

# New Fluorescent Monomers and Polymers Displaying an Intramolecular Proton-Transfer Mechanism in the Electronically Excited State. III. Thermogravimetric Stability Study of the Benzazolylynylene Derivatives

Leandra Franciscato Campo, Fabiano Severo Rodembusch, Valter Stefani

Universidade Federal do Rio Grande do Sul, Instituto de Química, Laboratório de Novos Materiais Orgânicos, Av. Bento Gonçalves, 9500. CP 15003 CEP 91501-970, Porto Alegre -RS Brazil

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**ABSTRACT:** Six fluorescent benzazolylynylene derivatives were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and related molecular parameters. The thermal stability was determined in terms of the steps of degradation and its fitting parameters, such as maximum degradation rate ( $R_{\max}$ ), maximum degradation rate temperature ( $T_{R_{\max}}$ ), degradation temperature range, which is related to the half-width at half-height values ( $\Gamma$ ), and the kinetic parameters: activation energy ( $E_a$ ), pre-exponential factor ( $A$ ), and reaction order ( $n$ ) obtained

by Barrett's method. Different organic substitutes and heteroatoms do not play a fundamental role in the thermal behavior of the studied dyes. The compensation effect between pre-exponential factor and activation energy was confirmed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 495–500, 2006

**Key words:** ESIPT; fluorescent monomers; thermogravimetric analysis; differential scanning calorimetry; kinetic parameters

## INTRODUCTION

A high fluorescence emission with a large Stokes shift can be observed in heterocyclics of the benzazole family due to an intramolecular proton-transfer mechanism in the electronically excited state (ESIPT)<sup>1–5</sup> (Fig. 1). ESIPT-exhibiting molecules often present a large Stokes shift. This phenomenon has widespread implications in UV-light stabilizers,<sup>6,7</sup> laser dyes,<sup>8</sup> new polymeric materials,<sup>9–11</sup> and also as fluorescent probes to labeling proteins.<sup>12,13</sup>

The UV light absorption through the enol conformer (E) produce the excited enol (E\*), which is quickly converted to an excited keto tautomer (K\*) by an intramolecular proton transfer. The excited keto tautomer decays emitting fluorescence to a keto tautomer in the ground state (K). Since the enol conformer (E) is more stable than the keto tautomer in the ground

state, the initial enol form is regenerated without any photochemical change.<sup>14,15</sup>

The present work aimed to characterize the thermal behavior and stability of these fluorescent monomers. This information is important for the production of new fluorescent polymers with high thermal and photochemical stability. Thermogravimetric analysis (TGA) is a well-known tool for thermal stability study.<sup>16,17</sup> Kinetic processes<sup>18</sup> related to cure and material composition<sup>19–21</sup> can be also investigated by this technique. Kinetic parameters, such as rate (frequency) factors, activation energies, and reaction orders can be obtained from TGA measurements.<sup>22,23</sup>

## EXPERIMENTAL

### DSC and TGA characterization

Thermal analysis was performed on a PL-DSC (Polymer Laboratories–Differential Scanning Calorimeter). Chloroform ( $T_m = -63.5^\circ\text{C}$ ,  $\Delta H_m = 73.65 \text{ J g}^{-1}$ ), benzene ( $T_m = 5.5^\circ\text{C}$ ,  $\Delta H_m = 127.40 \text{ J g}^{-1}$ ), In (6.404 mg;  $T_m = 156.60^\circ\text{C}$ ;  $\Delta H_m = 28.45 \text{ J g}^{-1}$ ), and Zn (2.815 mg;  $T_m = 419.47^\circ\text{C}$ ;  $\Delta H_m = 108.37 \text{ J g}^{-1}$ ) were used for temperature and fusion heat calibration. Approximately 30 mg of each dye sample was conditioned in a DSC aluminum sample pan. The samples were quenched with liquid N<sub>2</sub> before analysis. The thermograms were obtained by heating from 100 to 280°C at

Correspondence to: V. Stefani (vstefani@iq.ufrgs.br)

