



IX International Macromolecular  
Colloquium

306628



# 6º CONGRESSO BRASILEIRO DE POLÍMEROS

## IX INTERNATIONAL MACROMOLECULAR COLLOQUIUM

11 a 15 de novembro de 2001  
Centro de Convenções do Hotel Serrano  
Gramado/RS

Promoção:



Associação Brasileira de Polímeros

Instituto de Química da Universidade  
Federal do Rio Grande do Sul (IQ/UFRGS)

Fabiano S. Rodembusch<sup>1\*</sup>, Nádyá P. da Silveira<sup>1</sup>, Dimitrios Samios<sup>1</sup>, Leandra F. Campo<sup>2</sup>, Valter Stefani<sup>2</sup>

Universidade Federal do Rio Grande do Sul – Instituto de Química - Av. Bento Gonçalves 9500, CEP 91501-970  
Caixa Postal 15003 Fax: +55(051) 319-1499 Porto Alegre/RS Brazil  
e-mail: rodembusch@yahoo.com

<sup>1</sup>Laboratório de Instrumentação e Dinâmica Molecular – <http://www.iq.ufrgs.br/lindim>

<sup>2</sup>Laboratório de Novos Materiais Orgânicos – <http://www.iq.ufrgs.br/lnmo>

Photon Correlation Spectroscopy (PCS) was used in order to characterize the fluorescent ESIPT copolymers of Poly (methyl-methacrylate)-Benzazole dyes in solution with chloroform and THF in dilute regime. The obtained intensity autocorrelation functions,  $g_{(2)}(t)$ , were analyzed using the CONTIN software. The diffusional coefficient at infinite dilution,  $D_0$ , the hydrodynamic radius,  $R_h$  as well as the dynamic interaction parameter,  $k_D$  were measured for the samples in dilute solutions. The results are showing that the Benzazole dyes incorporation in PMMA does not affect the polymer dynamics in the dilute regime.

## Introduction

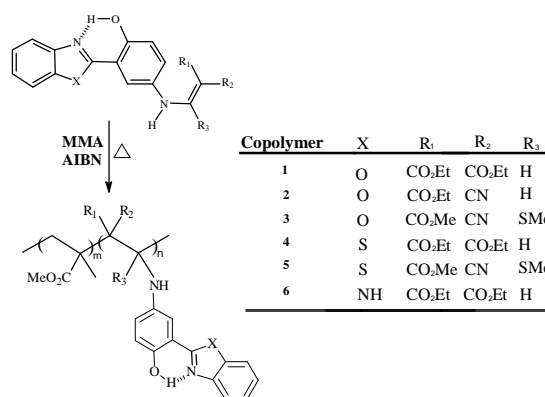
The excited-state intramolecular proton-transfer (ESIPT) phenomena have been widely studied in chemistry, biochemistry and physics in recent years [1-4]. Molecules emitting ESIPT fluorescence, as 2- (2'-hydroxyphenyl)benzazoles, have many uses as polymer ultraviolet stabilizers [5], laser dyes [6] and fluorescent probes [7]. According to, recently we described the synthesis of new fluorescent monomers and its copolymerization with methylmethacrylate [8] that yield new fluorescent polymers with good thermal and optical properties. In the present work we report dynamic light scattering data obtained from PMMA-Benzazole dyes copolymers dynamics in solution by Photon Correlation Spectroscopy (PCS). Six copolymers with different Benzazole dye structure and dye incorporations as well as PMMA were studied in dilute regime. The dynamics properties obtained in a wide range of scattering angles and concentrations are showing that the dye incorporation does not affect the copolymer dynamics behavior if compared to the PMMA in this dilution regime.

## Experimental

### Copolymer synthesis

The copolymer synthesis was made by heating a solution of Benzazole-dyes in MMA using AIBN as initiator. The initial temperature was 40° C and then increased up to 60° C during 6 days. The samples were

than heated for 2 hours at 70° C and for 8 hours at 80° C [8]. For the SLS measurement the copolymers were purified by solubilization-precipitation (1:20 mL solvent/non-solvent). The structure is depicted in Figure 1.



