Electrochemical Preparation of Highly Conducting Polythiophene Films

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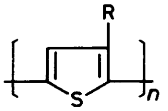
Electrochemical polymerization of thiophene, 3-methylthiophene, and 3-ethylthiophene in propylene carbonate gave tough films, having conductivities of 190, 510, and 270 S cm^{-1}, respectively.

Electrically conducting polymers have attracted a great deal of attention recently, since doping with iodine was found to increase the conductivity of polyacetylene by over seven orders of magnitude.[1] Polypyrrole was electrochemically prepared as free standing films in 1979.[2] This polymer is attractive because polypyrrole films can be easily grown in their oxidized conducting form on a conducting substrate by electrochemical polymerization of pyrrole monomer.

Electrochemical polymerization of 3-methylthiophene has been reported by two groups.[3] The conductivity of the polymer was 100—120 S cm^{-1}. From more than two hundred experiments we found the optimum conditions for the



(1)

electrochemical polymerization of 3-methylthiophene. Using these conditions, the conductivity is four times higher than previously reported values and the films are tough. We have also prepared highly conducting and tough films of polythiophene and poly(3-ethylthiophene) under the same polymerization conditions. The conductivity of the former is twice as high as previously reported values.[4] The latter is a new polymer which has not been reported previously. These films may have uses in electronic devices, electrochromic displays, and polymer batteries, as well as for fundamental research on conducting polymers.

The reaction vessel was a one-compartment cell equipped with an indium tin oxide conducting glass or platinum anode and a platinum or aluminium cathode. The thiophenes were dried over calcium chloride, distilled, and stored under dry nitrogen. Propylene carbonate (PC), supplied by Wako Pure Chemical Industries Ltd., was dried over 4 Å molecular sieve, distilled, and stored under dry nitrogen. The electrolytes were used without further purification. Electrochemical polymerization was carried out at 5 °C under an argon atmosphere and continued until the charge reached 2.4 C cm^{-2}. The films deposited on the surface of the anode were peeled off and washed with n-hexane. The direct current conductivity was measured using a four-point probe method.

The selection of the solvent is important to obtain coherent films. As for the polymerization of 3-methylthiophene, PC was the preferred solvent. Tetraethylammonium hexafluorophosphate (Et_4NPF_6) gives the most highly conducting films. $NaAsF_6$ and tetraethylammonium tetrafluoroborate are also good electrolytes.

The optimum concentration of 3-methylthiophene and Et_4NPF_6 was found to be 0.2 and 0.03 mol dm^{-3}, respectively. The optimum current density is 10 mA cm^{-2} for Et_4NPF_6 as an electrolyte. Below -15 °C no coherent films were obtained and above 10 °C the conductivity of films decreased with increase in temperature. The conductivity of the films is in the range of 450—510 S cm^{-1}, depending on electrolytes and conducting substrates.

We obtained highly conducting and tough films of polythiophene and poly(3-ethylthiophene) under the same polymerization conditions, but the current density was lowered to 5 mA cm^{-2} for $NaAsF_6$ because of the high resistivity of the reaction mixture. The conductivity of polythiophene and poly(3-ethylthiophene) is 190 and 270 S cm^{-1}, respectively.

Poly(3-methylthiophene) films are the most conducting among as-grown films obtained by electrochemical polymerization of heterocyclic compounds. An as-grown film of poly(3-methylthiophene) is blue and has a metallic lustre. It becomes red upon electrochemical reduction. From Fourier transform i.r. spectra of reduced films, the structure of poly(3-methylthiophene) and poly(3-ethylthiophene) can be formulated as shown in (**1**).

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