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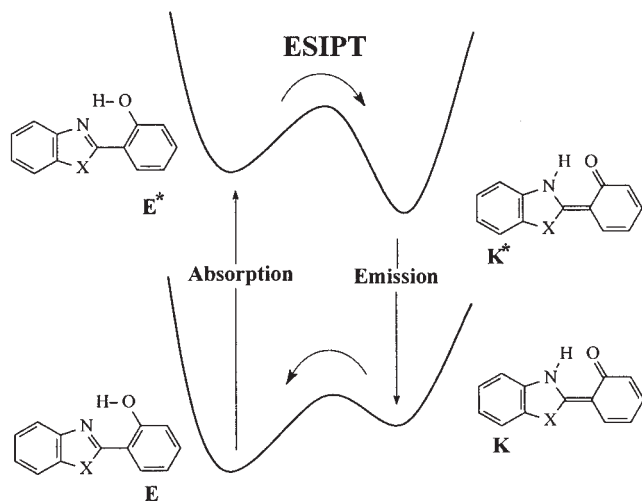


Figure 1 ESIP mechanism for benzazole dyes.

$10^{\circ}\text{C min}^{-1}$ . The runs were carried out with automatic baseline correction. All the samples were analyzed twice with reproducible results.

TGA was conducted with a TA Instruments, model 2050, thermal gravimetric analyzer under  $\text{N}_2$  atmosphere. Dry samples (3–4 mg) were weighed directly into aluminum pans. A heating rate of  $20^{\circ}\text{C min}^{-1}$  was applied. The temperature range was from 50 to  $600^{\circ}\text{C}$ .

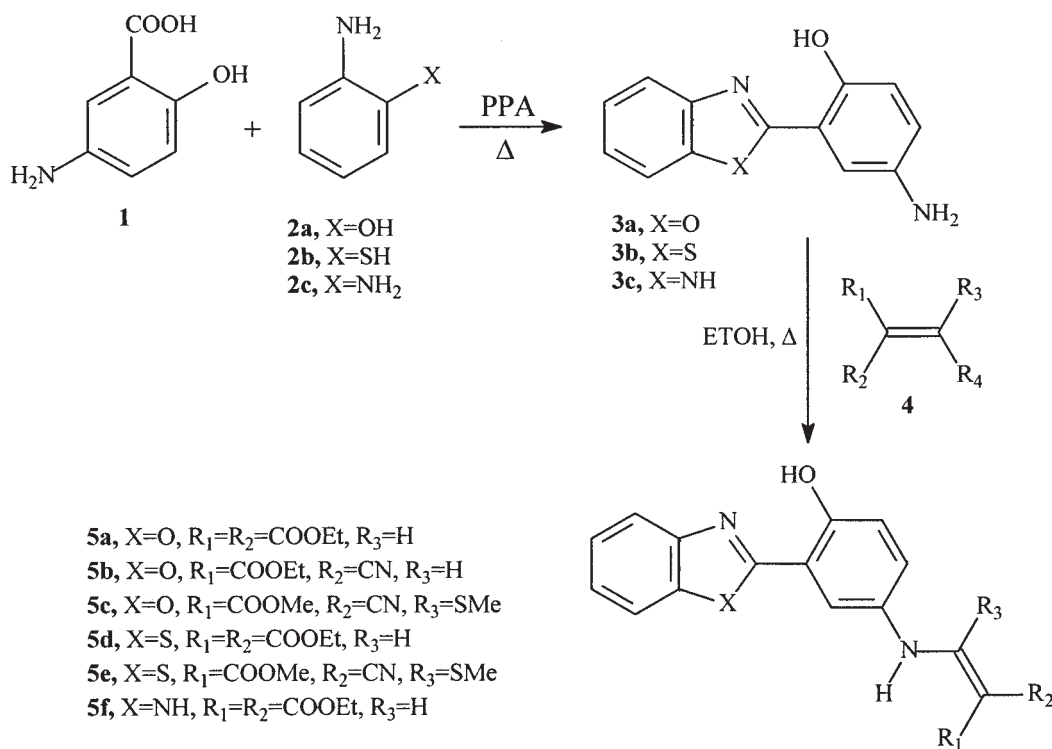


Figure 2 Synthesis of the fluorescent monomer dyes 5a-f.

