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Electrophotographic properties of copolyimide Langmuir–Blodgett films having different chemical structures

Zhi-Kang Xu [a,b,*], Zhen-Mei Liu [a,b], Bao-Ku Zhu [a,b], You-Yi Xu [a]

[a] Institute of Polymer Science, Zhejiang University, Hangzhou 310027, PR China
[b] State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, PR China

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Abstract

A series of copolyimide Langmuir–Blodgett (LB) films with different chemical structure was fabricated into xerographic photoreceptors and its electrophotographic properties were measured by photoinduced discharge method. Comparison was made between the LB films and the corresponding 1 μm solvent-cast films. It was found that the copolyimide LB films have the advantage of high electrophotographic performance. The results could be ascribed to charge-transfer complexes formation, nanometer film thickness, compact molecular packing and chain alignment in the copolyimide LB films. © 2001 Published by Elsevier Science B.V.

Keywords: Langmuir–Blodgett films; Solvent-cast films; Copolyimide

1. Introduction

Aromatic polyimides have very desirable characteristics, such as high thermal resistance, high modulus, high tensile strength, excellent chemical stability, and good electrical properties. That they are also photoconductive makes them highly interesting. Even during the pioneering stages, the photoconductive properties of the typical polyimide such as Kapton polyimide have been investigated [1–6]. LaFemina et al. [7] and Lee et al. [8] reported, respectively, that the radical anions of the electron-accepting pyromellitic imide moieties and the radical cations of biphenyl ether moieties formed by electron transfer resulted in the photoconductivity of Kapton polyimide. However, Kapton is weakly photosensitive. It has been 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 as compared to the virgin polymer. Wang et al. [9] have pointed out that increase in crystallinity of polyimides upon annealing can also lead to significant improvement of the photosensitivity. In previous papers [10,11], we have found that an increase in photoconductivity can be achieved by incorporating suitable electron donors, such as phthalocynine, into the polyimide backbone. One of the reasons for this increase in photoconductive performance is the formation of charge-transfer complexes, because 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.

As claimed in some literatures [12–14], high conductivity and photoconductivity could be achieved also in LB films because a stacked molecular organization and the small intermolecular distance in the films induce high charge mobility. In the past decade, a series of polyimide LB films with a monolayer thickness of 0.4 nm have been successfully prepared and much attention has been paid to their potential applications [15–21]. For example, photocurrent behavior and photoinduced surface potential of several polyimide LB films fabricated in photodiode or deposited on metal electrodes have been reported, respectively, by Nishikata et al. [18,19] and Iwamoto and Fukuda [20,21]. Because the LB film is much thinner than the spin-coated film, it is of interest to investigate the photoconductive properties of polyimide LB films fabricated in xerographic photoreceptors. In this paper, therefore, the electrophotographic properties of a series of copolyimide LB films with carbazole, phthalocyanine and porphyrin as electron donors were studied by using the photoinduced discharge technique. The results were discussed on the basis of charge-transfer complexes formation, film thickness and molecule packing.

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* Corresponding author. Present address: Institute of Polymer Science, Zhejiang University, Hangzhou 310027, PR China.
Tel.: +86-571-7951342-8218.
E-mail address: xuzk@ipsm.zju.edu.cn (Z.-K. Xu).

