

# New Fluorescent Monomers and Polymers Displaying an Intramolecular Proton-Transfer Mechanism in the Electronically Excited State (ESIPT). IV. Synthesis of Acryloylamide and Diallylamino Benzazole Dyes and Its Copolymerization with MMA

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**ABSTRACT:** Six new fluorescent monomers were synthesized by reaction of 2-(5'-amino-2'-hydroxyphenyl)benzazole derivatives with acryloyl chloride and allyl bromide. UV-vis and steady-state fluorescence in solution were used to characterize its photophysical behavior. The monomers are fluorescent in the blue, green, yellow, and red region, with a large Stokes shift between 92 and 226 nm. A dual fluorescence ascribed to a conformational equilibrium in solution in the ground state dependent on the solvent po-

larity could be observed in the fluorescence emission spectra of the monomers. The radical polymerization of the monomers with methyl(methacrylate) allowed the production of fluorescent polymers in the blue-green region, with good optical and thermal properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2109–2116, 2006

**Key words:** copolymerization; dyes/pigments; fluorescence; photophysics; functionalization of polymers

## INTRODUCTION

ESIPT-exhibiting dyes are very attractive molecules, since they are highly fluorescent with a large Stokes shift, due to an excited-state intramolecular proton-transfer mechanism in the electronically excited state (Fig. 1).<sup>1–5</sup> This phenomenon has implications in the UV-light stabilizers field,<sup>6,7</sup> laser dyes,<sup>8</sup> new polymeric materials,<sup>9–12</sup> and also as fluorescent probes to labeling proteins.<sup>13,14</sup>

The ESIPT mechanism is quite dependent on the solvent polarity,<sup>15–17</sup> and many studies regarding this dependence,<sup>17–21</sup> as well as, theoretical calculations involving the geometry of the conformers in solution<sup>22–27</sup> have been made. In protic and/or polar solvents the enol-cis open conformer ( $E_{II}$ ) can be stabilized by intermolecular hydrogen bond with the solvent.<sup>28</sup> This conformer is originated from the intramolecular hydrogen bond rupture between the hydrogen of the hydroxy group and the nitrogen in the third position followed by 180° rotation of the 2-hydroxyphenyl group under the  $C_2-C_{1'}$  bond. In nonpolar solvents, additional enol-trans ( $E_{III}$ ) con-

formers in benzoxazoles and benzothiazoles ( $X = O$  and  $S$ , respectively) and enol-trans open ( $E_{IV}$ ) in benzimidazoles ( $X = NH$ ) could also exist (Scheme 1). All these conformers ( $E_{II}-E_{IV}$ ) present normal relaxation and can compete with the keto tautomer responsible to the ESIPT mechanism.<sup>29</sup>

Recently, we described new fluorescent MMA-benzazole dye copolymers with good optical and thermal properties.<sup>9,10</sup> The synthesis and characterization of new acryloylamide and diallylamino derivatives and its radical polymerization with methyl(methacrylate), to produce new fluorescent polymers for optical application, were presented in this work.

## EXPERIMENTAL

### Materials

Acryloyl chloride and allyl bromide were purchased from Merck and used as received. The 2-(5'-amino-2'-hydroxyphenyl)benzazoles **1a–c** were synthesized and purified according to a methodology previously described.<sup>9</sup> Methyl(methacrylate) (MMA) (Aldrich) was purified before the polymerization reaction by passing on an activated alumina column. 2,2'-Azobisobutyronitrile (AIBN) was purchased from Merck and purified before use by recrystallization from methanol and maintained under vacuum. Silica-gel 60 (Merck) was used for chromatographic column

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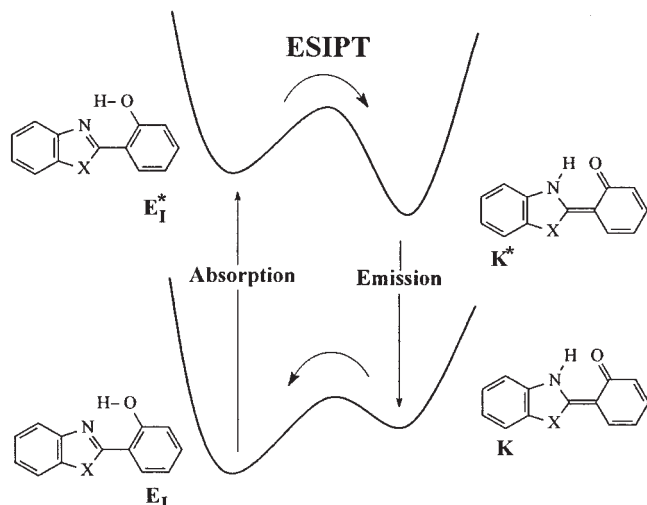


Figure 1 ES IPT mechanism.

purifications. All the solvents were used as received or purified using standard procedures.

### Instruments and methods

Infrared spectra were performed with a Mattson Galaxy Series FTIR 3000 in KBr. Melting points were measured with a Thermolyne apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were performed on a VARIAN model VXR-200 or INOVA-300, using tetramethylsilane (TMS) as the internal standard and DMSO- $d_6$  (Aldrich) or  $\text{CDCl}_3$  (Merck) as the solvent, at room temperature. UV-vis absorption data were taken on a Shimadzu UV-1601PC spectrophotometer. Fluorescence spectra were measured with a Hitachi spectrofluorometer model F-4500. Spectrum correction was performed to enable measuring a true spectrum by eliminating instrumental response such as wavelength characteristics of the monochromator or detector, using Rhodamine B as a standard (quantum counter). Elemental analyses were performed using Perkin-Elmer model 240.

