Bull. Chem. Soc. Jpn., 54, 2274—2277 (1981) [Vol. 54, No. 8

Optical Properties of Undoped and AsF_5 Doped "Poly(4,4'-biphenylylene)" Films

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(Received September, 3, 1980)

Optical absorption and reflection measurements are carried out on undoped and AsF_5 doped films of "poly(4,4'-biphenylylene)" over a wide wavelength region (300 —50000 cm^{-1}). In the doped polymer, the free carrier absorption band appears in the IR region and the dc conductivity is estimated from the observed spectrum. The obtained value ($\sigma_0=376$ S cm^{-1}) is two orders of magnitude larger than the value ($\sigma_0=2$ S cm^{-1}) observed by the conductivity measurement. The discrepancy may be due to the existence of many cracks on the films.

There is now a large and rapidly growing interest in conducting derivatives of organic polymers. Polymers such as doped polyacetylene,[1] doped poly(*p*-phenylene),[2] doped polypyrrole,[3-5] and doped poly(thio-*p*-phenylene)[6,7] were reported to exhibit high electrical conductivity. Polyacetylene is obtained as flexible and crystalline film, however, it is insoluble and infusible. Other polymers, such as electrochemically prepared polypyrrole, poly(thio-*p*-phenylene) are insoluble in common solvents.

We have recently reported the conducting polymer prepared by AsF_5 oxidation of benzene soluble polymer: "poly(4,4'-biphenylylene)."[8] In the present paper, we describe about the electrical and optical properties of pure and AsF_5 doped "poly(4,4'-biphenylylene)."

Experimental

"Poly(4,4'-biphenylylene)" was readily prepared by heating a suspension of the 4,4'-benzidinebis(diazonium) chloride–CuCl complex in pure water (80 °C, 1 h),[9,10] although poly(*p*-phenylene)[11,12] was synthesized by direct polymerization as is shown in Fig. 1. The dark-brown polymer was then separated into two fractions by extraction with benzene. The soluble portion was fractionally precipitated by adding petroleum ether and separated into two fractions by extraction with acetone.

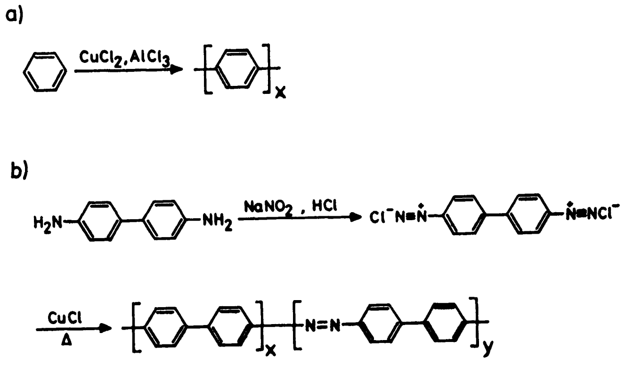

Fig. 1. Preparation of a) poly(*p*-phenylene), b) "poly(4,4'-biphenylylene)."

Reaction of AsF_5 gas with the benzene soluble and acetone insoluble polymer produced a blue-black material and the doped level were adjusted by doping time under 200 mmHg (1 mmHg=133.322 Pa) of AsF_5 gas. For the sample doped for 40 h, the uptake of AsF_5 measured by weight increases corresponds to *ca.* one AsF_5 molecule per phenyl group.

The film was made by dropping the dioxane solution of "poly(4,4'-biphenylylene)" on the four probe plate and then drying. The films were doped with AsF_5 and pumped for about one hour. After that, the doped films were connected to an apparatus for measuring the dc conductivity. The electrical conductivity was measured under nitrogen by the standard four probe method.

The absorption spectra of pure and AsF_5 doped films on a KBr or quartz plate were measured *in vacuo* with Hitachi IR 260-50 (300—4000 cm^{-1}) and Carl Zeiss M4Q (4000—50000 cm^{-1}) spectrophotometers. The reflection measurement of pure thick "poly(4,4'-biphenylylene)" film on a glass plate was made with Hitachi IR 260-50 and a microscopic spectrophotometer (4000—50000 cm^{-1}) made in our laboratory. It consists of an Olympus microscope, a Carl Zeiss Ultrafluar lens (×10), a Nikon crystal mount, a HTV 928 photomultiplier and a PbS tube, and an Intel 8080 microcomputer for data processing.

