PHOTOCONDUCTIVE OPS-POLYIMIDES AND THEIR APPLICATIONS FOR OPTO-ELECTRONIC DEVICES (I): XEROGRAPHIC PHOTORECEPTORS

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OPS-Polyimides (OPS-PI), which are composed of a series of thiophenylene moieties, \(-(\text{C}_n\text{H}_3\text{S})_n\)- oligo-p-phenylene sulfide (OPS), and imide groups, have been designed on the base of our proposed photoconduction mechanism and showed a high sensitivity. OPS-PI consist of two different functional groups. An imide group in OPS-PI generates carriers by absorbing the visible light. And carriers are transported in the paths formed by OPS segments. Carrier transport mechanism will be discussed on the band-conduction model. The sensitizing in the near infrared region by H_2Pc doping is proposed on the base of the energy diagram. The application of OPS-PI to xerographic photoreceptors is shown including doped OPS-PIs.
1. Introduction

Previously, we reported that we have succeeded in synthesizing a new class of photoconductive polymers based on the molecular design using highly crystalline and stacked phenylene sulfide molecules. Figure 1 shows chemical structures of novel photoconductive polyimides, oligo-p-phenylene sulfide polyimide (OPS-PI), which are composed of a series of thiophenylene moieties, -C_6H_4S-, and imide rings. OPS-PIs can have high sensitivity only in the crystalline phase. Coplanar conformations of polymer chains lead by the crystallizing give the overlapped π orbitals perpendicular to the polymer chains. First in the next chapter, the model of molecularly separated functions in photoconduction is given and discussed with the data on photocurrent measurements and the band structure of OPS-PI in the crystalline phase.

Organic photoconductors (OPCs) and photoconductive polymers have been widely studied for applying to xerographic photoreceptors of copies or printing machines. Previous our paper showed that OPS-PIs had high sensitivity in the visible light region and could be comparable to other commercial OPCs. In the chapter 3, the first application of OPS-PI to xerographic

![Chemical Structures of OPS-PIs](image)

Fig. 1 Chemical Structures of OPS-PIs
experimentally that both the absorption and photoconductivity of the OPS-PI film increased in the crystallizing. The optical energy gap, \( E_g \), in BPDA-Ph3, the most sensitive OPS-PI, changed from 2.5 eV for the amorphous phase to about 1.85 eV for the crystalline phase. So the new absorption band is imagined to be made by the crystallizing. The photosensitivity of BPDA-Ph3 increased with four orders of magnitude or more in that crystallizing. We have proposed that this remarkable changes in optical and electrical properties were lead by the coplanary conformations of OPS-PI, which overlap \( \pi \) orbitals between polymer chains.

One important experimental result supporting our model was given by the model polymer, in which sulfur atoms in OPS segments were replaced by the oxygen atoms. The model polymer in the crystalline phase showed much less photosensitivity with three orders of magnitude and a small \( E_g \) of 2.3 eV. This result indicated that OPS segments in the crystalline phase play a very important role of photoconductivity. Particularly the sulfoire atoms between the benzen rings have a key to induce the novel electronic structure of OPS-PI.

2-2. Electronic structure model

We will propose the electronic structure of BPDA-Ph3 as a particular example of OPS-PI by assuming the band-conduction. Conduction and valence bands are postulated to be arrised from extensively overlapped \( \pi \) orbitals of imide rings, benzens and sulphure atoms between polymer chains. Using the value of \( E_g \), 1.85 eV, given by the observation of UV visible absorption spectra, the value of ionization potential \( (I.P.) \), 5.9 eV evaluated by Surface Analyzer AC-1M (RIKEN KEIKI Co.,Ltd.) and the assumption of the fermi level \( (E_f) \) at the middle gap, the electronic structure was made as shown in figure 3. In this figure, the OPS-PI film is sandwiched between the electrodes of Au (work function of 5.4 eV) and Al (work function of 4.2 eV).

We examined the postulated electronic structure by the photocurrent measurements of BPDA-Ph3 thin film samples on Al substrates. They were covered with evaporated Au semitransparent
Fig. 3 Electronic Structure of BPDA-Ph3 sandwiched between Au and Al electrodes

Fig. 4 Photocurrents as a function of (a) applied voltage and (b) wavelength
top electrodes, which constructed the sandwich-type cells. Figure 4 (a) shows the voltage dependence of photocurrents. The magnitude of photocurrent ($i^+$) in illuminating under the positively biased Au electrode ($Au^+/OPS-PI/Al$) was much larger than that of photocurrent ($i^-$) in illuminating under the negatively biased Au electrode ($Au^-/OPS-PI/Al^+$). In these measurements, short wavelength light of 400nm was irradiated using the bandpass filter, so the light absorption was made near the front region of semitransparent electrode of Au. From the data on the absorption coefficient against the wavelength of 400 nm, more than 90% of electron-hole pairs were made between the depth of 0.1 μm in the film. Carriers to be transported through the bulk film were holes in the positively biased case ($Au^+$). On the contrary, in the negatively biased case ($Au^-$) electrons were moved. So as shown in fig. 3 (a), OPS-PI can move holes much more easily in the film than electrons and majority carriers are holes.

