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# LADDER POLYMERS AS NEW POLYMERIC CONDUCTORS

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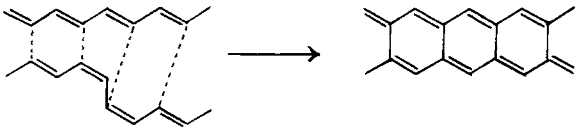
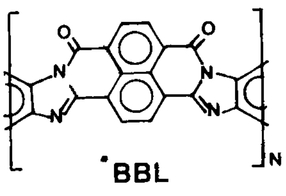
Electrical conductivity of heteroaromatic ladder polymers of the benzimidazobenzophenanthrolin type, BBL and BBB, and the phenothiazine type, PTL, was investigated. Doping studies of initially insulating BBL and BBB polymer films were carried out using various electron donors and acceptors. PTL polymer showed unexpectedly high conductivity ( $\sigma=10^{-5}$ $ohm^{-1}$ $cm^{-1}$); doping with $ASF_5$ brought about a minor increase in conductivity. With BBL and BBB polymers, a negligible doping effect was observed with halogens, a significant effect with $AsF_5$ and a marked effect with $SO_3$ ( $\sigma=1x10^{-2}$ $ohm^{-1}$ $cm^{-1}$) and $H_2SO_4$ ( $\sigma=2$ $ohm^{-1}$ $cm^{-1}$). A large increase of the thickness and the weight in the doped film is probably due to the planar layered structure of the polymers. The room temperature conductivity of potassium metal-doped (at 300-500°C) BBL film was $2x10^{-1}$ $ohm^{-1}$ $cm^{-1}$, while the potassium naphthalide-doped sample had a conductivity of 1 $ohm^{-1}$ $cm^{-1}$. In the acceptor-doped samples, band broadening was observed in the 1700 (C=O) and 1580 (C=N) $cm^{-1}$ regions, resulting from their frequency shifts (25 30 $cm^{-1}$) toward higher wave numbers. This can be explained by an increase of force constants in C=O and C=N bonds by $\pi$-polarization induced by the complexation with the acceptors on the imino-nitrogen which is the primary complexation site. The exact same band broadening was observed around these frequencies in protonic acid-doped samples. Therefore, acid doping is interpreted as a Lewis acid-type charge-transfer complexation, not merely a protonation.

## INTRODUCTION

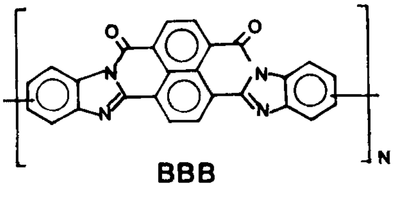
Graphite is a unique model for organic conducting polymers. The anisotropy of its electrical conductivity[1] is attributed to the oriented layered structure of two dimensional basal planes, along which electric current is carried with a great preference. The high conductivity of some synthetic polymers such as polyacetylene is said to be related to the chain backbone planarity[2] which can maximize the orbital overlap. This hypothesis is supported by the observation[3] that the conductivity drops sharply when two methylacetylene units are incorporated as comonomer in the polyacetylene chain.

The coplanarity of chain molecules can best be achieved when two randomly conformed conjugated chains are covalently bonded together as a rigid ladder structure. The solid state order of this conjugated ladder structure can be a mimic of graphite. Many ladder polymers however, are known to be insoluble and/or infusible, except for a few of the heteroaromatic ladder polymers such as the benzimidazobenzophenanthrolin type, BBL[4] and BBB[5], which are soluble and film-forming. In the form of a film, these polymers have nearly a two-dimensional layered structure with Bragg spacings of 3.5 and 7.5Å.



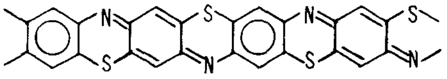


BBL



BBB

This scattering is the result of orientation[6] derived from the high degree of ordered packing of the material. Hence, a study of the conductivity of this class of polymers is well worth while. A more elaborate ladder structure polymer, a phenothiazine type, PTL, was synthesized for the same purpose.