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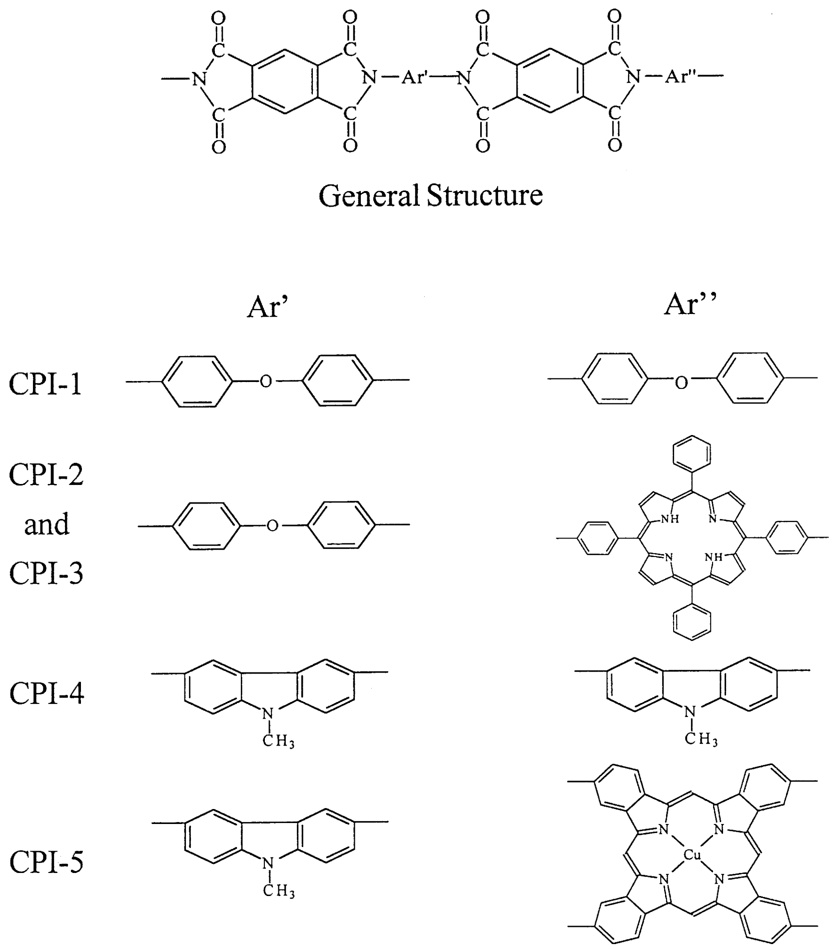

Fig. 1. Chemical structure and designation of the polyimides used in this work.

2. Experimental details

2.1. Materials

The details of the synthesis, characterization, and monolayer spreading behaviors of the "precursor" polymers, copolyamic acids (CPAAs) and the corresponding copolyimides studied in this work were described in previous papers [10,11,22]. The chemical structures of the corresponding copolyimides are shown in Fig. 1. The UV–Visible spectra of the polymers demonstrated that the mole ratio of porphyrin to oxydianiline is 1:40 in CPI-2 and 1:20 in CPI-3, and the mole ratio of phthalocyanine to carbazole is 1:4.85 in CPI-5. 4-(*N*,*N*′-diethylamino)-benzaldehyde-1,1-diphenyl-hydrazone (DEH) was synthesized and purified in our lab following the usual procedures. Dimethyl acetamide was distilled over CaH_2 under reduced pressure before use. All other reagents were of analytical degree and used without purification.

2.2. Preparation of LB films

Copolyimide LB films were prepared using the reported procedures. Deionized water (specific resistance $\geq$18 MΩ cm) was used as a subphase. *N*,*N*-dimethyloctadeylamine was used to form CPAA 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" [15,16], the obtained CPAA amine salts LB films were then converted to CPI LB films and the hydrocarbon chains removed by a solvent treatment.

2.3. Photoreceptor design and fabrication

The photoreceptor device configuration used to evaluate the copolyimide LB films was a four-layer structure. The electrode substrate, an aluminum plate, was overcasted with a poly(methyl methacrylate) (PMMA) charge blocking layer (or interface layer, IFL). The charge-generating layer (CGL) was the LB film of the copolyimides. The charge transport layer (CTL) was a solid solution of DEH in polycarbonate (PC) in 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

