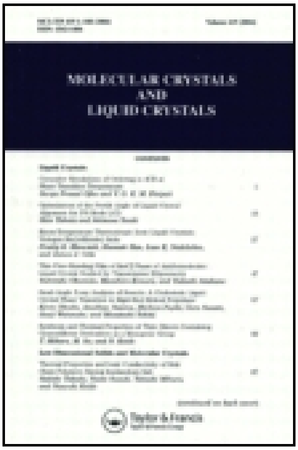

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Optical and electrical studies on polypyrrole and poly(4,4'-Biphenylylene)

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OPTICAL AND ELECTRICAL STUDIES ON POLYPYRROLE AND POLY(4,4'-BIPHENYLYLENE)

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Absorption and reflection spectra of polypyrrole and poly(4,4'-biphenylylene) are shown over the wide wavelength region, and the best fit of the calculated reflection or absorption spectra is presented to the observed spectra. Based on these results, the conduction mechanism of polypyrrole and poly(4,4'-biphenylylene) is discussed.

INTRODUCTION

In recent years, many polymers such as polysulfur nitride, $(SN)_x$,[1] and AsF_5 doped polyacetylene, $(CH)_x$,[2] have arrested attention because they exhibited metallic properties. These discoveries have encouraged the search for other polymer systems.

Diaz *et al.*[3] have synthesized a strongly adhered, durable film; polypyrrole by electrochemical polymerization. Ivory *et al.*[4] found out a novel method for the preparation of highly conducting polymers: the doping of polyphenylene with the action of AsF_5. We[5] have recently reported the conducting polymer prepared by AsF_5 oxidation of benzene soluble polymer: "poly(4,4'-biphenylylene)".[5] In the present paper, we report the absorption and reflection spectra of polypyrrole and poly(4,4'-biphenylylene). The electrical conductivity of these two polymers are measured over the wide temperature range and the conduction mechanism of poly-

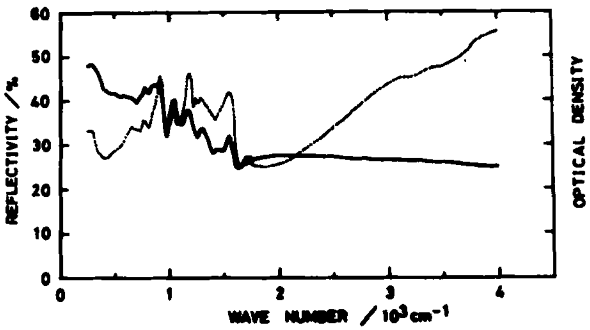

FIGURE 1 Comparing between the IR absorption and the reflection spectra of polypyrrole film prepared by using Et_4NBF_4.
----- : absorption spectrum, —— : reflection spectrum

pyrrole is discussed on these experimental results.

ABSORPTION AND REFLECTION SPECTRA OF POLYPYRROLE[10]

In figure 1 the IR absorption and reflection spectra of thin polypyrrole film prepared by using Et_4NBF_4 as supporting electrolyte are shown. The IR absorption spectra show the bands characteristic of pyrrole confirming the presence of the pyrrole rings in the polymer.[6] For example, the skeltal streching of the pyrrole ring is found at 1500 cm^{-1} region, the =C-H in-plane deformation is found at 1300 and 1180 cm^{-1}; the =C-H out-of-plane bending at 775 cm^{-1} and the ring breathing at 920 cm^{-1}. The peak near 1035 cm^{-1} is assigned to the BF_4^- ion since this band is observed in the spectra of Et_4NBF_4 in KBr disk.

Shown in figure 2 are the reflection spectra of polypyrrole films prepared by different supporting electrolytes. The reflectivity in the lower energy region increases and is intensified with increasing conductivities. The lower energy transition may be assigned to the free carrier absorption band.