## RESULTS AND DISCUSSION

### Benzazolylynylene derivatives

The benzazolylynylene derivatives were prepared using a methodology presented in the Figure 2. The reaction consists in the condensation of 5-aminosalicylic acid with *o*-substituted anilines in polyphosphoric acid (PPA) to yield the corresponding aminobenzazoles **3a–c**, which reacts with the vinylene derivatives **4**, in ethanol as solvent, to produce the fluorescent monomers **5a–f**.<sup>9</sup>

### DSC analysis

The DSC thermograms of the benzazolylynylene are presented in Figure 3. The dyes **5a–b** and **5f** present melting points higher than  $200^{\circ}\text{C}$ . The dye **5b** presents the higher one ( $247^{\circ}\text{C}$ ), while dyes **5c–e** presented melting points between 169 and  $195^{\circ}\text{C}$ .

### TGA

The DTG curves for all dyes were obtained from the TGA curves and were analyzed by least squares fit of multiGaussian functions, and its deconvolution are depicted in Figure 4. The Marquard algorithm for multifunctional fits was applied to analyze the overall degradation process by deconvolution into steps of degradation.

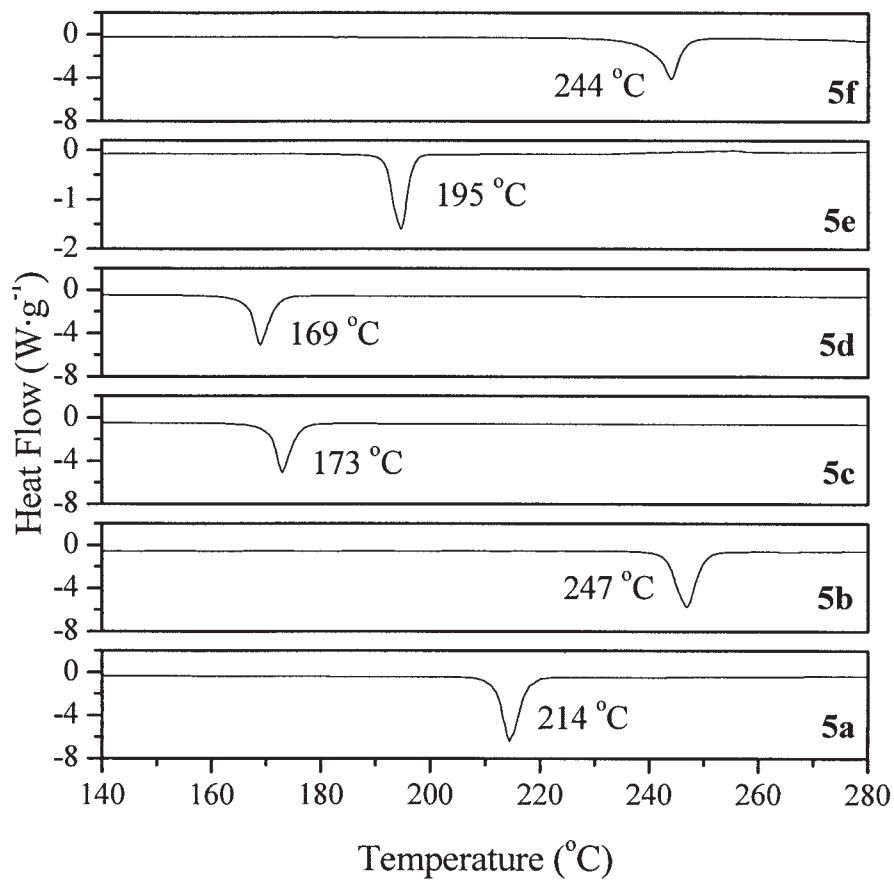


Figure 3 DSC thermograms of benzazolyvinylene 5a–f.

