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Strongly Fluorescent and Thermally Stable Functional Polybenzoxazole Film: Excited-State Intramolecular Proton Transfer and Chemically Amplified Photopatterning

Sanghyuk Park, Sehoon Kim, Jangwon Seo, and Soo Young Park*

School of Materials Science and Engineering, Seoul National University, ENG 445, Seoul 151-744, Korea

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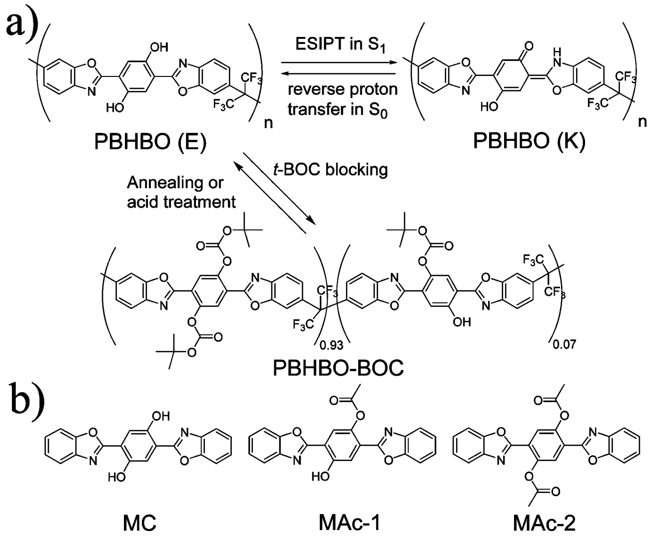
Polybenzoxazoles (PBOs) are rigid aromatic polymers of industrial significance, which have excellent mechanical, thermal, and various functional properties as well as good chemical resistance.[1−3] For the advanced application of these high-performance PBOs, particularly for the electronic and photonic devices, fabrication and patterning of high-quality polymer film are demanded in many cases. Because of the rigid molecular structure and consequent insolubility in organic solvents, however, fabrication and patterning of fine PBO films are seriously limited and remain as an important challenge. In one approach, bulky alkyl groups[4,5] or flexible linkages[6,7] are introduced into the main chain or side chain of PBO to improve their solubility, which inevitably sacrifices original thermal stability and functional properties of the parent PBO. As a different and more acceptable approach, *tert*-butyloxy carbonate (*t*-BOC) blocking and relevant photopatterning have been successfully employed for the fabrication of linear[8] and hyperbranched PBO films,[9] respectively. In this work, we employ the modified *t*-BOC blocking method to demonstrate the fabrication and specific fluorescence patterning of poly(2-benzooxazol-2-yl-5-[6-(2,2,2-trifluoro-1-trifluoromethylethyl)benzooxazol-2-yl]benzene-1,4-diol) (PBHBO) film for the first time. Unique fluorescent properties and the photopatterning of PBHBO film are originally discussed in this work, while the synthesis and excellent thermal stability of PBHBO were reported earlier by Dang et al.[3] As shown in Scheme 1, PBHBO comprises benzoxazole units and two aromatic hydroxyl groups virtually forming fused-ring structures by cyclic intramolecular hydrogen (H) bonds, of which the hydroxyl groups are used as the *t*-BOC attaching site. Importantly, PBHBO with intramolecular H-bonded hydroxyl group is also considered to be potentially active toward excited-state intramolecular proton transfer (ESIPT) fluorescence based on the structural similarity to the 2-(2-hydroxyphenyl)benzoxazole,[11] poly((benzodithiazole)-(1,4-(2-hydroxy)phenylene)),[12] and hydroxyphenylquinoline.[13−15] Therefore, *t*-BOC blocking of PBHBO is likely to suppress the ESIPT process, resulting in the effective fluorescence modulation.