DSC analysis was performed with a Perkin-Elmer DSC-4. The standard operating range of the instrument was 50–300°C. Dry samples, 5–7 mg, were prepared in aluminum pan and sealed. A three-cycle method, from 50 to 300°C at a rate of 20°C  $\text{min}^{-1}$ , was used, with a nitrogen purge. TGA analysis was conducted with a Perkin-Elmer TGS-2 thermal gravimetric analyzer. Dry samples, 3–4 mg, were directly weighted into aluminum pans. A heating rate of 20°C  $\text{min}^{-1}$  was maintained from 50 to 600°C. Size exclusion chromatography (SEC) was performed with a LDC Analytical Model Constametric 3200. Standard polystyrene was used as reference.

### Synthesis of the monomer dyes

#### Synthesis of the 2-[5'-(*N*-Acryloyl)-2'-hydroxyphenyl]benzazoles

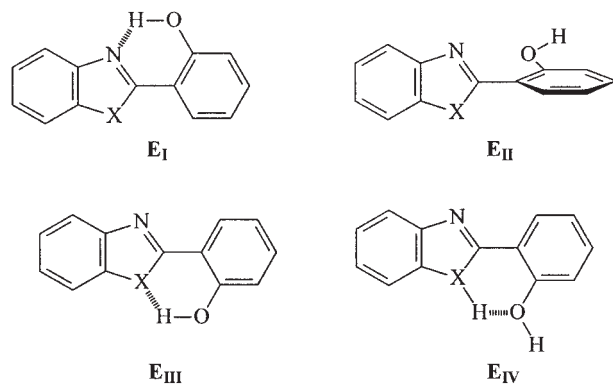
The acryloyl derivatives **2a–c** were prepared according to Scheme 2. To a solution of the corresponding benzazole **1a–c** in chloroform, cooled at 5°C, was added dropwise a solution of an equimolar amount of acryloyl chloride in chloroform. After the addition, the mixture was stirred for 2 h to prepare **2a** and **2b** and 8 h to prepare **2c**, cooled, and the resulting precipitate was filtered, washed with chloroform, dried at room temperature, and purified by column chromatography, eluted with chloroform.

#### 2-[5'-(*N*-Acryloyl)-2'-hydroxyphenyl]benzoxazole (**2a**).

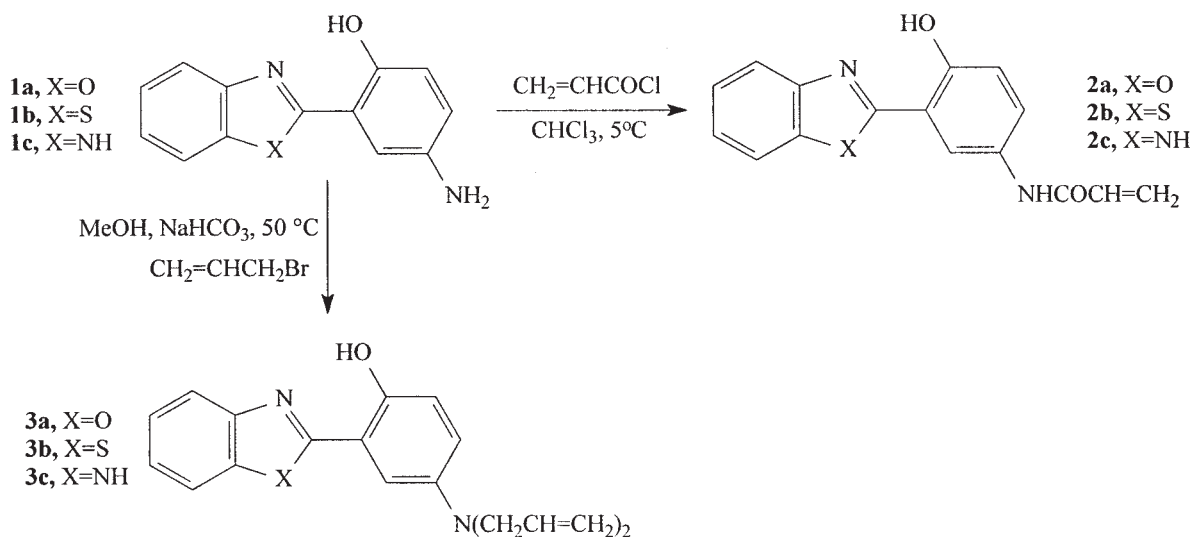
Yield: 83%. m.p.: 252–253°C. Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_3$ : C 68.56%, H 4.32%, N 9.99%. Found: C 68.27%, H 4.39%, N 9.76%. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3296 (NH), 1661 (C=O), 1610 (C=C).  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 11.0 (s, 1H, OH); 10.2 (s, 1H, NH); 8.6 (d, 1H,  $\text{H}_{6'}$ ,  $J_{\text{meta}} = 2.7$  Hz); 8.5–7.8 (m, 2H,  $\text{H}_5$  and  $\text{H}_6$  or  $\text{H}_4$  and  $\text{H}_7$ ); 7.6 (dd, 1H,  $\text{H}_{4'}$ ,  $J_{\text{meta}} = 2.7$  Hz,  $J_{\text{ortho}} = 9.0$  Hz); 7.5–7.4 (m, 2H,  $\text{H}_5$  and  $\text{H}_6$  or  $\text{H}_4$  and  $\text{H}_7$ ); 7.1 (d, 1H,  $\text{H}_{3'}$ ,  $J_{\text{ortho}} = 9.0$  Hz); 6.4 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{cis}} = 9.7$  Hz,  $J_{\text{trans}} = 17$  Hz); 6.3 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{gem}} = 2.2$  Hz,  $J_{\text{trans}} = 17$  Hz); 5.8 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{gem}} = 2.2$  Hz,  $J_{\text{cis}} = 9.7$  Hz).  $^{13}\text{C}$  NMR (50 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 163.8 (C=O); 152.6 ( $\text{C}_2$ ); 151.4 ( $\text{C}_2$ ); 150 ( $\text{C}_8$ ); 140.1 ( $\text{C}_9$ ); 131.3 ( $\text{C}_5$ ); 130.8 ( $\text{CH}_2=\text{CH}-$ ); 129.1 ( $\text{CH}_2=\text{CH}-$ ); 125.4 ( $\text{C}_5$  or  $\text{C}_6$ ); 124.4 ( $\text{C}_5$  or  $\text{C}_6$ ); 123.9 ( $\text{C}_1$ ); 121.8 ( $\text{C}_4$ ); 120.5 ( $\text{C}_4$ ); 120.3 ( $\text{C}_6$ ); 116.4 ( $\text{C}_3$ ); 110.8 ( $\text{C}_7$ ).

