

Photoconductivity of a Polyimide with an Alicyclic Diamine Doped with *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine

Sung Ae LEE, Takashi YAMASHITA, and Kazuyuki HORIE

*Department of Chemistry and Biotechnology, Graduate School of Engineering,
The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*

(Received March 13, 1997)

ABSTRACT: Photoconductivity of a polyimide with an alicyclic diamine [the polyimide film prepared from pyromellitic dianhydride and diaminodicyclohexylmethane PI(PMDA/DCHM)], and an aromatic polyimide [the polyimide film prepared from pyromellitic dianhydride and oxydianiline PI(PMDA/ODA)] was investigated by the addition of an electron donor, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). The addition of the electron donor increased the photocurrent generation of two polyimide films by about three orders of magnitude shifting to longer wavelength by forming intermolecular charge-transfer complex in the ground state of the polyimide films. The polyimide with the alicyclic diamine doped with the electron donor showed a larger enhancement of photocurrent probably due to the existence of only intermolecular charge-transfer complex in the polyimide film, compared to the case of the aromatic polyimide having charge-transfer complex both intra- and intermolecularly. The mechanism of the enhancement of photocurrent by the addition of the electron donor would be first due to photo-absorption by the intermolecular charge-transfer complex formed between the added electron donor and pyromellitic imide unit of the polymer backbone. Under an applied field, its excitation is followed by rapid electron transfer from the donor to pyromellitic imide to produce the radical anion of the polymer and the radical cation of the donor, resulting in the photoconductivity in the bulk polyimide films.

KEY WORDS Polyimides with Alicyclic Diamines / Electron Donor / *N,N,N',N'*-tetramethyl-*p*-phenylenediamine / Charge-Transfer Complex / Charge Carrier / Quantum Yield of Photocurrent / Photoconduction Mechanism /

Polyimides have been widely used as the materials for microelectronics due to their high thermal stability, solvent insensitivity, and good dielectric characteristics. The syntheses of new polyimides with various functional groups which show high photosensitivity, have also been carried out.¹ The photoconductivity of aromatic polyimide films has been reported in the literature by using UV and visible-light radiation²⁻⁸ as the excitation sources, while various organic photoconductors (OPCs) and photoconductive polymers have been widely investigated for applying to xerographic photoreceptors of copies or printing machines.⁹⁻¹⁰ Although polyimides are well known for their high thermal stability, solvent insensitivity, and good dielectric characteristics, the low quantum efficiency in photocurrent generation has limited their use as photoconductors.

Sensitization of photoconductivity in electron-donating polymers by the addition of electron acceptors has been widely reported, with most of the focus on poly(*N*-vinylcarbazole) (PVK).^{11,12} Sensitization of photoconductivity of Kapton polyimide film, [the polyimide film prepared from pyromellitic dianhydride and oxydianiline PI(PMDA/ODA)], was investigated by the addition of electron donors reported by Freilich,⁶ because the polyimide film falls into the class of electron-accepting polymers by virtue of the pyromellitic imide group in the polymer backbone. He has reported that the addition of the electron donor of dimethylaniline (DMA) increased the photocurrent generation by as much as 5 orders of magnitude in the applied field range of 10^5 – 10^6 Vcm⁻¹ in Kapton polyimide film. Iida *et al.*⁷ have investigated the effect of molecular orderiness on photoconductivity of Kapton polyimide film, reporting that stretching of polyimide film affected the photoconductivity, *i.e.*, as the film was stretched pho-

tocurrent increased.

In recent years, Jin *et al.*¹³⁻¹⁵ and Itoya *et al.*¹⁶ have reported that the polyimides prepared from alicyclic or aliphatic diamines are attracting much interest because they have good optical, photochemical and dielectric properties as well as good thermal stability. One of the reasons for their high performance is due to the elimination of charge transfer, because the charge transfer state of aromatic polyimides is formed between aromatic diamines as electron donors and aromatic dianhydrides as electron acceptors both intra- and intermolecularly.¹⁷⁻¹⁹ In our previous paper,²⁰ the photoconductivity of the polyimide film prepared from pyromellitic dianhydride (PMDA) and diaminodicyclohexylmethane (DCHM), PI(PMDA/DCHM) has been investigated, compared with that of an aromatic polyimide prepared from PMDA and oxydianiline (ODA), PI(PMDA/ODA). We have found that the polyimide film with the alicyclic diamine as well as the aromatic polyimide film showed the photoconductive properties even without the addition of any electron donors. In addition, the photoconductivity for the polyimide with the alicyclic diamine was larger than that for the aromatic polyimide film, even though it had no charge-transfer complex in the ground state of the polymer backbone. By the measurement of fluorescence spectra, in addition to monomer emission, red-shifting emission maxima were observed for the polyimide film with the alicyclic diamine when the film was excited at longer wavelengths which resulted also in the photoconductivity. These emissions were attributed to the intermolecular interaction in the ground state of the polymer backbone by comparing absorption and fluorescence excitation spectra. However, the photoconduction mechanism of the polyimide with the alicyclic diamine is not perfectly cleared up to now,

and we are investigating continuously.

In the present paper, sensitization of the photoconductivity of the polyimide with the alicyclic diamine, PI(PMDA/DCHM), as well as that of a typical aromatic polyimide, PI(PMDA/ODA), was investigated by the addition of electron donors, because polyimide films have electron acceptable properties by virtue of the pyromellitic imide group in the polymer backbone. The TMPD was chosen as an adequate electron donor, and the photocurrent generation of polyimide films doped with the electron donor is investigated as functions of applied field, wavelength, and polarity.