PTL

In our previous communication[7], we reported the preliminary results of BBL and BBB doping studies. In this article, we describe the details of doping studies with a particular interest in charge-transfer interactions between the polymers and dopants.

## EXPERIMENTAL

### Materials Synthesis

BBL polymer was synthesized by polycondensation reaction of naphthalene-1,4,5,8-tetracarboxylic acid with 2,3,5,6-tetraaminobenzene, according to the known procedure[4]. BBB polymer (kindly provided by Professor G. C. Berry, Carnegie-Mellon University) was prepared[5] from napthalene-1,4,5,8-tetracarboxylic acid and 3,3' diaminobenzidine. The films of the polymers can be made by filtration, casting, or spray techniques from methanesulfonic acid solution. The resulting films have a golden luster with a high tensile strength ($1 \times 10^4$ lb/in$^2$) and high thermal stability ($\geq 500°C$). PTL polymer was prepared by polycondensation reaction of 2,5-diamino-1,4-benzene-dithiol and 2,5-dichloro-p-benzoquinone. The product is a black-colored insoluble polymer. The details will be published elsewhere.

### Doping Reaction

The doping of an electron acceptor was carried out by charging the dopant into a tube containing the polymer sample under vacuum. The conductivity changes were monitored under the variable conditions of pressure and temperature versus elapsed time. For sulfuric acid (98%) doping, the acid was vacuum-pumped over the polymer film at ca. 35°C, and for $SO_3$ doping, fuming sulfuric acid (30% $SO_3$) was warmed to ca. 35°C to feed dry $SO_3$ into the sample tube. For the electron-donor doping, a solution of potassium naphthalide (0.5 M) in THF was transferred from a reservoir into the reaction tube where the sample was mounted on four probe wires. After a time, the doping solution was transferred back to the reservoir, the sample was washed with several aliquot of dry THF distilled out of the doping solution in the reservoir and dried under vacuum before measurement of the conductivity. For metallic potassium doping, the reaction was conducted in a specially designed vacuum tube in which a mass of freshly distilled metallic potassium and a sample film on four probe wires were kept apart from each other while a temperature difference between them was maintained using a double furnace (at 300~500°C).

## Conductivity Measurements

In most cases the electrical conductivity of polymer films ca. 0.2 mm in thickness was measured by a standard four point probe system made from four parallelly aligned wires on which a film sample was mounted and pasted with Electrodag to secure the contact. For powder samples a compaction disk (8mm diameter and 0.5 mm thickness) was made and the standard four point probe technique was applied for the conductivity measurement. Conductivities were also measured using a commercial pressure-loaded, metal-contact, four point probe.

## Spectroscopy

For the vibrational spectroscopy, thin films (ca.3 x $10^{-2}$ mm in thickness) were used. They were lightly ($\leq$10%) doped, since originally transparent BBL and BBB films become increasingly opaque in the IR with doping. The doped films were sandwiched between two pieces of round sodium chloride plates and the interface was then sealed with melted wax. These procedures were carried out in a dry box. FTIR spectra of various doped samples were recorded using a Digilab FTS-15C. For the electronic spectra (using a Shimadzu Double-Beam UV-200S spectrophotometer), extra thin films, (ca. 1 x $10^{-3}$ mm) were used, which were cast from methanesulfonic acid solution on the inside surface of a quartz cell by vacuum evaporation of the solvent. The cast films were very briefly exposed to the doping agents immediately before taking the spectra.