**Figure 1:** Chemical structure of the PMMA-Benzazole dyes copolymers.

The polymer and copolymers were characterized by Static Light Scattering (SLS) [9] were the weight average molar weight ( $\overline{M}_w$ ) and the radius of gyration ( $R_g$ ) were determined. The values are given in Table 1. The polydispersity ( $\overline{M}_w/\overline{M}_n$ ) obtained by Size Exclusion Chromatography (SEC) is also given in Table 1. In this work the overlap concentration has

been defined as  $c^* = A_2 \bar{M}_w c$  and was found to be around  $3 \text{ g}\cdot\text{L}^{-1}$  and  $2 \text{ g}\cdot\text{L}^{-1}$  for the system using THF and chloroform as solvent, respectively. The Benzazoles dyes incorporation showed in Table 2 was calculated using *UV-vis* data. It is assumed that the coefficients do not change by Benzazoles incorporation to the PMMA.

**Table 1:** Weight average molar weight,  $\bar{M}_w \times 10^3$  ( $\text{g}\cdot\text{mol}^{-1}$ ) and radius of gyration,  $R_g$  (nm), obtained by Static Light Scattering (SLS). Polydispersity  $\bar{M}_w/\bar{M}_n$ , obtained by Size Exclusion Chromatography (SEC).

	$\bar{M}_w/\bar{M}_n$ <sup>a)</sup>	THF		CHCl <sub>3</sub>	
		$\bar{M}_w$	$R_g$	$\bar{M}_w$	$R_g$
PMMA	1.37	166	62.3	171	69.8
Cop.1	1.39	171	66.1	173	67.0
Cop.2	1.32	164	63.3	175	66.9
Cop.3	1.33	166	66.2	177	67.2
Cop.4	1.45	169	67.4	178	73.2
Cop.5	1.28	163	65.4	178	65.5
Cop.6	1.39	179	66.7	175	67.5

<sup>a)</sup> Using polystyrene as reference.

**Table 2:** Benzazoles dyes incorporation,  $I$  (%).

	Cop.1	Cop.2	Cop.3	Cop.4	Cop.5	Cop.6
$I$ <sup>a)</sup>	36.0	29.5	24.3	49.7	26.3	61.7

<sup>a)</sup> Benzazole-dye incorporation taking in account the initial mass of the Benzazole-dyes used in the copolymerization. Data obtained by *UV-vis* as previous described.

### PCS Experiments

Solutions of PMMA and copolymers were prepared in THF and chloroform, with concentrations ranging between  $0.10$  and  $3 \text{ g}\cdot\text{L}^{-1}$  (dilute regime). They were filtered using a  $0.22 \mu\text{m}$  ( $13 \text{ mm}$  diameter) Durapore<sup>®</sup> membrane directly into the dust-free scattering cells. Measurements were made at room temperature ( $20 \text{ }^\circ\text{C}$ ) using a Brookhaven Instruments Goniometer BI200M/version 2.0 ( $200 \text{ mm}$ ) coupled to a BI9863 detection system. The intensity autocorrelation functions,  $g_{(2)}(t)$ , were obtained using a BI9000AT correlator. As light source a  $35 \text{ mW}$  Spectra Physics He-Ne Laser (model 127,  $I_0 = 632.8 \text{ nm}$ ) was applied. The scattered light was analyzed in the angular range between  $25^\circ$  and  $145^\circ$ , in steps of  $15^\circ$ .

### Results and Discussion

Typical normalized intensity autocorrelation functions  $g_{(2)}(t)$  are depicted in Figure 2 in dependence on the scattering angle. They were obtained with a dilute solution of the Copolymer 6 in THF as a function of the scattering angle  $q$ . The inset represents the functions for a dilute solution of PMMA. The  $g_{(2)}(t)$

were analyzed by inverse Laplace transformation using the Provencher's CONTIN software [10].