EXPERIMENTAL

Materials and Solvents

Pyromellitic dianhydride (PMDA) supplied by Tokyo Kasei Co., Ltd. was purified by recrystallization in distilled acetic anhydride, and dried at high temperature (150°C) under vacuum for 12 h. 4,4'-Diaminodicyclohexylmethane (mixture of isomers, DCHM) was supplied by Wako Pure Chemical Co., which was used without further purification. 4,4'-Diaminodiphenyl ether (ODA) and *n*-butylamine (*n*-BA) were supplied by Tokyo Kasei Co., Ltd., and used without further purification. Distilled *N,N'*-dimethylacetamide (DMAc) and *N,N'*-dimethylformamide (DMF) provided by Tokyo Kasei Co., were used as solvents for preparing poly(amic acid) (PAA) and a model compound, respectively. Aniline, *N*-methylaniline (NMA), *N,N*-dimethylaniline (DMA), *N,N*-diethylaniline (DEA), *N,N,N',N'*-tetramethylbenzidine (TMB), and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) provided by Tokyo Kasei Co., were used as electron donors without further purification.

Preparation of Polyimides and Its Model Compound

The poly(amic acid)s, PAA(PMDA/ODA) and PAA(PMDA/DCHM), were prepared at room temperature by 24 hour stirring of pyromellitic dianhydride (PMDA) with oxydianiline (ODA), and pyromellitic dianhydride with diaminodicyclohexylmethane (DCHM) in distilled *N,N'*-dimethylacetamide (DMAc) solution, respectively. The intrinsic viscosity, $[\eta]$, for these poly(amide acid)s were 1.02 dl g⁻¹ for PAA(PMDA/DCHM) and 1.21 dl g⁻¹ for PAA(PMDA/ODA) at 25°C in DMAc. A 10% solution of the poly(amide acid)s was spin coated onto conductive indium-tin-oxide coated glass (ITO glass) at 1500 rpm for 1 min, and then heated to the imidization temperature region, for 12 h at 50°C and for 1 h each at 160°C, 180°C, and 200°C under vacuum. Under these conditions, almost all of the poly(amide acid)s changed to the polyimides which was ascertained by IR spectroscopy. *N,N'*-di-*n*-butylpyromellitic diimide, M(PMDA/*n*-BA), was prepared as a model compound by using *n*-butylamine and pyromellitic dianhydride in *N,N'*-dimethylformamide (DMF), and recrystallized in CCl₄. The addition of electron donors were carried out by taking a direct doping method to the poly(amic acid) solution by 1 : 1 molar ratio.

These chemical structures are shown Figure 1.

Measurements of Photocurrent

Figure 2 shows the schematic diagram of the

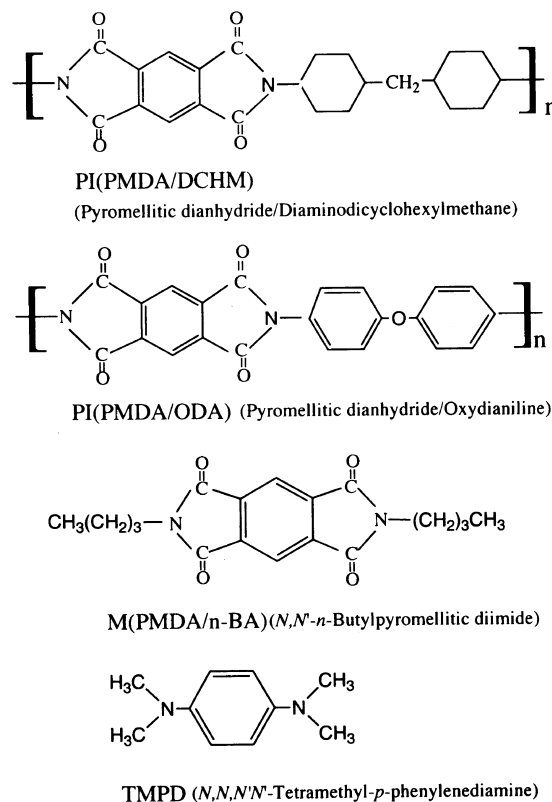


Figure 1. The chemical structure of two polyimides, PI(PMDA/DCHM) and PI(PMDA/ODA), a model compound for pyromellitic imide moiety, M(PMDA/*n*-BA), and an electron donor, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD).

photocurrent measuring instrument. The sample was placed in an aluminum box, which was electrically shielded. Steady-state DC photocurrent was measured in the sandwich configuration, using an electrode arrangement between a front electrode of conductive glass (ITO glass) and a back electrode of silver paste with $\phi = 0.6$ mm. Films were photoilluminated with the intensity of about 3 mW cm⁻² by the monochromatized light from a xenon lamp (100V/500W). Photocurrent was measured with a picoammeter (PM-18U, TOA Co., Ltd.).

RESULTS AND DISCUSSION

Effect of Electron Donors on Charge-Transfer Complex Formation

The nature of the charge-transfer complex was investigated first by using a model compound. By assuming that the imide unit is responsible for the acceptor characteristics of the polymer, a low-molecular-weight *N,N'*-di-*n*-butylpyromellitic diimide, M(PMDA/*n*-BA), was synthesized. There has been a fair quantity of work investigating the complex formation between pyromellitic dianhydride and electron donors.²¹⁻²³ However, little is known about the charge-transfer complexes of pyromellitic imides. Thus the charge-transfer complex between pyromellitic imides and electron donors was investigated using methylene chloride as a solvent.