The Kramers-Kronig (K-K) transformation of the reflection spectra and the best fit of the absorption and reflection spectra by SALS program were made on a Facom M-200 computer of Nagoya University.

Results and Discussion

"Poly(4,4'-biphenylylene)" was identified to be a copolymer of 1,4-biphenyldiyl and azo-1,4-biphenyldiyl compounds (x : y=4 : 1).[9,10] Accordingly, the excited wave function (Ψ_e) of this polymer can be expressed by the superposition of the locally excited configurations of polyphenyl (Φ_{ph}) and azo (Φ_{azo}) groups and the charge transfer (Φ_{CT}) configurations between these two groups.[13]

$$\Psi_e = c_1\Phi_{ph} + c_2\Phi_{azo} + c_3\Phi_{CT} \qquad (1)$$

and the transition moment between the ground (Ψ_0) and excited states can be given as follows,

$$(\Psi_e|M|\Psi_0) = c_1(\Phi_{ph}|M|\Psi_0) + c_2(\Phi_{azo}|M|\Psi_0). \qquad (2)$$

However, the azo group has a weak absorption band at 350 nm whose intensity has been reported to be $\varepsilon=5$.[14] Therefore, the second term of the right side in Eq. 2 can be neglected and the visible absorption spectra of "poly(4,4'-biphenylylene)" may be considered to be similar to that of polyphenyl group. A benzene molecule has six π-electrons which are considered free to delocalize along the phenyl ring. These π-electrons form two single and two double degenerate π-orbitals (ϕ_i, $i=$ 1—6). In the polyphenyl system, π-bands $\psi_i(k)$ can be expressed by the linear combination of π-orbitals in each ring

$$\psi_i(k) = \frac{1}{\sqrt{N}}\sum_{\mathrm{n}} \mathrm{e}^{ikR_{\mathrm{n}}}\phi^i_{\mathrm{n}} \qquad (i{=}1\text{—}6). \tag{3}$$

The energies $\varepsilon_i(k)$ of π-bands are calculated according to MO theory,

$$\begin{aligned}
\varepsilon_1(k) &= \alpha + 2\beta + \frac{1}{3}\beta' \cos\,(ka) \\
\varepsilon_2(k) &= \alpha + \beta - \frac{2}{3}\beta' \cos\,(ka) \\
\varepsilon_3(k) &= \alpha + \beta \\
\varepsilon_4(k) &= \alpha - \beta + \frac{2}{3}\beta' \cos\,(ka) \\
\varepsilon_5(k) &= \alpha - \beta \\
\varepsilon_6(k) &= \alpha - 2\beta - \frac{1}{3}\beta' \cos\,(ka),
\end{aligned} \tag{4}$$

where β is the resonance integral between successive carbon atoms in the same ring and β' in the different ring. All π-electrons are filled in the three bands of $\varepsilon_1(k)$, $\varepsilon_2(k)$, and $\varepsilon_3(k)$ as is shown in Fig. 2-a.

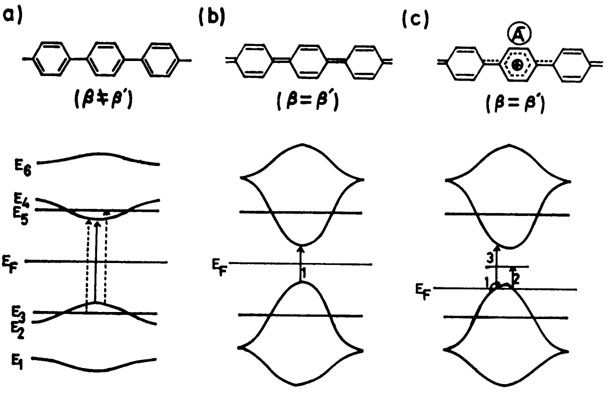

Fig. 2. Electronic structure of the polyphenyl system.

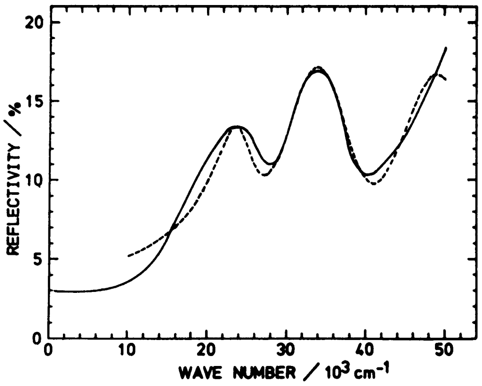

Fig. 3. Reflection spectra of "poly(4,4′-biphenylylene)."
——: Observed, ------: calculated (SALS).

