Photoconductive Studies on Langmuir-Blodgett Multilayers of a Copolyimide Containing Phthalocyanine and Carbazole

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ABSTRACT: The Langmuir-Blodgett multilayers of a copolyimide incorporating both copper-phthalocyanine and carbazole as electron donors were fabricated into a dual-layer photoreceptor as the charge-generating layer (CGL). The photoconductive properties of this photoreceptor were studied by photoinduced discharge measurement and compared with a reference photoreceptor in which the charge-generating layer was a solvent-casting film of the copolyimide. It was found that the photoreceptor consisting the copolyimide LB multilayers have the advantages of high photosensitivity, low residual potential, and high photodischarge rate. It was explained on the basis of the stacked molecule packing and charge−transfer complexes formation in the LB multilayers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1403–1408, 1998

Key words: aromatic polyimide; Langmuir-Blodgett multilayers; photoconductivity; charge−transfer complexes, photoreceptor

INTRODUCTION

Aromatic polyimides possess high thermostability and excellent mechanical, chemical, and electrical properties. That they are also photosensitive makes them highly interesting. Even during the pioneering stages, the photoconductive properties of the typical polyimide such as Kapton polyimide were established.[1−6] However, Kapton is weekly photoconductive. It was reported by Freilich[5] that the addition of electron donors to Kapton polyimide films results in an enhancement of photocurrent by as much as five orders of magnitude compared to the virgin polymer. Therefore, it is reasonably expected that incorporating of suitable electron donors, such as carbazole and/or phthalocyanine, into the polyimide backbone will lead to an increase of the photoconductivity. Several

poly(metal phthalocyanine)imide copolymers with a low to high degree of polymerization and superior thermal stability have been synthesized and their electric conductivity measured by Achar et al.[7] and Shirai,[8] respectively. However, no data are available on their photoconductive properties.

In the past decade, a various of polyimide Langmuir-Blodgett films with a monolayer thickness of 0.4 nm have been successfully prepared using a "Precursor Method" reported by Kakimoto and his co-workers.[9,10] Because stacked molecular organization and small intermolecular distance, leading to high charge mobility,[11] can be obtained in Langmuir-Blodgett films,[12,13] it is of interest to investigate the photoconductive properties of the polyimide LB films with various chemical structure. Photocurrent behavior and photoinduced surface potential of several polyimides LB films deposited on metal electrodes have been investigated respectively by Nishikata et al.[5,14] and Iwamoto et al.[15,16] In this work, the LB multilayers of a polyimide copolymer incorporating both copper phthalocyanine and carbazole as electron donors were fabricated into a photoreceptor and its pho-

toconductive properties were measured by means of photoinduced discharge technique. The results were compared with those of the corresponding coating film and were discussed on the basis of molecule packing and charge–transfer complexes formation.

EXPERIMENTAL

Materials

The details of the synthesis, characterization, and monolayer spreading behavior of the copolypyromellitamic acid (PAA) and the corresponding copolyimide (CPI) with both copper phthalocyanine and carbazole groups were described in a previous paper.[17] 1-Naphthaldehyde hydrazone (1-NH) was synthesized and purified in our lab according to the usual procedures. Dimethyl-acetalamide was distilled over CaH_2 at reduced pressure and stored under a nitrogen atmosphere. All other reagents were of analytical and used without purification.

Preparation of Langmuir-Blodgett Films

Deionized water (specific resistance 18M cm) was used as a subphase. N,N-Dimethyloctadeylamine was used to form PAA amine salts monolayer at the air–water interface. Measurement of surface pressure–area isotherms and deposition of the amine salts monolayer on substrates were carried out using a computer-controlled Langmuir trough. According to the "Precursor Method,"[9,10] the PAA amine salts LB multilayers were then converted to PI and the hydrocarbon chains removed by a solvent treatment.