Table I shows the charge-transfer absorption maxima and their extended tail formed between pyromellitic imide group of the model compound and electron donors in methylene chloride, which were measured by 1 : 1 molar ratio. Without the addition of electron donors, the model

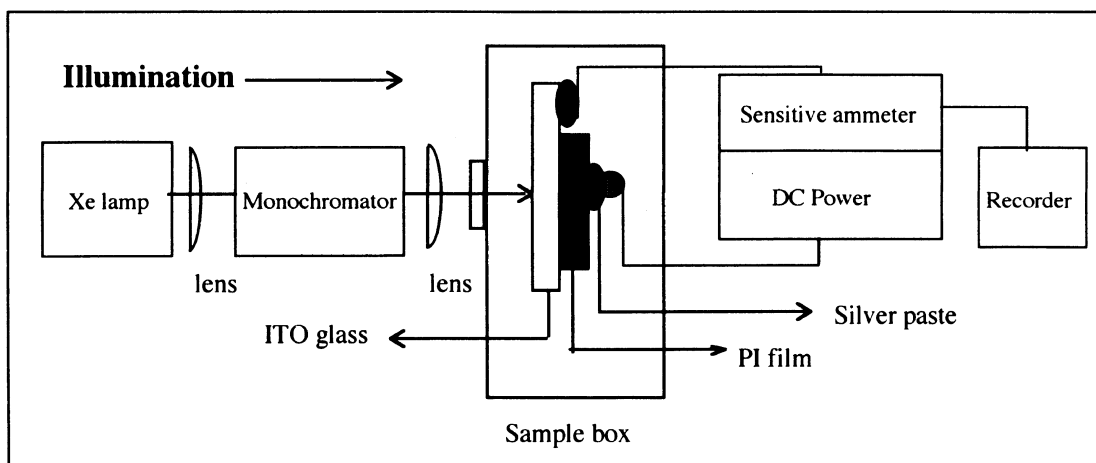


Figure 2. Experimental arrangement for photocurrent measurements.

Table I. The charge-transfer absorption maxima and tails formed between a model compound, M(PMDA/*n*-BA), and various electron donors in methylene chloride (CH₂Cl₂)

Model compound	Electron donor	CT maximum	Extended tail
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M Aniline		400 nm	650 nm
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M NMA (<i>N</i> -Methylaniline)		435	690
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M DMA (<i>N,N'</i> -Dimethylaniline)		470	690
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M DEA (<i>N,N'</i> -Diethylaniline)		490	710
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M HMB (Hexamethylbenzene)		400	530
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M TMB (Tetramethylbenzidine)		560	800
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M TMPD (Tetramethyl- <i>p</i> -phenylenediamine)		580	850
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M TTF (Tetrathiafulvalene)		440, 600	800
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M DMBP (Bis-(dimethylamino)benzophenone)		585	700
0.05 M M(PMDA/ <i>n</i> -BA)/0.05 M DEBP (Bis-(dimethylamino)benzophenone)		590	700
0.05 M M(PMDA/ <i>n</i> -BA)/without donor		309, 319	370

system showed an absorption spectrum extended to 370 nm with maxima of 309 and 319 nm. The addition of electron donors to this solution resulted in a change in the absorption spectrum, which showed a broad transition at longer wavelength. As shown in Table I, the charge-transfer absorption maxima shift to longer wavelength, as the number of amine groups and methyl groups in electron donors increases. Specially, electron donors containing an amine group than a number of methyl groups would be assumed to be stronger electron donors, because *N*-methylaniline (NMA) compared to hexamethylbenzene (HMB) showed a broad transition at longer wavelength with lengthened tail.

Figure 3 shows the relationship between ionization potential, I_p , of the electron donors and the absorption maxima of the charge-transfer complexes. It shows linear relationship between absorption energy and ionization potential agreed with the Mulliken charge-transfer theory.²⁴ It states that over a sufficiently small range of ionization potentials, the energy of charge-transfer absorption will depend linearly on ionization potential of the electron donor. As shown in Figure 3, the transition energy of the charge-transfer absorption formed between tetramethyl-*p*-phenylenediamine (TMPD) and pyromellitic imide group of the model compound is lowest, because ionization potential of TMPD is lower than those of any other donors. A maximum of the charge-transfer absorption of TMPD with the model compound is observed at 580 nm, and its absorption tail extends to above 850 nm by forming strong charge-transfer complex intermolecularly. There-

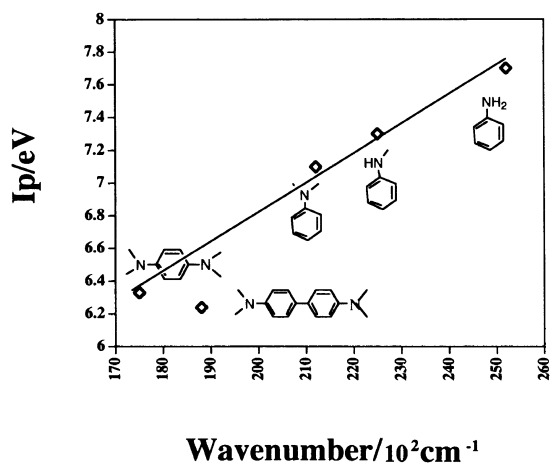


Figure 3. Relationship between ionization potential, I_p , of electron donor and absorption energy of the charge-transfer complex formed between a model compound of M(PMDA/*n*-BA) and electron donors in methylene chloride (CH₂Cl₂).

fore, TMPD was used as an electron donor to sensitize the photoconductivity of polyimide films by doping directly to poly(amic acid) solution with 1 : 1 molar ratio.