Figure 3 shows the reflection spectrum of the pure polymer film of "poly(4,4′-biphenylylene)." The first band at 24000 cm^{-1} has the reflectivity of 13.4% and the second band at 34000 cm^{-1} has that of 17.1%. The third band is located in the region of higher wave number than 50000 cm^{-1}. Accordingly, the first band at 24000 cm^{-1} can be assigned to the transition from the $\varepsilon_2(k{=}0)$ band to the $\varepsilon_4(k{=}0)$ band. The second band consists of the overlap of two transitions of $\varepsilon_2(k{=}0){\to}\varepsilon_5(k{=}0)$ and $\varepsilon_3(k{=}0){\to}\varepsilon_4(k{=}0)$. The dielectric function of pure "poly(4,4′-biphenylylene)" can be expressed by the following equation.[15]

$$\varepsilon(\omega) = 1 + \sum_j \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}, \tag{5}$$

where

$$\Omega_j = \left(\frac{4\pi N_j e^2}{m} f_j\right)^{1/2}. \tag{6}$$

ω_j and γ_j are the transition energy and the band width of the j-th band. N_j is the number density of electron contributing to the j-th band, f_j is the oscillator strength of the j-th band and m is the electron mass.

The reflectivity R can be expressed by using the dielectric function of Eq. 5,[15–17]

$$R = \frac{1+|\varepsilon| - \sqrt{2(|\varepsilon|+\varepsilon_1)}}{1+|\varepsilon| + \sqrt{2(|\varepsilon|+\varepsilon_1)}} \tag{7}$$

and

$$|\varepsilon| = \sqrt{\varepsilon_1^1 + \varepsilon_2^2}, \tag{8}$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric function. The parameters Ω_j, ω_j, and γ_j of undoped "poly(4,4′-biphenylylene)" can be determined by the best fit of the calculated reflection values to the observed spectra. The obtained parameters are shown in Table 1 and the best fit curve is plottted in Fig. 3 for comparison with the experimental curve.

The absorption coefficient $\alpha(\omega)$ based on these parameters can be obtained by the following equations,[15]

$$\alpha(\omega) = \frac{4\pi}{cn(\omega)}\omega\varepsilon_2(\omega) \tag{9}$$

and

$$n(\omega)^2 = \{\sqrt{\varepsilon_1^2+\varepsilon_2^2}+\varepsilon_1\}/2. \tag{10}$$

In Fig. 4, the obtained absorption spectrum is depicted together with the solution spectrum and the absorption spectrum calculated by the Kramers-Kronig transformation of the reflection spectrum.

Figure 5 shows the temperature dependence of the conductivity of the films doped with various concentrations of AsF$_5$. The room temperature conductivity was about $\sigma \simeq 2$ S cm^{-1} for the film doped for 40 h under

TABLE 1. BEST FITTED PARAMETERS OF THE DIELECTRIC FUNCTION OF PURE AND AsF$_5$ DOPED "POLY(4,4′-BIPHENYLYLENE)" FILM

Band	Pure film			AsF$_5$ doped film[a]		
j	Ω_j/cm^{-1}	ω_j/cm^{-1}	γ_j/cm^{-1}	Ω_j/cm^{-1}	ω_j/cm^{-1}	γ_j/cm^{-1}
1	16263.5	23742.5	5829.2	8678.9	0.0	3336.3
2	25736.2	32046.3	9400.9	26102.6	8933.6	10623.7
3	21906.9	44669.9	11791.3	25257.7	17488.5	7623.6
4				149223.0	51715.0	28382.0

a) Data of the "poly(4,4′-biphenylylene)" doped for 22 h under 200 mmHg of AsF$_5$ gas.