The dielectric function of a linear chain of free carrier absorption band may be expressed by the following equation,[7]

$$\varepsilon(\omega) = \varepsilon_{core} - \frac{\omega_p^{\,2}}{\omega^2 + i\,\omega\,\gamma}, \tag{1}$$

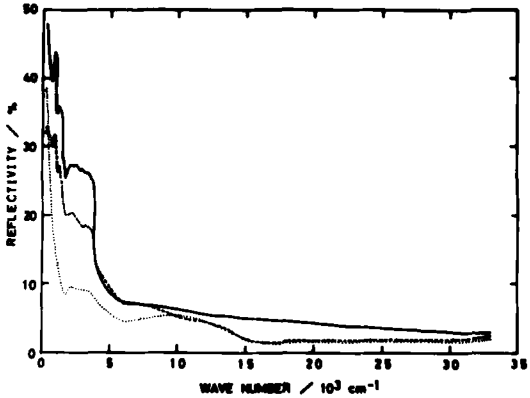

FIGURE 2 Reflection spectra of polypyrrole film prepared by using different supporting electrolytes.
——— : Et_4NBF_4 (σ_{295K} = 4.4 $\Omega^{-1}cm^{-1}$)
------: Et_4NBF_4 (σ_{295K} = 0.74 $\Omega^{-1}cm^{-1}$)
......: $LiClO_4$ (σ_{295K} = 0.016 $\Omega^{-1}cm^{-1}$)

$$\text{where} \quad \omega_p = \left(\frac{4\pi N e^2}{m^*}\right)^{1/2} . \tag{2}$$

γ is the band width, N is the number density of free carrier and m* is the effective electron mass.

The reflectivity R can be expressed by the following equation,[7]

$$R = \frac{1 + |\varepsilon| - \sqrt{2(|\varepsilon| + \varepsilon_1)}}{1 + |\varepsilon| + \sqrt{2(|\varepsilon| + \varepsilon_1)}} , \tag{3}$$

$$\text{and} \quad |\varepsilon| = \sqrt{\varepsilon_1^2 + \varepsilon_2^2} , \tag{4}$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric function. Accordingly, the best fit of equation 3 to the observed reflection spectra is obtained by using the following parameters with equation 1,

$$\omega_p = 17230\ cm^{-1}, \quad \gamma = 39340\ cm^{-1}, \quad \varepsilon_{core} = 2.4 . \tag{5}$$

The calculated reflection spectrum based on these values is in good agreement with the observed curve as is shown in figure 3.

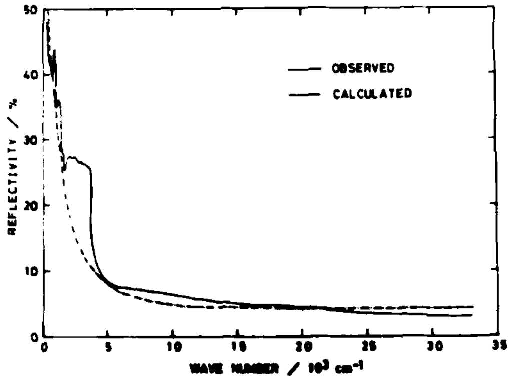

FIGURE 3 Observed and calculated reflection spectra of polypyrrole film prepared by using Et_4NBF_4.

Then, the number density, N, of the free carrier in the polypyrrole film can be estimated as 3×10^{21} cm^{-3} by substituting m* = m to the next equation,[7]

$$N = \frac{\omega_p^2 \, m^*}{4 \pi e^2} \quad . \tag{6}$$

This value corresponds to ca. 5% of the total π-electrons (7×10^{22} cm^{-3}) which is estimated from the density of the film ($\rho = 1.48$ g/cm^3).[8] This means that a few holes in the filled π-band contribute to the transport phenomenon.

