Photoconductivity of Aliphatic Polyimide

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ABSTRACT: Photoconductivity of an aliphatic polyimide, PI(PMDA/DCHM), was investigated, comparing with that of an aromatic polyimide, PI(PMDA/ODA). An enhanced photocurrent was observed for the aliphatic polyimide. The quantum efficiency of the aliphatic polyimide and the aromatic polyimide was 2.1×10^{-5} at 370 nm, as 5.6×10^{-6} at 420 nm respectively, where the film thickness is 1.0 μ . Initial photoresponse behavior was observed to investigate the photoconduction mechanism of the aliphatic polyimide, which shows a different behavior from the aromatic polyimide. The nature of the aliphatic polyimide film is investigated by using the model compounds. The emission spectra of the aliphatic polyimide shows the red-shifting with increasing of the excitation intensity, which indicates the existence of an aggregation of pyromellitic groups intra- and intermolecularly.

1. Introduction

Organic photoconductors (OPCs) and photoconductive polymers have been widely studied for applying to xerographic photoreceptors of copies or printing machines. [1-4] The photoconductivity of Kapton polyimide films has been reported in the literature, which used UV [5], X-ray [6-7], and visible radiation [8-11] as the excitation sources. 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-accepting polyimide, by the addition of electron donors has been reported. [12] Also, the synthesis of new polyimides with various functional groups which show high photosensitivity, was carried. [13-15]

In recent years, the polyimides prepared from alicyclic diamines are attracting much interests because they have good optical spectroscopic and dielectric properties as well as good thermal stability. [16-18] One of the reasons for their high performance is due to the elimination of charge transfer, while the charge transfer state of aromatic polyimides is formed between the aromatic diamines as electron donors and the aromatic dianhydrides as electron acceptors both intra- and intermolecularly. There has been no previous work on the photoconductivity of the aliphatic polyimides, comparing with those of aromatic polyimides.

2. Experimental

Synthesis of Polyimides and Model Compounds PI(PMDA/ODA) was prepared from pyromellitic dianhydride (PMDA) and oxydianiline (ODA). PI(PMDA/DCHM) was prepared from pyromellitic dianhydride and diaminodicyclohexylmethane (DCHM). *N-N'*-di-*n*-butylpyromellitic diimide, M(PMDA/*n*-BA), was synthesized by using *n*-butylamine and pyromellitic dianhydride. *N-N'*-di-*n*-cyclohexylpyromellitic diimide, M(PMDA/CHA), was synthesized from pyromellitic dianhydride and cyclohexylamine. The chemical structure is shown in Figure 1.

Figure 1. Chemical structure of PI(PMDA/DCHM) and PI(PMDA/ODA).

Preparation of Sample Films A 5% dimethylacetamide (DMAc) solution of the poly (amic acid) was spin-coated onto conductive indium tin oxide coated glasses (ITO glass), which has been washed with methylene chloride (CH_2Cl_2) in a ultrasonic chamber. Then the films were heated to the imidization temperature region, holded 1 hr at 160°C, 180°C, and 200°C, respectively.

Measurement of Photocurrent Figure 2 shows the schematic diagram of the 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. Photocurrent was measured with a picoammeter (PM-18U, TOA Co. Ltd.) Illumination was afforded by the monochromatized radiation from a xenon lamp (100V/500W).

Figure 2. Schematic diagram of the photocurrent measuring instrument.

3. Results and Discussion

Photocurrent Measurement of PI(PMDA/DCHM) Figure 3 shows the photocurrent of PI(PMDA/DCHM) and PI(PMDA/ODA) measured in the applied field range of $2.0 \times 10^4 \sim 5.0 \times 10^5$ V/cm, that is, 2~50 V. The film thickness of the samples is 1.0μ , and the samples were illuminated at 350 nm for PI(PMDA/DCHM), at 400 nm for PI(PMDA/ODA) in order to photo-irradiate at the same ODs. Normalized UV absorption spectra of the polyimide thin films casted onto ITO glasses are shown in Figure 4. The maximum photocurrents for PI(PMDA/DCHM) and PI(PMDA/ODA) were 1.8×10^{-8} A and 6.2×10^{-8} A, respectively, at an applied electric field of 5.0×10^5 V/cm. The darkcurrents are negligibly small compared to the photocurrents in this experiment. It is very interesting that the photocurrent of the aliphatic polyimide film is larger than that of the aromatic polyimide film in all applied electric fields, because there has been no previous work on the photoconductivity of aliphatic polyimides, though the photoconductivity of the aromatic polyimides is well known. [5-11, 12]

Figure 3. Photocurrent as a function of applied electric field, E , illuminated at 350 nm for PI(PMDA/DCHM) (○), at 400 nm for PI(PMDA/ODA) (□) film. Thickness of the films is both 1.0μ . The filled marks are the dark currents.