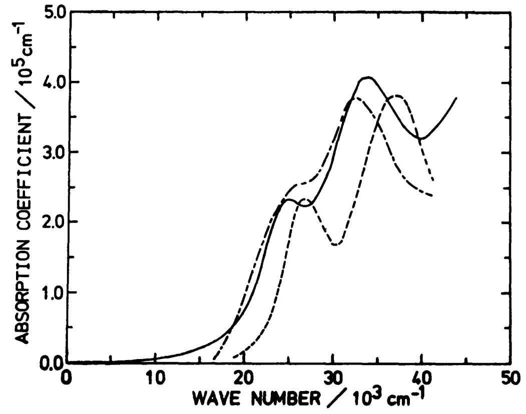

Fig. 4. Absorption spectra of pure "poly(4,4′-biphenylylene)."
------: Observed (dioxane solution), ——: calculated (SALS), – – –: calculated (Kramers-Kronig).

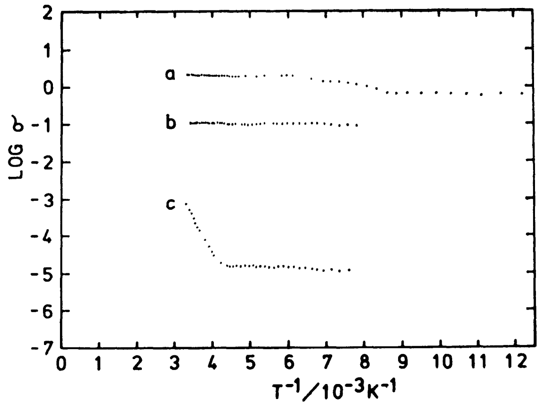

Fig. 5. Temperature dependence of the conductivity of the films doped with various concentrations of AsF_5.
a: 40 h, b: 20 h, c: 3 h.

200 mmHg of AsF_5 gas, although the conductivity for the undoped material is less than 10^{-4} S cm^{-1}. The plots of log σ *vs.* $1/T$ give straight lines near room temperature and the approximate thermal activation energy can be determined by the initial slope of $1/T$ plots. The resulting activation energy is about 0.36 eV for the sample doped for 4 h and reaches to almost zero for the films doped for more than 20 h.

Figures 6 and 7 are the visible and IR absorption spectra of thin "poly(4,4′-biphenylylene)" films doped with various concentrations of AsF_5. On doping the film with AsF_5, the absorption intensity of the 27000 cm^{-1} band decreases and the new band appears at about 18500 cm^{-1}. An isosbestic point at 23200 cm^{-1} may be explained by an equilibrium between the highly conjugated polymer ($\beta=\beta'$) and the twisting polymer ($\beta\neq\beta'$). That is, each phenyl ring seems to twist about the central bond in the pure polymer and $|\beta'|$ is smaller than $|\beta|$. For the lightly doped polymer, each phenyl group lies in the same plane and π-electrons become to be highly conjugated between phenyl rings ($|\beta'|=|\beta|$). As a consequence, the first band at 27000 cm^{-1} shifts to the shorter wave number region as is shown in Fig. 2-b. After that, doping produces the broad band in the region of 5000 cm^{-1} to 10000 cm^{-1} and a background absorption in the IR region in addition to the vibrational bands of $AsF_6^-H_3O^+$ at 400, 700, and 3000 cm^{-1}.[18] Figure 2-c shows that the Fermi level comes below the top of $\varepsilon_2(k)$ band by transfering a few π-electrons to AsF_5 molecules and the impurity level appears at the midpoint of the gap between the $\varepsilon_2(k)$ and $\varepsilon_4(k)$ bands. This broad band may be explained by the transition band from the $\varepsilon_2(k)$ band to the impurity level.

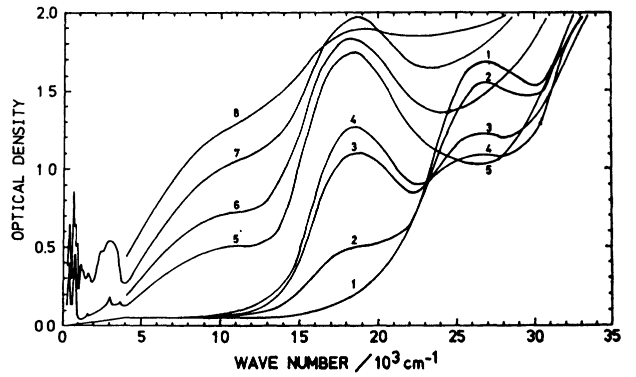

Fig. 6. Absorption spectra of AsF_5 doped "poly(4,4′-biphenylylene)."
1: 0 min, 2: 5 min, 3: 30 min, 4: 1 h, 5: 3 h, 6: 19 h, 7: 22 h, 8: 32 h.

