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Photoconductivity of Copolyimide Films Containing Tetraphenylporphyrin and Carbazole Moieties

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A series of polyimide copolymers based on pyromellitic dianhydride, 3,6-diaminocarbazole, and tetrakis(4-aminophenyl)porphyrin were synthesized. The “precursors”, copolyamic acids, and the copolyimides were characterized by IR, UV–visible, and emission spectra and thermogravimetry. The mole ratios of tetraphenylporphyrin (TPP) to carbazole (Cz) in the polymers calculated from the UV–visible spectra indicate that TPP and Cz were incorporated into the polymer backbones as expected. The copolyimide films were fabricated into bilayer photoreceptors as a charge-generating layer to investigate their photoconductivity. It was found that the photosensitivity of the copolyimides increases with the incorporation of TPP into the polymer chains. These results were compared with those of the tetraphenylporphyrin-doped pyromellitic/3,6-diaminocarbazole polyimide film and explained on the basis of charge-transfer complex formation.

Introduction

Polyimide specialty polymers are finding growing usage in applications such as high-temperature thermostable insulators and dielectrics, coatings, and high-performance composites. The versatility of polyimide-based materials has been providing stimulus for accelerating research and development activity in many fields.¹ Among these, the investigation of photoconductive polyimide proceeded smoothly in the past one and one-half decades. It has been reported that typical Kapton polyimide films are weakly photoconductive in the presence of high electric fields.^{2–5} When electron donors were added to Kapton polyimide films, however, the photocurrents increased by as much as 5 orders of magnitude as compared with the virgin polymer. The author has related this enhancement in photoconductivity to the formation of charge-transfer complexes (CTC) between the imide units and the electron donors.⁶ It is reasonable to expect, therefore, that incorporating suitable donors into the polyimide backbones will result in more photoconductive polyimides. Takimoto et al.⁷ have found that polyimides consisting of thiophenylene moieties are photosensitive in the visible region. Nishikata and co-workers⁸ have reported that SnO₂ modified with a monolayer of polyimide-containing porphyrin moieties possesses a photocurrent quantum efficiency of 17.8%.

We have investigated the electrophotographic properties of poly(metal-phthalocyanine)imide coatings and Langmuir–Blodgett films and confirmed that these polyimide films have high photosensitivity.^{9,10} In this work, a series of copolyimides (CPIs) containing tetraphenylporphyrin (TPP) and carbazole (Cz) units were synthesized. Photoreceptors (PRs) in which the CPIs acting as a charge-generating layer were fabricated, and their electrophotographic properties were measured by the photoinduced discharge (PID) technique.

