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Uv-Visible, Fluorescence Spectroscopy Data and Thermogravimetric Analysis of PMMA Copolymers Containing Benzazolylvinylene Chromophores

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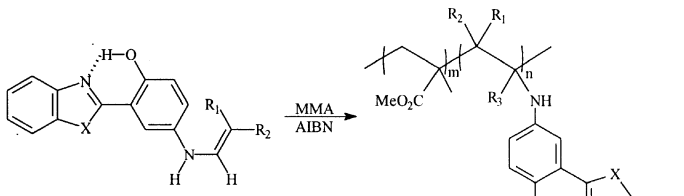
In this work we describe the Uv-vis and fluorescence spectroscopy data of the 2-[(5'-*N*-vinylene)-2'-hydroxyphenyl] benzazoles and its copolymers with MMA as well as its thermal properties.

Keywords Fluorescence; ESIPT; Benzazoles; PMMA.

INTRODUCTION

Heterocyclic compounds like 2-(2'-hydroxyphenyl) benzazoles are important dyes which emit fluorescence with large Stokes shift ascribed to an intramolecular-proton transfer mechanism in the electronically excited state- ESIPT. The proton transfer occurs along previously existent hydrogen bonding involving the azole nitrogen atom and hydrogen from phenolic group, and is very fast, occurring in the picosecond scale. Fluorescent dyes which presents ESIPT when dispersed or covalently bonded in a polymeric matrix are potentially useful as solid laser-dyes, materials for opto-electronics and as UV-light stabilizer [1-7].

The polymethylmethacrylate copolymers containing benzazolylvinylene chromophores were synthesized according to the references [7]. Figure 1 shows the structure of the copolymers.



Copolymer	X	R_1	R_2	R_3
1a	O	CO_2Et	CO_2Et	H
1b	O	CO_2Et	CN	H
1c	O	CO_2Me	CN	SMe
1d	S	CO_2Et	CO_2Et	H
1e	S	CO_2Me	CN	SMe
1f	NH	CO_2Et	CO_2Et	H

FIGURE 1 The structure of the PMMA copolymers containing benzazolylvinylene chromophores

RESULTS AND DISCUSSION

Uv-vis and Fluorescence Spectroscopy Analysis

The UV-vis (Figure 2) and fluorescence (Figure 3) spectra of all copolymers were measured in $CHCl_3$ solutions (10^{-3} mol/L). The UV-vis spectra of copolymers present two main bands, whose maxima are located in the 317-367 nm regions and the other band blue-shifted located in the 283-304 nm. The long-wavelength band are attributed to the strong intramolecular hydrogen bond between the benzazole nitrogen and the adjacent hydroxy group [4], indicating that the benzazole moiety in the PMMA copolymers retains the planar structure.

The emission spectra of copolymers **1a-b** and **1f** show only one band with λ_{max} values of about 510 nm and 500 nm for **1a-b** and **1f** respectively. It is also noticed that the emission spectra of cop **1a-b** and **1f** are very similar to that of monomers itself, indicating the presence of similar pathways for radiative decay for the benzazolylvinylene monomers and the copolymers. In contrast to, the copolymers **1c-e** present one band with λ_{max} values about 550 nm for copolymers **1d-e** and 500 nm for copolymer **1c**, and other band blue-shifted with λ_{max} value about 420 nm and 440 nm for copolymers **1d-e** and copoplymer **1c**, respectively. It is important to note that the copolymers **1c-e** have in common one sulfur atom in the structure. This can be indicate that the presence of the sulfur atom lead to the formation of an another

pathways of emission. Further studies are in progress and will be reported elsewhere.

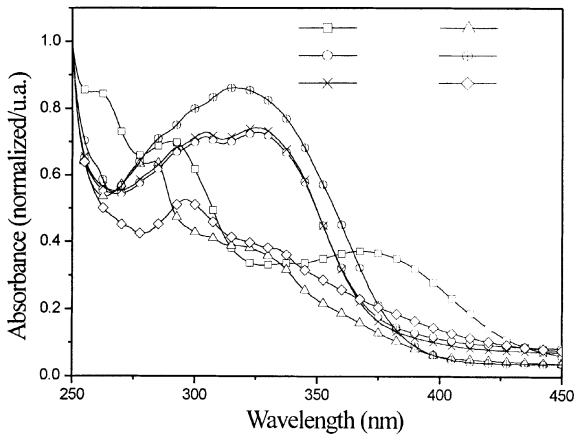


FIGURE 2 Normalized UV-vis spectra of copolymers **1a-f** at room temperature in $CHCl_3$.

