Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Comparison of Optical Properties of Porphyrin Dispersed Polyimide and Porphyrin Incorporated Polyimide into the Main Chain

Hooi-Sung Kim [a], Tae-Wook Heo [a], Mi-Ra Kim [a], Chang-Sik Ha [a] & Jin-Kook Lee [a]

[a] Dept. of Polym. Sci. and Eng., Pusan National University, Jangjundong, Kumjung-ku, Pusan, 609-735, Korea E-mail:

Version of record first published: 24 Sep 2006

To cite this article: Hooi-Sung Kim, Tae-Wook Heo, Mi-Ra Kim, Chang-Sik Ha & Jin-Kook Lee (2001): Comparison of Optical Properties of Porphyrin Dispersed Polyimide and Porphyrin Incorporated Polyimide into the Main Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 281-284

To link to this article: http://dx.doi.org/10.1080/10587250108024741

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 281-284

Comparison of Optical Properties of Porphyrin Dispersed Polyimide and Porphyrin Incorporated Polyimide into the Main Chain

HOOI-SUNG KIM, TAE-WOOK HEO, MI-RA KIM, CHANG-SIK HA and JIN-KOOK LEE*

Dept. of Polym. Sci. and Eng., Pusan National University, Jangjundong, Kumjung-ku, Pusan 609-735, Korea
E-mail: csha@hyowon.pusan.ac.kr

Optical properties of polyimide film with dispersed metalloporphyrin (ZnTPDPI) and those of polyimide film containing tetraphenylporphyrinzinc in polymer backbone (POTPPI) were compared. For ZnTPDPI, the increase of the content of ZnTPP in PI film exhibited the increase of absorption and emission. POTPPI showed higher emission and absorption than ZnTPDPI. Relative fluorescence quantum yield of POTPPI was 0.218, while that of ZnTPDPI was 0.125.

Keywords optical property; polyimide; porphyrin; photocurrent

Introduction

The investigation of photoconductive polyimide proceeded in the past one and half decades. It has been reported that typical Kapton polyimide films are weakly photoconductive in the presence of high electric fields [1]. When electron donors were added to Kapton polyimide films, however, the photocurrents increased by as much as 5 orders of magnitude as compared with the virgin polymer, although polyimides are well-known for their thermal stability, solvent instability,

and good dielectric characteristics [2].

Porphyrins are well known as sensitizers working in the photosynthesis in plant [3], and in the artificial solar energy conversion systems [4]. Fujihira et al. reported that the photocurrent was observed in the tetraphenylporphyrin modifying electrode with high efficiency by irradiation of light [5]. We assume that the polyimide–porphyrin composite system can be one of promising material systems for novel photoconductive applications. In this work, optical properties of the polyimide film dispersed with metalloporphyrins(ZnTPDPI) and those of polyimide film containing tetraphenylporphyrine zinc in polymer backbone(POTPPI) were compared. Porphyrins were used as an electron donor to increase the charge-transfer in polyimide.

Experimental

Metalloporphyrin dispersed poly(4,4'-oxydiphenylene pyromellitic acid) (PMDA-ODA) polyimides(ZnTPDPIs) were prepared by adding metalloporphyrins to PMDA-ODA precursor with a mole ratio of 0.482 with stirring for 1 days[1]. The amount of metalloporphyrins was 60 mg. The solution was passed through 0.2 μm filter and spin-coated on a glass plate and themally imidized to give a final polymer film. POTPPI was prepared by slowly adding PMDA(0.28g, 1mmol) to ODA(0.2g, 0.9mmol) and Meso-tetra(o-aminophenyl)porphyrinatozink(0.07g, 0.1mmol) dissolved in DMAc(3g) with vigorously stirring for 2 days.[6]

UV-visible spectroscopic measurements were performed using Perkin-Elmer Lambda-20 spectrometer. Fluorescence emission spectroscopic measurements were made at room temperature using SPEX-750 monochrometer with a Photomultiplier-Tube. The 422 nm of monochromatic light was used as an excitation source. The relative quantum yield (ϕ_f) was obtained by comparing the ratio of the fluorescence emission intensity maximum to the absorbance at the exicitation wavelength used for the sample with that of *N,N'*-dicyclohexylperylenebisimide dye dispersed in poly(methyl-methacrylate) (ϕ_f = 0.91) [7]. For each sample, quantum yield was measured at least five times, then averaged.

