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Electrochemical Synthesis of Poly(p-phenylene xylylidene), a New Electrically Conducting Polymer

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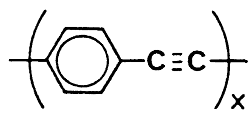
Electroreduction of α,α,α,α',α',α'-hexachloro-p-xylene at a copper electrode in n-Bu_4NBF_4-propylene carbonate gave a free-standing film of poly(p-phenylene xylylidene), PPX, a new conducting polymer with phenylenic and acetylenic backbones. The PPX film exhibited a conductivity of 70 $S\,cm^{-1}$ on doping with SO_3.

Considerable attention has been afforded recently to the preparation and properties of new electrically conducting polymers. Electrochemical synthetic methods are attractive on account of the great convenience and simplicity and of the film forming ability that is useful in application to electronic sensors and devices. We have recently demonstrated the validity of electroreduction of organic halides as a synthetic method of conducting polymer films by preparing poly(p-phenylene vinylene) (PPV) from α,α,α',α'-tetrabromo-p-xylene (**1**).[1] We report herein the second preparation of a free-standing film by this electroreduction method, which provides poly(p-phenylene xylylidene) (PPX), a new electrically conducting polymer with a straight chain composed of phenylenic and acetylenic backbones.[2]



PPX

In a typical synthetic procedure, constant-potential electrolysis of α,α,α,α',α',α'-hexachloro-p-xylene (**2**) was performed at a copper electrode in 0.1 M[3] n-Bu_4NBF_4-propylene carbonate under a nitrogen atmosphere in a standard three-electrode cell equipped with a platinum counter and a Ag/Ag^+ reference electrode. Electrolysis of **2** (0.1 M) at -1.7 V vs. Ag/Ag^+ for 24 h afforded a ca. 40 μm of uniform brownish-yellow film (3.2 mg/cm^2). The structure of the polymer thus formed can be expected to be $(C_6H_4{-}CCl_2{-}CCl_2)_x$, $(C_6H_4{-}CCl{=}CCl)_x$ and/or $(C_6H_4{-}C{\equiv}C)_x$, according to the degree of reduction. The chlorine content of the film was 8.7 wt%[4] and this is much lower than 41 wt% for $(C_6H_4{-}CCl{=}CCl)_x$. Accordingly, it is assumed that the monomer **2** undergoes mainly six electron reduction under these conditions.

Infrared and Raman spectra of the film are displayed in Fig. 1. In the Raman spectrum, a characteristic band assignable to the C≡C stretching mode can be seen at 2205 cm^{-1},[5] but this band scarcely appears in the infrared spectrum, indicating a highly symmetrical structure in a unit of the polymer. In addition two other strong signals at 1583 and 1118 cm^{-1} due to the C=C and C-C stretching vibrations are observed. The absorptions at 1450-1650 cm^{-1} and 600-

800 cm^{-1} in the infrared spectrum are ascribable to 1,4-substituted benzene.[5)] These analytical and spectroscopic data can draw a conclusion that the major part of the film consists of $(C_6H_4-C\equiv C)_x$, PPX. The chlorine content mentioned above suggests that the polymerization degree, n, is ca. 19, provided that the film is simply composed of $Cl_3C(C_6H_4-C\equiv C)_nC_6H_4CCl_3$,[4)] although elements other than C, H and Cl such as Cu were contained in the film and a part of the moieties generated by reduction of 2 may be hydrogenated judging from a little high hydrogen content of the film.[4)] These impurities could be derived from the electrode materials, electrolyte and/or solvent.

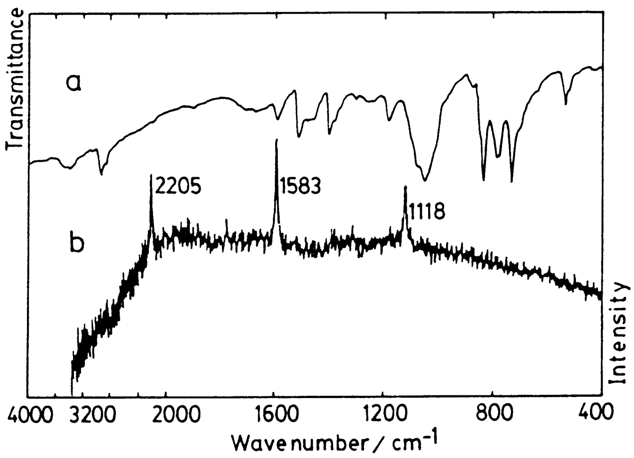


Fig. 1. Infrared (a) and Raman (b) spectra of the PPX film.

The film as grown exhibited 2 × 10^{-8} S cm^{-1} in electric conductivity at 25 °C, and showed a disorder in Arrhenius plots of conductivity measured at the first raise in temperature (see Fig. 2). This is attributable to the impurities in the film. Conductivity of the film at 25 °C estimated from a straight line in the Arrhenius plots was 4 × 10^{-10} S cm^{-1}. This almost undoped PPX can be doped with I_2 or SO_3 to become dark brown or black, respectively. The I_2-doping raised the conductivity at most to 3 × 10^{-7} S cm^{-1}, whereas the SO_3-doped film measured by the four-contact method exhibited a high conductivity, 70 S cm^{-1} at 25 °C.

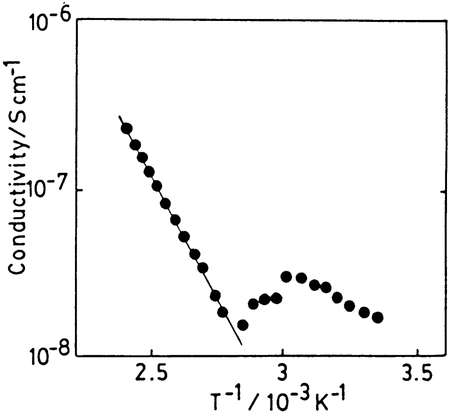


Fig. 2. Temperature dependence of electrical conductivity of undoped PPX.

In order to infer whether the polymerization in the electroreduction of the halides occured at the film/solution interface or at the electrode surface, an experiment of two-step polymerization from 2 and secondly from 1 in a liquid flow electrochemical cell was performed. The PPV film was formed between the electrode and the preformed PPX film. Thus it is concluded that the polymerization reaction of the halides proceeds at the electrode surface.

References

1) H. Nishihara, M. Tateishi, K. Aramaki, T. Ohsawa, and O. Kimura, Chem. Lett., 1987, 539.
2) A quantum chemical calculation has been carried out for PPX, see: J. L. Brédas, R. H. Baughman, and R. Silbey, J. Chem. Phys., 76, 3673 (1982).
3) 1 M = 1 mol dm^{-3}.
4) Anal. Found: C, 78.52; H, 4.21; Cl, 8.70%; Cu, 7.61. Calcd for $Cl_3C(C_6H_4-C\equiv C)_{19}C_6H_4-CCl_3$ plus others (8.57%): C, 79.32, H, 3.33; Cl, 8.78%.
5) "The Infra-red Spectra of Complex Molecules," 3rd ed, ed by L. J. Bellamy, Chapman and Hall, London (1975).

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