## RESULTS AND DISCUSSION

BBL and BBB polymers are insulators, but thermal annealing gave some conductivity. When BBL polymer film, for example, was thermally annealed at ca. 500°C, 24 hrs in vacuo, it became semiconductive ($\sigma \simeq 10^{-6}$ ohm$^{-1}$ cm$^{-1}$) without appreciable changes in dimension and appearance, except that the original golden luster became slightly greyish. The reason for this is not clear, but is suspected to be due to an increased structural perfection of the ladder. When treated with Lewis acids or protonic acids, the golden colored films became green, dark green, or green-black depending on the doping level. Halogens such as iodine and bromine had a negligible doping effect on these polymers, which indicates that they are insufficiently strong oxidizing agents; a green color of the doped films faded away in a short while after the doping was discontinued. Results of doping with other reagents are summarized in Table 1. A minor doping effect was observed with $BF_3$ and a significant effect with $AsF_5$. In the $AsF_5$-doped samples, $AsF_6^-$ anion was confirmed from the characteristic absorption at 705 cm$^{-1}$ as in other $AsF_5$-doped polymers. A marked enhancement in the conductivity was observed with sulfuric acid or with $SO_3$. With either treatment, the doped films remained flexible but underwent an enormous change in thickness and a concomitant weight change. After two days of the acid doping the film thickness increased 20-25% and the weight increase was nearly 200%, corresponding to the molar ratio of $H_2SO_4$ (or $SO_3$) with respect to the repeating unit of the polymers of approximately 6:1. Such a high doping level in the polymer is suspected to result from the layered structure of the polymer film. Another observation relating to the layered structure was that in the case of potassium doping the doped sample conductivity changed reversibly depending on the sample temperature when the potassium temperature was kept constant. Such a behavior of these polymers is reminiscent of the staging effect of graphite intercalation.

PTL polymer consists of a nearly planar structure of diphenodithiazine units, and the electronic structure of this molecule is assumed to be similar to that of phenothiazine which is known[8] for its ease of oxidation and subsequent formation of stable radical cations. PTL

TABLE 1. Conductivities (at room temperature) of BBL, BBB and PTL polymers doped with various doping agents

| Polymer | Dopant | Conductivity (ohm$^{-1}$cm$^{-1}$) | Appearance | [Dopant] per BBL Unit |
|---|---|---|---|---|
| BBL (BBB) | None* | $10^{-12}$ $(10^{-14})$** | Gold | |
| | $I_2$ | $10^{-10}$ | Brown | |
| | $Br_2$ | $10^{-10}$ | Brown | |
| | $BF_3$ | $10^{-7}$ | Blue-Green | |
| | $AsF_5$ | $10^{-3}$ | Dark Green | |
| | $SO_3$ | $1\text{x}10^{-2}$ $(10^{-3})$** | Dark Green | 6 |
| | $H_2SO_4$ | 2.1 (1)** | Green-Black | 6 |
| | K (Metal) | $2\text{x}10^{-1}$ | Silver-Black | |
| | $\overset{+}{\mathrm{K}}$ $\overset{\overline{\cdot}}{\mathrm{Naph}}$ | 1.1 | Green-Black | |
| PTL | None | $3\text{x}10^{-5}$ | Black | |
| | $AsF_5$ | $10^{-3}$ | Shiny Black | |

*When undoped BBL film is thermally annealed, it becomes a semi conductor:

200°C 24 hrs. in vacuo, $10^{-9}$ ohm$^{-1}$ cm$^{-1}$
500°C 24 hrs. in vacuo, $10^{-6}$ ohm$^{-1}$ cm$^{-1}$

**Values of BBB Polymer

showed an exceptionally high intrinsic semiconductivity. This is mainly the result of long-range coplanarity of the conjugated ladder polymer besides the electronic structure of phenothiazine units. However, conductivities of some partial ladder polymers[8] are known to be nearly comparable to those of full ladder polymers as in the case of BBB and BBL conductivities. This suggests that the partial ladder polymers assume a rigid planar configuration as do full ladder polymers in the solid state. On the other hand, less rigid but potentially planar polymers like poly(9,10-anthracene diylidene)[10] in which anthracene rings are linked with double bonds exist virtually as insulators, due probably to non-planar conformation caused by torsional motions. A preliminary experiment of doping with $AsF_5$, however, revealed only a minor increase in the conductivity. The reason is not clear. Further doping studies of this polymer are underway.