In the present experiments, the PAA doped with TMPD was spin-coated onto conductive ITO glass by 1500 rpm, dried at 50°C under vacuum for 24 h, and then heated to the imidization temperature region under nitrogen atmosphere to prevent the evaporation of TMPD. We have confirmed that TMPD exists in the bulk film after the imidization by calculating the losing weight with increasing imidization temperature using

an electronic balance. The addition of the electron donor of TMPD resulted in a marked change in the color of the polyimide films forming intermolecular charge-transfer complex in the ground state.

Photocurrent Generation

Figure 4(a) shows absorption spectra for $1\ \mu\text{m}$ undoped polyimide films and $1\ \mu\text{m}$ donor-doped polyimide films with TMPD, and Figure 4(b) shows their difference spectra which reveal intermolecular charge-transfer between TMPD and pyromellitic imide unit of two polyimide films. By the addition of the electron donor, the absorption of polyimide film with the alicyclic diamine extended from 390 to 600 nm, while the absorptions of the aromatic polyimide film lengthened from 490 to 600 nm. It is thought that the addition of the electron donor forms the intermolecular charge-transfer complex with electron acceptable pyromellitic imide unit in the ground state, resulting in the extended absorption to longer wavelength. Figure 5 shows the photocurrent and the darkcurrent of undoped polyimide films and TMPD-doped polyimide films with about $1\ \mu\text{m}$ thickness as a function of applied field. The sample was arranged in the sandwich type and photoirradiated with intensity of $3\ \text{mW cm}^{-2}$ at 350 nm for PI(PMDA/DCHM), at 400 nm for PI(PMDA/DCHM)/TMPD, at 420 nm for PI(PMDA/ODA), and at 460 nm for PI(PMDA/ODA)/TMPD where optical density is small enough (0.3–0.5). The photocurrent generation increased with increasing applied field for all polyimide

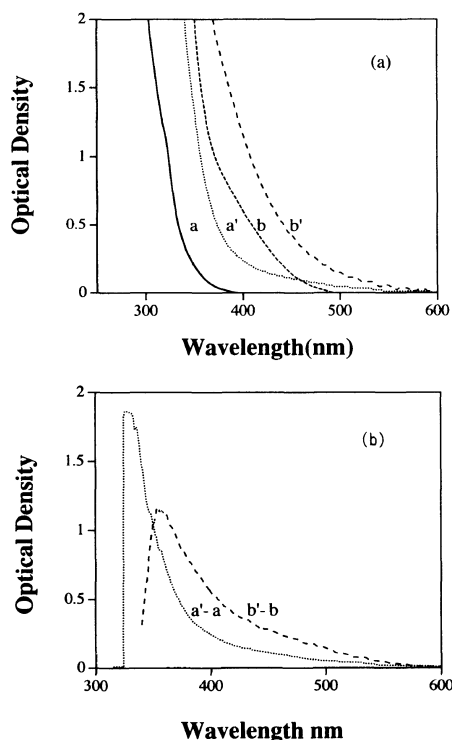


Figure 4. Absorption spectra of undoped polyimide films and TMPD-doped polyimide films with the film thickness of about $1\ \mu\text{m}$ (a), and their difference spectra which reveal intermolecular charge-transfer absorption between TMPD and pyromellitic imide unit of two polyimide films (b). a, PI(PMDA/DCHM) (—); a', PI(PMDA/DCHM)/TMPD (·····); b, PI(PMDA/ODA) (-----); b', PI(PMDA/ODA)/TMPD (----); a'-a, PI(PMDA/DCHM)/TMPD-PI(PMDA/DCHM) (·····); b'-b, PI(PMDA/ODA)/TMPD-PI(PMDA/ODA) (----).

films. No photocurrent generation was observed when an applied field is zero, which indicates that the carrier generation of photocurrent depends upon the applied field. It would be assumed that the applied field helps the transport of generated carriers by preventing from geminate recombination and lengthening their lifetime. The darkcurrents of all polyimide films shown with filled symbols in Figure 5 were low enough, however, the addition of the electron donor increased the darkcurrent to some extent at the high applied electric fields.

As is shown in Figure 5, the presence of the electron donor results in an enhancement of photocurrent in the polyimide films at all applied electric fields. The addition of the electron donor increased the photocurrent generation of polyimide films by as much as 2–3 orders of magnitude in the applied electric field range of 10^5 – $10^6\ \text{V cm}^{-1}$. Between them, the donor-doped polyimide film with the alicyclic diamine compared to the donor-doped aromatic polyimide film showed higher photocurrent generation with lower darkcurrents in all the applied electric field range. Figure 6 shows action spectra of the photocurrent for $1\ \mu\text{m}$ undoped polyimide films and $1\ \mu\text{m}$ TMPD-doped polyimide films, under an