#### 2-[5'-(*N*-Acryloyl)-2'-hydroxyphenyl]benzothiazole (**2b**).

Yield: 84%. m.p.: 243–246°C. Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ : C 64.85%, H 4.08%, N 9.45%. Found: C 64.66%, H 4.33%, N 9.41%. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3271 (NH), 1658 (C=O), 1630 (C=C).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 11.4 (s, 1H, OH); 10.9 (s, 1H, NH); 8.5 (d, 1H,  $\text{H}_{6'}$ ,  $J_{\text{meta}} = 3.0$  Hz); 8.2–8.0 (m, 2H,  $\text{H}_5$  and  $\text{H}_6$  or  $\text{H}_4$  and  $\text{H}_7$ ); 7.7 (dd, 1H,  $\text{H}_{4'}$ ,  $J_{\text{meta}} = 3.0$  Hz,  $J_{\text{ortho}} = 9.0$  Hz); 7.6–7.4 (m, 2H,  $\text{H}_5$  and  $\text{H}_6$  or  $\text{H}_4$  and  $\text{H}_7$ ); 7.0 (d,



Scheme 1



Scheme 2

1H,  $H_{3'}$ ,  $J_{\text{ortho}} = 9.0$  Hz); 6.4 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{cis}} = 9.0$  Hz,  $J_{\text{trans}} = 17$  Hz); 6.3 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{gem}} = 2.4$  Hz,  $J_{\text{trans}} = 17$  Hz); 5.8 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{gem}} = 2.20$  Hz,  $J_{\text{cis}} = 9.0$  Hz).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 171.4 ( $\text{C}_2$ ); 163.0 ( $\text{C}=\text{O}$ ); 153.5 ( $\text{C}_9$ ); 151.4 ( $\text{C}_{2'}$ ); 133.9 ( $\text{C}_8$ ); 131.3 ( $\text{C}_{5'}$ ); 130.0 ( $\text{CH}_2=\text{CH}-$ ); 129.2 ( $\text{CH}_2=\text{CH}-$ ); 125.8 ( $\text{C}_5$  or  $\text{C}_6$ ); 125.1 ( $\text{C}_5$  or  $\text{C}_6$ ); 123.9 ( $\text{C}_{1'}$ ); 122.7 ( $\text{C}_7$ ); 122.1 ( $\text{C}_4$ ); 121.8 ( $\text{C}_{4'}$ ); 120.3 ( $\text{C}_{6'}$ ); 116.4 ( $\text{C}_{3'}$ ).

**2-[5'-(*N,N*-Dipropylamin-2-ene)-2'-hydroxyphenyl]benzimidazole (2c).** Yield: 55%. m.p.: 289–290°C.  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 13.2 (s, 1H, OH or NH azolic); 12.9 (s, 1H, OH or NH azolic); 10.1 (s, 1H, NH amide); 8.5 (d, 1H,  $H_{6'}$ ,  $J_{\text{meta}} = 2.0$  Hz); 7.7–7.6 (m, 2H,  $H_5$  and  $H_6$  or  $H_4$  and  $H_7$ ); 7.4 (dd, 1H,  $H_{4'}$ ,  $J_{\text{meta}} = 2.0$  Hz,  $J_{\text{ortho}} = 9.0$  Hz); 7.3–7.2 (m, 2H,  $H_5$  and  $H_6$  or  $H_4$  and  $H_7$ ); 7.0 (d, 1H,  $H_{3'}$ ,  $J_{\text{ortho}} = 9.0$  Hz); 6.3 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{cis}} = 10.0$  Hz,  $J_{\text{trans}} = 27$  Hz); 6.3 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{gem}} = 5.0$  Hz,  $J_{\text{trans}} = 27$  Hz); 5.8 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ,  $J_{\text{gem}} = 5.0$  Hz,  $J_{\text{cis}} = 10.0$  Hz).  $^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 163.8 ( $\text{C}=\text{O}$ ); 151.4 ( $\text{C}_{2'}$ ); 141.5 ( $\text{C}_2$ ); 137.9 ( $\text{C}_8$  and  $\text{C}_9$ ); 131.5 ( $\text{C}_{5'}$ ); 130.2 ( $\text{CH}_2=\text{CH}-$ ); 129.1 ( $\text{CH}_2=\text{CH}-$ ); 123.9 ( $\text{C}_{1'}$ ); 122.9 ( $\text{C}_5$  and  $\text{C}_6$ ); 121.8 ( $\text{C}_{4'}$ ); 120.3 ( $\text{C}_{6'}$ ); 116.4 ( $\text{C}_{3'}$ ); 115.5 ( $\text{C}_4$  and  $\text{C}_7$ ).

#### Synthesis of the 2-[5'-(*N,N*-Dipropylamin-2-ene)-2'-hydroxyphenyl]benzazoles

The diallylamino derivatives **3a–b** were prepared according to Scheme 2. To a solution of the corresponding benzazole **1a–c** in methanol was added an equimolar amount of sodium bicarbonate and stirred. To this solution was added allyl bromide (2:1 with respect to the benzazole dye) in methanol and it was allowed to react for 12 h at reflux. The dyes **3a–c** that

precipitate into the reactional mixture were filtered, washed with chloroform, and dried at room temperature. The resulting products were purified by column chromatography, using chloroform as the eluent.