Experimental Details

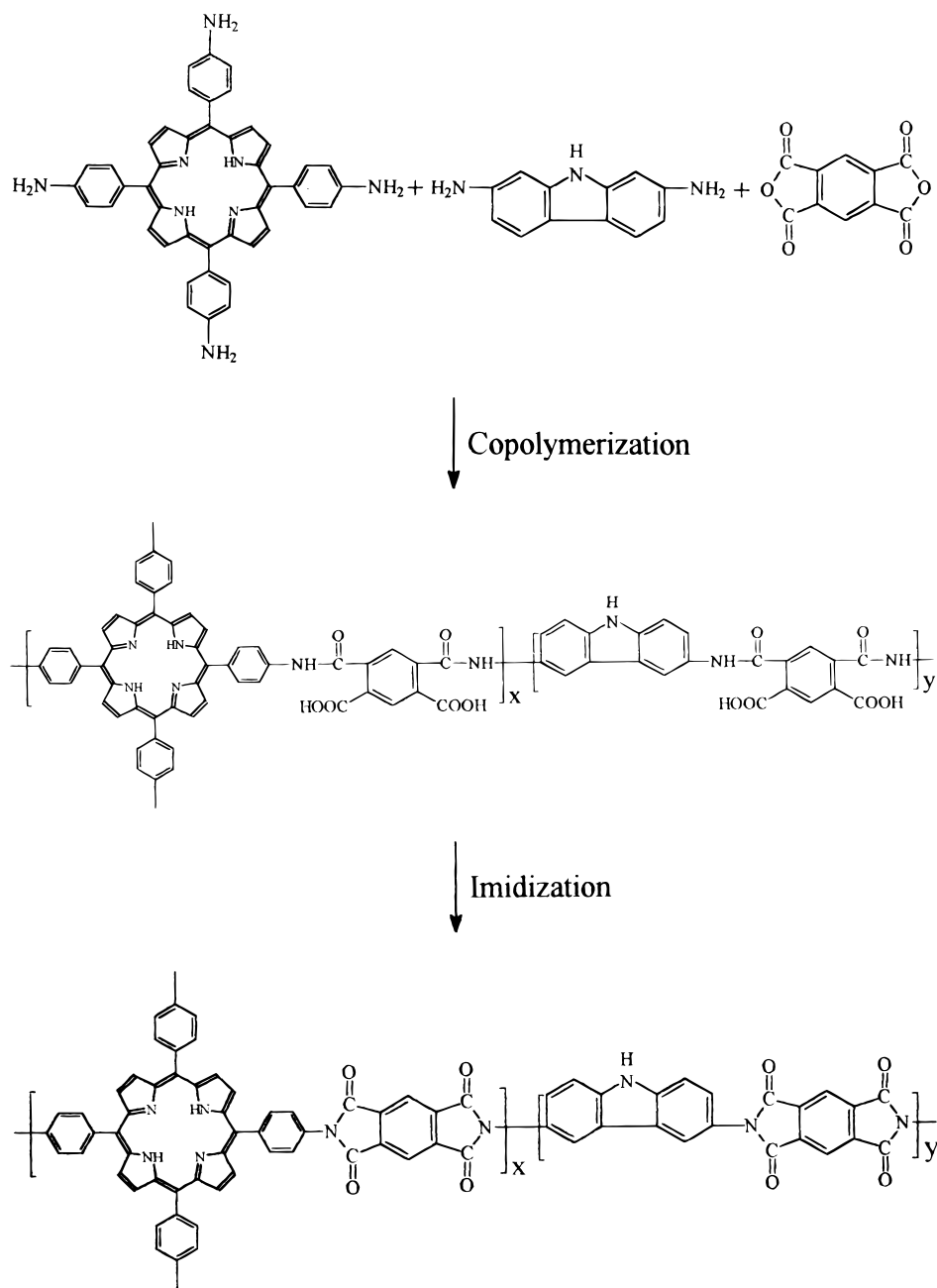
Materials. Tetra(4-aminophenyl)porphyrin and tetraphenylporphyrin were synthesized according to our previous paper.¹¹ 3,6-Diaminocarbazole was prepared by the procedures of Biswas and Das.¹² Pyromellitic dianhydride (PMDA) was recrystallized in dry acetic anhydride prior to use. *N,N*-Dimethyl acetamide (DMAc) was dried by P₂O₅ and distilled under reduced pressure before use. 4-(*N,N*-Diethylamino)-benzaldehyde-1,1-diphenylhydrazone (DEH) was synthesized and purified in a usual way. All other reagents were analytical degree and used as received.

Synthesis and Characterization of CPAs and CPIs. The copolyimides were prepared following a normal two-step reaction sequence. The amino-monomers, tetra(4-aminophenyl)porphyrin and 3,6-diaminocarbazole, with different mole ratios were dissolved in dry DMAc. PMDA was added slowly to these solutions under vigorous stirring. The mixtures were stirred at 5 °C for 2 h and then at 25 °C for another 2 h in N₂ atmosphere. Copolyamic acids (CPAs), the precursors of the copolyimides, were obtained by pouring the final reaction mixtures into cold methanol and then drying the precipitates under reduced pressure at room temperature. The thermal condensation of CPAs at 250 °C in N₂ for 8 h yielded

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Scheme 1



corresponding CPIs. The inherent viscosities of CPAs were measured at the concentration of 0.5 g/dL in DMAc at 30 °C. The UV–visible and IR spectra were measured using UV-240 and NIC-50X spectrometers, respectively. The thermal behaviors of the polymers under nitrogen atmosphere were evaluated by thermogravimetric analysis with a PRT-1 thermogravimeter. A JSM-T20 electron microscope was used to analyze the features of the CPIs and the TPP-doped polyimide films.

Photoreceptor Design and Fabrication. Bilayer photoreceptors consisting of a charge-generating layer (CGL) of the copolyimides and a charge-transporting layer (CTL) of DEH-doped polycarbonate (DEH:PC) were used to evaluate the photoconductivity of the CPIs. The bilayer devices were fabricated on an aluminum substrate, as shown in Figure 1.

