Fabrication of Poly(3-hexylthiophene) Thin Films by Vapor-Phase Polymerization for Optoelectronic Device Applications

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ABSTRACT The vapor-phase polymerization (VPP) of poly(3-hexylthiophene) (P3HT) was achieved successfully as an alternative method to conventional solution-based thin film fabrication. Using FeIIICl3·6H2O, a spontaneous reaction of 3-hexylthiophene monomers resulted in the rapid formation of conducting P3HT thin films directly on substrates, such as glass, indium–tin-oxide, and poly(ethylene terephthalate), at thicknesses ranging from 50 to 1000 nm. The VPP of P3HT was achieved using ferric chloride hexahydrate and a 1:1 ratio of a methanol/ethanol mixture as the solvent system. The developed VPP technique can provide good processing consistency with an electrical conductivity, a transmittance, and a surface roughness of ∼10−2 S/cm, >90%, and <10 nm, respectively.

KEYWORDS: poly(3-hexylthiophene) • vapor-phase polymerization • conducting polymers • thin films • electronic devices

INTRODUCTION Since π-conjugated polymers were first reported (1, 2), they have been studied extensively primarily for their high conductivity and potential applications in semiconductors of electronic devices. For example, polythiophenes (PTs) (2) and poly(3-alkylthiophene)s (P3ATs) (3–5) with a higher regioregularity (2, 6) have been examined for use in light-emitting diodes (LEDs), field-effect transistors (FETs), all-polymer integrated circuits, and thin-film transistors (TFTs) (7–13). Similarly, photovoltaic cells have adopted P3ATs as an electron-donor layer because they are one of the most promising active components for this application (14, 15). Furthermore, P3AT polymer lasers are attractive devices because of their light weight, flexibility, and low-cost fabrication (16).

Among the P3ATs, such as poly(3-octylthiophene) and poly(3-dodecylthiophene) (3), poly(3-hexylthiophene) (P3HT) is used most widely because of its low cost and superb properties. P3HT is the best of the P3ATs, even though it is either annealed to improve the degree of crystallinity or exposed to oxygen (4, 5). Depending on the doping level, P3HT thin film has many potential uses in applications such as biosensors, wettability switch devices, flexible electronic displays, microchips, electrochromic windows, and radiation screens (17–20). P3HT is also one of the most indispensable materials in organic TFTs, providing solution-processable capability and relatively high mobility (0.1 cm2 V−1 s−1) (11, 21). In particular, in organic solar cells, P3HT has recently been used as an active matrix material incorporated with CuPc, TiO2, perylene, or fullerene (C60) derivatives, such as methanofullerene and phenyl C61-butyric acid methyl ester (14, 15).

P3HT is usually synthesized in powder form by chemical oxidative polymerization, electrochemical polymerization, Grignard polycondensation, oxidative coupling, and quasiliiving polymerization (22–26). However, there are several drawbacks to be addressed with this polymer. For example, the light transmittance is not usually enhanced up to 90% and the surface morphology of fabricated P3HT films is generally poor because film formation is usually achieved by a wet-coating process, which is also limited by the wetting characteristics of the P3HT solution with the substrate materials (27, 28).

This study investigated P3HT thin films deposited using a vapor-phase polymerization (VPP) technique (29, 30), which desirably ensures thin-film formation in various substrate materials without the additional processes to liquefy polymers. To the best of the authors’ knowledge, there are no reports showing the successful VPP of P3HT even though this method is simple, easy to use, and inexpensive. It is believed that the VPP technique for P3HT will allow the