Photoreceptor Design and Fabrication

The photoreceptor device configuration used to evaluate the LB multilayers of the copolyimide was dual-layer structure. The electrode substrate, a aluminum plate, was overcoated with a poly (methyl methacrylate) (PMMA) charge blocking layer (or interface layer—IFL). The charge generating layer (CGL) was the Langmuir-Blodgett multilayers of the copolyimide. The charge transport layer (CTL) was a solid solution of 1-naphthaldehyde hydrazone (1-NH) in PMMA (1 : 1 by weight).

The charge blocking layer was prepared from a 1% by weight solution of PMMA in chloroform and coated with 0.5-mm wet gap. It was cured at 100°C for 20 min. The multilayers of the copolyimide, acting as charge-generating layer (CGL), was then deposited using the method as mentioned above. The 1-NH/PMMA charge transport layer (CTL) was coated from a 10-mL chloroform solution of 0.5 g 1-NH and 0.5 g PMMA. The device thus obtained was dried under vacuum at 60°C for 24 h before photoconductivity measurement.

For comparison with the photoreceptor containing LB charge-generating layer, a reference photoreceptor was prepared in which the CGL was a coating film of the copolyimide. The IFL and CTL were deposited by the same procedures used for the photoreceptor containing LB CGL. The charge generating layer was coated from a 10-mL DMAc solution of 0.2 g copolypyromellitamic acid with a blade having a 1.0-mm gap. The device was then dried in nitrogen at 250°C for 6 h to form the copolyimide charge-generating layer.

Photoconductivity Measurement

A computer-controlled GDT-II system was used to measure the photoconductive properties of the photoreceptors. The samples were mounted onto the flat-plate scanner. A corotron wire was used for charging the samples to a negative potential. A 5 W visible lamp was used as a light source to plot the photoinduced discharge curve (PIDC) of the photoreceptors.

RESULTS AND DISCUSSION

Scheme I illustrates the synthesis and preparation of the copolyimide (CPI) Langmuir-Blodgett multilayers with both copper phthalocyanine and carbazole groups. The UV-visible spectra of the copolymer demonstrated that the mol ratio of copper phthalocyanine to carbazole in the copolyimide is 1 : 4.86. A typical surface pressure–surface area curve (π-A curve) of the copolyamic acid salt is shown in Figure 1. Deposition of the salt was successfully carried out at a surface pressure of 20 mN m^{-1} onto an appropriate plate by dipping through the air–water interface at a rate of 5 mm min^{-1} at 20°C.

Figure 2(a) shows a cross-section through the four-layer photoreceptor that was constructed to evaluate the performance of the copolyimide Langmuir-Blodgett multilayers as the charge-generating layer. It consists of a 3-mm aluminum plate
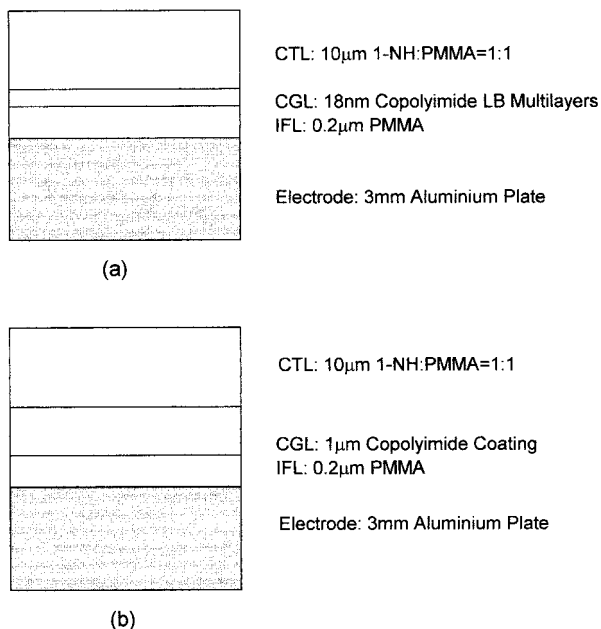
Figure 1 Surface pressure–area isotherm of the co-polyamic acid salt at 20°C.

