Enhanced Photoconductive Properties of Polyimide Films Based on Controlled Charge Transfer Interactions

Shinji Ando, Sho Fukuchi, Shigeo Asai, and Kazuhiro Takizawa

Department of Chemistry & Materials Science, Tokyo Institute of Technology,
Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo, 152-8552 Japan
Tel: + 81-3-5734-2137, Fax: +81-3-5734-2889 E-mail: sando@polymer.titech.ac.jp

Introduction Polyimides (PIs) are widely-used in photonic and electronic industries owing to their high thermal stability and mechanical toughness, though their electro-conductive and photoconductive properties have not been well investigated. We have recently examined the temperature dependence of electric current of PI films to clarify their electric conduction mechanisms[1]. Since PIs containing triphenylamine (TPA) moiety are reported to represent high photoconductivity[2], we have recently reported that the intensity of UV-vis absorptions and photocurrents increase with increasing the electron affinity (E_A) of dianhydride moiety, which is due to the enhanced CT interactions[3]. In this study, the photoconductive propeties of PIs derived from four dianhydrides having large E_As were investigated based on the UV-vis absorption spectra and photo-electrical measurements.

Experimental The structures of PIs used in this study are shown in Fig. 1. DMAc solutions of poly(amic acid)s, precursors of PIs, were spin-coated onto ITO substrates, followed by thermal imidization at 300°C. Silver electrodes (ϕ=1 mm) were directly formed on PI films by magnetron sputtering under vacuum. UV-vis spectra were measured using a Hitachi U-3500 spectrophotometer, and electrical measurements were performed using a home-built equipment. A DC electric field (50 kV/cm) was applied for 9 min, and the film was photo-irradiated for 3 min in the middle. Photocurrent density was determined as a difference between the current densities at 3 min after applying DC field (dark current density) and that at 6 min (maximum photo-current density).

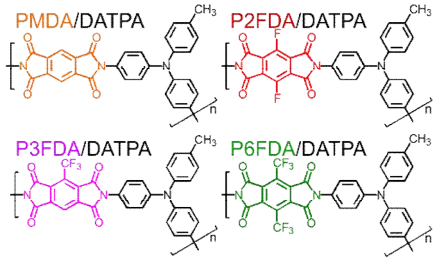

Fig.1 Molecular structures of PIs.

Results and Discussion The UV-vis absorption and photo-current spectra for the four PIs are shown in Fig. 2. The absorption around 500 nm increases with increasing the E_A of dianhydride moiety (PMDA < P3FDA < P2FDA < P6FDA), which is attributable to the enhanced charge transfer (CT) interactions. However, the photoconductivity does not show clear correlation with the degree of CT interactions. The photoconductivity of the PIs derived from P2FDA and P3FDA are the highest, though that from P6FDA is much lower. The photoconductive mechanism consists of three steps: (1) excited CT complexes (e.g. excitons) are generated by irradiation, (2) the excitons are dissociated to free carriers and (3) they are conducted under strong electric field. The enhanced CT interactions can increase the amount of excitons, but the charge separation and conduction process are closely related to aggregation structures of polymer chains. The dense molecular packing and strong intermolecular interactions in PIs from P2FDA and P3FDA enhance their photoconductivity.

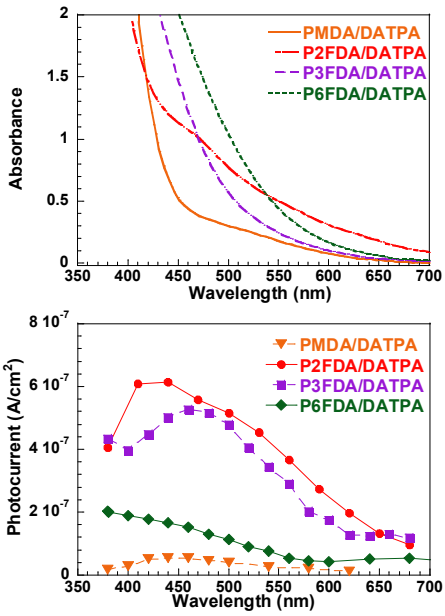

Fig. 2 (a) UV-vis absorption spectra and (b) photocurrent spectra of PI films.

References [1] K. Takizawa, S. Asai, S. Ando, *Polymer J.*, **46**, 201 (2014). [2] E.L. Aleksandrova, *Opt. Spectr.*, **93**, 118 (2002). [3] K. Takizawa, S. Fukuchi, S. Asai, S. Ando, *13th Pacific Polymer Conf.* (Kaohsiung, Taiwan) S7-005 (2013).