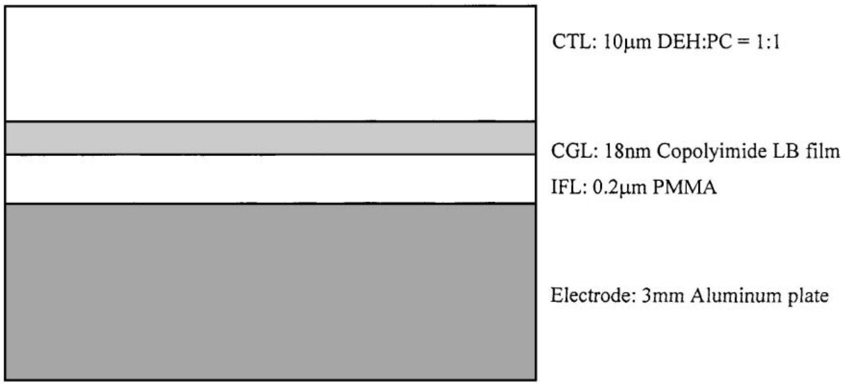

Fig. 2. Structure of the four-layer photoreceptor CTL, CGL, IFL.

multilayer films of the copolyimides, acting as CGL, were then deposited using the method as mentioned above. The DEH/PC CTL was coated from a 10 ml chloroform solution of 0.5 g DEH and 0.5 g PC. The devices thus obtained were dried under vacuum at 60°C for 24 h before photoconductivity measurement.

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

2.4. Measurement

UV/Vis adsorption spectra were recorded on Shimizu UV-240 spectrometer. X-ray diffraction analysis was performed on Rigakudenki/Max-3B System with a Cu Kα X-ray source (40 kV, 100 mA). 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 curves (PIDCs) of the photoreceptors.

3. Results and discussion

Fig. 2 shows a cross-section through the four-layer photoreceptor that was constructed to evaluate the performance of the copolyimide LB films. It consists of a 3 mm aluminum plate that acts as both a support and a conducting substrate, a coating layer consisting of 0.2 μm PMMA, an LB layer consisting of 30 transferred monolayer, and a charge-transporting top layer consisting of a concentrated dispersion of DEH in a PC binder. Fig. 3 provides a typical PIDC for the photoreceptor with CPI-5 LB film as CGL. From the PIDC, several important parameters, including photosensitivity, dark decay (R_d), residual potential (V_r), photodischarge rate (R_p), the percentage of potential discharge during 1 s exposure (ΔV_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 electrophotographic performance of a material finds expression in high photosensitivity, low dark decay, high photodischarge rate and low residual potential. Table 1 summarizes the data of electrophotographic properties for these copolyimide LB films. It was found that incorporating large π systems such as porphyrin and phthalocyanine into the polyimide backbone enhanced the photoconductivity significantly. As can be seen from Table 1, the photosensitivity, reciprocal of $t_{1/2}$, increases with increasing porphyrin mole fraction in the copolyimides

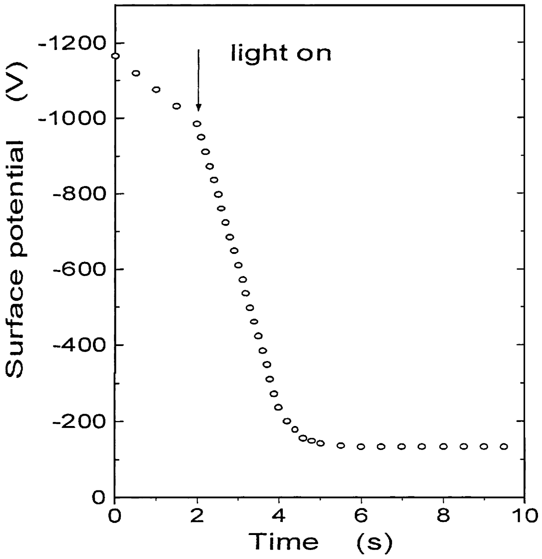

Fig. 3. Photoinduced discharge curve for the photoreceptor using CPI-5 LB film as CGL.