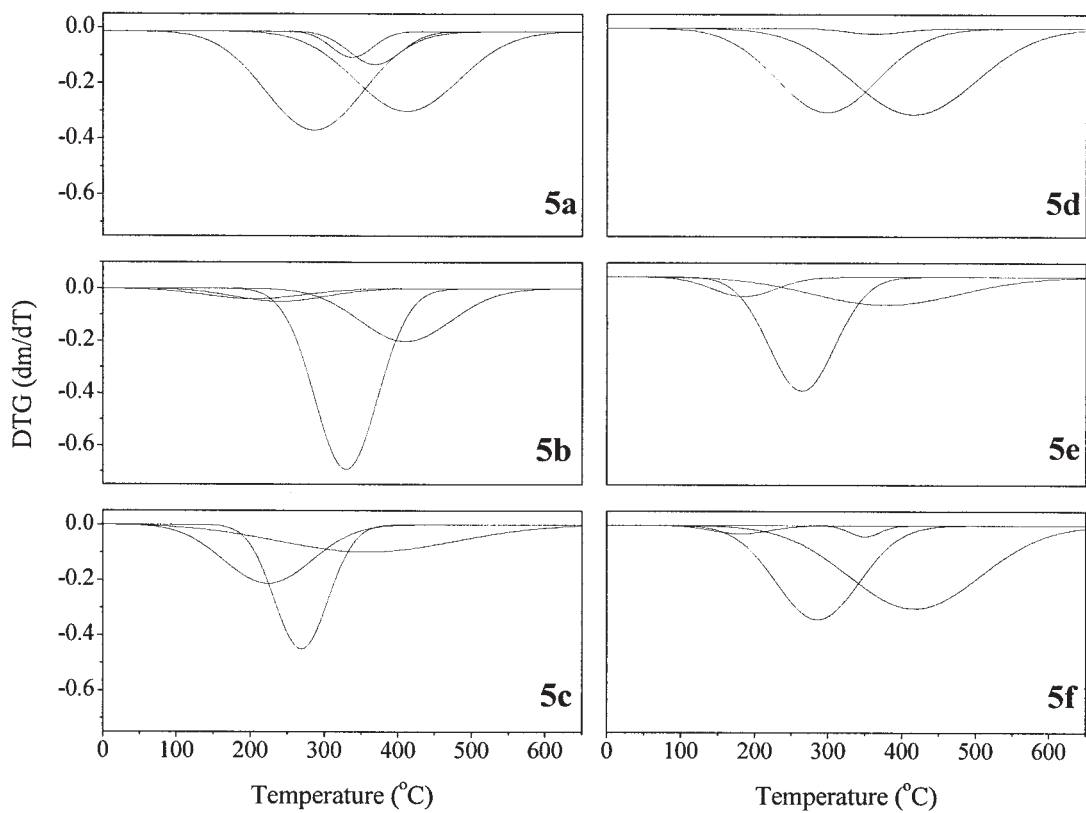


Figure 4 Deconvoluted curves from the experimental DTG curves for benzazolyvinylene 5a–f.

**TABLE I**  
Fitting Results of Thermogravimetric Derivative Curves

Dye	$N_{ri}$	$T_{R_{\max}}$ (°C)	$\Gamma$ (°C)	$R_{\max}$ (%m °C <sup>-1</sup> )
5a	1	285.80	65.78	-0.36
	2	336.56	28.06	-0.09
	3	367.84	35.37	-0.12
	4	411.27	70.51	-0.29
5b	1	204.90	66.78	-0.04
	2	239.47	62.14	-0.05
	3	329.35	42.75	-0.65
	4	409.70	62.08	-0.21
5c	1	223.71	59.52	-0.21
	2	268.78	36.17	-0.45
	3	356.92	120.54	-0.10
5d	1	297.84	68.75	-0.30
	2	362.51	35.69	-0.02
	3	415.36	84.26	-0.31
5e	1	184.89	43.15	-0.07
	2	263.84	45.02	-0.41
	3	377.03	99.52	-0.09
5f	1	181.25	39.89	-0.03
	2	285.68	56.27	-0.35
	3	349.87	20.59	-0.04
	4	417.30	89.40	-0.29

$N_{ri}$ : step of degradation number;  $T_{R_{\max}}$ : maximum degradation rate temperature;  $\Gamma$ : degradation temperature range, related to the half-width at half-height and  $R_{\max}$ : maximum degradation rate ( $dm/dT$ ).

