Fluorescence and Phosphorescence Properties of Sulfur-containing Semi Aromatic Polyimides

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Introduction

Highly fluorescent polyimides (PIs) are expected to be applied to solar spectrum down-convertors owing to their excellent optical properties such as high transparency and tunable fluorescent colors as well as outstanding physical properties like thermal stability, light weight, flexibility, chemical and light resistance, and mechanical strength originated from their rigid and polar primary structures [1]. However, the fluorescence PIs in the first generation have small Stokes shifts (*SS*), which is a difference in wavelengths between absorption and emission peaks. In general, phosphorescence can exhibit much enlarged *SS* than that of conventional fluorescence because it includes intersystem crossing (ISC) process from the excited singlet state to the excited triplet state with a slight energy dissipation. It is well known that ISC can be enhanced by introducing heavy atoms due to the enlarged spin-orbit coupling. For example, our group have reported that PIs substituted by bromine atoms as heavy halogens exhibit bright room temperature phosphorescence (RTP) [2,3]. Furthermore, we have recently found that a series of oxygen-containing PIs emit phosphorescence under vacuum and lower temperatures [4]. In this study, we investigated the fluorescence and phosphorescence properties of newly synthesized PIs containing sulfur atoms. Since sulfur is one of the chalcogens in group 16 of the periodic table and its weight is twice as heavy as oxygen, more efficient ISC can be expected within PI skeletal structures.

Experimental

2SDEA dianhydride was synthesized according to the literature [5]. An alicyclic diamine (1,4-*t*-DACH) and aromatic dianhydrides (ODPA, SDPA, 2SDEA, or 3SDEA, **Fig. 1**) were stirred in DMAc under nitrogen to give poly(amic acid) (PAA) precursor solutions. The PAA solutions were spin-coated onto a fused silica substrate, followed by soft-baking at 70 °C for 50 min and subsequent thermal imidization at 220 °C for 1.5 h, and then obtained PI thin films. Abbreviation of each PI is presented in **Fig.1**.

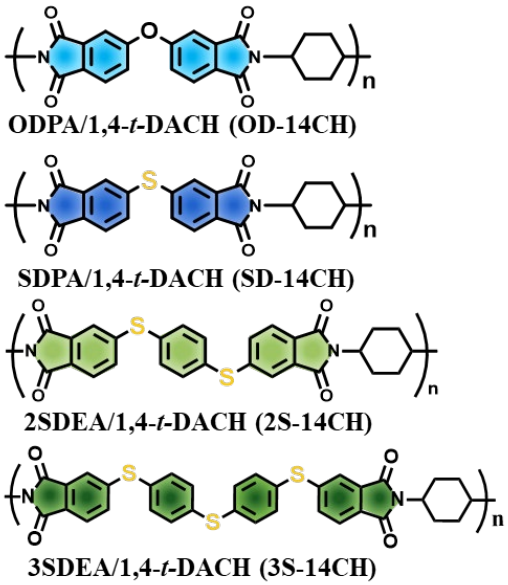

Fig. 1 Chemical structures of photo-luminescent polyimides.

Results and Discussion

The PI films of OD-14CH and SD-14CH are colorless, transparent, and emit blue fluorescence under UV irradiation (λ = 365 nm). On the other hand, 2S-14CH and 3S-14CH films show pale yellow color and emitted green fluorescence under UV irradiation. **Fig. 2** shows the excitation / emission spectra and the photograph of each PI film. **Fig. 3** shows the quantum yields and lifetimes of the fluorescent emission of each PI (excitation: 365 nm for OD-14CH and 2S-14CH, 405 nm for SD-14CH and 3S-14CH, and the wavelength represents peak position of each spectrum). By substiting thioether (−S−) for the ether (−O−) linkages of OD-14CH, the excitation and fluorescence peak of SD-14CH is shifted toward longer wavelengths. These shifts could be caused by lowering of transition energies due to the widely distributed molecular orbitals around the sulfur atom. Moreover, the excitation and fluorescence peaks of 2S-14CH and 3S-14CH are additionally shifted to longer wavelengths with enhanced *SS* values (*SS* = 5000 ~ 6316 cm^{-1}). According to **Fig. 3**, the sulfur-containing PIs showed smaller quantum yields and shortened fluorescence lifetimes than that of OD-14CH. These results indicate that the ISC was enhanced by the sulfur atoms, and a part of the excited singlet electron transferred to the triplet state. However, the PIs listed in **Fig. 1** did not emit RTP in air. It could be attributable to the non-radiative deactivation from the triplet state induced by the molecular motion and/or by energy quenching via energy transfer to oxygen absorbed in the PI films. However, the PIs shown in **Fig. 1** did not emit RTP even under vacuum condition. We will proceed analyses on the optical properties of these PIs at lower temperatures (RT~77 K) and investigate the effect of sulfur atoms and local molecular motion on the phosphorescence properties of PIs.

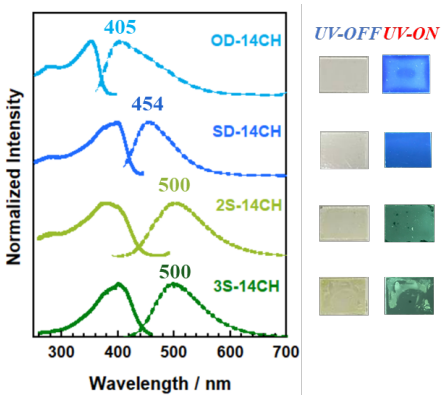

Fig. 2 Excitation / emission spectra and photographs of OD-14CH, SD-14CH, 2S-14CH and 3S-14CH PIs.

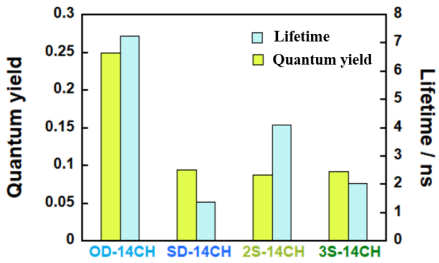

Fig. 3 Quantum yields and lifetimes of fluorescence of OD-14CH, SD-14CH, 2S-14CH and 3S-14CH PIs.

References

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