Table 1
Photoconductive properties of the copolyimides

Polymer for charge generating layer	V_0[a] (V)	V_R[b] (V)	R_d[c] (V/s)	R_p[d] (V/s)	ΔV_1%[e]	$t_{1/2}$[f] (s)	$t_{1/2}^{-1}$[g] (s^{-1})
CPI-1							
Coating	−1226	−132	18	312	32.4	1.63	0.61
LB film	−1007	−134	15	350	37.8	1.56	0.64
CPI-2							
Coating	−716	−96	33	375	65.5	0.56	1.79
LB film	−684	−66	33	450	77.3	0.29	0.84
CPI-3							
Coating	−703	−82	34	437	75.4	0.43	2.33
LB film	−657	−52	33	450	83.8	0.25	4.00
CPI-4							
Coating	−1734	−374	17	500	29.9	2.31	0.43
LB film	−1015	−257	15	250	38.3	1.62	0.62
CPI-5							
Coating	−1195	−195	21	250	51.8	1.02	0.98
LB film	−1164	−132	90	375	82.4	0.25	4.00

[a] V_0: charge acceptance.
[b] V_R: residual potential.
[c] R_d: rate of dark decay.
[d] R_p: rate of photo-discharge.
[e] ΔV_1%: percentage of potential discharge after 1 s exposure.
[f] $t_{1/2}$: time from the original potential to half under exposure.
[g] $t_{1/2}^{-1}$: reciprocal of $t_{1/2}$.

from CPI-1 to CPI-2 to CPI-3. The CPI-5 LB film exhibits the highest photosensitivity in this series. These results are not surprising, as similar behaviors have been already observed by Freilich [5] in electron-donor doped Kapton polyimide systems. 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 formation in the polyimide matrix [23–25]. Concerning their photoconductive properties, the donor–acceptor interaction between the structure elements of chains is the main factor determining the photosensitivity [5]. For the copolyimides studied in this work, it could be presumed that incorporating large π systems such as porphyrin into the polymer chain promotes the interaction between electron donor (porphyrin groups) and electron acceptor (imide portion of the polymer backbone). The enhanced interaction allow the charge-transfer complexes (CTCs) to form conveniently between the copolyimide chains and to result in increasing the photosensitivity. On the other hand, one could expect that the porphyrin rings, phthalocyanine rings and the imide benzene rings in the CPI-2, CPI-3 and CPI-5 LB films enhance coplanarity more than those in the CPI-1 LB film. Therefore, the former three CPI LB films have more expanded conjugate system along the chains. The overlapped orbital, both along and between, chains also lead to high photosensitivity.

Nevertheless, an unexpected result of these studies is that the photoconductive performance of CPI-4 LB film is poor, being characterized by a high residual potential V_r of −257 V, a low percentage of photodischarge ΔV_1% of 38.3%, and a low photosensitivity $t_{1/2}^{-1}$ of 0.62 s^{-1}. The value shows that the photosensitivity is smaller by about 6-fold than CPI-5 and is almost the same as CPI-1. These mean that the incorporation of carbazole into the polyimide backbone does not improve the photosensitivity as expected. The reason for these results is not clear at present.

Comparison was made between the LB films and the corresponding 1 μm solvent-casting films of the copolyimides. Data presented in Table 1 quite clearly indicate that the copolyimide LB films have the advantage of high photoconductive performance, especially being characterized by the large values of $t_{1/2}^{-1}$, ΔV_1% and R_p. These results may be explained considering the differences in film thickness, molecular packing and chain alignment between the LB films and the casting films.

Firstly, the thickness of the solvent-casting films is about 1 μm, while that of the LB films with 30 monolayers is only 18 nm. Recently, preliminary results have been reported by Zhang et al. [26] to explore nanoscale size effects on semiconducting polymers through photoconductivity experiments on electrophotographic photoreceptors as the thickness of a conjugated polymer coating, acting as CGL in the photoreceptor, was varied in the nanoscale range. A 3-fold increase in quantum efficiency for photogeneration and an enhancement of photosensitivity have been observed when the thickness of the CGL was reduced from ∼100 to ∼10 nm.

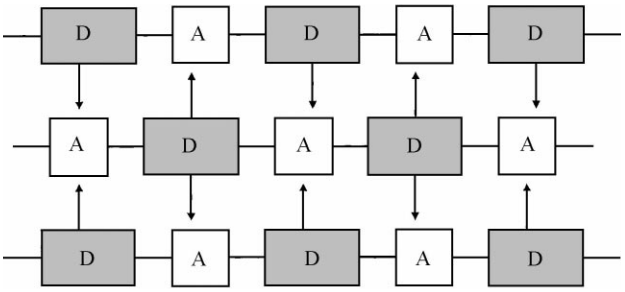

Fig. 4. Schematic representation of charge-transfer between polymer chains in the LB film; D represents the donor part and A the acceptor part in the polyimide molecule. The arrows show the direction of charge-transfer.