PBHBO was prepared by the reaction of 2,5-dihydroxyterephthalic acid and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane in poly(phosphoric acid) according to the literature method.[3] After the purification by successive Soxhlet extraction with water for 1 day and ethanol for 2 days, PBHBO was obtained as a yellowish powder with orange fluorescence, which is insoluble in most organic solvents including tetrahydrofuran (THF), chloroform, dimethylformamide, and dimethyl sulfoxide. PBHBO is soluble only in strong acid such as H_2SO_4 and methanesulfonic acid and shows no T_g up to 300 °C due to the rigidity and planarity from the seven virtual fused rings formed by double H-bondings in every repeating unit, as reported in the literature.[3] However, *t*-BOC blocked polymer (PBHBO−BOC) is highly soluble in most organic solvents, enabling solution-state measurements and film fabrication. The blocking was carried out for the dispersion of PBHBO powder in THF containing excess of di-*tert*-butyl dicarbonate and a catalytic amount of (dimethylamino)pyridine at 0 °C. The insoluble polymer dispersion became completely dissolved with the progress of *t*-BOC blocking reaction; concomitantly the initial orange fluorescence ($\lambda_{\text{max,em}} = 597$ nm) of the PBHBO dispersion turned to the strong green fluorescence ($\lambda_{\text{max,em}} = 524$ nm). After successive reprecipitation from dichloromethane solution into ethanol, green-fluorescent PBHBO−BOC was obtained which showed weight-average molecular weight (M_w) of 13 700 from gel permeation chromatography (against polystyrene standard) and inherent viscosity [η] of 0.20 dL/g at a concentration of 0.5 g/dL in *N*-methylpyrrolidinone at 30 °C. In the ^{1}H NMR spectrum of PBHBO−BOC in $CDCl_3$ solution, only a small amount of residual hydroxyl proton peaks was identified, indicating that 93.2% of the total hydroxyl sites of PBHBO are blocked with *t*-BOC groups. The thermal property of PBHBO−BOC powder was examined by differential scanning calorimetry (DSC) at a rate of 20 K/min. The first heating run shows a large and broad exotherm peaking at 183 °C just after the glass transition at 135 °C, which is most likely attributed to the thermal deblocking of *t*-BOC group. On and after the second heating run, the exotherm as well as the apparent glass transition are no more observed up to 300 °C, which is consistent with the thermal behavior of the parent polymer PBHBO.[3] Moreover, it was noted that the complete insolubility

Scheme 1. (a) Schematic Diagram of the Excited-State Intramolecular Proton Transfer (ESIPT) in PBHBO and *t*-BOC Blocking/Deblocking Conversions; (b) Model Compound of PBHBO (MC) and Its Acetyl-Blocked Derivatives, MAc-1 and MAc-2



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* Corresponding author. E-mail: parksy@snu.ac.kr.

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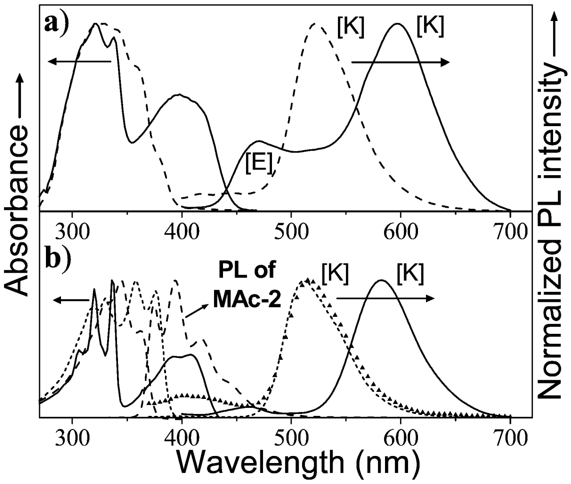

Figure 1. (a) UV−vis absorption and emission spectra of PBHBO−BOC (dashed line) and PBHBO (solid line) thin film, which were excited at 365 and 380 nm, respectively. The PBHBO film was obtained by the heat treatment of PBHBO−BOC thin film at 195 °C for 20 min. (b) Absorption and emission spectra of MC (solid line), diblocked MAc-2 (dashed line), monoblocked MAc-1 (short dashed line), and emission spectrum of MAc-2:MAc-1=9:1 mixture (▲); each compound was dispersed in PMMA film (7 wt %).