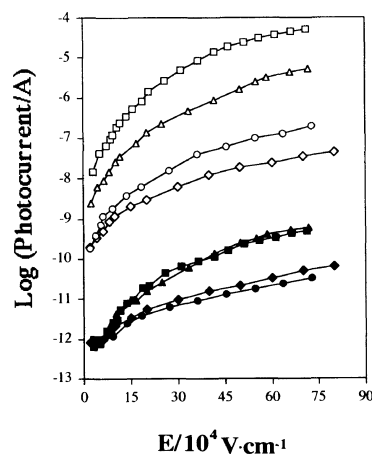


Figure 5. Photocurrent generation as a function of applied field for $1\ \mu\text{m}$ undoped polyimide films and $1\ \mu\text{m}$ TMPD-doped polyimide films. Films were photoirradiated with the intensity of $3\ \text{mW cm}^{-2}$ at 350 nm for PI(PMDA/DCHM) (○), at 400 nm for PI(PMDA/DCHM)/TMPD (□), at 420 nm for PI(PMDA/ODA) (◇), and at 460 nm for PI(PMDA/ODA)/TMPD (△) where optical density is 0.3–0.5. Filled symbols denote darkcurrents for corresponding system.

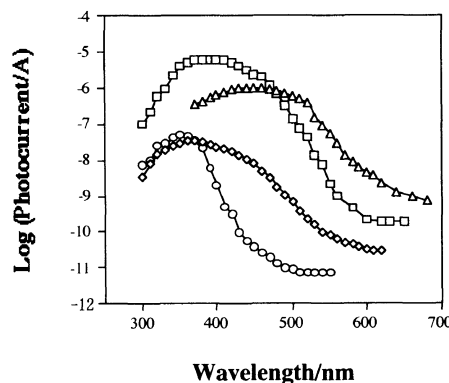


Figure 6. Action spectra of the photocurrent under an electric field of $5.0 \times 10^5\ \text{V cm}^{-1}$ for $1\ \mu\text{m}$ undoped polyimide films and $1\ \mu\text{m}$ TMPD-doped polyimide films. Undoped polyimide films; PI(PMDA/DCHM) (○), PI(PMDA/ODA) (◇), and TMPD-doped polyimide films; PI(PMDA/DCHM)/TMPD (□), PI(PMDA/ODA)/TMPD (△).

applied electric field of $5.0 \times 10^5 \text{ V cm}^{-1}$. The marked red-shift of action spectra for the photocurrent and the increase in its generation by 2–3 orders of magnitude by the addition of TMPD to both PI(PMDA/DCHM) and PI(PMDA/ODA) suggest that the first step in the photoconduction process of donor-doped polyimide films would be an photo-excitation of the intermolecular charge transfer complex between a pyromellitic imide unit and TMPD.

The quantum yield for photocurrent generation, Φ , is defined as the ratio of the number of charge carriers producing photocurrent generated by photoexcitations to the number of photons absorbed by the material during the same period of time, and it can be expressed as

$$\Phi = J_{\text{ph}}/e\alpha I_0 T \quad (1)$$

where J_{ph} in A cm^{-2} is the photocurrent density, e is the elementary charge in C , $\alpha = (1 - 10^{-OD})$ is the absorption coefficient with OD being the optical density, I_0 in $\text{photon cm}^{-2} \text{ s}^{-1}$ is the intensity of incident light per unit area and per second, and T is the transmittance of the illuminated electrode ($T=1$ was used for the ITO glass). The quantum yields for carrier generation, Φ , normalized by the absorption of the bulk film are demonstrated in Figure 7. The value of Φ for undoped polyimide films shows wavelength dependence at shorter wavelength, and the addition of the electron donor, TMPD, increases the Φ for photocurrent generation by 10^2 times with the shifts to longer wavelength. The value of Φ for the undoped PI(PMDA/ODA) film at 370 nm excitation agrees well with the literature value (9.0×10^{-6}).³ By the addition of TMPD, the effective wavelength of Φ for the polyimide films red-shifted and broadened from 370–400 nm to 370–530 nm for PI-

(PMDA/DCHM)/TMPD, and red-shifted from 370–500 nm to 400–600 nm for PI(PMDA/ODA)/TMPD, where the optical density is small enough. The marked decrease in Φ with increasing optical density in the region below the effective wavelength would be due to the presence of other absorptions besides the intermolecular absorption contributing to the photocurrent generation. The region which shows the enhanced photocurrent by the addition of TMPD is attributed to the intermolecular charge-transfer complex formed between the pyromellitic imide unit and TMPD. In our previous paper,²⁰ fluorescence spectra of the polyimide film with the alicyclic diamine, PI(PMDA/DCHM), showed a strong monomer emission for 300–320 nm excitation and red-shifting emission for longer wavelength (380–450 nm) excitation, suggesting that species responsible to this red-shifting emission is related to the photoconductivity of the polyimide film with the alicyclic diamine without an electron donor. However, for TMPD-doped PI(PMDA/DCHM) and PI(PMDA/ODA) films, we observed the intermolecular charge-transfer complex formed between pyromellitic imide unit and TMPD by measuring absorption spectra (Figure 4) and also fluorescence spectra with very weak structureless broad band at 590 nm. Consequently, the enhanced photocurrent of the donor-doped polyimide films is attributed to the formation of the intermolecular charge-transfer complex in the ground state, indicating that the intermolecular charge-transfer complex is responsible for the generation of charge carriers in these systems.