Figure 4. UV absorption spectra of PI(PMDA/DCHM) (—) and PI(PMDA/ODA) (---) films normalized by their thickness.

Action Spectra and Quantum Efficiency Figure 5 shows the action spectra of the photocurrents of PI(PMDA/DCHM) and the PI(PMDA/ODA), whose film thickness is 1.0μ under an applied electric field of 5.0×10^{-5} V/cm. A maximum in the photocurrent of PI(PMDA/ODA) is observed in Figure 5, however the optical density of PI(PMDA/ODA) below 350 nm is so large that the absorption of light is heterogeneous. And so the action spectra below 350 nm cannot be discussed and the maximum is not regarded as a peak. The small increase in the photocurrent over 400 nm in PI(PMDA/ODA) film has been attributed to the formation of the charge transfer complexes in the ground state. [12, 20, 21] On the other hand, the PI(PMDA/DCHM) film

shows a maximum in the photocurrents at 350 nm, when the optical density is small enough. Figure 6 shows the wavelength dependence of the quantum yields of PI(PMDA/DCHM) and PI(PMDA/ODA), which are normalized by assuming that the photocurrent is based on the absorption of the bulk film. The quantum yields of the aliphatic polyimide film above 400 nm is negligibly small, while those below 400 nm become longer. The strong wavelength dependence of the quantum yields of the PI(PMDA/DCHM) is very interesting, and it cannot be explained if we assume that photo-generated carriers are transported in the homogeneous aliphatic polyimide medium. There are two possible reasons for the wavelength dependence of the quantum yields of PI(PMDA/DCHM). One is because the photocurrent is based on the excitation of another activated species whose UV absorption is different from the bulk absorption. The other reason is that photocurrent is dependent on the absolute value of the optical density of the sample, though the charge generation is based on the bulk absorption.

Figure 5. Action spectra of PI(PMDA/DCHM) (○) and PI(PMDA/ODA) (◁) under an applied electric field of 5×10^5 V/cm. The data whose OD is greater than 1 are plotted with filled marks.

Figure 6. Wavelength dependence of the quantum yield of PI(PMDA/DCHM) (○) and PI(PMDA/ODA) (▷) under an applied electric field of 5×10^5 V/cm. The data whose OD is greater than 1 are plotted with filled marks.

Thickness and Light Intensity Dependence To confirm the latter assumption, the effects of film thickness and light intensity are measured. Figure 7 shows the thickness dependence of the photocurrents of PI(PMDA/DCHM), measured for the films whose film thickness is 1.0, 4.4 μ , respectively. The absorption of the both films above 450 nm is regarded as homogeneous because their ODs are small enough, however the photocurrent of the 4.4 μ film is much greater than that for 1.0 μ , though the difference in the absorption light is estimated as only 4 times. This results shows the strong OD dependence of the photocurrent of PI(PMDA/DCHM) even at the same wavelength. One of the reason for the OD dependence of the photocurrent is thought that the photoconduction is affected by the concentration of the carriers, and that the extent of the mobility