Results and Discussion

FIGURE 1 shows the Soret bands of tetraphenyl-porphyrinzinc (ZnTPP) in a 10^{-4} M solution of ZnTPP in chloroform and ZnTPDPI film. The red shift of ZnTPDPI film in comparison to ZnTPP solution shows an obvious evidence of the charge transfer (CT). While ordinary absorption bands of ZnTPP are observed at 424, 554, and 597 nm, a single remarkable absorption peak was observed at 432 nm in the ZnTPDPI film. The shift of the Soret band means that the intrer-molecular or intra-molecular CT from porphyrin moiety (donor) to imide moiety (acceptor) took place in the ZnTPDPI film. FIGURE 2 shows UV-vis absorption spectra of ZnTPDPI film as a function of the contents of ZnTPP. Absorbance increases as the contents of ZnTPP increases. More dyes induced higher absorption and a slight red shift of the Soret band from 433 nm for 6 wt% of ZnTPP to 435 nm for 16 wt% of ZnTPP. Emission spectra of ZnTPDPI are shown in FIGURE 3. PI-related bands are observed at 533 nm in the

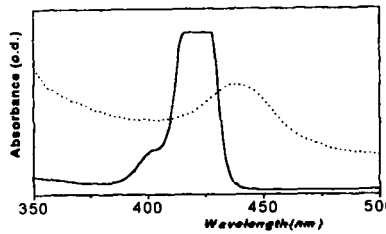

FIGURE 1. Soret bands of ZnTPP (bold) in a 10^{-4} M solution of ZnTPP in chloroform and ZnTPDPI film (dotted).

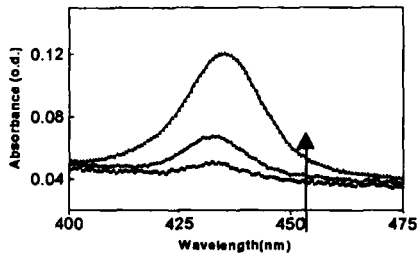

FIGURE 2. UV-vis absorption spectra of ZnTPDPI with different contents of ZnTPP; The arrow indicates the increasing ZnTPP contents from 0, 6 to 16 wt%.

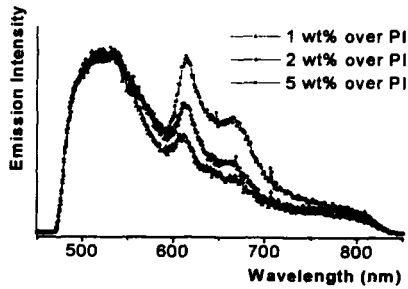

FIGURE 3. Emission spectra of ZnTPDPI films.

emission spectra. ZnTPP-related emission bands are observed at 612 nm and 664 nm. One can see that the porphyrin related bands at shorter wavelength at 606 nm, 610 nm, and 615 nm, showed different emission bands, depending on the ZnTPP contents. On increasing the contents of ZnTPP, the emission intensities of the ZnTPP-related bands increased. Relative fluorescence quantum yield (ϕ_f) was measured. The ϕ_f of ZnTPDPI film was 0.125 and that of POTPPI was 0.218, which was a quantitative evidence for stronger charge transfer in the POTPPI in comparison to ZnTPDPI.

Conclusion

POTPPI and ZnTPDPI films were fabricated and their optical properties were compared. The increase of the content of ZnTPP in PI flim exhibited the increase of absorption and emission. Both ZnTPDPI and POTPPI films showed higher emission and absorption than PI films without porphyrins, which implies the inter- and intra-molecular charge transfer between polymers and dyes. Relative fluorescence quantum yield of POTPPI was 0.218, while that of ZnTPDPI was 0.125, which led us to conclude that the polymer with dye on main chain produces more emitted photons and shows higher quatum yield than the dye dispersed polymer system.

Acknowledgements

The work was financially supported by the Brain Korea 21 Project.

References

[1] Freilich SC. Macromolecules 1986;20:973.
[2] Takai Y, Kim M, Mitzutani T, Ieda M. Jpn J Appl Phys 1982;21:1542.
[3] Lehninger AL. in Biochemistry, 2nd ed. Worth, New York 1975.
[4] Lichtin NN. Chemtech 1980;10:254.
[5] Fujihira M, Kubota T, Osa T. J Electroanal Chem 1981;119:379
[6] Nshkata Y, Morikawa A, Kakimoto M, Imai Y, Nishyama K, Fujihira M, Polym. J. 1990;22:593
[7] Phelan JC, Sung CSP. Macromolecules 1997;30:6837.