The bilayer photoreceptors were fabricated by casting of 5 wt % solutions of copolyamic acids in DMAc onto an aluminum plate electrode with a size of 20 × 20 × 3 mm³. The resulting copolyamic acid films were then imidized as mentioned above to give copolyimide films of about 1 μm thickness. Charge-transporting layers of 8–10 μm thickness were deposited onto

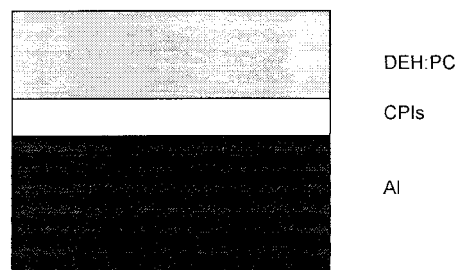


Figure 1. Schematic of the bilayer photoreceptor.

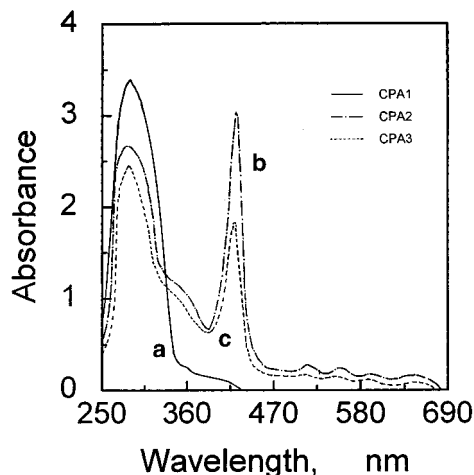
the copolyimide films from a 16 wt % solution of DEH/PC (1:1 by weight) in 1,2-dichloroethane. The devices thus obtained were dried at 60 °C for 4 h in a vacuum before electrophotographic measurements.

Electrophotographic Properties Measurement. A computer-controlled GDT-II system was used to measure the electrophotographic properties of the PRs. The samples were mounted onto the flat scanner and negatively charged by a

Table 1. Synthesis and Viscosity of Copolyamic Acids

CPAs	TPP/Cz mole ratios		η_{inh} (dL/g)
	in feed	in polymer ^a	
CPA1	0.00	0.000	2.1
CPA2	0.05	0.048	3.3
CPA3	0.10	0.098	2.9

^a Calculated from the UV-visible spectra of CPAs.

**Figure 2.** UV-visible spectra of (a) CPA1, (b) CPA2, and (c) CPA3.

corotron charger in the dark. After a 2.5 s dark decay, the samples were exposed to a 5 W visible lamp. The decay of surface potential was recorded as the PID curve.

Results and Discussion

Synthesis and Characterization of Copolyamic Acids and Copolyimides. Similar to the usual method for common polyimide synthesis, copolyimides containing tetraphenylporphyrin and carbazole moieties in this work were synthesized by a two-step reaction procedure. Scheme 1 illustrates the synthesis of the CPI. The first step of the reaction led to CPAs, the "precursors" of the corresponding copolyimides. Vigorous stirring, slow addition of PMDA, and low reaction temperature were adopted for this step to obtain CPAs with high molecular weight. Table 1 summarizes the relevant information about the synthesis of CPAs. The molar concentration of TPP and Cz were varied with respect to the fixed concentration of PMDA in such a way that the total amine functionality of the amines kept equivalent to the dianhydride. At high concentrations of TPP relative to Cz, the degree of cross-linking due to the four reacting groups of the tetra(4-aminophenyl)porphyrin increased to a considerable extent to give insoluble copolyamic acids. This unfavorable effect can be completely eliminated by increasing the length of the connecting group between the two porphyrin moieties, which can be done by selecting the suitable molar ratios of TPP/Cz.

The UV-visible absorption spectra of the CPAs are shown in Figure 2. It can be seen that CPA2 and CPA3 have absorption maxima (λ_{max}) at 427 and 285 nm, whereas CPA1 has λ_{max} at 285 nm only. The absorption spectra of the CPAs demonstrated that the mole ratio of TPP to Cz in the resultant polymers is 0.048 in CPA2 and 0.098 in CPA3, nearly matching with the monomer mole ratio of TPP to Cz. The IR spectra of the CPAs exhibit amide characteristic absorption bands around 3400, 1715, 1650, 1300, and 805 cm^{-1} .