#### 2-[5'-(*N,N*-Dipropylamin-2-ene)-2'-hydroxyphenyl]benzoxazole (3a).

Yield: 78%. m.p.: 93–95°C. Anal. Calcd for  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ : C 74.49%, H 5.92%, N 9.14%. Found: C 74.10%, H 6.10%, N 8.95%. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3471 (NH), 2973 (C–H), 1637–1631 (C=C).  $^1\text{H}$ -NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 10.90 (s, 1H, OH); 7.74–6.91 (m, 7H aromatic); 6.00–5.80 (m, 2H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ); 5.28–5.17 (m, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ); 4.06–3.92 (m, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 152.6 ( $\text{C}_2$ ); 150.0 ( $\text{C}_8$ ); 145.3 ( $\text{C}_{2'}$ ); 140.9 ( $\text{C}_9$ ); 137.6 ( $\text{C}_{5'}$ ); 134.3 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ); 125.4 ( $\text{C}_5$  or  $\text{C}_6$ ); 124.4 ( $\text{C}_5$  or  $\text{C}_6$ ); 124.6 ( $\text{C}_{1'}$ ); 120.7 ( $\text{C}_4$ ); 117.7 ( $\text{C}_{3'}$ ); 114.9 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ); 114.0 ( $\text{C}_{4'}$ ); 113.0 ( $\text{C}_{6'}$ ); 110.8 ( $\text{C}_7$ ); 59.6 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ).

#### 2-[5'-(*N,N*-Dipropylamin-2-ene)-2'-hydroxyphenyl]benzothiazole (3b).

Yield: 82%. m.p.: 60–62°C. Anal. Calcd for  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{OS}$ : C 70.78%, H 5.63%, N 8.69%. Found: C 70.58%, H 5.78%, N 8.83%. IR  $\nu$  ( $\text{cm}^{-1}$ ): 2926 (C–H), 1633–1591 (C=C).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 12.50 (s, 1H, OH); 8.10–7.10 (m, 7H aromatic); 6.20–6.00 (m, 2H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ); 5.42–5.35 (m, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ); 4.07–4.04 (m, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ).  $^{13}\text{C}$ -NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 171.4 ( $\text{C}_2$ ); 153.5 ( $\text{C}_9$ ); 145.3 ( $\text{C}_{2'}$ ); 137.6 ( $\text{C}_{5'}$ ); 134.0 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ); 133.9 ( $\text{C}_8$ ); 125.8 ( $\text{C}_5$  or  $\text{C}_6$ ); 125.1 ( $\text{C}_5$  or  $\text{C}_6$ ); 124.3 ( $\text{C}_{1'}$ ); 122.7 ( $\text{C}_4$  or  $\text{C}_7$ ); 122.1 ( $\text{C}_4$  or  $\text{C}_7$ ); 117.5 ( $\text{C}_{3'}$ ); 114.5 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ); 114.0 ( $\text{C}_{4'}$ ); 113.2 ( $\text{C}_{6'}$ ); 59.3 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ).

TABLE I  
AIBN, Fluorescent Dye, and MMA Amounts Used in the  
Polymerization

Copolymer	Dye	$n_{\text{dye}}$	$n_{\text{MMA}}$ ( $\times 10^{-2}$ )	$m_{\text{AIBN}}$ (mg)
Cop 2a	2a	$1.5 \times 10^{-5}$	9.3	12
Cop 2b	2b	$1.4 \times 10^{-5}$	9.3	12
Cop 2c	2c	$1.6 \times 10^{-5}$	9.3	12
Cop 3a	3a	$9.8 \times 10^{-6}$	6.5	16
Cop 3b	3b	$6.2 \times 10^{-6}$	6.5	16
Cop 3c	3c	$8.1 \times 10^{-4}$	6.5	16

2-[5'-(*N,N*-Dipropylamin-2-ene)-2'-hydroxyphenyl]benzimidazole (**3c**).

Yield: 80%. m.p.: 234°C (decomp.). Anal. Calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}$ : C 74.73%, H 6.27%, N 13.76%. Found: C 74.51%, H 6.00%, N 13.70%. IR  $\nu$  ( $\text{cm}^{-1}$ ): 2925 (C—H), 1626–1593 (C=C).  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 7.90–7.10 (m, 7H aromatic); 5.92–5.77 (m, 2H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ); 5.32–5.20 (m, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ); 4.07–3.90 (m, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ).  $^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 145.5 ( $\text{C}_2$ ); 141.5 ( $\text{C}_2$ ); 137.9 ( $\text{C}_8$  and  $\text{C}_9$ ); 137.0 ( $\text{C}_5$ ); 134.5 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ); 124.6 ( $\text{C}_1$ ); 122.9 ( $\text{C}_5$  and  $\text{C}_6$ ); 117.1 ( $\text{C}_3$ ); 115.4 ( $\text{C}_4$  and  $\text{C}_7$ ); 114.9 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ); 114.0 ( $\text{C}_4'$ ); 113.5 ( $\text{C}_6'$ ); 60.0 ( $\text{N}-\text{CH}_2\text{CH}=\text{CH}_2$ ).