of the carrier is limited. The samples in the present investigation are in the sandwiched configuration between electrodes, so the carriers are thought to be produced from a photoexcited state of PI(PMDA/DCHM). Suppose that the mobility of the carriers is limited, the conductivity is expected to be large when the carrier concentration is so high that the mobile regions are overlapped, while the photoconductivity is small below the critical concentration. In order to investigate the effect of the carrier concentration on the photocurrents, the quantum yields of PI(PMDA/DCHM) and PI(PMDA/ODA) were measured at various light intensities. As shown in Figure 8, the quantum yields have strong light intensity dependence until 1.5×10^{-9} Einstein $\text{cm}^{-2} \text{s}^{-1}$, and the dependence becomes saturated after then. This observation suggests that the photoconduction may include more than single mechanism. Figure 9 shows response of the photocurrent of the polyimides at 4.0×10^4 V/cm of applied electric field and illuminated at 350 nm for PI(PMDA/DCHM), at 400 nm for PI(PMDA/ODA) in order to photo-irradiate at the same ODs. The photocurrent of the PI(PMDA/ODA) film, stands up in the initial stage, followed by the decay to an equilibrium within 50 seconds. As stop of the illumination, it reaches to the dark current level immediately within a few seconds. However, the photocurrent of PI(PMDA/DCHM) film reaches to an equilibrium gradually after a small decay, suggesting that the photoconduction of the aliphatic polyimide contains a different kind of phenomena, while the photoconduction of the aromatic polyimides is reported owing to the charge carrier transport formed in the ground state. [12, 20]

Figure 7. Thickness dependence of photocurrent of PI(PMDA/DCHM) films under an applied electric field of 5×10^5 V/cm. The data whose OD is greater than 1 are plotted with filled mark. Film thickness is 1.0 μ (○), 4.4 μ (◁)

Figure 8. Quantum efficiency as a function of light intensity under an applied electric field of 5×10^5 V/cm, at 350 nm for PI(PMDA/DCHM) (●) and at 400 nm for PI(PMDA/ODA) (□) film. The ODs of the films are the same.

Figure 9. Initial photoresponse with time of PI(PMDA/DCHM) (---) and PI(PMDA/ODA)(—) under an applied electric field of 4.0×10^{-4} V/cm, at 350, 400 nm, respectively.

Fluorescence Spectra of the Aliphatic Polyimide Film and Its Model Compounds

Figure 10 shows the absorption and the emission of *N*-substituted imides in dichloromethane (CH_2Cl_2). Red shift of the absorption of the models was observed in the order of M(PMDA/CHA), M(PMDA/*n*-BA), and PMDA at 380, 355, and 330 nm, respectively, due to the electron donating ability of the substituents. They have fluorescence at 430, 420, and 350 nm respectively. Those emissions are originated in the locally excited state of PMDA moieties, while an aromatic imide has charge transferred fluorescence in the longer wavelength region. [21]

Figure 11 shows the excitation and emission spectra of PI(PMDA/DCHM) film,

whose thickness is 0.5μ . When the film is excited at 300 nm, fluorescence is observed at 430 nm, which is identical to the fluorescence of the locally excited state of PMDA moieties. The emission maxima shift to the longer wavelength as the sample is excited at longer wavelength.

Figure 10. UV absorption and emission spectra of model compounds in CH_2Cl_2 . a; PMDA $5.1 \times 10^{-4}\text{M}$, b; M(PMDA/*n*-BA) $5.4 \times 10^{-4}\text{M}$, c; M(PMDA/CHA) $5.0 \times 10^{-4}\text{M}$

Figure 11. Excitation and emission spectra of PI(PMDA/DCHM) film. Excitation spectra were obtained by observing the emission at 450, 500, 520 nm respectively. Emission spectra were recorded by exciting at 300, 350, 370, 380, 390, 400, 450 nm respectively.

This continuous shift of the emission shows that there are various absorption and emission sites in the aliphatic polyimide matrix, whose energy levels are slightly different each other. These sites

are regarded to be related to the intermolecular aggregates of pyromellitic moieties, whose aggregation size is different site by site. The excitation maxima of the aggregates is located above 350 nm region. The quantum yields in Figure 6 were calculated based on the absorption of bulk films, which is mainly corresponds to the absorption of monomeric units of the chromophores. The wavelength dependence of the quantum yields may be attributed to assumption that the origin of the photocurrent is based on the excitation of the aggregates of PMDAs, but it is not clear upto now.

4. Conclusion

We observed that the aliphatic polyimide have higher photoconductivity than the aromatic polyimide below 400 nm region. The quantum yields of the polyimides depend on the irradiation wavelength. Main reason for the wavelength dependence is thought that the photocurrent of PI(PMDA/DCHM) is affected by the concentration of carriers. However the effect of light intensity and the time response experiments suggest the involvement of some mechanism, which are not perfectly clear upto now. The fluorescence of PI(PMDA/DCHM) shows the existence of various ground state aggregate of pyromellitic moieties.

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