As it can be observed in Figure 4, the benzazolylylvi-nylenes **5a–b** and **5f** present a four-step degradation process, and the dyes **5c–e** present a three-step process. All the dyes presented similar thermal degradation behavior with relatively high maximum degradation rate ( $R_{\max} < -0.41\%m\ ^\circ C^{-1}$ ). A higher value was only detected for dye **5b** ( $R_{\max} = -0.65\%m\ ^\circ C^{-1}$ ). These values show that the heteroatom and the different organic substitutes do not play a fundamental role in the degradation process. The values of  $T_{R_{\max}}$  were found to be around 285°C to the dyes **5a** and **5f** and 329 and 412°C to **5b** and **5d**, respectively.

For a degradation process  $i$ , the conversion factor  $\alpha_i$  is the ratio of the partial mass loss  $\Delta m_{T,t}^i$  until the time  $t$  caused by this specific process, divided by the total mass loss  $\Delta m_{\text{tot}}^i$  for the same degradation process  $N_{ri}$  as presented in eq. (1)

$$\alpha = \Delta m_{T,t}^i / \Delta m_{\text{tot}}^i \quad (1)$$

The steps of degradation were analyzed according to Barrett's method.<sup>24</sup>

$$d\alpha_i/dt = A_i e^{(-E_a^i/RT)} (1 - \alpha_i)^n \quad (2)$$

The eq. (2) can be written in logarithmic form, resulting

$$\ln(d\alpha_i/dt) = \ln A_i - E_a^i/RT + n \ln(1 - \alpha_i) \quad (3)$$

where  $i$  refer to the degradation process  $N_{ri}$ ,  $A$  is the Arrhenius pre-exponential frequency factor,  $E_a^i$  is the activation energy, and  $n$  is the reaction order. The coefficient  $d\alpha_i/dt$  in eq. (3) can be described as

$$d\alpha_i/dt = dm/dt \cdot 1/m_{\text{tot}} = dm/dT \cdot 1/m_{\text{tot}} \cdot \phi \quad (4)$$

where  $m_{\text{tot}}$  can be obtained by the overall integration of the degradation process, and  $\phi$  is the heating rate (°C min<sup>-1</sup>). The eq. (4), in terms of temperature  $T$ , reads

$$d\alpha_i/dt = dm/dT \cdot 1/m_{\text{tot}} \cdot \phi \quad (5)$$

This allows the eq. (3) to be written as

$$\ln(dm/dT \cdot 1/m_{\text{tot}} \cdot \phi) - n \ln(1 - \alpha_i) = -E_a^i/RT + \ln A_i = \ln k. \quad (6)$$

A plot of  $k$  as a function of  $1/T$  gives the kinetic parameters  $A_i$ ,  $E_a^i$ , and the reaction order  $n$ .

The data obtained from DTG curves (Fig. 4) are summarized in Table I, for each step of degradation; maximum degradation rate ( $R_{\max}$ ), maximum degradation rate temperature ( $T_{R_{\max}}$ ), the corresponding half-width at half-height ( $\Gamma$ ). The data obtained from

**TABLE II**  
Corresponding Kinetic Parameters Obtained by Barrett's Method

Dye	$N_{ri}$	$E_a^i$ (kJ mol <sup>-1</sup> )	$\ln A$	$n$	$r$
5a	1	44 ± 1	5.3 ± 0.1	1.4	0.999
	2	184 ± 12	34 ± 2	1.6	0.991
	3	149 ± 2	25 ± 1	2.0	0.999
	4	66 ± 1	7.4 ± 0.2	1.3	0.998
5b	1	28 ± 1	2.8 ± 0.1	1.2	0.999
	2	43 ± 1	6.2 ± 0.1	1.5	0.999
	3	110 ± 3	19 ± 1	1.8	0.997
	4	92 ± 2	13 ± 1	1.8	0.998
5c	1	40 ± 1	5.7 ± 0.3	1.3	0.995
	2	128 ± 6	26 ± 1	1.9	0.989
	3	28 ± 1	0.6 ± 0.1	1.2	0.996
5d	1	48 ± 1	6.8 ± 0.2	1.4	0.998
	2	133 ± 6	21 ± 1	1.4	0.993
	3	53 ± 1	5.9 ± 0.1	1.3	0.999
5e	1	59 ± 1	12.5 ± 0.4	1.7	0.998
	2	67 ± 2	11 ± 1	1.3	0.993
	3	31 ± 1	2.9 ± 0.1	1.1	0.998
5f	1	57 ± 1	11 ± 1	1.4	0.998
	2	60 ± 1	9.5 ± 0.2	1.5	0.998
	3	232 ± 14	42 ± 3	1.4	0.990
	4	49 ± 1	4.5 ± 0.1	1.3	0.999