Photocurrents ($i^+$ and $i^-$) changed with the n-th power of the applied voltage ($i \propto V^n : n=2.5 \sim 4.5$), which indicated the Onsager's type photogeneration mechanism, which has often well explained the photogeneration efficiency in organic materials.89

Figure 4 (b) shows the spectral dependence of photocurrents ($i^+$ and $i^-$) in applying the voltage of 20 v. The $i^+$ shows the flat profile in the visible light region of wavelengths between 400-600 nm and the rapid decrease over the absorption edge of the film, $E_g=1.85$ eV ($\lambda =670$nm). This result indicated that the absorption edge of the film coincidented with the mobility edge of the carrier transport. So it might be cleared that BPDA-Ph3 had a band structure. The $i^-$ shows the photocurrent peak at the wavelength of 520 nm. In illuminating the light with longer wavelength, electron-hole pairs can be generated in the whole film and the number of holes transported in the film are increasing in negatively biased case ($i^-$). The appearence of photocurrent peak in the $i^-$ can be reasonably explained on the condition of larger mobility of hole than that of electron.

We examined the energy transport and dye sensitizing effects by doping the phthalocyanine complexes (metal-free phthalocyanine, $H_2Pc$, Copper phthalocyanine, $CuPc$). The complexes
are well known materials often used for sensitizing of OPCs in the near infrared region. The relative energy levels of LUMOs and HOMOs of the dopants are also shown in fig. 3. Doping of H2Pc with the ratio of less than 1 weight % to the OPS-PI gave the extreme increase of the sensitivity in the wavelength region of 600-900 nm. On the contrary, CuPc showed no significant increase of sensitivity. As shown in the postulated energy diagram of OPS-PI and dopants, HOMO of H2Pc can give holes generated by absorbing the long wavelength light to the valence band of OPS-PI. Then OPS-PI transports holes in the valence band. On the other hand, electrons in the conduction band dissipated from LUMO of CuPc can not travel in the OPS-PI because of a low ability of electron transfer.

From these experimental results, we thought that the assumed electronic structure as shown in fig. 3 explained the optical and electrical properties of BPDA-Ph3. The discussions in this chapter, we assumed the band-type conduction of polymers. The band-type conduction needs the microscopic mobility larger than a value of 1 cm²/Vsec.9 Well known photoconductive polymer PVK has a microscopic mobility of about 2 × 10⁻² cm²/Vsec, so the band-conduction mechanism is not valid. In PVK there assumed to be intermolecular jump mechanism of conduction. The carriers may move along the polymer chains and may jump from one chain to another. To make sure that OPS-PIs satisfy the condition of microscopic mobility mentioned above or not, further investigations will be needed.

3. Application to xerographic photoreceptors

Xerographic photoreceptors of OPS-PIs were made according to the same method in ref. 2. Figure 5 shows the typical light-decay curve of the surface potential of BPDA-Ph3 with the film thickness of 7 µm. Measurements were performed by Electrophotographic Paper Analyzer model SP-428 (Kawaguchi Electronic Works). In positively charging up the film by +9 kV corotron charger, the initial surface potential (Vo) was +760 V and the exposing energy of 0.7 µJ/cm² (550 nm) was needed for decreasing the surface potential to the half value of Vo, which defines the
electrophotosensitivity $E_{1/2}$. Residual surface potential ($V_{re}$) was less than 30 V. In negatively charged case, sensitivity was less than the other because of an electron transfer type photoreceptor.

Figure 6 shows the reciprocal value of $E_{1/2}$ as a function of wavelength. The $E_{1/2}$ of BPDA-Ph3 is less than 1.0 $\mu$J/cm$^2$ in the 400-570 nm wavelength region.

From the discussions of the chapter 2, the sensitivity of the OPS-PI film was remarkably decreased near the wavelength of the optical energy gap, $E_g$. Spectral sensitivities of another types of photoreceptors are also shown in that figure. Inorganic photoreceptors have larger sensitivities than OPCs in the 400-700nm, but in applications to laser printers using GaAs lasers, high sensitivity for red wavelength longer than 700 nm, is necessary.

Figure 7 shows the spectral sensitivities of BPDA-Ph3 doped with $H_2Pc$ of the doping ratio range 0.01-1 weight %. The energy band diagram for the indicates that the doping of $H_2Pc$ comes to an effective sensitizing. The increase of dopants lead
the rapid increase of photosensitivity in long wavelength region 600-900nm, which is coincidented with the absorbing range of H$_2$Pc. In turn, doping of more than 1 weight % decreased of the sensitivity in the whole wavelength region 400-900nm. It is reasonable to consider that dopants in OPS-PI films act as carrier trapps and prevent carriers from transporting. Because an excess of dopants in the crystalline phase of OPS-PI would destroy the crystallinity to disturb the carrier transport paths. So the moderate doping ratio was existed.

4. Conclusions

We proposed the electronic structure of BPDA-Ph$_3$, the most sensitive OPS-PI made with the experimental results. The determined band-conduction model explained the optical and electrical properties of OPS-PI well. And we could prepare the sensitized BPDA-Ph$_3$ by doping H$_2$Pc using the energy diagram. Xerographic photoreceptors consisted of mono-layer, which had a high sensitivity over the wide wavelength region including 400-900nm, could be applied to the positively charged use.
5. References
1) A.Takimoto, H.Wakemoto, E.Tanaka, M.Watanabe and H.Ogawa, 
3) H.Hoegl, J.Phys.Chem.69(1965)755
4) P.J.Regensburger, Photochem.Photobiol.8(1968)429
5) W.D.Gill, J.Appl.Phys.43(1972)5033
7) L.Onsager, Phys.Rev.54(1938)554
   68(1978)637
9) R.C.Penwell,B.N.Ganguly and T.W.Smith, Macromolecular Reviews
   13(1978)148