that acts as both a support and a conducting substrate, a coating layer consisting of 0.2 μm poly (methyl methacrylate) (PMMA), a Langmuir-Blodgett layer consisting of 30 transferred monolayer, and a charge-transporting top layer consisting of a concentrated dispersion of 1-NH in a PMMA binder. Figure 3(a) provides a typical photoinduced discharge curve (PIDC) for this photoreceptor. Comparison was made with photoreceptor in which the charge-generating layer was a 1-μm solvent-cast copolyimide coating, as can be seen from Figure 2(b) and Figure 3(b). From PIDC, several important parameters, including

Scheme 1

CTL: 10μm 1-NH:PMMA=1:1

CGL: 18nm Copolyimide LB Multilayers
IFL: 0.2μm PMMA

Electrode: 3mm Aluminium Plate

(a)

CTL: 10μm 1-NH:PMMA=1:1

CGL: 1μm Copolyimide Coating
IFL: 0.2μm PMMA

Electrode: 3mm Aluminium Plate

(b)

Figure 2 Structure of the four-layer photoreceptors. CTL: charge transfer layer; CGL: charge-generating layer; IFL: interface layer.

photosensitivity, dark decay (R_d), residual potential (V_r), photodischarge rate (R_p), the percentage of potential discharge after 1 s of exposure $(\Delta V_1\%)$, and the time from the original potential to half under exposure $(t_{1/2})$, can be obtained. Here, the photosensitivity can be characterized by the reciprocal of $t_{1/2}$.

Generally, high photoconductive performance of a material finds expression in high photosensitivity, low dark decay, high photodischarge rate, and low residual potential. Table I summarizes the photoconductive data for these two photoreceptors. The performance of the photoreceptor with copolyimide coating as charge-generating layer is poor, being characterized by a high residual potential V_r of -195 V, a low percentage of photodischarge $\Delta V_1\%$ of 30.6%, a low photodischarge rate R_p of 250 V/s, and a low photosensitivity $t_{1/2}^{-1}$ of 0.48 s^{-1}. However, as can be seen from Table I, it also showed a relatively high charge acceptance V_0 of -945 V and a relatively low dark decay R_d of 31.2 V/s, which were due to the thickness of the CGL. On the other hand, it was found that the photoreceptor with the copolyimide Langmuir-Blodgett multilayers as the charge-generating layer has a very high percentage of photodischarge $(\Delta V_1\% = 63.3\%)$, a fast rate of photodischarge $(R_p = 375$ V/s$)$, and significantly a short time of half-discharge $(t_{1/2} = 0.63$ s$)$.

On the whole, these results indicate quite clearly that the copolyimide LB multilayers have the advantage of high photosensitivity, especially being characterized by the large value of $t_{1/2}^{-1}$. Because the aromatic polyimides contain an alternating sequence of electron-rich donor and electron-deficient acceptor structure elements, it has been suggested that their physical properties are dependent on the existence of charge–transfer complexes formed between their polymer chains. Recent studies of fluorescence spectroscopy and X-ray diffraction provide strong support for the existence of these charge–transfer complexes formations in the polyimide matrix.[18–20] Concerning their photoconductive properties, the donor–acceptor interaction between the structure elements of chains is the main factor determing the photosensitivity.[5] For the copolyimide studied in this work, it could be expected that incorporating large systems such as phthalocyanine and carbazole into the polymer chain will promote the interaction between electron donor (copper phthalocyanine and carbazole groups) and electron acceptor (imide portion of the polymer backbone). The charge–transfer complexes (CTC) will form between the polyimide chains and result in increasing the photosensitivity. However, it is well known that the efficiencies of intermolecular charge–transfer complexes formation are influ-
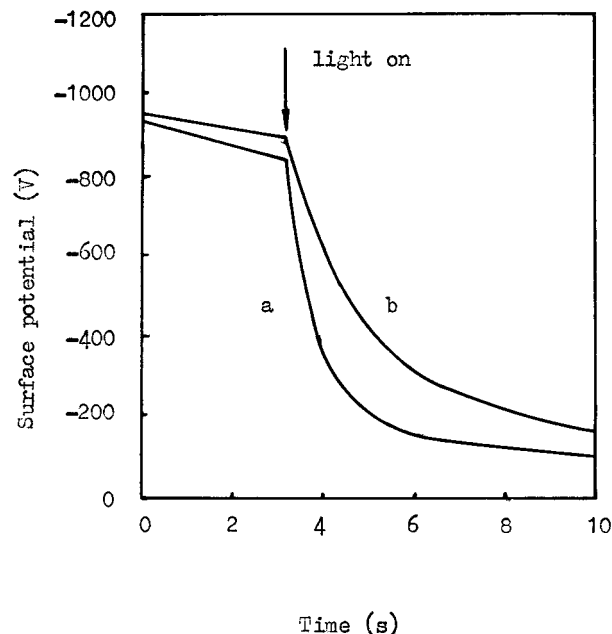