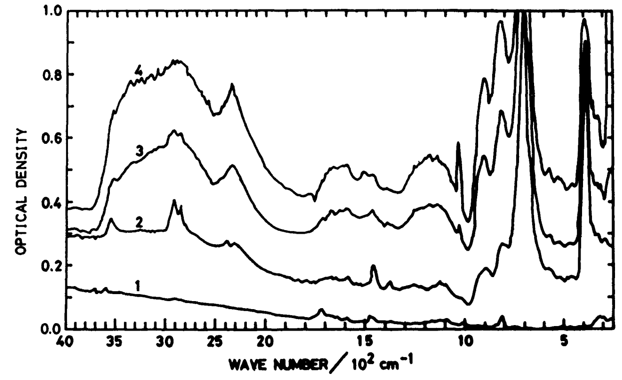

Fig. 7. IR absorption spectra of AsF_5 doped "poly(4,4′-biphenylylene)."
1: 0 min, 2: 2 h, 3: 4 h, 4: 22 h.

The maximum absorption coefficient of the 27000 cm^{-1} band of the pure film is determined to be 2.6×10^5 cm^{-1} in Fig. 4. Accordingly, the absorption coefficient of the AsF_5 doped film can be estimated as is shown in Fig. 8. Then, the parameters of the dielectric function of the doped film were decided by the optimum fit of Eq. 7 to the experimental data. The best fitted parameters are shown in Table 1. The calculated absorption spectrum based on these values is plotted for comparison with the experimental curve in Fig. 8.

The band 1 has the zero transition energy $\omega_j=0$ and is the back ground absorption in the IR region which can be assigned to the intraband transition. This means that doping makes the π-electrons in the polymer to be transferred to the AsF_5 molecule according to the following reaction,

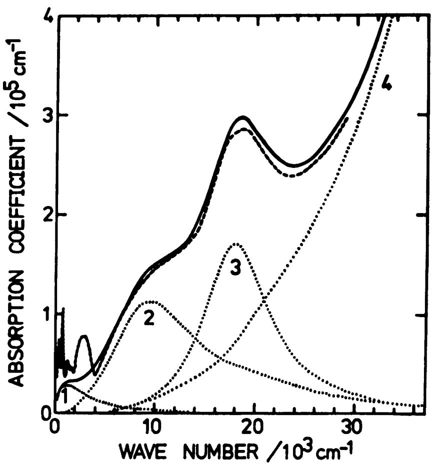

Fig. 8. Absorption spectra of "poly(4,4'-biphenylylene)" doped with AsF_5 (22 h).
——: Calcualted (SALS), ⋯⋯: calculated(SALS), ------: observed.

$$3AsF_5 + 2e \longrightarrow 2AsF_6^- + AsF_3 \qquad (11)$$

and one of the π-bands becomes partially unfilled. The plasma frequency of the first band is given in Table 1.

$$\Omega_1 = \left(\frac{4\pi Ne^2}{m^*}\right)^{1/2} = 8678.9\ \mathrm{cm}^{-1} \qquad (12)$$

Then, the number density (N) of the free carriers in the AsF_5 doped film can be estimated to be about $8\times10^{20}\ \mathrm{cm}^{-3}$ by substituting $m^*=m$ to the next equation,

$$N = \frac{\Omega_1^2 m^*}{4\pi e^2}. \qquad (13)$$

This value corresponds to 1.4% of the total π-electrons ($6\times10^{22}\ \mathrm{cm}^{-3}$) in the polymer film, judging from the density of the film ($\rho=1.38\ \mathrm{g/cm^3}$). This means that a few holes in the unfilled π-band contribute to the transport phenomenon.

Furthermore, the dc conductivity, σ_0, is given by the following equation,[15)]

$$\sigma_0 = \frac{\Omega_1^2}{4\pi\gamma_1} \qquad (14)$$

and is calculated by using the observed plasma frequency, Ω_1, and the band width, γ_1. The obtained value ($\sigma_0\simeq376\ \mathrm{S\ cm^{-1}}$) is two orders of magnitude larger than the observed values ($\sigma_0\simeq2\ \mathrm{S\ cm^{-1}}$) of the dc conductivity of AsF_5 doped films. The discrepancy may be due to the existence of many cracks on the film.

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