

ORGANIC METALS : FILMS OF AsF_5 DOPED POLY-4,4'-BIPHENYLENE

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Metallic film of poly-4,4'-biphenylene is prepared by the AsF_5 oxidation and the conductivity of AsF_5 doped film is measured as a function of temperature. The maximum conductivity at 295 K of the heavily doped film becomes $\sigma_{295\text{K}} \approx 6 \Omega^{-1}\text{cm}^{-1}$, although the conductivity for the undoped material is less than $10^{-4} \Omega^{-1}\text{cm}^{-1}$. The film doped for one day under 300 mmHg of AsF_5 gas is metallic between 295 and 250 K.

There is now a large and rapidly growing interest in conducting derivatives of organic polymers and polymers such as doped polyacetylene,¹⁾ doped poly-*p*-phenylene,²⁾ doped polypyrrole,³⁾ and doped poly-*p*-phenylene sulphide^{4,5)} were reported to exhibit high electrical conductivities. We describe here the conducting polymer prepared by AsF_5 oxidation of a solution-processible polymer : poly-4,4'-biphenylene.

Poly-*p*-phenylene⁶⁾ has a long chain of phenylene nuclei and was synthesized by direct polymerization of benzene as is shown in Fig. 1-a. However, poor solubility makes it difficult to characterize poly-*p*-phenylene completely. Poly-4,4'-biphenylene⁷⁾ was readily prepared by the reaction of CuCl and benzidinetetrazonium chloride as is shown in Fig. 1-b. The dark brown polymer of higher molecular weight was then separated into two fractions by extraction with benzene. The soluble portion precipitated by adding petroleum ether was separated into two fractions by extraction with acetone. The benzene soluble and acetone insoluble portion has molecular weight distribution of 5,000 to 16,000 and the elemental analyses⁷⁾ indicated that there are no oxygen, one azo group nitrogen, and two to three chlorines for each ten phenyl nuclei.

Fig. 2 is the IR spectra of poly-*p*-phenylene, pure and AsF_5 doped poly-4,4'-biphenylene. Poly-*p*-phenylene has the vibrational modes at 1450, 990, and 780 cm^{-1} . These peaks are also observed with *p*-terphenyl and *p*-quaterphenyl. Poly-4,4'-biphenylene has the additional absorption peaks at 1595 and 1090 cm^{-1} in addition to three peaks of 1460, 1000, and 810 cm^{-1} . These are also found in the spectra of azobenzene. Therefore, this polymer is identified to be a poly-4,4'-biphenylene azo compound. AsF_5 doped poly-4,4'-biphenylene has one sharp peak at 700 cm^{-1} , one shoulder at about 860 cm^{-1} and one broad band at about 1650 cm^{-1} in addition to five bands of poly-4,4'-biphenylene. The sharp peak at 700 cm^{-1} is assigned to the AsF_6^- anion⁸⁾ and two bands at 860 and 1650 cm^{-1} seems to correspond to the 900 and

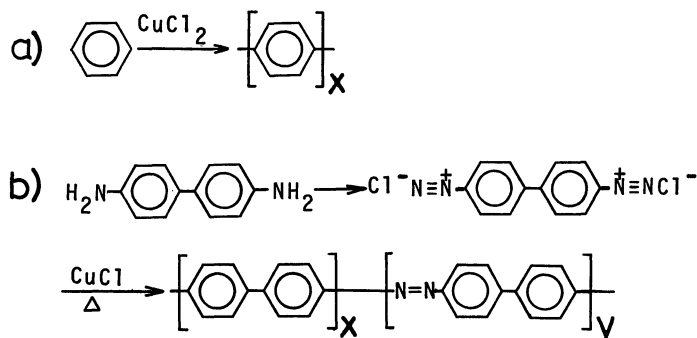


Fig. 1 Reaction of the polymerization of poly-*p*-phenylene and poly-4,4'-biphenylene.

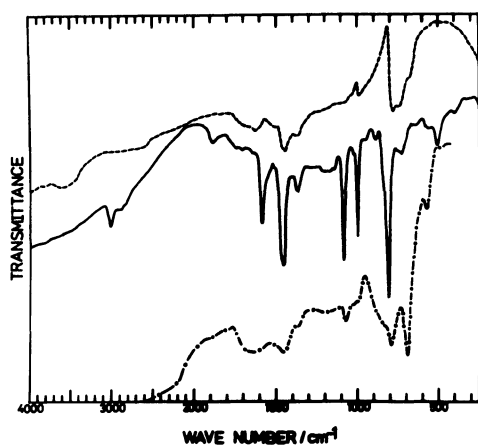


Fig. 2 Infrared spectra of polymers ;
 a) ——— poly-4,4'-biphenylene,
 b) - - - - AsF₅ doped poly-4,4'-biphenylene,
 c) - - - - - poly-p-phenylene.

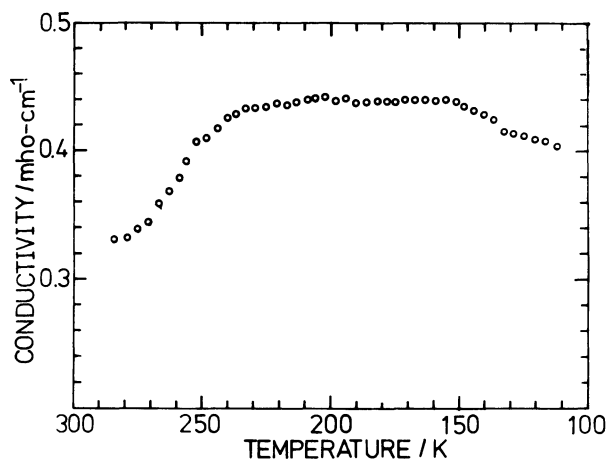


Fig. 3 Temperature dependence of the conductivity of the poly-4,4'-biphenylene film doped for one day under 300 mmHg AsF₅ gas.

1370 cm⁻¹ bands observed in the IR spectra of doped polyacetylene.^{9,10} Furthermore, doping produces a background absorption which may be due to the free carrier absorption.

A reddish thin film is deposited on a electrical copper plate of the four probe by slowly dropping a dioxane solution of poly-4,4'-biphenylene. After that, the polymer was exposed with AsF₅ gas. The doped film was pumped for about two hours and the electrical conductivity was measured under nitrogen by the four probe method. The film had the size of 1.0×0.5×0.001 cm³. Fig. 3 shows the temperature dependence of the conductivity of the metallic behavior between 295 and 250 K. The maximum room-temperature conductivity ($\sigma_{295K} \approx 6 \Omega^{-1}\text{cm}^{-1}$) was obtained for the film doped for two days under 300 mmHg of AsF₅ gas.

The conductivity of AsF₅ doped poly-4,4'-biphenylene is quite stable for heat and dry air.

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