#### Polymer synthesis

The copolymers **Cop 2a–c** and **Cop 3a–b** were prepared by heating a solution of the fluorescent monomers in MMA. The amounts used for each polymer are presented in Table I. The initial temperature was 40°C for 2 days and then was increased up to 60°C. After 6 days, the samples were heated for 2 h at 70°C and subsequently the temperature was maintained at 80°C for 8 h.<sup>9,10</sup> During the polymerization the temperature was maintained with an accuracy of  $\pm 0.5^\circ\text{C}$ . The copolymers were purified by solubilization in

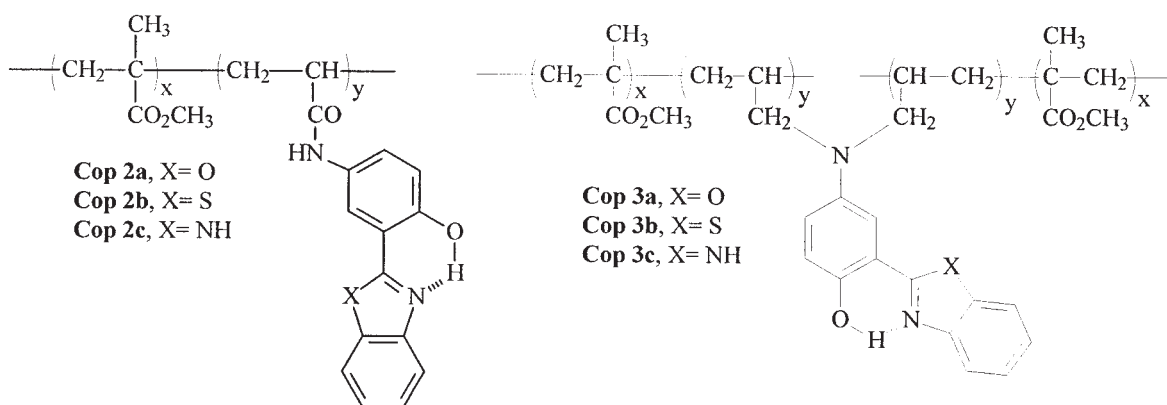
chloroform and precipitation into cyclohexane (1:20 mL solvent/nonsolvent). The resulting fluorescent copolymers are presented in the Scheme 3.

## RESULTS AND DISCUSSION

### UV–vis and fluorescence characterization of monomer dyes

The UV–vis absorption and fluorescence emission spectra were made in dichloromethane (DCM) and ethanol. All experiments were performed at room temperature, in a concentration of  $10^{-6}\text{M}$ . The UV–vis absorption and fluorescence emission spectra are normalized. The relevant photophysical data are presented in Table II. As seen in Figure 2, the dyes **2a–c** present an absorption maximum ( $\lambda_{\text{max}}^{\text{abs}}$ ) between 335 and 357 nm, with molar extinction coefficients  $\epsilon$  values ( $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) in agreement with  $\pi-\pi^*$  transitions ( $\text{S}_0 \rightarrow \text{S}_1$ ). The absorption maximum of the dye **2c** presents a smooth dependence ( $\sim 5 \text{ nm}$ ) on the solvent polarity. An intense band around 300 nm can be also observed, attributed to a charge-transfer mechanism due to the azole chromophore.<sup>21</sup>

The fluorescence emission spectra of the monomers **2a** and **2c** show the corresponding ESIPT band at 517 and 486 nm in ethanol, respectively, and at 517 and 495 nm in DCM. The monomer **2b** presented one main emission band at 547 nm in DCM, ascribed as the ESIPT band. However, in ethanol, an intense blue-shifted band at 414 nm and the ESIPT band at 548 nm can be observed, indicating the conformational equilibrium in solution in the ground state. Usually, a dual fluorescence emission presents a band at higher wavelengths attributed to an excited keto tautomer ( $\text{K}^*$ ), which arises from the enol-cis conformer ( $\text{E}_1$ ) in the excited state, and a blue-shifted one due to the conformational forms, which present a normal relaxation,<sup>23,28</sup> and the structure depends on the solvent polarity. In this way, for the dye **2b** in aprotic and/or



Scheme 3

TABLE II  
UV-Vis and fluorescence emission data of the dyes 2a-c and 3a-c.

Dye	Solvent	$\lambda_{\max}^{\text{abs}}$ (nm)	$\epsilon_{\max} \times 10^{-4}$ ( $1 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )	$(\lambda_{\max}^{\text{em}})_{\text{enol}}$ (nm)	$\Delta\lambda_{\text{ST}}^{\text{enol}}$ (nm)	$(\lambda_{\max}^{\text{em}})_{\text{keto}}$ (nm)	$\Delta\lambda_{\text{ST}}^{\text{keto}}$ (nm)
2a	Dichloromethane	345	1.32	—	—	517	172
	Ethanol	345	0.58	—	—	517	172
2b	Dichloromethane	357	0.82	—	—	547	190
	Ethanol	357	0.89	414	42	548	191
2c	Dichloromethane	340	1.20	—	—	495	155
	Ethanol	335	0.75	—	—	486	151
3a	Dichloromethane	394	0.54	480	86	591	197
	Ethanol	397	0.66	474	77	584	187
3b	Dichloromethane	405	0.51	470	65	631	226
	Ethanol	408	0.58	500	92	—	92
3c	Dichloromethane	387	0.25	433	46	565	178
	Ethanol	373	0.55	436	63	545	172

low polar solvents, the conformational equilibrium is probably between the  $E_I$  and  $E_{III}$  conformers, which will emit fluorescence by normal relaxation. In protic solvents it is due to the conformers  $E_I$  and  $E_{II}$ .

