kinetics and mechanism of pyrrole chemical polymerization

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ABSTRACT

Proton NMR spectroscopy was used to study the kinetics of the chemical polymerization of pyrrole in water using ferric chloride as an oxidant. A kinetics model was proposed in which the consumption of pyrrole is due to a fast oxidation reaction, and a relatively faster reaction with the oxidized oligomers of pyrrole. This suggests the commonly used mechanism for polymerization of pyrrole to polypyrrole, which is an important conductive polymer, is not correct for polymerization in water. Instead the polymerization is based on a mechanism where the pyrrole monomer is attacked by a radical cation, leading directly to the pyrrole reacting with the oxidized oligomer. We conducted kinetics studies as a function of temperature and determined the activation energy, activation entropy and enthalpy for each step of the polymerization process for the first time. The activation enthalpy and activation entropy are respectively $77,091 \pm 17$ J and 24.25 ± 0.06 J/K for the initial step, and $70,971 \pm 14$ J and 24.25 ± 0.06 J/K for the propagation step.

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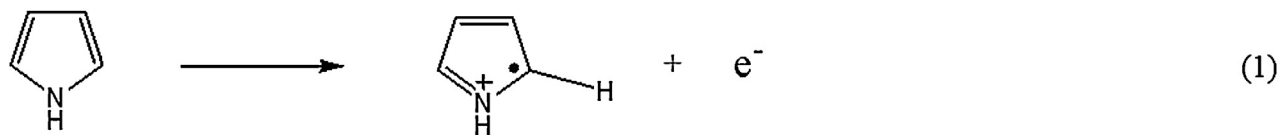
1. Introduction

Conjugated conducting polypyrrole (PPy) has been well known for many years [1–4]. It is one of the promising conducting polymers applied in the industry and new technology with unique properties, such as relatively high conductivity, easy synthesis and stability [2]. The kinetics study of pyrrole chemical polymerization at different temperatures contributes to developing our understanding of polymerization mechanism, optimizing the synthesis method and designing reaction processes of pyrrole oligomers with other chemical reagents. For example, if we know the mechanism and the temperature dependence of the kinetics of the polymerization, a desired chemical reagent can be added at a proper time and with the choice of proper temperature to have a reaction with the

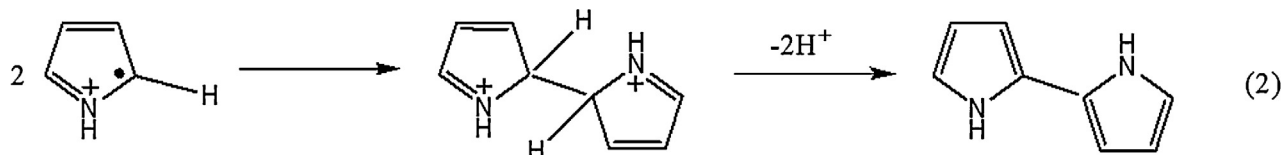
monomer or oligomers in order to modify the polymer. The yield and rate constants which are obtained at different temperatures for this chemical polymerization would benefit both laboratory and industrial applications.

The polymerization of pyrrole is proposed to involve complex reactions including oxidation, deprotonation and crosslinking [5]. Synthesis of polypyrrole by electropolymerization is an easily controlled process, so the kinetics of pyrrole electropolymerization has received more attention than chemical polymerization [5–8].

The mechanism of PPy formation by chemical method is controversial [9–11]. The most widely accepted polymerization mechanism of PPy is the coupling between radical cations [12]. In the initiation step, the oxidation of a pyrrole monomer yields a radical cation.

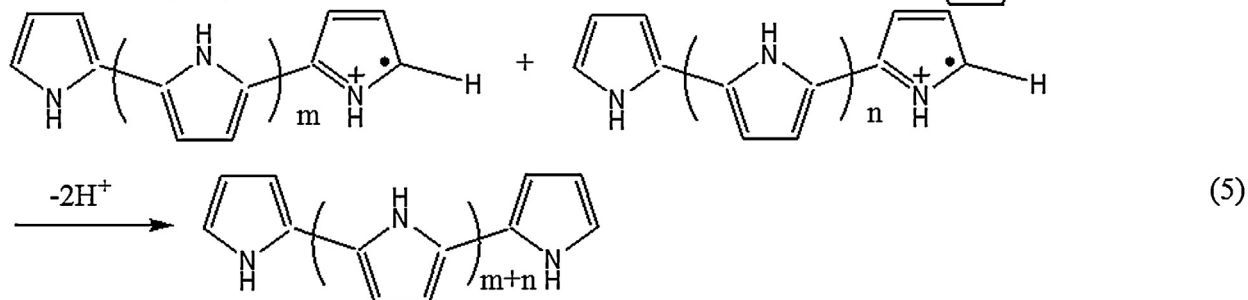
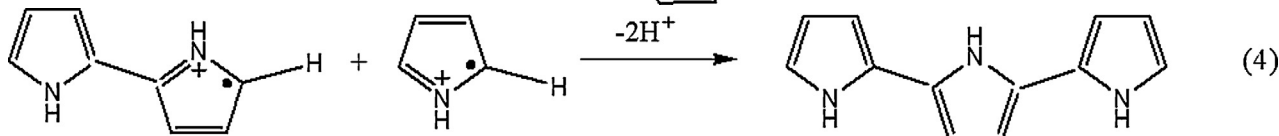
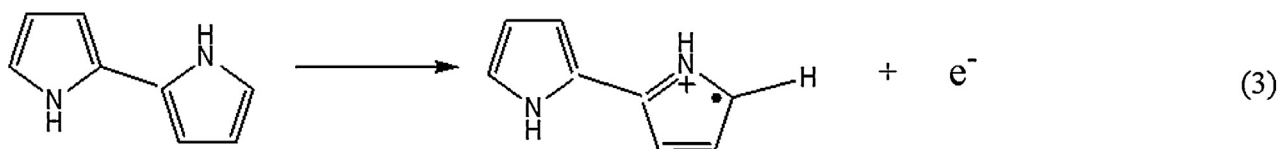


