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Recent advances in the synthesis of conducting polymers from the vapour phase

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ABSTRACT

Inherently conducting polymers (ICPs) combine the electrical properties of metals and semiconductors with a polymer's ability to flex and/or stretch. In general, polymers are relatively simple to synthesise, however, ICPs themselves have had limited uptake in consumer devices. This lack of uptake is in part related to the insolubility of many ICPs in common industrial solvents, and hence methods to manufacture them in a usable form have been problematic. Vapour phase polymerisation (VPP) is one method that provides a convenient route to producing thin films of both soluble and insoluble ICPs, and nanocomposites thereof. In this critical review the VPP process will be discussed from the fundamental viewpoint of the proposed polymerisation mechanism and the parameters affecting polymer growth for a range of different monomers (thiophene, 3-hexylthiophene, pyrrole, 3,4-ethylenedioxythiophene, *etc.*). Looking forward into the future, new areas of polymer design and fabrication using VPP will be discussed, such as the enhancement of ICPs through additives, and next generation device fabrication based upon VPP ICPs.

Contents

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1. Introduction

With the development and uptake of consumer electronics over the past decades, daily life has undergone and continues to undergo rapid transformation. At the heart of this development, conductive organic materials present as one means to realise new and innovative devices. Electrical devices that utilise these organic materials, namely inherently conductive polymers (ICPs), have the opportunity to be light weight, flexible and potentially wearable.

The field of organic electronics was born in 1977 upon the discovery by Shirakawa et al. [1] of the first ICP, polyacetylene, possessing the ability to conduct electricity. In the solid state, the extended pi-bonded network of the conjugated polymer backbone allows for electrical charge to be transported, once doping anions are introduced to stabilise the charge carriers [2]. To illustrate the simplistic difference between traditional (insulating) polymers and ICPs, example structures of insulating, conjugated, and ICPs are presented in Fig. 1.

The development since of such ICPs has been thorough and rapid, and as a result now form potential components in devices such as organic light emitting diodes (OLEDs) [3–5], organic transistors [6–8], electrochromic devices [9–12] and fuel cells [13–18]. The ever broadening list of potential applications for ICPs highlights the need to develop efficient, cost effective methods of synthesis which maximise their advantages over inorganic alternatives. Despite the vast amount of research into enhancing ICPs [19,20], they are only sparingly used in commercially available devices. The issues limiting this class of material from being widely adopted by industry relate to practical considerations such as their potential degradation in air, thermal decomposition at elevated temperature, and the problematic nature of specific synthesis. Beginning with synthesis issues, the common pathway to synthesise ICPs is to utilise a molecule or compound (oxidant) to deprotonate the monomer, hence initiating the process of polymerisation. This chemical reaction is summarised in Eq. (1) with Fe^{3+} as the oxidant, X as the doping anion and M as the monomer [21,22]. Fe^{3+} is used herein as one of the most common oxidants used in the soon to be discussed vapour phase polymerisation (VPP) field [5,12,23,24]. The studies of Gleason and co-workers on the oxidative chemical vapour deposition of conducting polymers presents a similar mechanism, where removal of an electron from the monomer by an oxidant leads to the initiation of the polymerisation process [25,26]. This is in contrast to the catalyst transfer condensation polymerisation using the Yokozawa method, where monomer modified with a leaving group (such as Br) is reacted with a catalyst (such as Ni-ligand-Cl molecule) to achieve a chain-growth polymerisation [27].

$$Fe^{3+}X_3^- + M \rightarrow Fe^{2+}X_2^- + M^* + X^- \quad (1)$$

Early successful polymerisation techniques combined oxidants and monomer together in solution, a process known as chemical oxidation [28,29]. This method, while simple to implement in practice, has limitations for producing polymers with conjugated structures, often leading to the formation of a poorly conducting powder. Diaz et al. [30] devised an electropolymerisation technique that overcame the issue of ICP solubility (see [31,32] for reviews of this technique). This technique relied on the application of a bias to a conductive substrate in order to extract electrons from the monomer species, thus initiating the polymerisation process. Electropolymerisation therefore gives some control over the ICP film thickness,

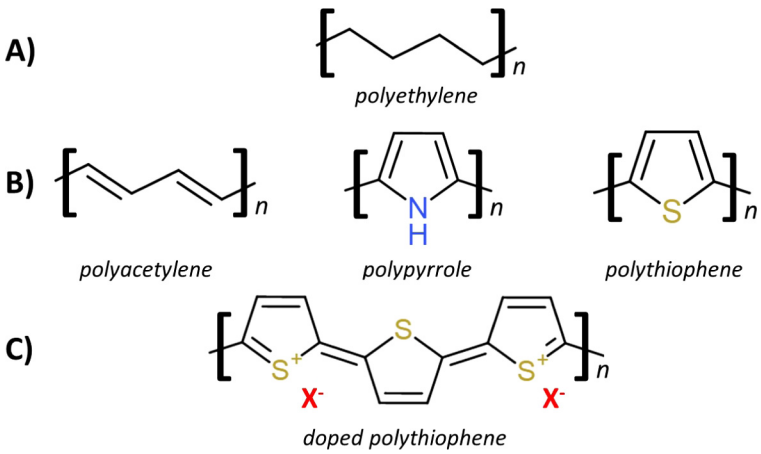

Fig. 1. The difference between (A) insulating, (B) conjugated (examples of polyacetylene, polypyrrole and polythiophene shown), and (C) ICPs (doped polythiophene).