New Electrochromic Polymers

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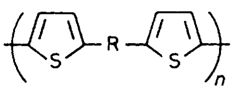
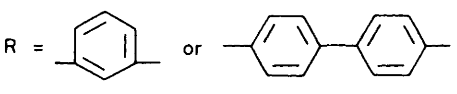
Poly-1,3-bis(2-thienyl)benzene and poly-4,4′-bis(2-thienyl)biphenyl films have been prepared which show green colours in doped states; thus the three primary colours, blue, green, and red, may be produced using polythiophene and its derivatives.

Electrically conducting polymers have attracted a great deal of attention recently, not only from the scientific point of view but also as regards industrial applications of this new class of polymer. Since some conducting polymers can be cycled electrochemically between doped and undoped states, they seem to offer possibilities as electrochemical materials, such as electrochromic films and rechargeable battery electrodes. The doping and undoping reactions of polythiophenes are accompanied by reversible colour changes. Yoshino *et al.* fabricated an electrochromic display device using polythiophene films on transparent electrodes, but the colours were limited to blue and red.[1] In the course of studies on the chemical structure and properties of polythiophenes, we have found new compounds which may be cycled between green and faint yellow.

The reaction of 1,3-di-iodobenzene with 2-thienylmagnesium bromide in the presence of a nickel catalyst yielded 1,3-bis(2-thienyl)benzene (T13B). 4,4′-Bis(2-thienyl)biphenyl (TBP) was prepared by the reaction of 4,4′-di-iodobiphenyl with 2-thienylmagnesium bromide in tetrahydrofuran. These monomers were polymerized electrochemically in a one-compartment cell equipped with two electrodes and an argon inlet. No reference electrode was used in the electrochemical polymerization. Polymerization was carried out at a constant current density of 1 mA/cm^2 at 25 °C for T13B and 40 °C for TBP. Potentials between the cathode and anode were 2.9 and 2.2 V for T13B and TBP, respectively. Polymerization times were 20—30 s for films used in spectroscopic measurements. The solvent and electrolyte were nitrobenzene and tetrabutylammonium tetrafluoroborate, respectively. Nitrobenzene was dried over calcium chloride



(1)



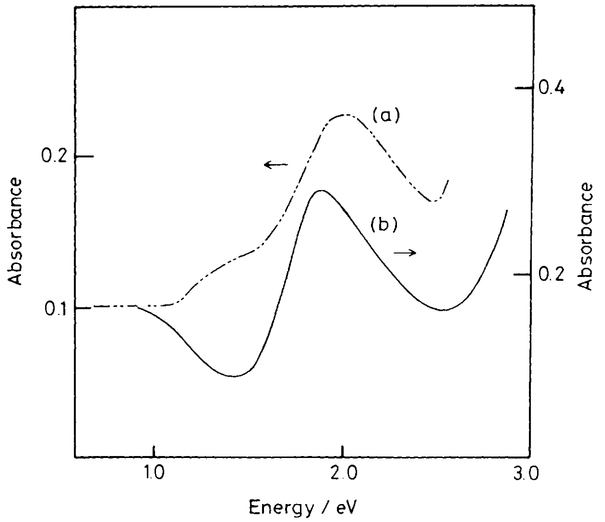


Figure 1. Absorption spectra of the polymers in doped states. (a) Poly-T13B; (b) poly-TBP.

and distilled just before use. Reference electrodes consisting of Ag/Ag^+ were used in cyclic voltammetry, and spectroscopic measurement during doping. The solvent and electrolyte used in these measurements were acetonitrile and tetrabutylammonium tetrafluroborate, respectively.

The i.r. spectra of the polymers were consistent with the structure (**1**).

The conductivity of BF_4-doped poly-T13B was about 1×10^{-4} S/cm. After the films had been deposited on electrodes, the polymerization solution was replaced with acetonitrile containing tetrabutylammonium perchlorate and silver perchlorate. Spectra were measured *in situ* at various levels of doping as described in ref. 2. Figure 1 shows the spectra when the applied voltage was 0.9 V. Well-defined peaks were observed at 2.0 and 1.9 eV for poly-T13B and poly-TBP, respectively. Since the absorbance decreased sharply on both sides of the peaks, the films were green in colour. The green colour did not change in the absence of an applied voltage. The films were faintly yellow in undoped states. They were stable to cycling between −0.4 to 0.9 V *vs.* Ag/Ag^+. The dry film retained the green colour in air for several months.

Poly-1,4-bis(2-thienyl)benzene was reported recently.[3] We have also prepared this polymer and examined its spectra.[4] The spectra had a peak at 2.2 eV and absorbance did not decrease so sharply on the higher-energy side, hence the film looked blackish. As far as we have been able to determine, the present polythiophenes are the only ones to show green colours.

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