In Figure 3 are presented the absorption and fluorescence emission spectra of the dyes 3a–c. All these dyes present a smooth dependence in the absorption maximum ( $\lambda_{\max}^{\text{abs}}$ ) on the solvent polarity. The dyes 3a–c

presented the  $\lambda_{\max}^{\text{abs}}$  at 397, 408, and 373 nm in ethanol, respectively, and 394, 405, and 387 nm in DCM, with molar extinction coefficients  $\epsilon$  values ( $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) also in agreement with  $\pi-\pi^*$  transitions. The intense band around 300 nm can also be observed, attributed to a charge transfer mechanism due to the azole chromophore.<sup>21</sup>

The fluorescence emission spectra of the monomers 3a–c in DCM show the corresponding ES IPT band at

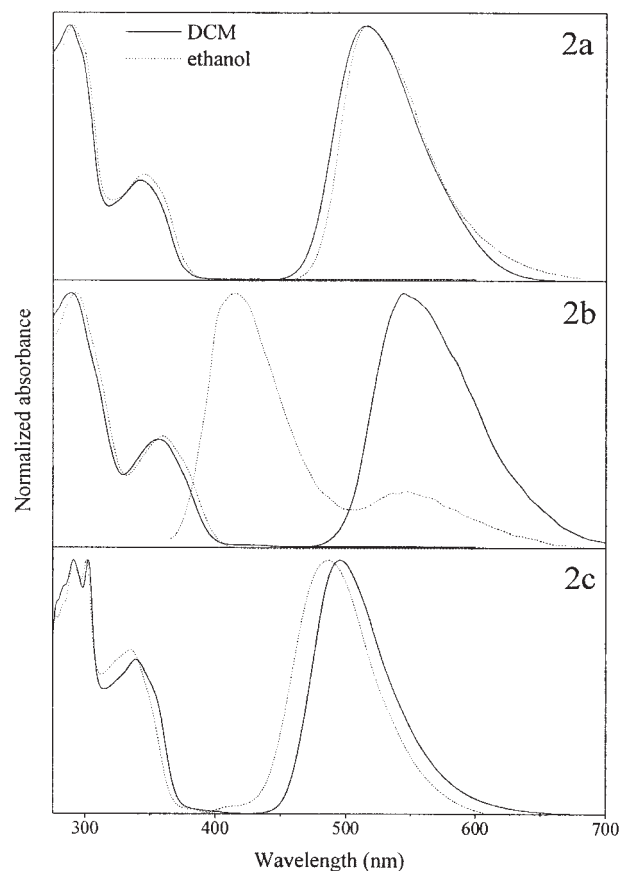


Figure 2 Normalized absorption and fluorescence emission spectra of 2a–c.

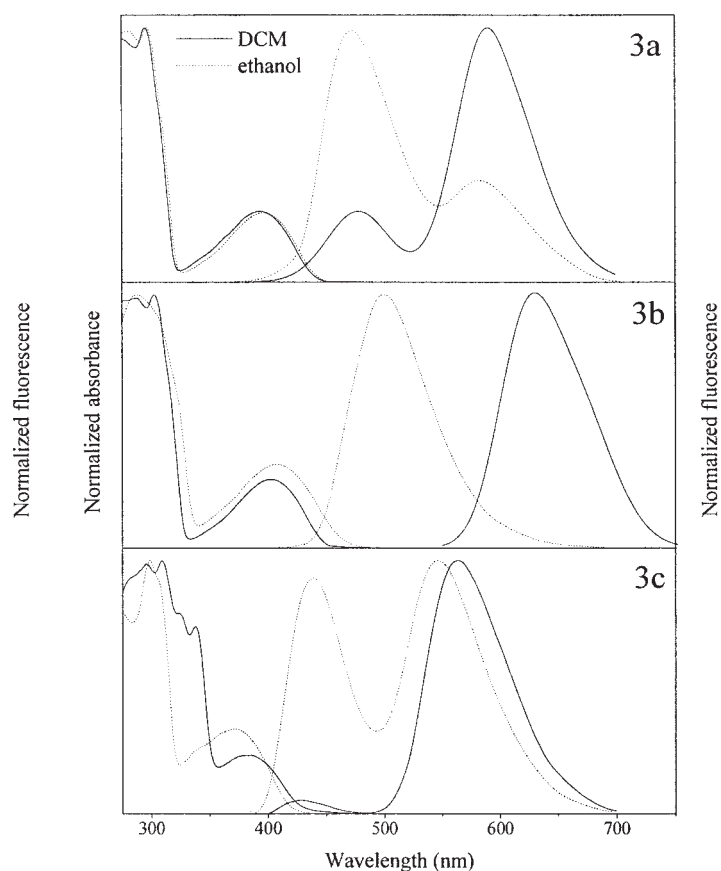
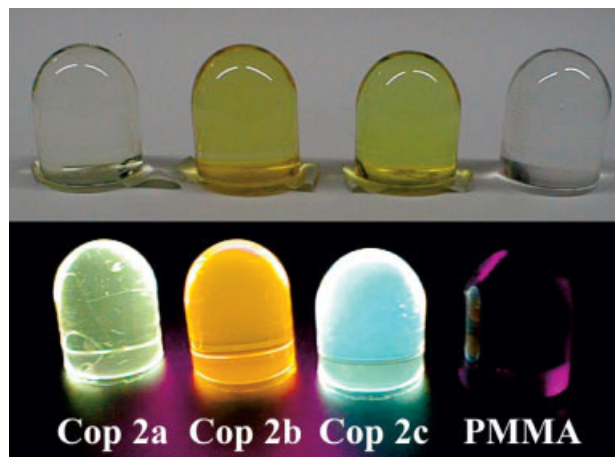


Figure 3 Normalized absorption and fluorescence emission spectra of 3a–c.





**Figure 4** Acryloyl copolymers under visible light (top) and UV radiation (bottom). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

591, 631, and 565 nm, respectively. Small blue-shifted bands can also be observed around 433–480 nm for **3a** and **3c**, indicating the conformational equilibrium in solution in the ground state, as already observed in the monomers **2a–c**. In the polar-protic solvent ethanol, the dual fluorescence can also be observed for **3a** and **3c**; however, with the blue-shifted band more intense, at 436–500 nm, in spite of the ESIPT band being above 545 nm. This behavior indicates that in ethanol, the conformers that present normal relaxation are in higher concentration in the ground state. The dye **3b** present one main emission band at 500 nm, ascribed to the ESIPT band.