Furthermore, the dc conductivity, σ_0, is given by the following equation,[7]

$$\sigma_0 = \frac{\omega_p^2}{4 \pi \gamma} \quad . \tag{7}$$

The value is calculated by using the observed plasma frequency, ω_p, and the band width, γ. The obtained value (σ_0 = 126 Ω^{-1}cm^{-1}) is two orders of magnitude larger than the observed value (σ_0 = 4.4 Ω^{-1}cm^{-1}) of the dc conductivity of polypyrrole prepared by using Et_4NBF_4.

The difference between these two values may be explained by the mechanism as shown below. That is, the temparature dependence of the electrical conductivity was measured on the polypyrrole films prepared by using Et_4NBF_4. As is shown

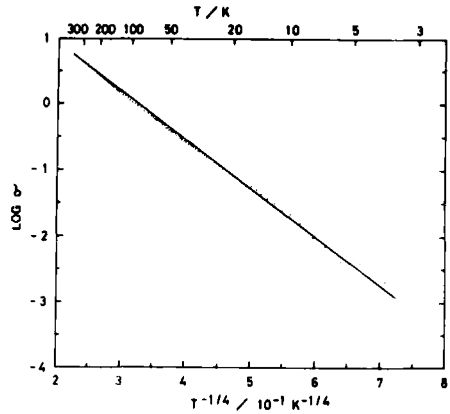

FIGURE 4 Electrical conductivity of polypyrrole film prepared by using Et_4NBF_4 in the form of log σ *vs.* $T^{-1/4}$.

in figure 4, a plot of log σ *vs.* $T^{-1/4}$ gives a straight line over the temperature region of 4.2 - 300 K.

Such behavior suggests a hopping model for the conduction mechanism. Namely, the resistivity ($\rho = 1 / \sigma$) in the film is composed of the sum of the resistivity ($\rho_0 = 1 / \sigma_0$) in the polypyrrole chain and the resistivity ($\rho_h = 1 / \sigma_h$) between the chains,

$$\rho = \rho_0 + \rho_h \,. \tag{8}$$

The intrachain conductivity, σ_0, can be explained by the conduction mechanism for the band model and corresponds to the optically determined value ($\sigma_0 \simeq 126\ \Omega^{-1}cm^{-1}$), which is larger than the conductivity, σ_h, between the chains. Accordingly, the observed conductivity, σ, of the film may be correlated with the conductivity, σ_h, for the hopping electron between the chains. Mott[9] presented a conduction mechanism for a hopping process, which is depicted in figure 5.

Every time an electron moves between the polymer chains, an electron just below the Fermi level jumps normally to a state just above it with energy W, and transfers from the one chain to the adjacent chain, of which the wave function overlaps that of the first chain. The hopping probability is then of the form,

$$\sigma \simeq \nu_{ph} \exp(- 2 \alpha R - W / k T), \tag{9}$$

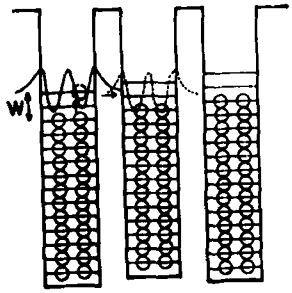

FIGURE 5 A conduction mechanism of the hopping electron between the polypyrrole chains.

where α denotes the rate of a fall-off of the envelope of the wave function. The average spacing, W, between energy levels can be written by the density of states, N(E), and the mean distance, a, between atoms as follows,

$$W = 1/\ (4\pi/3)\ a^3\ N(E) \quad . \tag{10}$$

If $a \simeq R$, the maximum conductivity can be found at $R \simeq (9/8\pi\alpha kTN(E))^{1/4}$ and can be expressed by the following equation,

$$\sigma \simeq A \exp\{ - (Q / k T)^{1/4} \} \quad . \tag{11}$$

A good consistency between the observed and the theoretical relation of log σ *vs.* $T^{-1/4}$ means that the mechanism of the conduction of polypyrrole films can be explained by a hopping model.