Conductivity changes of BBL polymer versus doping time are illustrated in Fig. 1. The low doping

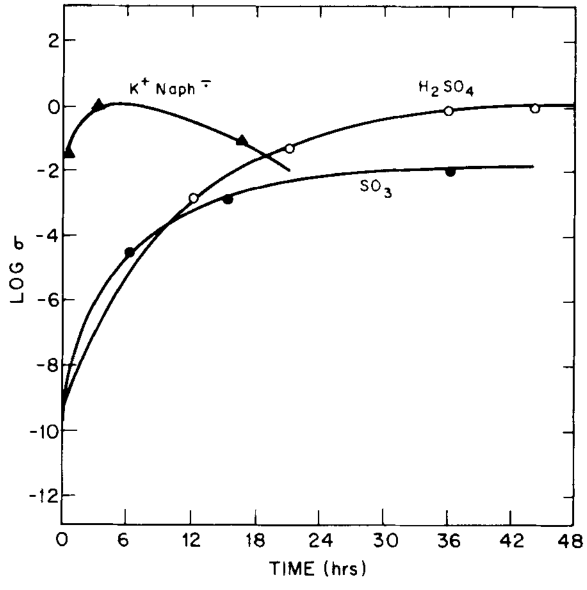


FIGURE 1 Conductivity changes of BBL polymer versus time of exposure to doping agents at room temperature for $K^+Naph^-$ and at 35°C for $H_2SO_4$ and $SO_3$

rate by election acceptors such as $H_2SO_4$ and $SO_3$ is partly due to the low dopant pressure in the reaction but also due to the unusually high doping level required for the conductivity as shown in Table 1. This may be related to the insufficiently low ionization potential of BBL polymer. On the other hand, potassium naphthalide doping was much faster and a maximum conductivity resulted in a few hours while further doping decreased the conductivity, suggesting that a further reaction is progressing in the doped polymer. BBL polymer was found to be very stable to electrochemical cycling,[11] and it exhibited no change in wave shape during numerous reduction-oxidation cycles in sulfuric acid over a period of weeks in air. This implies that electrochemical reduction is different from the reduction by potassium naphthalide. As has been observed in other conducting polymers, the treatment of acceptor-doped BBL polymers with ammonia rapidly reduced the sample conductivity.

As shown in Table 1, sulfuric acid doping is the most effective. The question is whether sulfuric acid acts as a protonic acid or an oxidizing agent, although sulfuric acid-doped sample colors (dark green) are the same as other acceptor-doped ones. IR spectra of various doping samples are compared in an attempt to identify the primary site of polymer-dopant interactions. Samples were lightly doped to moderate the optical transmission, because the spectra of heavily doped samples show a strong featureless absorption throughout the infrared region, and this tendency is marked with sulfuric acid doping. This broad absorption band is known to be typical of conducting polymers. As shown in Fig. 2, the largest shifts are observed in two bands, 1583 $cm^{-1}$, $\nu$ (C=N), and 1700 $cm^{-1}$, $\nu$(C=O), in the lightly doped samples. The band broadening in these particular frequency regions is toward higher wave number, while other bands remain at the same band position with a relative reduction in transmittance upon doping. This band broadening is interpreted to be a result of the characteristic frequency shift of the groups responsible for complexation with the doping agents and thus represents a vibrational mixing of "free" and "complexed" states of the particular components in the lightly-doped polymer. The band broadening, or band overlap, is even greater with an increase of doping level as seen in the spectra of $SO_3$-doped samples where sample 1 is less doped than sample 2. The pattern of the band