Figure 3 Photoinduced discharge curves for the photoreceptors. (a) Langmuir-Blodgett multilayers as CGL; (b) coating film as CGL.

Table I Photoconductive Properties of the Copolyimide

CGL	V_0 (V)	V_R (V)	R_d (V/s)	R_p (V/s)	$\Delta V_1\%$	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s^{-1})
Coating film	−945	−195	31.2	250	30.6	2.06	0.48
LB film	−921	−140	43.2	375	63.3	0.63	1.60

V_0: charge acceptance; V_R: residual potential; R_d: rate of dark decay; R_p: rate of photodischarge; $\Delta V_1\%$: percentage of potential discharge after 1s exposure; $t_{1/2}$: time from the original potential to half under exposure; $t_{1/2}^{-1}$: reciprocal of $t_{1/2}$.

enced by various structural and thermodynamic factors, including the driving force for interaction, orientation factors, reorganization energy of donor and acceptor, and especially the distance of separation between species. (CTC just form when the distance between donor and acceptor is less than 6 Å[21]). In the solvent casting film, it may be assumed that the bending and twisting configuration, due to the steric hindrance effect of the phthalocyanine groups, and the rigid characteristic of the copolyimide chains disturb a packed structure formation of the polymer chains, in turn, disturb the formation of charge−transfer complexes. In the Langmuir-Blodgett multilayers, on the other hand, compact packing and a high degree alignment of polyimide chain could be reached. This was borne out in the characterization of various polyimides LB films, which involved FTIR, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atom force microscopy (AFM), and liquid crystal alignment properties studies.[22] As can be seen by Figure 4, the compact packing and alignment of the chains are favorable to the formation of charge−transfer complexes as well as improve charge mobility, which lead to high photosensitivity of the LB multilayers. Furthermore, carriers
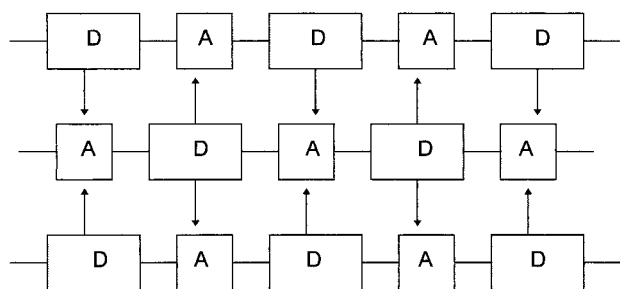
in the polyimide matrix would be transported perpendicular to the polymer chains and so the shorter distance between the neighboring chains in the LB multilayers makes carriers transport more easily. On the other hand, the phthalocyanine rings, carbazole rings, and the imide benzene rings in the copolyimide LB multilayers enhanced coplanarity more than those of in the casting film and, thus, the PI LB multilayers had the more expanded conjugate system between the chains. The overlapped orbitals both along and between chains will also lead to a high photosensitivity. Ongoing experiments are under way to elucidate the above hypothesis and to evaluate a correlation between the charge−transfer complexes and the photosensitivity.

Figure 4 Schematic representation of charge transfer between polymer chains in the Langmuir-Blodgett multilayers; D represents the donor part, and A the acceptorpart in the polyimide molecule. The arrows show the direction of charge transfer.

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