### Polymer characterization

The polymerization of the benzazolylylene dyes with MMA lead new fluorescent ESIPT polymers with the dyes covalently bonded into the polymer chain. The obtained fluorescent acryloyl copolymers **Cop 2a–c**, under visible light and UV radiation, are presented in Figure 4. The copolymers were analyzed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and size exclusion chromatography (SEC). The relevant data from the copolymers are summarized in the Table III. The fluorescent copolymers were also investigated by  $^1\text{H}$  NMR and IR spectroscopy, where only the signals from the MMA polymer chain could be detected, as expected, since a very low concentration of the dyes were used in the polymerizations.<sup>9</sup>

**Cop 2a–c** and **Cop 3a–c**: IR  $\nu$  (KBr pellets,  $\text{cm}^{-1}$ ): 3020 (st C–H), 1740 (st C=O), 1240 (def C–O–C).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 3.61 (3H,  $\text{OCH}_3$ ), 1.87–1.81 (2H,  $\text{CH}_2$ ), 0.85 (3H,  $\text{CH}_3$ ).

The **Cop 2a–c** present similar values of the glass transition temperature ( $T_g$ ) when compared with PMMA. The **Cop 3a–c** presented higher  $T_g$  values, since the monomers are quite different than those used in the **Cop 2a–c**. In this way the polymer chain of **Cop 3a–c** seems to be more entangled than **Cop 2a–c**. The results from TGA show that the **Cop 3a–c** are more thermally stable than the **Cop 2a–c**, since values around 300°C were observed to the initial decomposition temperature ( $T_{\text{di}}$ ) in relation to the **Cop 2a–c** ( $T_{\text{di}} \sim 381^\circ\text{C}$ ).

The normalized absorption spectra and fluorescence emission of the **Cop 2a–c** in DCM ( $10^{-5}\text{M}$ ) are presented in Figure 5, and those of the monomers are also depicted for comparison. To these copolymers, the absorption maximum presented a small shift (1–4 nm) if compared to the monomers **2a–c**. The fluorescence emission spectra of the **Cop 2a–c** show no changes in its ESIPT band localization. However, the **Cop 2b–c** present additional blue-shifted bands at 421 and 400 nm, respectively, more intense to the **Cop 2b** in respect to the **Cop 2c**. The dual fluorescence emission, as already observed to the correspondent monomer, is probably due to the interaction of the phenolic OH with the polymer matrix, which contributes to the stabilization of the conformers that present normal relaxation.

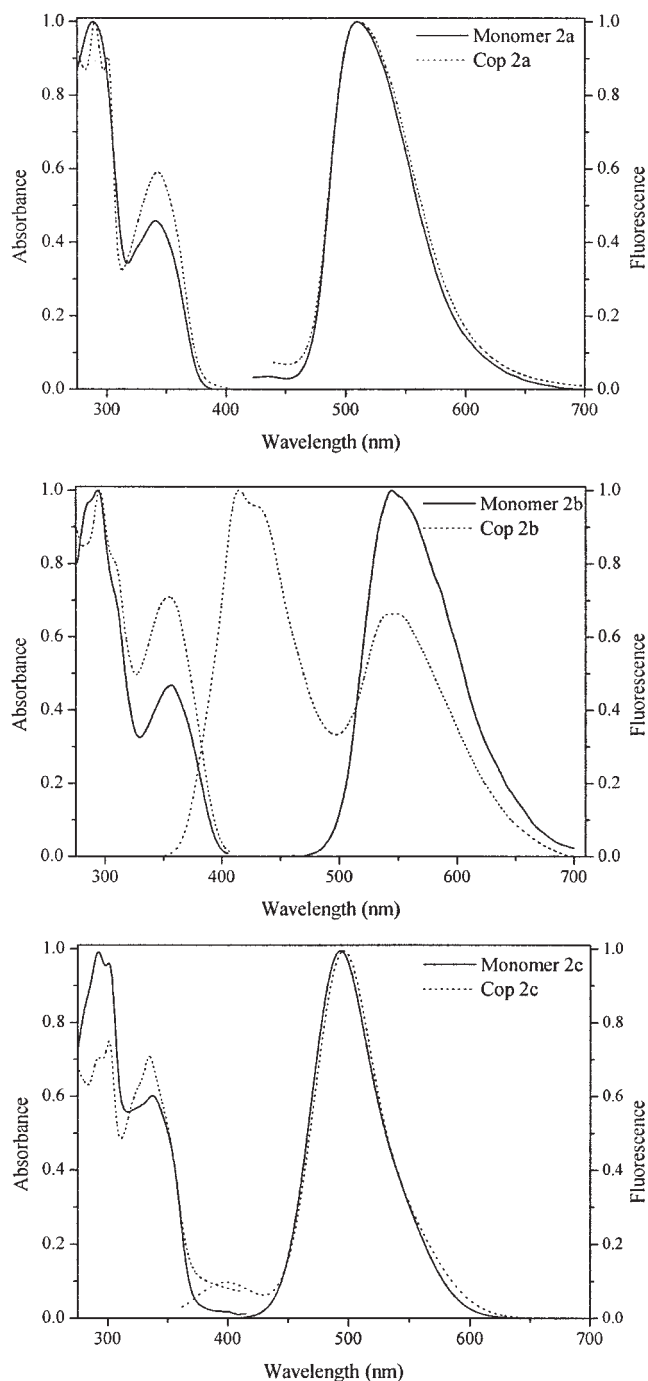
The **Cop 3a–c** present a quite different photophysical behavior when compared with the monomers **3a–c** (Fig. 6). The absorption maximum of the monomers could not be observed in the absorption spectra of the **Cop 3a–c**. All copolymers presented blue-shifted bands in the fluorescence emission spectra, indicating that the polymer matrix play a fundamental role in the photophysical behavior of the fluorescent dyes. The interaction of the phenolic OH with the MMA monomers seems to be more intense in the allyl than the acryloyl copolymer.

