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# Novel fluorescent copolymers of styrene with benzazole chromophores

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**Abstract**

Novel green fluorescent copolymers of styrene and 2-[(5′-*N*-acryloyl)-2′-hydroxyphenyl]benzoxazole or 2-[(5′-*N*-acryloyl)-2′-hydroxyphenyl]benzothiazole were synthesized by radical polymerization. The copolymers were characterized by size exclusion chromatography, thermal analyses (DSC, TGA), UV–Vis and fluorescence spectrophotometry. The glass transition temperatures of the fluorescent copolymers were similar to that of the parent polystyrene and the average molecular weight was lower due to the chain transfer effect of the benzazole dyes. The maximum fluorescence emission wavelength of the copolymers in the solid state or in chloroform solution accessed by fluorescence spectrophotometry was also similar. The Stokes shift of the styrene–benzoxazole or –benzothiazole copolymers was similar to those presented by fluorochromes that exhibit an excited state intramolecular proton transfer mechanism.


*Keywords:* Fluorescence; ESIPT; Benzazole; Fluorescent copolymer

## 1. Introduction

Fluorescent polymers are used as a probe in analytical technique, a suitable indicator that changes the fluorescence intensity when in contact with an analyte [1,2], as a polymeric sensor [3], in light-emitting diodes (OLEDs) [4–6] or in laser dyes [7–9]. These materials are made of a polymeric matrix and a fluorescent dye covalently bounded to the polymer chain [10–12] or physically blended with the polymer. In order to be used as a matrix for fluorescence purposes, the polymer must be amorphous [13] and transparent so that the fluorescent light propagates through it. In this field, studies on benzazole derivatives have been done due to their photophysical stability [14]. The fluorescence of these compounds is the consequence of the mechanism known as excited state intramolecular proton transfer (ESIPT) [15,16]. In the ESIPT mechanism (Fig. 1), the enol tautomer ($E_0$) of the 2-(2′-hydroxyphenyl)benzazole presents a strong intramolecular bond between the phenolic proton

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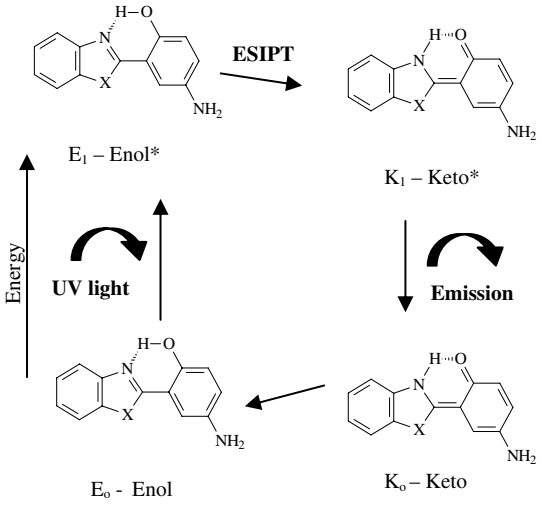


Fig. 1. Chemical structure and tautomeric forms of 2-(2′-hydroxyphenyl)benzazole in the emission light-ESIPT mechanism.

and azolic nitrogen and it is the most stable structure. The UV light absorption by $E_0$ structure produces an excited enol form ($E_1$), which eliminates the overload energy converting to an excited keto tautomer ($K_1$) by intramolecular proton transfer. The $K_1$ structure decays to a keto tautomer in the ground state ($K_0$) emitting fluorescence. The $K_0$ structure again becomes the $E_0$ structure without any photochemical change.

Compounds that exhibit the ESIPT mechanism have been extensively studied [17–19]. Lee and coworkers [17] have investigated a fluorescence temperature sensor based on poly(vinly alcohol)/borax/2-naphthol hydrogel network as a surfactant-free system. Grabchev and Betcheva [18] have reported on the ability of two 1,8-naphthalimide fluorescent brighteners to copolymerize with methyl methacrylate (MMA) in a bulk process as well as on photophysical characteristics of monomeric and polymeric fluorescent brighteners obtained.

In this work, new copolymers of styrene with 2-[(5′-*N*-acryloyl)-2′-hydroxyphenyl]benzoxazole or 2-[(5′-*N*-acryloyl)-2′-hydroxyphenyl]benzothiazole were synthesized and their thermal and optical properties were evaluated for application in fluorescent devices.

## 2. Experimental

### 2.1. Materials

Styrene polymerization grade supplied by INNOVA S.A. (Brazil) was used as received. The benzazole fluorescent brighteners used as comonomers 2-[(5′-*N*-acryloyl)-2′-hydroxyphenyl]benzoxazole and 2-[(5′-*N*-acryloyl)-2′-hydroxyphenyl]benzothiazole, called here dye 1 and 2, respectively, were synthesized according to the literature [20]. 2,2′-Azobisisobutyronitrile (AIBN) was used after recrystallization from methanol. All solvents used for the synthesis of copolymers and their characterizations were used as received.

### 2.2. Polymer synthesis

In a sealable 5 mL tube, 3.2 g (30 mmol) of styrene, 2.80 mg (0.01 mmol) of dye 1 or 2.96 mg (0.01 mmol) of dye 2 and 16 mg (0.1 mmol) of AIBN as initiator were added. The polymerization tube was sealed using nitrogen gas and then inserted into an isothermal bath. All polymerization reactions were carried out at 50 °C for 67 h and then at 60 °C for 24 h. The obtained products were milled and dissolved in chloroform. The polymer solutions were filtered and added dropwised into ethyl ether to precipitate the copolymer. This procedure was extensively repeated in order to remove completely the unreacted benzazole dye and oligomers. The copolymers were recovered by filtration and dried under vacuum to constant weight. The reaction yield was about 2.6 g or 83%.

### 2.3. Polymer characterization assays

Infrared spectra of polymers and their respective monomers were performed with a FT-IR Perkin–Elmer spectrum 1000 using KBr pellets. The average molecular weights ($M_w$, $M_n$ and $M_z$) of the polymers were determined in THF solution at room temperature by size exclusion chromatography (SEC) in a Waters model 515 pump chromatographer. A 2410 differential refractometer detector and three polymer PLgel 5 μm (10000, 500 and 100 Å) columns in a serial fashion were used. The calibration curve was built with polystyrene monodisperse standards obtained from Waters. The dyes and polymers UV–Vis spectra in chloroform solution were recorded with a Shimadzu UV-1601PC spectrophotometer. The benzazole dye content in the copolymers was estimated by the Lambert and Beer Law equation using a standard calibration procedure with dye 1 or 2 chloroform solutions. The fluorescence of the dyes and polymers was checked with a Hitachi spectrofluorimeter model F-4500. The fluorescence quantum yield ($\phi_{fl}$) of