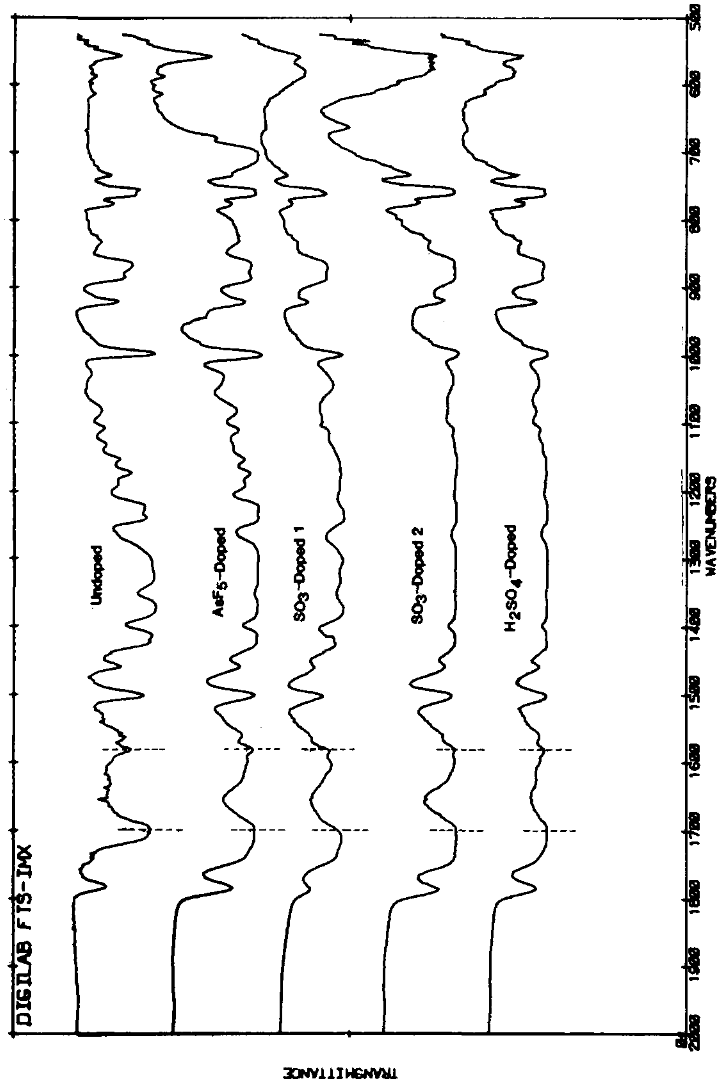
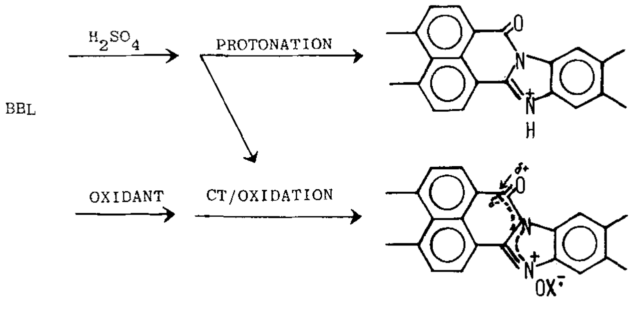


FIGURE 2. FTIR spectra of lightly doped and undoped BBL polymers

broadening is the same regardless of the acceptor species used, suggesting that the interaction mode of sulfuric acid is the same as that of other acceptor dopants. Moreover, the spectra of other protonic acid-doped samples showed the same behavior as observed with the $H_2SO_4$-doped sample. The spectral change seen in doped BBL polymer was also observed in doped BBB polymer.

The blue shifts (25-30 $cm^{-1}$) of the particular frequencies, 1583 and 1700 $cm^{-1}$ ($\nu$(C=N) of imidazole and $\nu$(C=O) of amide, respectively) provide a useful probe for the complexation site. Obviously, this amide carbonyl does not act here as donor for the complexes with Lewis acids and even with sulfuric acid; if it did, the carbonyl stretching frequency should shift to a lower wavenumber. Therefore, the nitrogen of the imidazol moiety may be the donor site. However, the possibility for other compexation sites cannot be excluded at high doping level because the unusually heavy acceptor doping required for high conductivity (Table 1) exceeds the stoichiometry of imino-nitrogen. Nitrogen-containing donors of heterocyclics such as pyridines and imidazoles are known to show[12] a negligible frequency change upon protonation, but a considerable frequency shift to higher wavenumber takes place when they are complexed to metal halides and halogens. In contrast to that, the IR spectra (particularly the region around 1583 $cm^{-1}$) of $H_2SO_4$-doped samples are not different from those of other Lewis acid-doped samples, suggesting that the sulfuric acid doping is not simple protonation but a type of charge-transfer (CT) complexation. A question arises then as to how to explain the shift of C=O band to higher frequency as a result of the complexation. Such a frequency shift to higher wavenumber is a consequence of an increase in the stretching force constant of the C=O band. The increase in this case can be explained in