ABSORPTION SPECTRA OF POLY(4,4'-BIPHENYLYLENE)[11]

Poly(4,4'-biphenylylene) was readily prepared by heating a suspension of the 4,4'-benzidinebis(diazonium)chloride - CuCl complex in pure water as is shown in figure 6. Poly(4, 4'-biphenylylene) was identified to be a copolymer of 1,4-biphenyldiyl and azo-1,4-biphenyldiyl compounds (x : y = 4 : 1). However, the visible absorption spectra of this polymer may be considered to be similar to that of polyphenylene group.

Pure polymer has the first band at 27000 cm^{-1} (curve 1 in figure 7) which can be assigned to the transition from

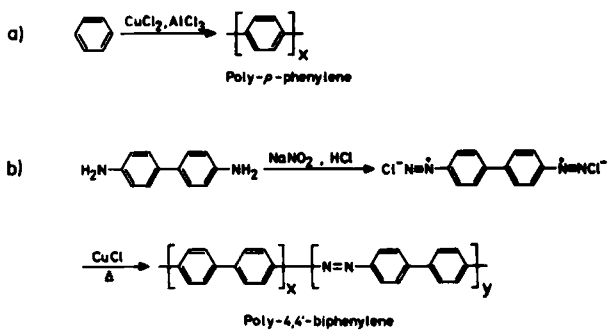

FIGURE 6 Preparation of a) poly(p-phenylene) and b) poly-(4,4'-biphenylylene).

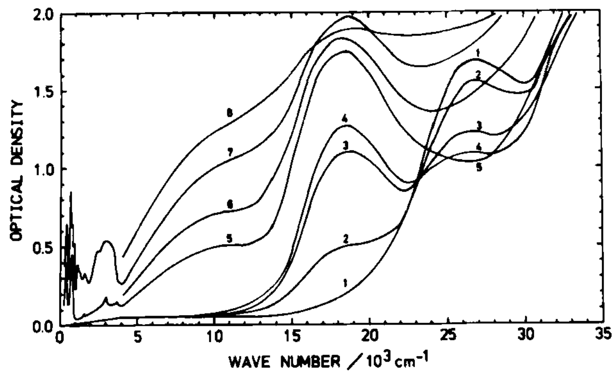

FIGURE 7 Absorption spectra of AsF_5 doped poly(4,4'-bi-phenylylene).

the ε_2 band to the ε_4 band as shown in figure 8-a. Figure 7 shows that the absorption intensity of the 27000 cm^{-1} band decreases and the new band appears at about 18500 cm^{-1} when the polymer is doped with AsF_5. An isosbestic point at 23200 cm^{-1} may be explained by an equilibrium between the highly conjugated polymer($\beta=\beta'$) and the twisting polymer($\beta\neq\beta'$) as shown in figure 8. After that, doping produces the broad band in the region of 5000 cm^{-1} to 10000 cm^{-1} and a back ground absorption in the IR region. The broad band may be explained by the transition band from the ε_2 band to the impurity level. The back ground absorption in the IR region

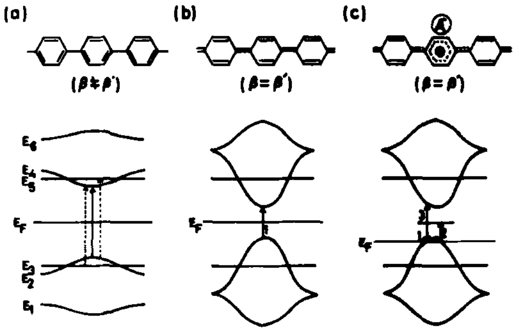

FIGURE 8 Electronic structure of polyphenylene system

can be assigned to the free carrier absorption band which contributes to the conductivity of 2 $\Omega^{-1}cm^{-1}$ for the polymer doped under 200 mmHg of AsF_5 gas during 40 h.

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