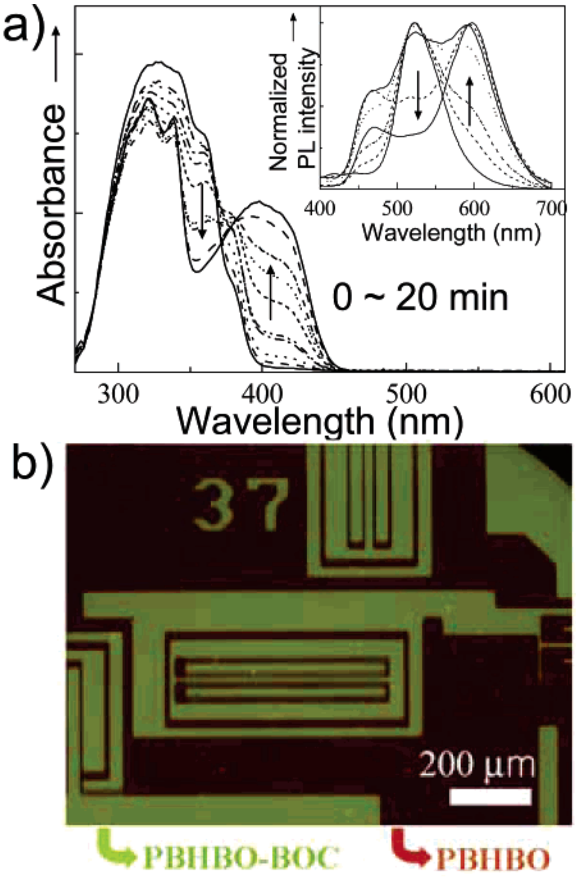

Figure 2. (a) Changes of UV−vis absorption spectra and emission spectra (inset) of PBHBO−BOC film depending on the annealing time at 195 °C. (b) Fluorescence micropatterned image of PBHBO−BOC. The dark orange areas are the irradiated parts through the photomask.

and characteristic orange fluorescence of PBHBO were recovered as well after the first DSC scan. Accordingly, the exotherm in the first scan of PBHBO−BOC certainly indicates the thermal cleavage of the *t*-BOC group and the vaporization of the resultant volatiles (i.e., isobutene and CO_2),[10] restoring the initial structure and properties of PBHBO.