By the addition of the electron donor, the polyimide with the alicyclic diamine showed an larger enhanced photocurrent compared to the aromatic polyimide. The aromatic polyimide film, PI(PMDA/ODA), is known to have not only intermolecular but also intramolecular charge-transfer states,¹⁷ and the photoconductivity measurements on anisotropic samples of PI(PMDA/ODA)²⁵ have shown that in-plane photocurrent is larger in the normal direction to the molecular chain than in the parallel direction, leading to the conclusion that the electrons move along the stacking direction of the phenyl and imide rings. The *in-situ* existence of intramolecular charge-transfer state in PI(PMDA/ODA) might reduce the electron-attracting ability of pyromellitic imide groups compared to the case in PI(PMDA/DCHM) where no intramolecular charge-transfer state exists. Thus the present results also suggest that the intermolecular charge-transfer formation is important for carrier generation and/or transport steps in the photoconductivity of polyimide films. The elimination of intramolecular charge-transfer state by introducing the alicyclic diamine gives a possibility of improving photoconductivity of thermostable polyimide films.

Polarity and Electrode Material Dependence

Polarity dependence of the photoconductivity was measured to investigate the photoconduction mechanism of the donor-doped polyimide films with about $15 \mu\text{m}$ thickness. This experiment is to investigate the type of carriers in the photocurrent generation, because electron or hole as a free carrier can be measured by photoilluminating a negative electrode or a positive

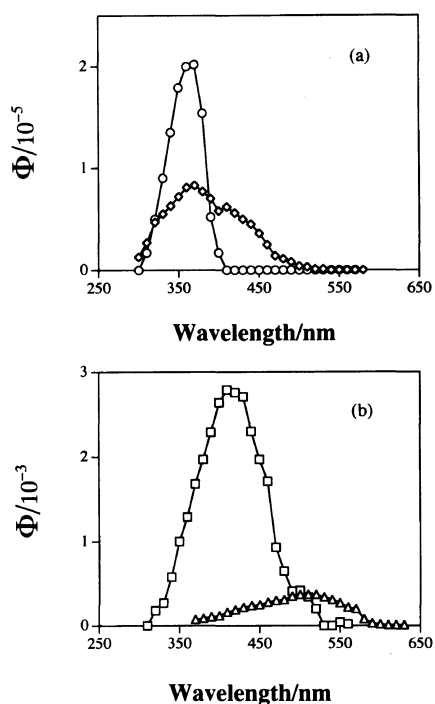


Figure 7. Quantum yield of the photocurrent generation as a function of wavelength under an electric field of $5.0 \times 10^5 \text{ V cm}^{-1}$ for undoped polyimide films and TMPD-doped polyimide films. (a) undoped polyimide films; PI(PMDA/DCHM) (\circ), PI(PMDA/ODA) (\diamond), (b) TMPD-doped polyimide films; PI(PMDA/DCHM)/TMPD (\square), PI(PMDA/ODA)/TMPD (\triangle).