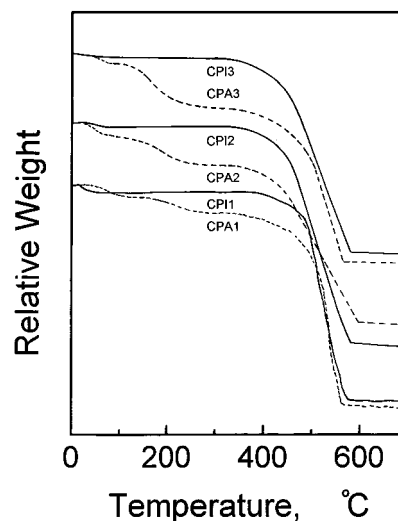
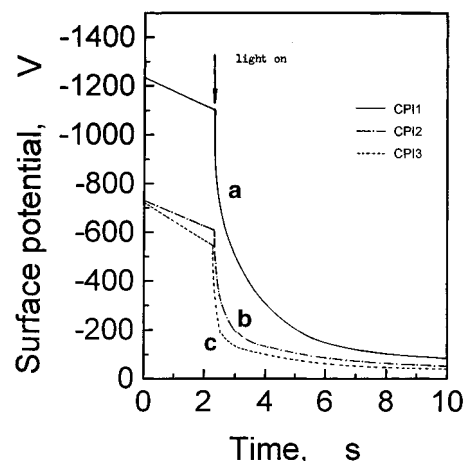
**Figure 3.** Thermogravimetry curves of CPAs and CPIs.**Figure 4.** Photoinduced discharge curves of PRs (a) CPI1, (b) CPI2, and (c) CPI3.

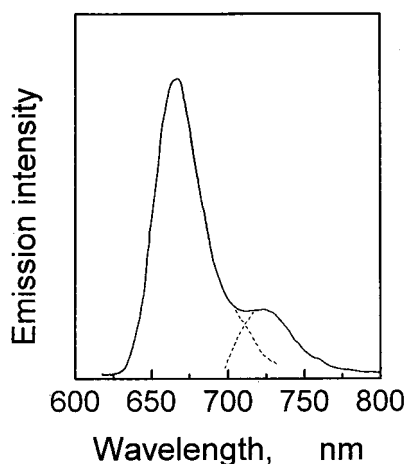
Figure 3 represents the thermogravimetry curves of the CPAs. It is clear that the three CPAs show similar thermal behaviors. The curves consist of three parts: removal of volatile substances under 150 °C, imidization between 150 and 250 °C, and thermolysis above 500 °C. Therefore, 250 °C was chosen as the imidization temperature in this study. After 8 h of heating, complete conversion of the CPAs to the CPIs was obtained, which was confirmed by the complete disappearance of the amide absorption bands at 3400, 1715, 1650, 1300, and 805 cm^{-1} and the appearance of the imide absorption bands at 1775, 1380, and 724 cm^{-1} . The thermogravimetric curves of the CPIs, which were shown in Figure 3 also, indicate that the polymers remain stable up to approximately 500 °C; thereafter, they undergo continuous weight loss due to oxidative degradation.

Photoconductive Properties of CPIs. It is well known that the bilayer photoreceptors and the photoinduced discharge technique are usually used to evaluate the photoconductivity of a material. Figure 4 shows the typical PID curves for the bilayer PRs. The electrophotographic parameters, derived from the PID curves, are summarized in Table 2. It can be seen that, with the increases of TPP content in the CPIs, the rate of photodischarge (R_p) is raised to 500 V/s, whereas the residual potential (V_R) is reduced to -108 V for CPI3.

Table 2. Electrophotographic Data of Copolyimides in PRs^a

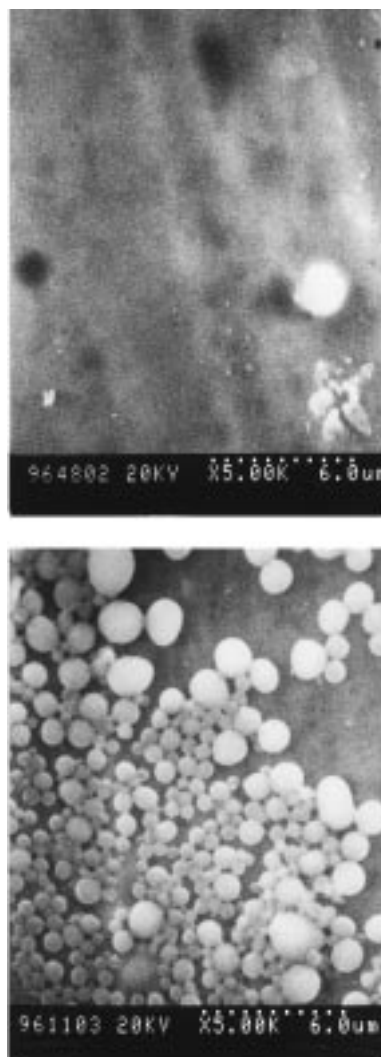
CGL	V_0 (V)	R_D (V/s)	V_R (V)	R_p (V/s)	ΔV_1 (%)	$T_{1/2}$ (s)	$T_{1/2}^{-1}$ (s ⁻¹)
CPI1	-1226	18	-132	312	32.4	1.63	0.61
CPI2	-716	33	-96	375	65.5	0.56	1.79
CPI3	-703	34	-82	437	75.4	0.43	2.33
TPP-doped CPI1 ^b	-978	34	-67	625	68.7	0.63	1.59

