

Optical and Photoconductive Properties of Polyimide Thin Films with Main Chain Triphenylamine Structure

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Introduction: Polyimides (PIs) are widely-used in photonic and electronic industries owing to their high thermal stability and mechanical toughness, although their electro-conductive and photoconductive properties have not been clarified. We have recently examined the temperature dependence of electric current of PI films to clarify their electric conduction mechanisms[1]. PIs containing triphenylamine (TPA) moiety have been reported to exhibit high photoconductivity (PC)[2], and we have 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 properties of PIs derived from eight kinds of dianhydrides having a wide range of E_A s are investigated based on the UV-vis absorption spectra and dark- and photo-electric measurements under DC electric field.

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 ($\phi = 1$ 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. DC electric field (50 kV/cm) was applied to PI films under dark condition for 3 min, followed by photo-irradiation with monochromatic light for 3 min. A value of photocurrent density was determined as a difference between the current density at 3 min after applying DC (dark current density) and that at 6 min (maximum photo-current density).

Results and Discussion: The photo-current spectra for eight kinds of PIs are shown in Fig. 2. The absorption around 500 nm (not shown) increases with increasing the E_A of dianhydride moiety (e.g. PMDA < P3FDA < P2FDA < P6FDA), which is attributable to the enhanced charge transfer (CT) interactions. However, the PC does not show clear correlation with the degree of CT interactions. Those of PIs derived from P2FDA and P3FDA are the highest, though that from P6FDA is much lower. The photoconductive mechanism is known to pass the three stages: (1) formation of excited CT complexes (e.g. excitons) by irradiation, (2) dissociation of excitons to free carriers, and (3) electric conduction under strong DC field. The photocurrent quantum yield (Φ) of PIs derived from P3FDA, s-BPDA and s-TDPA increase with increasing the irradiation wavelength, which indicates that the lower probability of charge recombination due to the lower optical absorption is dominant. In contrast, the Φ values of PIs from P2FDA and PMDA decrease above ~450 nm, which indicates the weak wavelength dependences of charge recombination due to the small variations in optical absorption, and thereby the reduced dissociation efficiency became dominant at longer wavelengths. The enhanced CT interactions can increase the amount of excitons, though the charge separation and conduction process are closely related to aggregation structures of PI chains. The dense chain packing and strong intermolecular interactions enhance the PC of PIs from P2FDA and P3FDA significantly.

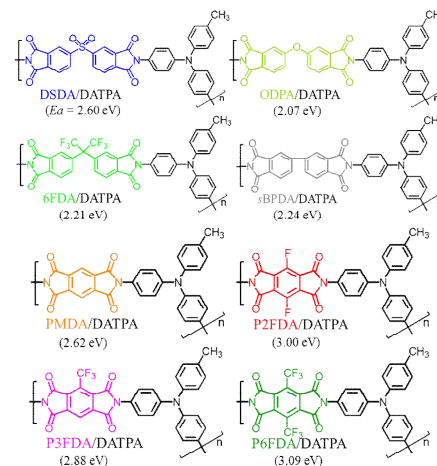


Fig.1 Molecular structures of PIs.

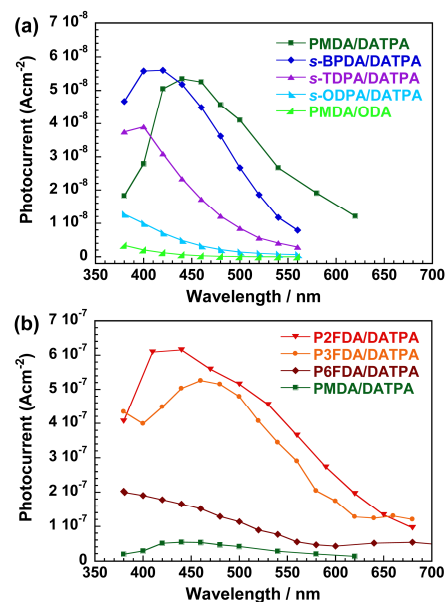


Fig. 2 photocurrent spectra of the PI films.

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).