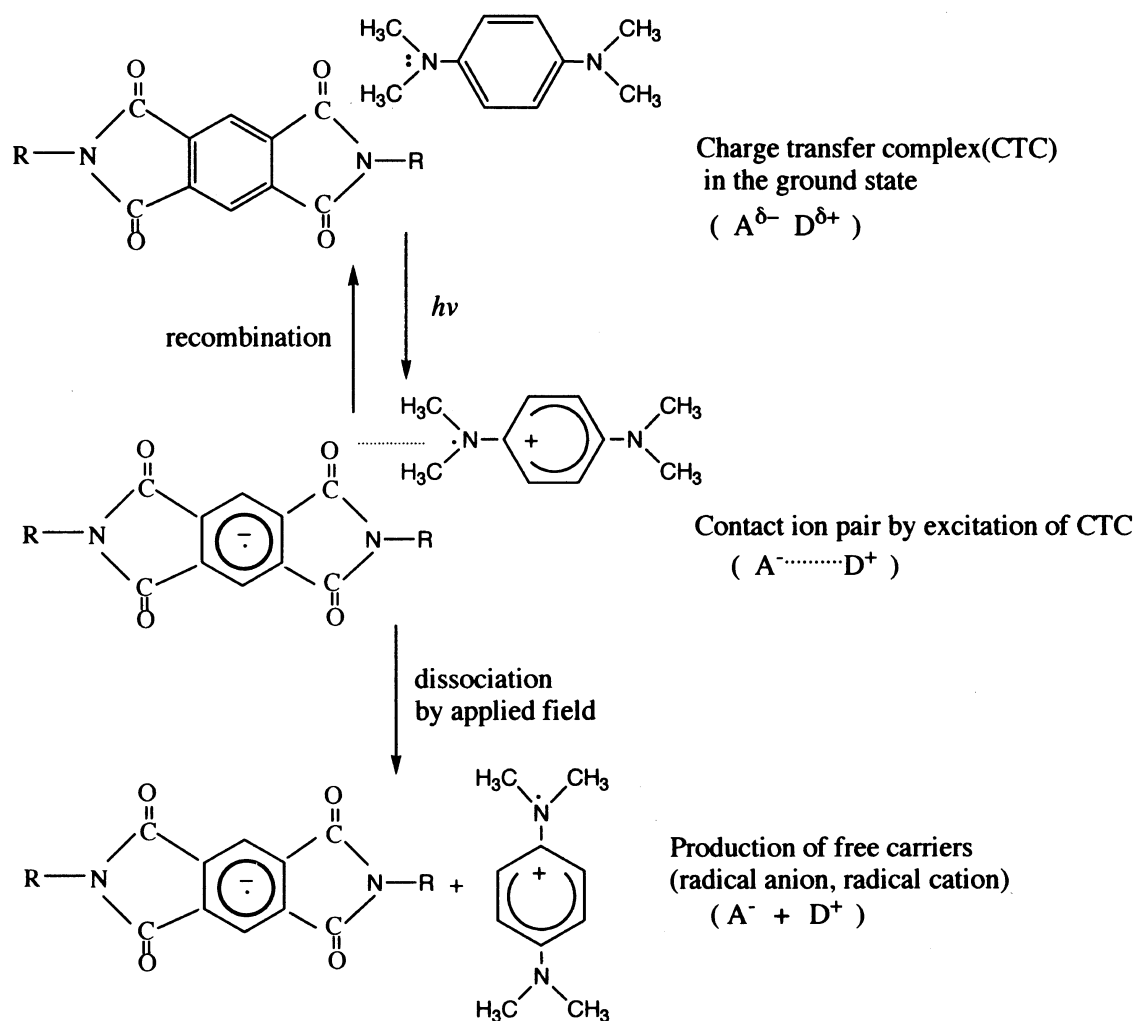


Figure 8. Scheme for charge carrier photogeneration in TMPD-doped polyimide films.

electrode, respectively. The photoconduction mechanism of pure poly(*N*-vinylcarbazole) (PVK) film is well known to be dominated by holes.^{26,27} Pfister *et al.*²⁶ have reported that although pure poly(*N*-vinylcarbazole) film has only the electron donating properties in the polymer backbone, electron transfer reactions occur in the excited state of carbazole with impurities such as oxygen that has acceptable properties by optical excitation and exhibits the strong charge transfer character in the excitation state. Gill²⁷ has investigated hole and electron drift mobility in thin films of charge-transfer complex of trinitrofluorenone (TNF) with PVK, and reported that by the addition of the electron acceptor with 1 : 1 molar ratio, the photoconduction of PVK film is dominated by electrons.

In this experiment, the photocurrent of polyimide films doped with TMPD showed no dependence on polarity. It would be suggested with some probabilities that charge carriers may be produced uniformly by photoillumination in the bulk film, or that the drift mobility of photogenerated carriers of electrons and holes may be almost the same. The electrode material dependence was also investigated by replacing a silver paste electrode with a gold evaporation electrode. In the measurement of electrode material dependence, the photocurrent was independent upon the electrode materials. Similar results were obtained by Takai *et al.*^{4,7} These results may mean that electrode effect is negligible.

Charge Carrier Generation

Law²⁸ has reported that although photoconductors from different chemical classes are structurally different, most of their electronic state are charge-transfer states. Having demonstrated that photoconductivity depends upon excitation of charge-transfer complexes and from the analogy to the photoconduction mechanism of poly(*N*-vinylcarbazole) (PVK) loaded with electron acceptors,²⁹⁻³¹ it can be supposed that the charge carriers are generated by an electron transfer during the excited state from the electron donor to the electron acceptable pyromellitic unit of the polymer backbone, resulting in the formation of contact ion pairs. Williams³² has reported that the radical cation of PVK and the radical anion of dimethyl terephthalate (DMT) were noticeable within 100 ps following the excitation of the polymer and acceptor in a toluene solution. Yokoyama *et al.*^{33,34} have reported that the fluorescence assigned to the exciplex formed between PVK and a poor donor of DMT was quenched by an applied field whose effect was attributed to field-assisted thermal dissociation of the photogenerated exciplex to form separated ion pairs. They also have reported that charge-transfer fluorescence in PVK film doped with a strong donor of 1,2,4,5-tetracyanobenzene (TCNB) is quenched by an applied field, attributed to the carrier photogeneration due to the field-induced thermal dissociation of ion pairs. We have investigated the active species of an aromatic polyimide

film, (PMDA/ODA), by using picosecond pulse radiolysis,³⁵ and observed the radical anions at 660 and 720 nm by electron transfer from electron donating diphenyl ether to the electron acceptable pyromellitic imide moieties, which are respected to the charge carrier in the photoconductivity of Kapton film. Freilich⁶ has also investigated the transient absorption by flash photolysis for an aromatic polyimide film doped with an electron donor of *N,N*-dimethylaniline (DMA), PI(PMDA/ODA)/DMA, reporting that the radical anions of pyromellitic imide moieties were observed at 653 and 721 nm by intermolecular electron transfer from DMA to pyromellitic imide moieties of the polymer backbone.

In the present system, the photoconduction mechanism of the TMPD-doped polyimide films would be explained by the extrinsic carrier generation as shown in Figure 8. We could observe the intermolecular charge-transfer complex formation in the ground state of the films by measurement of UV absorption spectra and its fluorescence in the excited state. The photocurrent generation of the photoilluminated films under the applied field resulted from the separation of the ion pair, because no photocurrent was observed when an applied field was zero.

Consequently, the enhanced photocurrent generation of donor-doped polyimide films is attributed to the formation of intermolecular charge-transfer complex, because they are doped with the strong electron donor of TMPD. By the absorption of light, charge-transfer complex states form contact ion pairs, and produce charge carriers of the radical anion and the radical cation under an applied field, resulting in the photocurrent by a hopping mechanism throughout the bulk film.

