Electrochemical Preparation of High Quality Poly(*p*-phenylene) Film

Masaharu Satoh, Keiichi Kaneto, and Katsumi Yoshino

Faculty of Engineering, Osaka University, Yamada-Oka, Suita, Osaka, Japan

A high quality poly(*p*-phenylene) film which is green in colour, with an electrical conductivity of *ca.* 100 S/cm, has been obtained by the electrochemical polymerization of benzene.

Electrochemical polymerization of aromatic compounds has been shown to be a useful method for obtaining uniform and flexible conducting polymer films. Many attempts have been made to produce new conducting polymers; however, only a limited number of polymers such as poly(pyrrole),[1] poly(thiophene),[2] poly(aniline),[3] and poly(pyridazine)[4] have been synthesized by this method. Among the many conducting polymers, chemically synthesized poly(*p*-phenylene) powder[5] has been widely investigated in view of both the fundamental physical interest and the practical viewpoint because of its possible applications,[6] *e.g.*, as active material for secondary batteries. This polymer becomes high conductive (*ca.* 150 S/cm)[7] upon doping with either electron acceptors or electron donors. Recently, films have been prepared by the electrochemical polymerization of benzene utilizing a two-phase system in HF–benzene[8,9] and a composite electrolyte of $AlCl_3$ and $Bu^n_4NClO_4$ in nitrobenzene.[10] However, the films obtained were not flexible, and had a rough and dull surface. Their conductivity (10^{-5}—10^{-4} S/cm) was also small in comparison with the chemically prepared poly(*p*-phenylene) powder.

We have found that electrochemical polymerization of benzene utilizing a composite electrolyte of $CuCl_2$ and $LiAsF_6$ gives a flexible film with a conductivity of *ca.* 100 S/cm, and now report our results and properties of the poly(*p*-phenylene) produced.

The electrochemical polymerization of benzene was performed in a one-compartment cell at room temperature using an In–Sn oxide conducting glass (ITO) as a working electrode and an Ni plate as counter electrode. A solution of benzene in nitrobenzene (1.2 mol/l) was electrolysed utilizing a composite elecrolyte of $CuCl_2$ and $LiAsF_6$ (each 0.1 mol/l). Benzene, nitrobenzene, $CuCl_2$, and $LiAsF_6$ were purified in the usual manner before use. The poly(*p*-phenylene)film grew on the ITO anode surface at a rate of about 0.07 μm/min at a typical current density of *ca.* 2 mA/cm^2. The film obtained was flexible and its surface was quite smooth. The thickness of the film depended directly on the current density and the reaction time. The charge passed during the film growth was used to determine the film thickness on the ITO. The as-grown film containing acceptor dopants easily became semiconducting with a brown colour on electrochemical or chemical undoping.

Elemental analysis of the undoped film gave a C : H ratio of 1.45—1.58 : 1, which agreed satisfactorily with the calculated value (1.5 : 1) for poly(*p*-phenylene). Residual electrolyte (*e.g.* $CuCl_2$) may remain in the film, because of insufficient washing, but the copper content has not been analysed in detail yet. The polymer has i.r. absorptions at 1580, 1480, 1000, 810, 760, and 700 cm^{-1} which are also consistent with data for chemically prepared poly(*p*-phenylene).

Figure 1 shows the absorption spectra of as-grown (a) and undoped (b) poly(*p*-phenylene) film. The absorption spectrum below 2 eV changes markedly on undoping, although a large peak at 3.4 eV is observed for both as-grown and

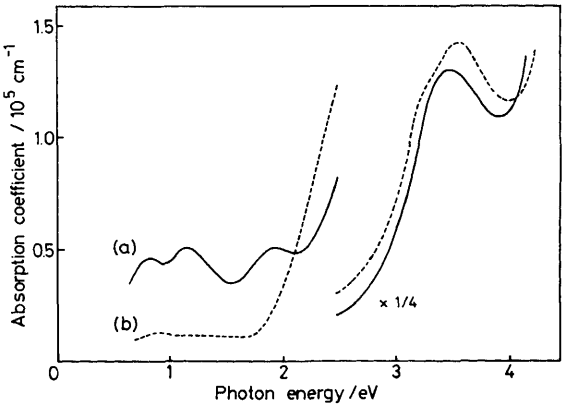

Figure 1. Absorption spectra of (a) as-grown and (b) undoped poly(*p*-phenylene) films.

undoped samples. The peaks below 2 eV may be related to polarons and/or bipolarons,[11] but a detailed study is needed for the assignment of these peaks.

The electrical conductivity of the poly(*p*-phenylene) film is *ca.* 100 S/cm, measured by the d.c. four-probe technique under argon atmosphere. This figure is much larger (more than six orders of magnitude) than values reported previously for poly(*p*-phenylene) films.[10] The conductivity of the as-grown film decreased to *ca.* 0.1 S/cm after exposure to air for several hours, indicating the neutralization or release of dopants probably due to moisture. Reproducible doping and undoping by the electrochemical and chemical methods has been successfully demonstrated, suggesting the possible application of this film. Detailed discussion of the properties will be reported elsewhere.

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