The most important optical property of PBHBO identified in this work is the ESIPT[11−17] and relevant fluorescence emission (see Scheme 1). ESIPT is a fast enol (E) to keto (K) prototropy occurring in the excited state of intramolecularly H-bonded molecules.[20] Since the ESIPT molecules are normally more stable in E form in the ground states but in K* form in the excited states, photoexcitation drives four-level cyclic proton-transfer reaction ($E \rightarrow E^* \rightarrow K^* \rightarrow K \rightarrow E$) via intramolecular H-bond accompanied by the characteristic $K^* \rightarrow K$ fluorescence. It has been generally observed that absorption from E and emission from K* give rise to an abnormally large Stokes' shift without self-absorption,[20] providing an ideal scheme for the proton-transfer laser[12,16−18] and UV photostabilizer.[21] As shown in Figure 1a, PBHBO absorbs UV light ($\lambda_{max,abs}$ = 364 nm) and emits dual fluorescences, composed of weaker E emission ($E^* \rightarrow E$; $\lambda_{max,em}$ = 470 nm) and stronger K emission ($K^* \rightarrow K$; $\lambda_{max,em}$ = 597 nm), exhibiting orange fluorescence overall. As indicated by dashed lines in Figure 1, the *t*-BOC blocked structures showed a hypsochromic shift of $\lambda_{max,abs}$ relative to H-bonded (nonblocked) materials due to the distorted conjugation by reduced planarity. In contrast to the normal Stokes' shift (6195 cm^{-1}, 106 nm) of E emission, abnormally large Stokes' shift (10722 cm^{-1}, 233 nm) of K emission is certainly due to the ESIPT process leading to the generation of K* tautomer of PBHBO.[13−15,22] On the other hand, *t*-BOC blocking of the ESIPT site in PBHBO must eliminate the K* generation, and thus the blue fluorescence of E emission is expected to be left behind. Actually, PBHBO−BOC shows blue emission with slight green tail (see Supporting Information, Figure S-2) in diluted $CHCl_3$ solution (1×10^{-5} mol/L), while fabricated thin film shows dominant green emission ($\lambda_{max,em}$ = 524 nm) with trace of blue emission. It was found from ^1H NMR spectra that PBHBO−BOC contains 93% of *t*-BOC-blocked hydroxyl group and 7% of free hydroxyl group, the latter of which presumably exists mainly as the monofunctionalized structure (see Scheme 1a). Förster-type energy transfer from the doubly *t*-BOC blocked unit to the mono-blocked one is quite probable in the PBHBO−BOC film due to the favorable spectral overlap between the absorption band of mono-blocked structure and emission band of double-blocked structure.[19] The green emission from PBHBO−BOC film, thus, is most likely the ESIPT fluorescence from the residual ESIPT hydroxyl group in PBHBO−BOC. To provide direct evidence, a model compound (MC) of PBHBO and its hydroxyl group-blocked derivatives, MAc-1 and MAc-2 shown in Scheme 1, were synthesized, and their optical properties were identified. As seen in Figure 1b, MC ($\lambda_{max,em}$ = 584 nm) and MAc-1 ($\lambda_{max,em}$ = 513 nm) show the almost same spectral behaviors as PBHBO and PBHBO−BOC in the film state, respectively. To ensure the presence of energy transfer process in the PBHBO−BOC film, we deliberately measured the fluorescence emission from the mixtures of MAc-1 and MAc-2 (MAc-1:MAc-2 = 1:9 by mole ratio) in dye-dispersed poly(methyl methacrylate) (PMMA) film. As shown in Figure 1b, despite the small portion of MAc-1, the green ESIPT emission of it was clearly observed from the dye-doped film, which clearly supports the idea of efficient energy transfer from MAc-2 to MAc-1 and also explains the green emission of PBHBO−BOC.

Deblocking of the *t*-BOC group from PBHBO−BOC and accompanied fluorescence modulation could be effected either by acid[9] or heat treatment.[23] First, the thermal cleavage of *t*-BOC group was optically monitored by the spectral changes of UV−vis absorbance as well as photoluminescence in PBHBO−BOC film, as shown in Figure 2a. Upon annealing at 195 °C, the absorption band of PBHBO−BOC at 354 nm decreased and that of PBHBO at 400 nm increased gradually with two isosbestic points at 366 and 388 nm, supporting the idea of stepwise cleavage of the *t*-BOC group. For the fluorescence photopatterning of PBHBO film, chemical amplification resist method was employed for the *t*-BOC deblocking.[24] A polymeric thin film consisting of PBHBO−BOC and photoacid generator (PAG, triphenylsulfonium trifluoromethanesulfonate, $\lambda_{\mathrm{max,abs}} =$ 250 nm, PBHBO−BOC:PAG = 19:1 by weight) was spin-coated from chloroform solution. Upon irradiation with a hand-held UV lamp (1.2 mW cm^{-2}) through the photomask, the images were successfully transferred to the polymer film as the dual color fluorescence patterns. It was the result of the localized deblocking of *t*-BOC group (Figure 2b) in the irradiated parts. For the high contrast and fine resolution, postexposure baking at 100 °C was carried out to ensure complete diffusion of generated photoacid.[22] It was also noted that the solubility difference between PBHBO and PBHBO−BOC was large enough to allow the fabrication of lithographic patterns.

In summary, a novel method of fabrication and fluorescence patterning of high-performance ESIPT-active polybenzoxaole film was demonstrated in this work. Remarkable increase of solubility and accompanied fluorescence change was obtained by the *t*-BOC blocking of hydroxyl groups in PBHBO. Dual color fluorescence photopatterning was successfully achieved by using the polymer film consisting of PBHBO−BOC and PAG.

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Supporting Information Available: TGA trace of PBHBO and PBHBO−BOC; absorption and emission spectra of PBHBO−BOC, MAc-1, and MAc-2. This material is available free of charge via the Internet at http://pubs.acs.org.

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