The reason of donor-doped polyimide film with the alicyclic diamine showing the large enhanced photocurrent compared to the donor-doped aromatic polyimide film would be assumed that a polymer film with only intermolecular charge-transfer complex is more effective for charge generation and/or transport of the polyimide films, because the polyimide with the alicyclic diamine forms the intermolecular charge-transfer complex with the added electron donor, while aromatic polyimide has charge-transfer complexes both intra- and intermolecularly. In addition, we are investigating more detailed studies on lifetime and drift mobility of carriers, because longer lifetime and/or effective drift mobility of carriers would also be expected for the enhanced photoconductivity of the polyimide with an alicyclic diamine by the addition of an electron donor.

CONCLUSION

Photoconductivity of a polyimide with an alicyclic diamine, PI(PMDA/DCHM), and an aromatic polyimide, PI(PMDA/ODA), was investigated by the addition of an electron donor of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). The addition of the electron donor increased the photocurrent generation of both polyimide films by 2–3 orders of magnitude with the shift of action spectra to longer wavelength by forming intermolecular charge-transfer complex in the ground state of the polyimide films. Between them, the polyimide with the alicyclic diamine doped with the

electron donor showed a larger enhancement of photocurrent due to the presence of only intermolecular charge-transfer complex in the polyimide film. The enhancement of photocurrent by addition of the electron donor resulted from the light absorption by the intermolecular charge-transfer complex formed between the added electron donor and pyromellitic imide unit of the polymer backbone. Under an applied field, its excitation is followed by the rapid electron transfer from the donor to pyromellitic imide to yield the radical anion of the polymer and the radical cation of the donor, resulting in the photoconductivity in the bulk polyimide films by a hopping mechanism.

REFERENCES

1. K. Horie and T. Yamashita, Ed., "Photosensitive Polyimides: Fundamentals and Applications," Technomic, Lancaster, PA, 1995.
2. P. K. C. Pillai and B. L. Sharma, *Polymer*, **20**, 1431 (1979).
3. L. Kan and K. C. Kao, *J. Chem. Phys.*, **98**, 3445 (1993).
4. Y. Takai, M. M. Kim, A. Kurachi, T. Ieda, and M. Mizutani, *Jpn. J. Appl. Phys.*, **10**, 21 (1982).
5. . Rashmi, Y. Takai, T. Mizutani, and M. Ieda, *Jpn. J. Appl. Phys.*, **22**, 1388 (1983).
6. S. C. Freilich, *Macromolecules*, **20**, 973 (1987).
7. K. Iida, M. Waki, S. Nakamura, M. Ieda, and G. Sawa, *Jpn. J. Appl. Phys.*, **23**, 1573 (1984).
8. A. Takimoto, H. Wakemoto, and H. Ogawa, *J. Appl. Phys.*, **70**, 2799 (1991).
9. W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).
10. G. Pfisher, *Phys. Rev.*, **B16**, 3676 (1977).
11. H. Hoegl, *J. Phys. Chem.*, **69**, 755 (1965).
12. R. C. Penwell, B. N. Ganguly, and T. W. Smith, *J. Polym. Sci., Macromol. Rev.*, **13**, 63 (1978).
13. Q. Jin, T. Yamashita, K. Horie, I. Mita, and R. Yokota, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 2345 (1993).
14. Q. Jin, T. Yamashita, and K. Horie, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 503 (1994).
15. Q. Jin, T. Yamashita, K. Horie, and R. Hayase, *Rep. Prog. Polym. Phys. Jpn.*, **38**, 376 (1995).
16. K. Itoya, Y. Kumagai, M. Kakimoto, and Y. Imai, *Macromolecules*, **27**, 4101 (1994).
17. J. P. LaFemina, *J. Chem. Phys.*, **90**, 5154 (1989).
18. J. P. LaFemina, *Chem. Phys. Lett.*, **159**, 307 (1989).
19. M. Hasegawa, I. Mita, M. Kochi, R. Yokota, *J. Polym. Sci., Polym. Lett.*, **27**, 263 (1989).
20. S. A. Lee, T. Yamashita, and K. Horie, *J. Photopolym. Sci. Technol.*, **9**, 355 (1996).
21. L. L. Ferstandig, W. G. Toland, and C. D. Heaton, *J. Am. Chem. Soc.*, **83**, 1151 (1961).
22. Y. P. Pilette and K. Weiss, *J. Phys. Chem.*, **75**, 3805 (1971).
23. I. Ilmet and P. M. Rashba, *J. Phys. Chem.*, **71**, 1140 (1967).
24. R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).
25. K. Iida, T. Takemoto, S. Nakamura, M. Ieda, and G. Sawa, *Jpn. J. Appl. Phys.*, **25**, 1542 (1986).
26. G. Pfister and D. J. Williams, *J. Chem. Phys.*, **61**, 2416 (1974).
27. W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).
28. K. Y. Law, *Chem. Rev.*, **93**, 449 (1993).
29. K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 2623 (1973).
30. M. Yokoyama, Y. Endo, and H. Mikawa, *Chem. Phys. Lett.*, **34**, 597 (1975).
31. K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 2613 (1973).
32. U. Laschish, R. Anderson, and D. J. Williams, *Macromolecules*, **13**, 1143 (1980).
33. M. Yokoyama, A. Matsubara, S. Shimokihara, and H. Mikawa, *Poly. J.*, **14**, 73 (1982).
34. M. Yokoyama, S. Shimokihara, A. Matsubara, and H. Mikawa, *Polym. J.*, **14**, 77 (1982).
35. S. A. Lee, T. Yamashita, and K. Horie, *J. Phys. Chem.*, In press.