Novel fluorescent copolymers of styrene with benzazole chromophores

M.R. Becker a,*, V. Stefani b, M.M.C. Forte a

a UFRGS, Escola de Engenharia, Laboratório de Materiais Poliméricos, Av. Bento Gonçalves, 9500, Caixa Postal 15010, 91501-970 Porto Alegre, RS, Brazil
b UFRGS, Instituto de Química, Departamento de Química Orgânica, Av. Bento Gonçalves, 9500, Caixa Postal 15003, 91501-970 Porto Alegre, RS, Brazil

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.

© 2006 Elsevier B.V. All rights reserved.

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 (E0) of the 2-(2'-hydroxyphenyl)benzoxazole presents a strong intramolecular bond between the phenolic proton...
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 co-workers [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 ($M_w$, $M_p$ 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 ($\phi_f$) of
the samples was determined in chloroform solution at room temperature with absorbance intensities lower than 0.05 by comparing the integrated intensities of fluorescence spectra with that of standard quinine sulphate in H_2SO_4 1 M (\(\phi_H = 0.55\)) [21–23]. The investigation of the thermal properties of the polymers was performed on a TA Instruments DSC 2010 analyzer at a heating rate of 10 °C/min. The thermogravimetric analyses (TG) of the samples were carried out in a TA Instruments TGA 2050 analyzer at a heating rate of 20 °C/min under nitrogen.

3. Results and discussion

Fluorescent polymers were synthesized by free radical copolymerization of styrene (a) with dye 1 (b), at two molar ratios (St:dye 1), named CPSOA and CPSOB or with dye 2 (c), named CPSS as shown in Fig. 2. Homopolymerization of styrene was carried out as a blank reaction producing parent polystyrene. The styrene copolymers were obtained at very low benzazole dye concentration, since a small amount of it is enough for fluorescent purposes. The obtained copolymers are amorphous and showed good solubility in acetone, chloroform and THF. The infrared spectra of the copolymer CPSOA and dye 1 and of the copolymer CPSS and dye 2 are shown in Fig. 3a and b, respectively. CPSOA and CPSS present IR absorptions in the range 3120–2800 cm\(^{-1}\) due to the saturated carbon bonds and at 1600 cm\(^{-1}\) due to C–C aromatic bonds (benzene ring). No absorptions related to the benzazole dyes were detected in the copolymers infrared spectra since their contents in the polymer backbone are too low or to dilute to be detected. Nevertheless, the presence of the benzazole dyes in the copolymers could be detected by the UV–Vis spectrophotometry.

Table 1 summarizes the results of average molecular weights (\(M_n, M_w\)), polydispersity (\(M_w/M_n\)) and glass transition (\(T_g\)) and decomposition (\(T_d\)) temperatures of the parent PS and styrene–benzazole dye copolymers. The difference between benzazole dyes 1 and 2 is in the heteroatoms present in their structure, which are oxygen and sulfur, respectively. The CPSOA and CPSOB copolymers were obtained at St:dye 1 molar ratio of 30:0.005 and 30:0.01, respectively. The CPSS copolymer was obtained at the same St:dye molar ratio of the CPSOB copolymer. The copolymers presented lower molecular weight than the parent PS (800,000 g mol\(^{-1}\)) probably because the benzazole dyes act as a chain transfer agent. Since the dye vinyl group is much less reactive than the styrene, the dye can promote the chain transfer during chain growing, reducing the polymer molecular weight. The PS and its copolymers did not show difference in their \(T_g\) values that was around 108 °C, since the benzazole dyes incorporated into the backbone did not affect the chain mobility due to the low content of it in the copolymer. The \(T_d\) determined as the apex of the peak of the loss mass derivate curve was the same for both homo and copolymer as well as the curve profiles, thus the incorporation of the dyes in the chain did not change the thermal degradation behaviour of the polymer.

Table 2 presents the benzazole dye content in the copolymer and the spectral characteristics of the benzazole dyes and copolymers analyzed in the solid state and in chloroform solution, including the maximum absorption (\(\lambda_{\text{abs max}}\)) and emission (\(\lambda_{\text{em max}}\)), the molar extinction coefficient (\(\varepsilon_{\text{max}}\)), the Stokes shift (\(\Delta\lambda_{\text{ST}}\)) and the fluorescence quantum yield (\(\phi_H\)). The dye 1 contents in the CPSO copolymers were similar, being 0.3 mg/g in the CPSOA (0.3 wt%) and 0.4 mg/g in the CPSOB (0.4 wt%). These values correspond to around 80 and 40%, respectively, of the dye 1 concentration in the CPSO feeding. This
unexpected behavior can be predicted by a limiting factor related to the dye solubility in styrene or in the reaction medium. The benzazole dye content values in the copolymers are in reasonable agreement with those recently reported [10,18]. The benzazole copolymers and respective dyes 1 and 2 in chloroform solution did not present significant difference in their maximum absorption spectra as can be seen in Figs. 4 and 5. The close similarity between the respective spectra indicates that the dye structures, if in the polymer backbone or not, are very similar and it does not matter if the N-acryloyl group is free or attached to the copolymer chain.