The fluorescent dye incorporation was determined using the copolymers' UV–vis data,<sup>9,12</sup> through the benzazole molar extinction coefficient  $\epsilon$  values at a

**TABLE III**  
Relevant Data of the Fluorescent Copolymers **2a–c** and **3a–c** Obtained by SEC ( $\bar{M}_n$  and  $\bar{M}_w/\bar{M}_n$ ), DSC ( $T_g$ ), TGA ( $T_{\text{di}}$  and  $T_{\text{dr}}$ )

Sample	$T_g$ ( $^\circ\text{C}$ )	$T_{\text{di}}$ ( $^\circ\text{C}$ )	$T_{\text{dr}}$ ( $^\circ\text{C}$ )	$\bar{M}_n$ ( $\times 10$ g mol $^{-1}$ )	$\bar{M}_w/\bar{M}_n$
PMMA	125	240	381	469	1.4
Cop2a	116	260	385	560	2.2
Cop2b	127	290	383	698	2.1
Cop2c	126	305	387	594	2.1
Cop3a	132	295	461	915	1.6
Cop3b	120	317	458	188	3.7
Cop3c	130	302	461	282	2.6

PMMA was also prepared for better comparison.

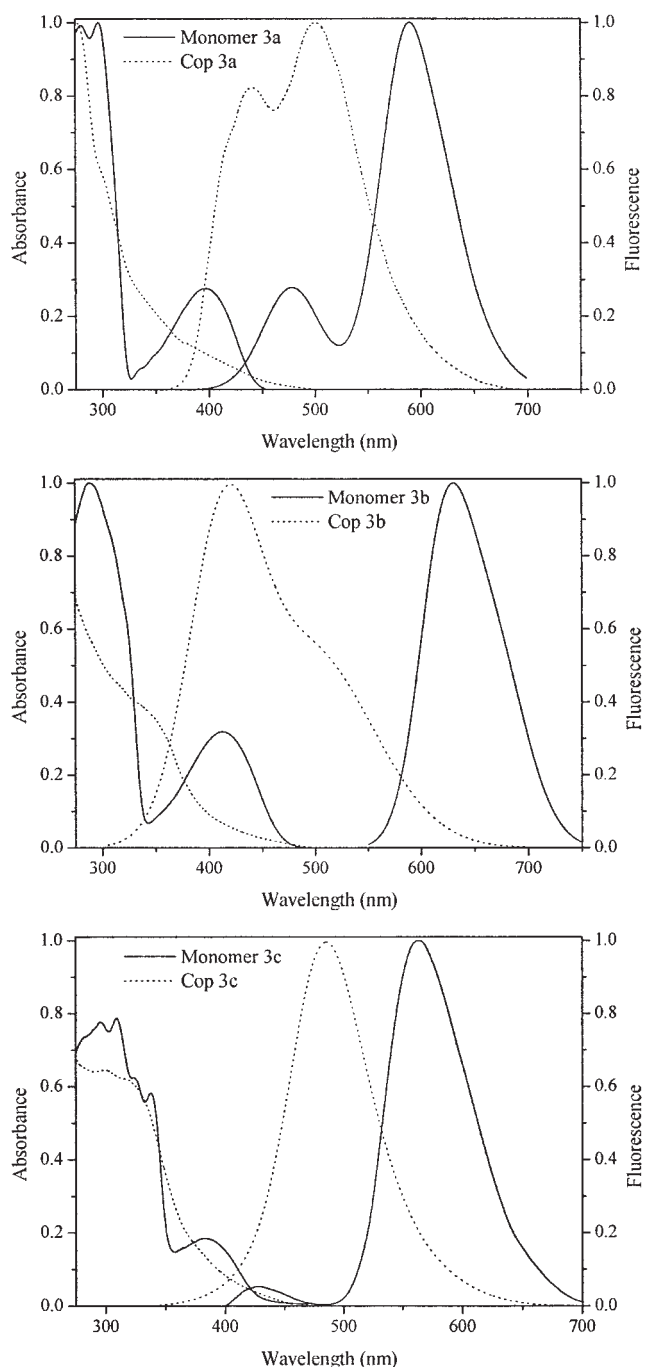


**Figure 5** Normalized absorption and fluorescence emission spectra of **Cop 2a–c** and monomers **2a–c**.

specific wavelength (Lambert–Beer law). It was assumed that  $\epsilon$  did not change when the benzazole was incorporated into the polymer chain. Values from 25 to 30% (w/w) [or 1.00–3.60% (mol/mol)] were found for the **Cop 2a–c**. Since the absorption maximum of the monomers could not be clearly observed in the absorption spectra of the **Cop 3a–c**, the dye incorporation in these samples could not be calculated.

## CONCLUSIONS

New fluorescent acryloyl and allyl monomers were synthesized, purified until optical purity grade, and characterized by elemental analysis,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, UV–vis, and steady-state fluorescence spectroscopy. The monomers are fluorescent in the blue–green–yellow–red region and present a Stokes shift between 92 and 226 nm. The absorption maximum dependence on the solvent polarity and the dual flu-



**Figure 6** Normalized absorption and fluorescence emission spectra of **Cop 3a–c** and monomers **3a–c**.

orescence indicated a conformational equilibrium in solution in the ground state. The emission at higher wavelength (ESIPT band) is due to an excited keto tautomer which arises from an enol-cis ( $E_1$ ) conformer in the excited state. The blue-shifted bands are due to conformational forms with a normal relaxation. The new monomers are found to be very sensitive to solvent polarity. All the synthesized monomers were totally soluble in MMA and were used to produce new fluorescent polymers. The resultant copolymers are transparent in the visible light and present fluorescence when illuminated with UV radiation. The new monomers and polymers showed to be very attractive to be used as new fluorescent materials.

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