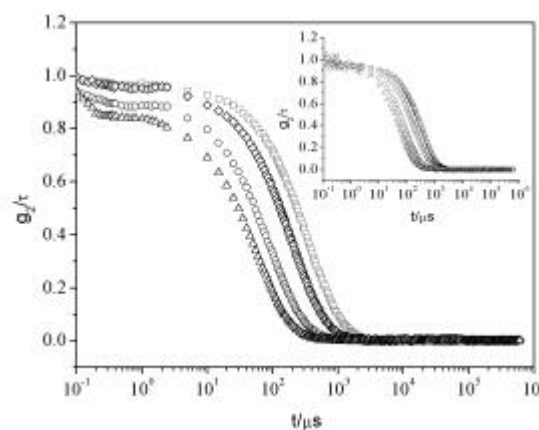
Since the molar weight distribution (see Table 1) of the samples was determined to be relatively small and the samples have been previously purified, the values of  $G$  should not be affected by the sample polydispersity.

The amplitude of the relaxation rates,  $G$  ( $\text{s}^{-1}$ ) can be calculated, being related to the translational diffusion coefficient  $D_c$ , through the relation [11]:

$$D_c = \frac{G}{q^2} \quad (1)$$

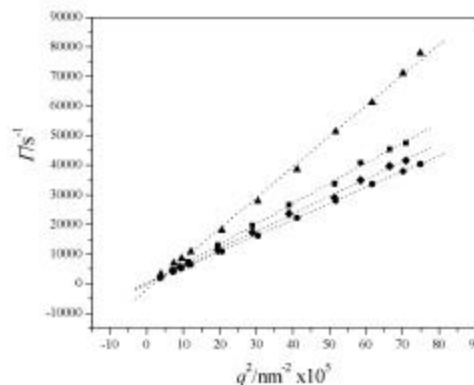
In equation (1)  $q$  is the scattering wave vector [12]:

$$q = \frac{4\pi n_o}{\lambda_o} \sin \frac{q}{2} \quad (2)$$



**Figure 2:** Normalized intensity autocorrelation functions of the Copolymer 6.  $\square$ :  $45^\circ$ ,  $\diamond$ :  $60^\circ$ ,  $\circ$ :  $90^\circ$  and  $\Delta$ :  $120^\circ$ . The inset shows the PMMA normalized intensity autocorrelation functions in THF ( $2.0 \text{ g}\cdot\text{L}^{-1}$ ).

A single exponential decay related to the polymer chains translational dynamics, can be observed for the copolymers as well as for the PMMA. The same behavior was detected for the solutions in chloroform. The amplitude of the relaxation rates  $G$  ( $\text{s}^{-1}$ ) depicted in Figure 3 are showing a linear dependence on  $q^2$ , with zero intercept, as expected for a diffusive dynamics.



**Figure 3:** Relaxation rate  $G$  as a function of  $q^2$  in the dilute regime.  $\blacksquare$ : PMMA/THF ( $2.0 \text{ g}\cdot\text{L}^{-1}$ ),  $\blacklozenge$ : Copolymer 6/THF ( $2.0 \text{ g}\cdot\text{L}^{-1}$ ),  $\circ$ : PMMA/CHCl<sub>3</sub> ( $1.5 \text{ g}\cdot\text{L}^{-1}$ ) and  $\bullet$ : Copolymer 6/CHCl<sub>3</sub> ( $1.5 \text{ g}\cdot\text{L}^{-1}$ ).

Since  $D_c$  depends on concentration, the diffusion coefficient at infinite dilution,  $D_o$  was calculated for each sample extrapolating  $D_c$  to zero concentration [13]:

$$D_c = D_o(1 + k_D c), \quad (3)$$

where  $k_D$  is the dynamic interaction parameter that describes the dependence of the translational diffusion coefficient on the concentration. The hydrodynamic radius  $R_h$  of the polymers in solution have been calculated applying the well-known Stokes-Einstein relationship [11]:

$$D_o = \frac{k_B T}{6\pi\eta_o R_h}, \quad (4)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature and the  $\eta_o$  is the solvent viscosity. The results are listed in Table 2.