The authors have related their results to the generally small exciton diffusion lengths in semiconducting polymers and the interfacial nature of the charge photogeneration process in the bilayers. Following this argument one could ascribe the high photosensitivity of the copolyimide LB films in this work partially to their nanoscale size thickness.

Secondly, it is well known that the efficiencies of intermolecular CTC formation are influenced by various structural and thermodynamic factors, including the driving force for interaction, orientation factors, reorganization energy of donor and acceptor, and the distance of separation between species. Among them, it is important to consider the distribution of the donor–acceptor distance [27]. In the solvent-casting films, it may be assumed that the bending and twisting configuration, due to the steric hindrance effect of the phthalocyanine or porphyrin groups, and the rigid characteristic of the copolyimide chains disturb a packed structure formation of the polymer chains. In the LB multilayers, on the other hand, compact packing and high degree alignment of copolyimide chains could be obtained more easily. This was borne out in the characterization of various polyimide LB films, which involved FT-IR, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and liquid crystal alignment properties studies [28]. As can be represented by Fig. 4, the compact packing and alignment of the chains are favorable to the formation of CTC as well as improves their charge mobility, which lead to high photosensitivity of the LB films. Furthermore, carriers in the copolyimide matrix would be transported perpendicular to the polymer chains and so the shorter distance between the neighboring chains in the LB films makes carrier transport more convenient.

To examine the orientation of polyimide chain in the CPI-3 LB film, X-ray diffraction analysis was carried out in this work. As can be seen from Fig. 5, the X-ray pattern indicated obviously that this copolyimide LB film has ordered structure.

Fig. 6 shows the absorption spectra of the LB film and solvent-casting film of CPI-3 on a quartz plate from the UV to Visible region. The UV/Vis spectrum (b) of the CPI-3 solvent-casting film displays typical adsorption of porphyrin and polyimide. The absorption band centered at 416 nm was assigned to the Soret band of porphyrin and was separated clearly from the absorption of polyimide backbone existing in the UV region (260–330 nm). The Soret band adsorption of porphyrin in the corresponding LB film (455 nm) shows a red shift compared with that of the solvent-casting film. This phenomenon of red shift could be attributed to the formation of CTC.

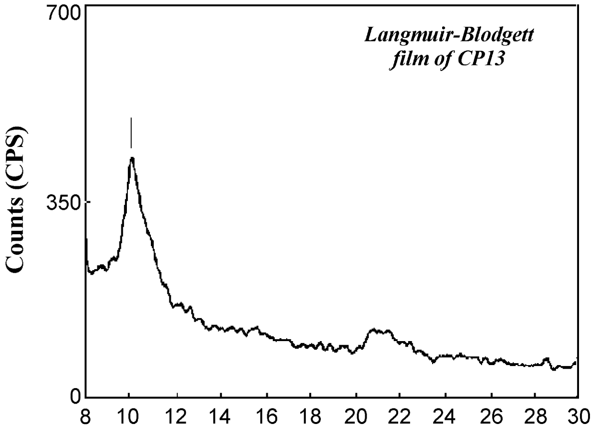

Fig. 5. X-ray diffraction pattern of copolyimide LB film deposited from CPI-3.

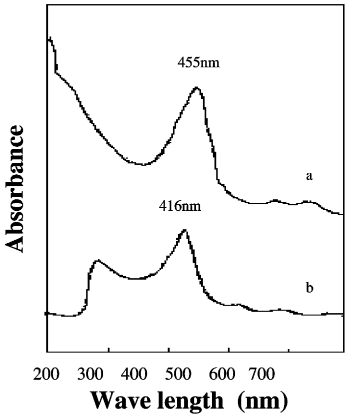

Fig. 6. UV–Visible spectra of (a) CPI-3 LB film and (b) CPI-3 solvent-casting film on quartz.

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