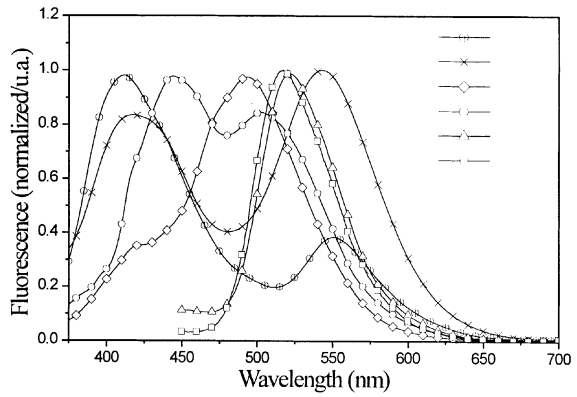


FIGURE 3 Normalized fluorescence spectra of copolymers **1a-f** in $CHCl_3$ at room temperature. The sample solutions were excited at 355 nm.

Thermal analysis

The analysis of the thermogravimetric curves (Figure 4) show a significant increase in the decomposition temperature (Td) values for the copolymers containing the benzazolylvinylene dyes when compared with the PMMA itself. This fact indicate that the copolymers present a

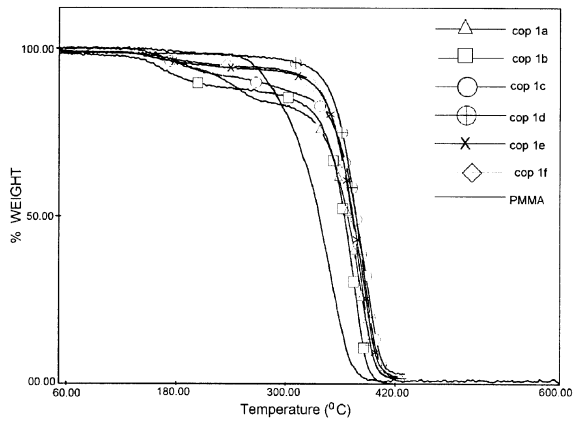


FIGURE 4 TGA curves of copolymers **1a-f** at a heating rate of 20°C/min in nitrogen.

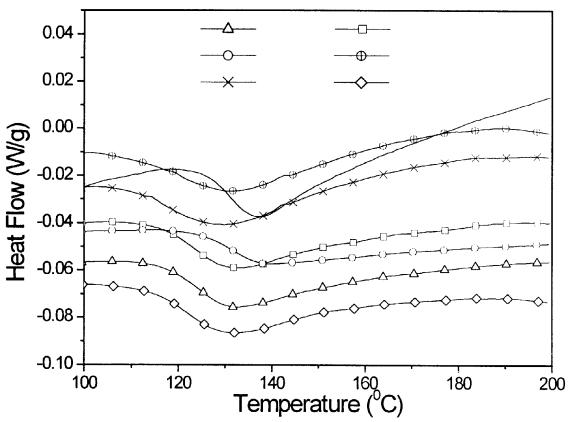


FIGURE 5: DSC curves of copolymers **1a-f** at a heating rate of 40^0C/min in nitrogen.

greater thermal stability when compared with PMMA itself. The TGA curves also show a single mass loss over a fairly broad temperature range for all the copolymers.

The differential scanning calorimetry (DSC) curves show that the copolymer **1c** have a greatest glass transition temperature (Tg) and the copolymers **1d** and **1e** present the smallest Tg (Figure 5). The M_W of copolymers **1a-f** stayed between 0,9 -1,5x10^6 g/mol and 1,5x10^6 g/mol for the PMMA itself.

CONCLUSIONS

The copolymerization of the benzazolylvinylene dyes with MMA lead a new fluorescent ESIPT polymers with the dyes covalently bonded in the main chain of the rigid polymers. These new polymers containing the benzazole moiety combine the high thermal stability of rigid-rod polymers with the photochemical stability and resistance to degradation by free radicals of benzazole moieties. The copolymers **1a-f** show optical transparency in the region of the visible spectra, condition indispensable for the application in solid state laser-dye and materials for opto-electronics. All the copolymers are non fluorescent when observed at the visible light and fluorescent when irradiated with UV light.

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REFERENCES

[1] V. Stefani, A.A. Souto, A.U. Acuña, F. Amat-Guerri, *Dyes Pigm.*1992, 20, 97.
[2] N.S. Domingues Jr., C. Krug, P.R. Livotto, V. Stefani, *J. Chem. Soc., Perkin Trans. 2*, 1997, 9, 1861.

[3] M. Segala, N. S. Domingues Jr., P. R. Livotto, V. Stefani, *J. Chem. Soc., Perkin Trans. 2*, 1999, 6, 1123.
[4] D. Kuila, G. Kvakovszky, M. A. Murphy, R. Vicari, M. H. Rood, K. A. Fritch, J. R. Fritch, *Chem. Mater. 11*, 1999, 109.
[5] M. L. Ferrer, A. U. Acuña, F. Amat-Guerri, A. Costela, J. M. Figuera, F. Florido, R. Sastre, *Appl. Opt.*,
1994, 33, 2266.
[6] L. F, Campo, M. Sc. Thesis, UFRGS,1999.
[7] L. F. Campo, D.S. Corrêa, M.A. de Araújo, V.Stefani, *Macromol. Rapid Commun., 2000, 21(12), 832*