Table 1
Molecular and thermal data of the homo and copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye</th>
<th>Feeding St:dye (molar ratio)</th>
<th>$M_w$ (×10³ g mol⁻¹)</th>
<th>$M_n$ (×10³ g mol⁻¹)</th>
<th>$M_w/M_n$</th>
<th>$T_g$ (°C)ᵃ</th>
<th>$T_d$ (°C)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent PS</td>
<td></td>
<td></td>
<td>800</td>
<td>420</td>
<td>1.9</td>
<td>108</td>
<td>434</td>
</tr>
<tr>
<td>CPSOA</td>
<td>1</td>
<td>30:0.005</td>
<td>610</td>
<td>340</td>
<td>1.8</td>
<td>108</td>
<td>ND</td>
</tr>
<tr>
<td>CPSOB</td>
<td>1</td>
<td>30:0.01</td>
<td>590</td>
<td>270</td>
<td>1.8</td>
<td>108</td>
<td>438</td>
</tr>
<tr>
<td>CPSS</td>
<td>2</td>
<td>30:0.01</td>
<td>650</td>
<td>280</td>
<td>2.3</td>
<td>108</td>
<td>442</td>
</tr>
</tbody>
</table>

ᵃ DSC at a heating rate of 10 °C/min.
ᵇ DTG at a heating rate of 20 °C/min under nitrogen.
The dyes and copolymers present two different absorptive regions, one region in the range of 260–320 nm regarding the azole chromophore absorption and the other at a longer wavelength from 320 to 400 nm, attributed to a \( \pi \rightarrow \pi^* \) state with charge transfer character [24]. As expected, the dyes and the copolymers present molar extinction coefficients \( (e_{\text{max}}) \) between 1.1 and 2.1 \( \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \) that are typical values for allowed \( \pi \rightarrow \pi^* \) transitions.

The copolymers synthesized were fluorescent and emitted a green light in either chloroform solution or solid state when irradiated with UV-light. Then 0.5% (wt/wt) of the fluorescent dye into the polymer backbone was enough for fluorescent purpose. The copolymers in solid state or in chloroform solution and their respective dyes did not differ in their maximum emission values of wavelength as can be seen in Figs. 4 and 5. The Stokes shifts of CPSOA, CPSOB or CPSS are in agreement with those presented by fluorochromes that exhibit ESIPT [25]. Interestingly, there is no overlap of the absorption and the fluorescence spectra indicating that the emitted light is not quenched or absorbed by unexcited chromophores. The fluorescence quantum yield \( (\phi_f) \) was given by a fraction of chromophore that emits a photon after direct excitation by a source. The \( \phi_f \) value for dye 1 was 0.026 and for CPSO copolymers were 0.016 and 0.019, whereas those for the dye 2 and CPSS copolymer were 0.006 and 0.005, respectively. These results show that the quantum yield values in the copolymers decreased slightly compared with the respective dyes monomers. It is due to a self-quenching of the dyes in the PS matrix but this decreasing is relatively small given the experimental error associated with the quantum yield measurements.

### Table 2

Spectral characteristics of the fluorescent copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye content in the copolymer (mg/g)</th>
<th>( \lambda_{\text{abs}}^{\text{max}} ) (nm)</th>
<th>( \epsilon_{\text{max}} \times 10^4 )</th>
<th>( \lambda_{\text{em}}^{\text{max}} ) Solid state (nm)</th>
<th>Solution (nm)</th>
<th>( \Delta \lambda_{\text{ST}} ) (nm)</th>
<th>( \phi_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye 1</td>
<td>–</td>
<td>342</td>
<td>1.9</td>
<td>509</td>
<td>167</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>Dye 2</td>
<td>–</td>
<td>356</td>
<td>1.1</td>
<td>542</td>
<td>186</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>CPSOA</td>
<td>0.3</td>
<td>342</td>
<td>1.6</td>
<td>510</td>
<td>508</td>
<td>166</td>
<td>0.016</td>
</tr>
<tr>
<td>CPSOB</td>
<td>0.4</td>
<td>342</td>
<td>1.7</td>
<td>510</td>
<td>510</td>
<td>168</td>
<td>0.019</td>
</tr>
<tr>
<td>CPSS</td>
<td>0.5</td>
<td>357</td>
<td>1.4</td>
<td>545</td>
<td>547</td>
<td>190</td>
<td>0.005</td>
</tr>
</tbody>
</table>

* Molar extinction coefficient in L mol\(^{-1}\) cm\(^{-1}\) at the maximum of the band, 342 nm for dye 1 and 356 nm for dye 2.

* Excited at 342 nm or 356 nm.

* Chloroform solution.

Fig. 4. Normalized absorption and fluorescence spectra of the CPSOB in chloroform solution (2 g/L) [(—)/(–)] and solid state (–), and of dye 1 in chloroform solution (1.5 mg/L) [(----)/(–)] (excitation wavelength = 342 nm).
4. Conclusions

Two fluorescent copolymers based on benzazole dyes could be obtained by free radical copolymerization of styrene and fluorescent benzazole derivatives. The copolymers in solid state or in chloroform solution emitted intense green fluorescence as the pure dyes although the dye content incorporated into the polystyrene backbone was less than 0.5% (wt/wt). Thus, the 2-[(5′-N-acryloyl)-2′-hydroxyphenyl] benzoxazole or benzothiazole is suitable as a monomer for fluorescent polymers. The thermal properties of the fluorescent copolymers and parent polystyrene were similar but the molecular weight of the copolymer was lower due to the chain transfer effect of the benzazole dyes.

Acknowledgements

The authors acknowledge the support and scholarships from the Brazilian Agencies CNPq and FAPERGS.

References