terms of a π-polarization mechanism[13] by which an electron-withdrawing doping species on the imino nitrogen upon complexation induces a polarization of the amide carbonyl group. This results in a strengthening of the C=O force constant and a charge redistribution in the extended system. This situation is similar to the case of pyridine-metal halide complexes where the CN stretching band shifts to higher frequency,[14] particularly so in the complexes of the pyridines substituted by electron withdrawing groups. The electronic spectra of such acceptor-doped samples show slight blue shifts around 580 and 360 nm. The reason is unclear because this is contrary to the trend commonly found for conducting polymers. The intensity of bands around 350 nm decreases, whereas the intensity of bands around 550 nm increases, an effect which may be associated with the free carrier formation.

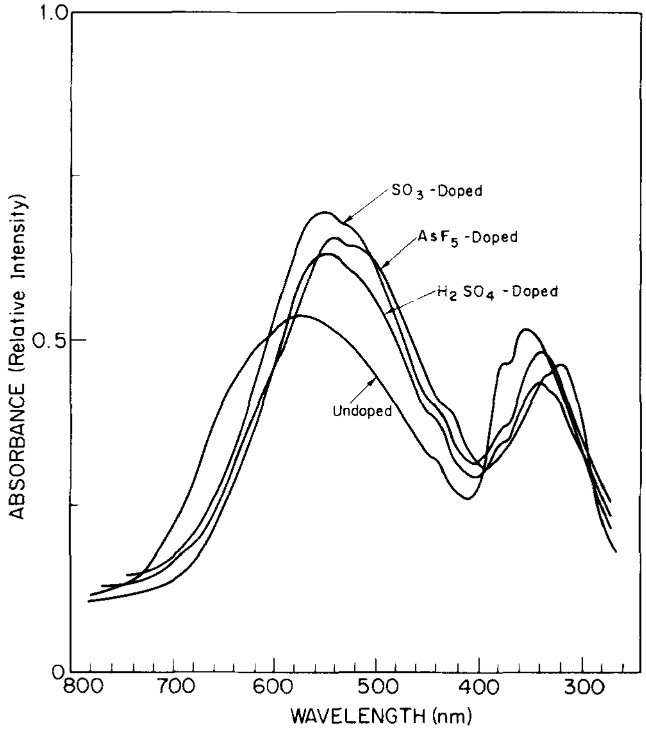


FIGURE 3 UV-visible spectra of lightly doped and undoped BBL polymers

The conductivity of acid-doped BBL polymer samples deteriorated in air down to $10^{-3}$ $ohm^{-1}$ $cm^{-1}$ after one week, but very slowly thereafter. A potassium napthalide-doped sample was very unstable even in vacuo, probably because of chemical degradation which might destroy the ladder structure, while a postassium-metal doped sample was fairly stable; the conductivity change was negligible in vacuo over six months and decreased one order of magnitude in air over one month.

## CONCLUSION

Electrical conductivity of heteroaromatic ladder polymers, BBL, BBB and PTL was studied by doping with Lewis acids, protonic acids and potassium metal and salt. Ladder structures including partial ladders are found to enhance polymer conductivity. The mode of acid doping suggests a Lewis acid type complexation and not merely a protonation. Complexation with acceptor dopants is found to occur on the imino-nitrogen. The high dopant concentration required for maximum conductivity is probably a consequence of the layered structure of ladder polymers.

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