Coupling of the two generated radical cations then deprotonation produces a bipyrrrole [13]. The bipyrrrole is oxidized again and couples with another oxidized segment.



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In the propagation step, re-oxidation, coupling, and deprotonation continue to form oligomers and finally PPy.



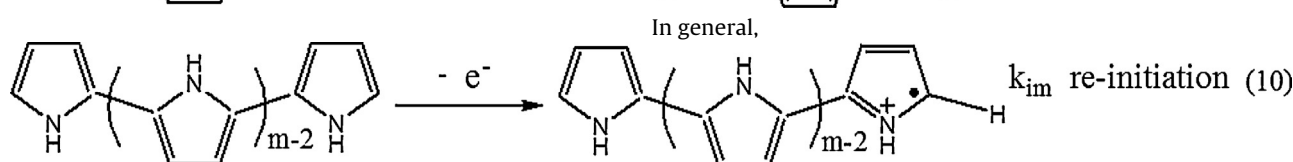
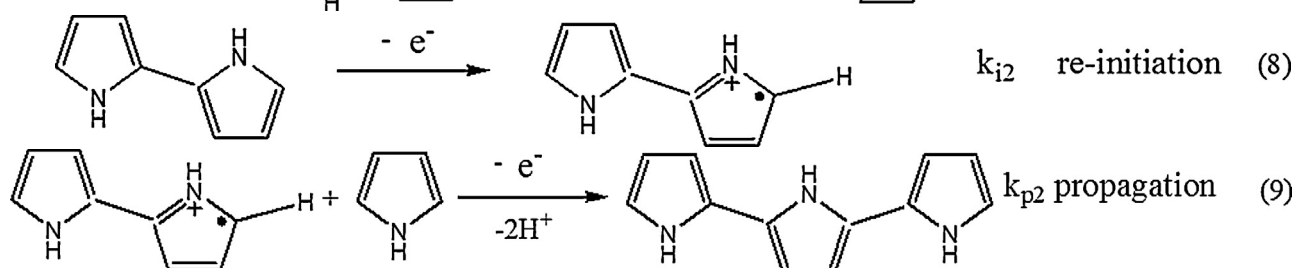
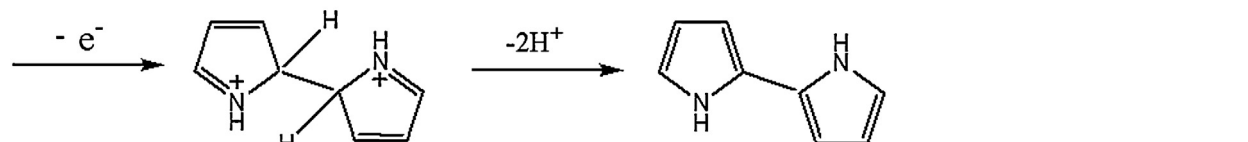
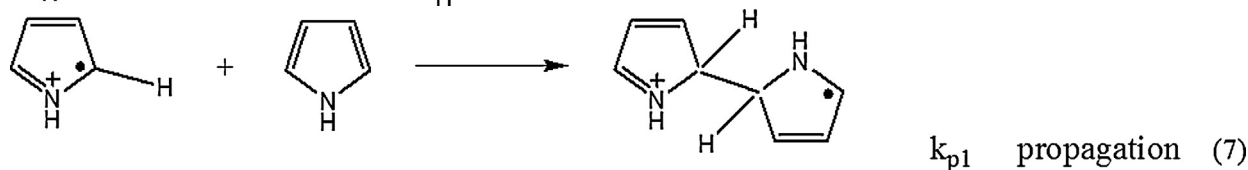
On the other hand, another mechanism for the chain growth of polypyrrole has been proposed:

- (1) The radical cation reacts with a neutral monomer [11,14,15] (reaction (6)).
- (2) This will be followed by oxidation and deprotonation to yield a dimer.

(3) This dimer will be oxidized immediately, and form a dimeric radical cation (reaction (8)).

(4) The dimeric radical cation will attack another neutral monomer leading to the formation of a trimer (reaction (9)).

By this repeated process, the polymer chains grow and finally lead to the polymer. The polymerization of pyrrole can be described by the following scheme:



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