**Table 2:** Diffusion coefficient at infinite dilution,  $D_o \times 10^8$  ( $\text{cm}^2 \cdot \text{s}^{-1}$ ), hydrodynamic radius  $R_h$  (nm) and dynamic interaction parameter  $k_D$  ( $\text{cm}^3 \cdot \text{g}^{-1}$ ), obtained by Photon Correlation Spectroscopy in the dilute regime for the PMMA and copolymers.

System	THF			CHCl <sub>3</sub>		
	$D_o$	$R_h$	$k_D$	$D_o$	$R_h$	$k_D$
PMMA	6.04	64.6	397.4	4.15	89.1	875.9
Cop.1	5.78	67.5	354.7	3.73	99.2	874.0
Cop.2	5.83	66.9	418.5	4.22	87.6	824.6
Cop.3	5.79	67.4	394.6	4.10	90.2	814.0
Cop.4	5.67	68.8	370.4	3.87	95.6	878.6
Cop.5	5.53	70.5	409.1	3.50	105.7	828.6
Cop.6	6.04	64.6	372.5	4.13	89.5	836.4

Positive  $k_D$  values means that THF and CHCl<sub>3</sub> are good solvents [14] for the PMMA and the copolymers studied. Another way, higher values of  $k_D$  indicate that CHCl<sub>3</sub> is a better solvent than THF.

## Conclusions

The PMMA and Copolymers normalized autocorrelation functions obtained by PCS in dilute regime show a single exponential decay. The dynamics is related to the polymer chain translational diffusion. In this dilution regime, the Benzazole dye does not affect the polymer dynamics.

The interaction parameter values obtained in dilute regime indicate that THF and CHCl<sub>3</sub> are good solvents for PMMA and copolymers, with CHCl<sub>3</sub> being the better one.

## Acknowledgements

Financial support and Scholarships from the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), the Conselho Nacional de Pesquisa (CNPq) and the Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS) in Brazil is gratefully acknowledged.

## References

1. N.S. Domingues Jr.; C. Krug; P.R. Livotto; V. Stefani *J. Chem. Soc. Perkin Trans.2* 1997, 9, 1861.
2. R.S. Iglesias; P.F.B. Gonçalves; P.R. Livotto *Chem. Phys. Lett.* 2000, 23, 327.
3. V.I. Minkin; A.D. Garnovskii; J. Elguero; A.R. Katritzky; O.V. Denisko *Adv. Heterocycl. Chem.* 2000, 76, 157.
4. M. Segala; N.S. Domingues Jr.; P.R. Livotto; V. Stefani *J. Chem. Soc. Perkin Trans.2* 1999, 6, 1123.
5. D. Kuila; G. Kvakovszky; M.A. Murphy; R. Vicari; M.H. Rood; K.A. Fritch; J.R. Fritch *Chem. Mater.* 1999, 11, 109.
6. A. Douhal; F. Amat-Guerri; A.U. Acuña; K. Yoshihara *Chem. Phys. Lett.* 1994, 217, 619.
7. G.M. Holler, M.Sc. Dissertation, UFRGS, 1998.
8. L.F. Campo; D.S. Corrêa; M.A. Araújo; V. Stefani *Macromol. Rapid Commun.* 2000, 21, 832.
9. F.S. Rodembusch, M.Sc. Dissertation, UFRGS, 2001.
10. S.W. Provencher *Computer Phys. Commun.* 1982, 27, 213.
11. R. Pecora, *Dynamic Light Scattering*, Plenum Press, New York, 1985.
12. W. Brown, *Light Scattering. Principles and Developments*, Clarendon Press, Oxford, 1996, 1<sup>st</sup> edition.
13. W. Brown, *Dynamic Light Scattering. The method and some applications*, Clarendon Press, Oxford, 1993, 1<sup>st</sup> edition.
14. Y. Tomai; T. Konishi; Y. Einaga; M. Fujii; H. Yamakawa *Macromolecules* 1990, 23, 4067.