$E_a^i$ : activation energy;  $A$ : pre-exponential frequency factor;  $n$ : reaction order and  $r$ : correlation factor.

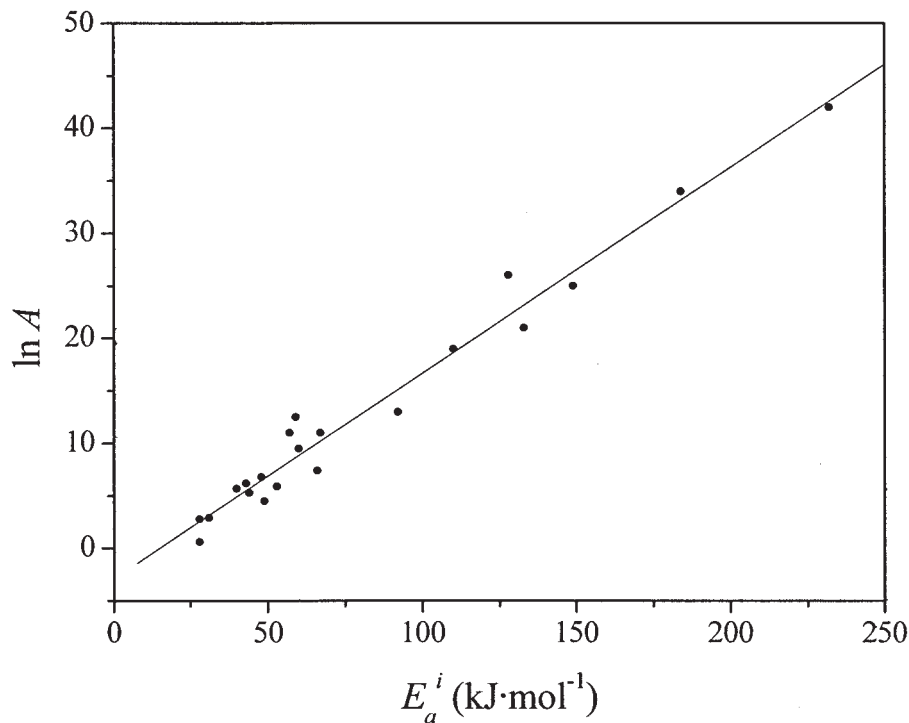


Figure 5 Plot of  $\ln A$  vs.  $E_a^i$  for the monomer dyes.

Barrett's method, pre-exponential factor ( $\ln A$ ), activation energy ( $E_i$ ), and reaction order ( $n$ ), are listed in Table II.

The values of the pre-exponential factor for all decomposition processes as a function of activation energies using the linear relation  $\ln A = a + bE_a^i$  were plotted in Figure 5. A linear behavior with intercept and slope of  $-2.92, 105$  and  $0.19, 603$ , respectively, with a correlation factor of  $0.98, 558$ , could be observed for all compounds independent of the nature of organic substitute or heteroatom present in the molecule. The whole thermal study carried out with the dyes presented different thermal parameters, but the compensation effect is observed in all cases, indicating that they belong to the same compound family.

### CONCLUSIONS

Six fluorescent monomers, with a large Stokes shift, were studied by standard thermal analysis. A single thermal event of first order related to the dye fusion could be observed in all samples. Values higher than  $200^\circ\text{C}$  could be observed for dyes **5a–b**, **5f** with the **5b** presenting the highest one ( $247^\circ\text{C}$ ). Intermediate values could be detected for **5c–e** dyes. The organic substitutes and heteroatoms do not play a fundamental role in the thermal behavior. The studied dyes obey the same compensation effect.

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