^a V_0 , charge acceptance; V_R , residual potential; R_D , rate of dark decay; R_p , rate of photoinduced discharge; ΔV_1 %, percentage of potential during 1 s exposure; $T_{1/2}$, time from the original potential to the half under exposure; $T_{1/2}^{-1}$, reciprocal of $T_{1/2}$. ^b The molar ratio of TPP/Cz is 0.20.

**Figure 5.** Emission spectrum excited at 320 nm for CPI3 films.

Furthermore, data presented in Table 2 also shows that the percentage of photoinduced discharge during 1 s of exposure (ΔV_1 %) rises from 32.4% for CPI1 to 75.4% for CPI3 gradually. On the other hand, the time from original potential to the half under exposure ($T_{1/2}$) decreases from 1.63 s for CPI1 to 0.43 s for CPI3. The photosensitivity ($T_{1/2}^{-1}$) of CPI3, characterized by the reciprocal of $T_{1/2}$, increases to 2.32 s⁻¹, almost 4 orders larger than that of CPI1. Although the V_0 decreases from -1226 for CPI1 to -703 for CPI3 and the rate of dark decay (R_D) increases slightly, all results mentioned above demonstrated clearly that the photoconductivity of the CPIs studied increase significantly with the increasing of TPP content in the copolyimide backbone.

Because tetraphenylporphyrin is a compound with some photosensitivity, it is reasonable to expect that dispersing TPP in polymer binder will produce a photoconductive material. Combining the photosensitivity of TPP with the intrinsic photoconductivity of the CPI1 discussed above may result in polyimide materials with high photoconductive performance. Table 2 also provides the electrophotographic data of TPP-doped CPI1 in which the mole ratio of doped-TPP to the carbazole unit in CPI1 chain is 0.20. The results show that the electrophotographic properties of CPI1 can be improved also by TPP-doping. As can be seen from Table 2, the R_p and ΔV_1 % of TPP-doped CPI1 are 2 times larger than

**Figure 6.** Scanning electron micrograph of (top) CPI3 and (bottom) TPP-doped CPI1.

those of CPI1, while the $T_{1/2}^{-1}$ of the former is 160% higher than that of CPI1. Comparing with the performance of CPI3, however, the results clearly infer that incorporating TPP into the copolymer backbone seems to be a more effective method to improve the photoconductivity than doping TPP into the polyimide matrix.

Because the aromatic polyimides contain an alternating sequence of electron-rich donor and electron-deficient acceptor subunits, it has been suggested that their physical properties are dependent on the existence of charge-transfer complexes formed between their polymer chains.¹³⁻¹⁵ It is well known that TPP is much more electron-rich than carbazole moieties. When TPP is incorporated into the CPI chains, CTCs might form between the TPP (donor) unit in one CPI molecule and the imide (acceptor) unit in another adjacent CPI molecule. The recent studies of spectroscopy and X-ray diffraction provide strong support for the existence of charge-transfer complex formation of polyimides. Figure 5 gives the result of the emission spectrum in CPI3 films measured using a fluorescence spectrophotometer. CPI3 films have emission spectra bands at 666 and 720 nm when excited at 320 nm. This finding supports that the charge-transfer complexes in CPI3 films are undoubtedly formed. Formation of this complex in poly-

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imides appears to increase the photosensitivity effectively. It could be expected that the CTCs formed between TPP and imide units possess a relatively narrower energy gap from base state to excited state. When exposed to light, the CTCs can be easily excited to bound electron–hole pairs (excited CTC) and further excited to separated ions (charge carrier, hole and electron). Alternatively, charge carriers might be relatively difficult to generate from the CTCs formed between Cz and imide units in CPI1 due to their wider

energy gap. For the TPP-doped CPI1 films, on the other hand, the phase separation figure in the films was found by scanning electron microscopy, as can be seen from Figure 6. The separated aggregation domains of TPP lead to an island sea structure. This inhomogeneity prevents the formation of CTCs effectively between TPP and imide units in the films. Further work is necessary to evaluate a correlation between the charge-transfer complex and the photosensitivity.

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