P10 Development of Colorless and Transparent Polyimide Copolymer Films Displaying Large Stokes Shifted Orange-color Photoluminescence

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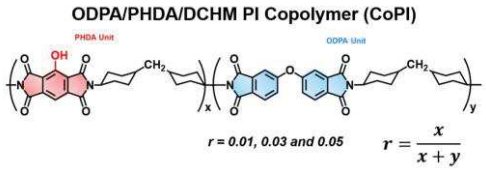
Introduction:

Our group has reported a highly fluorescent PI derived from 1-hydroxy pyromellitic dianhydride (PHDA) and 4,4'-diamino-dicyclohexylmethane (DCHM), which exhibits a large Stokes shifted photoluminescence through excited-state intramolecular proton transfer (ESIPT). This ESIPT process competes with an emission from aggregated forms of the PHDA unit in the excited states [1,2]. To suppress the aggregation formation, we prepared a series of PI copolymers (CoPIs) based on 4,4'-oxydiphthalic anhydride (ODPA), PHDA, and DCHM, as shown in **Scheme 1**. Among these CoPI films, a copolymer with a molar ratio of PHDA unit (r) at 0.03 (CoPI-0.03) is most suitable for solar converting applications because of its high optical transparency, colorlessness, and bright orange photoluminescent color (on fused silica substrates) based on ESIPT of the PHDA moieties. However, the CoPI-0.03 film showed an intense yellowish color as well as yellowish fluorescence on soda-lime glass substrates due to anion ($-O^-$) formation of −OH group of PHDA moiety, which is different from the PI films formed on fused silica substrates (colorless and orange fluorescence). This study examines the effect of substrate materials and developed a novel method to obtain colorless and transparent PI films exhibiting bright orange fluorescence on both the substrates.

Results and Discussion:

To obtain colorless PI films with orange fluorescence, anion formation must be suppressed. We tried to reduce deprotonation of the PHDA moiety by doping CoPI films with non-volatile acids. Because CoPI is prepared at a high temperature (220 °C) and insoluble in organic solvents, the acid should be added to poly amic acid (PAA) solution before thermal imidization. Thus, we chose sulfuric acid (H_2SO_4) due to its high boiling temperature without vapor pressure, and its concentration was varied from 1 to 3 equivalents (eq.) to the OH group of PHDA moiety. **Fig. 1** displays the UV-Vis absorption spectra of CoPI-0.03 films doped with H_2SO_4. The film without H_2SO_4 (0 eq.) shows an obvious anion absorbance at 470 nm, which was confirmed by a model compound, whereas it was totally suppressed by adding 2 eq. of H_2SO_4. We successfully obtained a colorless and transparent CoPI film exhibiting UV-excited bright photoluminescence by adding 2 eq. H_2SO_4 to a CoPI-0.03 film formed on a soda-lime glass substrate, as presented in **Fig. 1** (inserted). The CoPI film which displays excellent transparency and orange-color fluorescence is suitable and promising for solar down-converter applications.



Scheme 1. Chemical Structure of PI Copolymers.

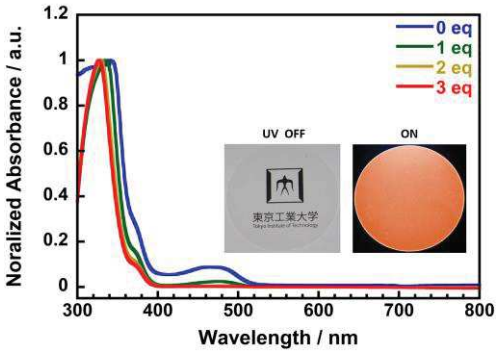


Fig. 1. Steady-state UV/Vis absorption spectra of CoPI films prepared with different H_2SO_4 concentrations (formed on glass substrates). **Inserted graphs**: Photos of a CoPI-0.03 film with 2 eq H_2SO_4. (on glass substrate) Left: without UV light. Right: under UV light (375 nm).

References: [1] K. Kanosue, R. Augulis, D. Peckus, R. Karpicz, T. Tamulevicius, S. Tamulevicius, V. Gulbinas, S. Ando, *Macromolecules*, **5**, 49, 2016. [2] J. Wakita, S. Inoue, N. Kawanishi, S. Ando, *Macromolecules*, **8**, 43, 2010.

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