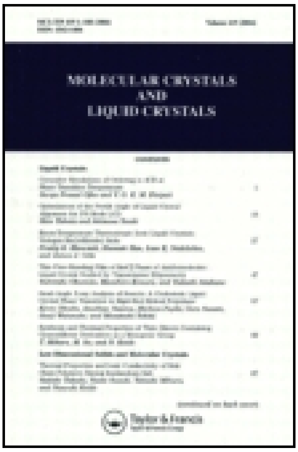

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Static Light Scattering from ESIPT Copolymers of Poly(methyl methacrylate) - Benzazole Dyes

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Static Light Scattering from ESIPT Copolymers of Poly(methyl methacrylate) – Benzazole Dyes

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Static Light Scattering (SLS) was used for characterization of the fluorescent ESIPT copolymers of PMMA - Benzazole dyes in solution with chloroform ($CHCl_3$) and tetrahydrofuran (THF) were studied. The results show that macromolecular parameters and copolymers architectures in solution are not changing in relation to those of PMMA. In this way, the incorporation of Benzazole dyes in PMMA does not affect the final polymer properties and conformations in the investigated dilution regime.

Keywords Static Light Scattering; ESIPT; PMMA; fluorescence.

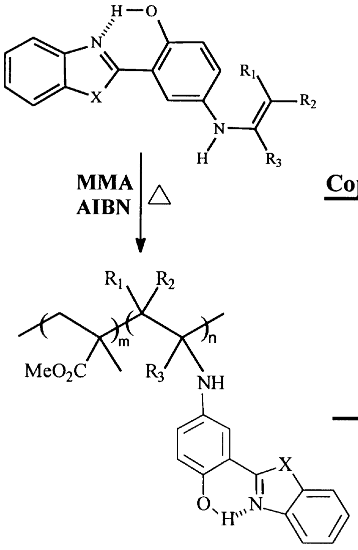
INTRODUCTION

The excited-state intramolecular proton-transfer (ESIPT) phenomena has been widely studied in recent years because of it widespread in chemistry, biochemistry and physics [1-4]. Molecules emitinhg ESIPT fluorescence, as 2-(2'-hydroxyphenyl)benzazoles, have many uses as polymer ultraviolet stabilizers [5], laser dyes [6] and fluorescent probes [7]. 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.

SLS is usually applied in polymer dilute solutions in order to obtain parameters such as the macromolecular weight average molar weight ($\overline{M}_w$) and the radius of gyration (R_g) as well as the second virial coefficient (A_2), which is characteristic of the polymer-solvent interaction. In addition, SLS allows the determination of macromolecular structural parameters in solution.

EXPERIMENTAL

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 (1:20mL solvent/non-solvent). Their structure is depicted in Figure 1.



Copolymer	X	R_1	R_2	R_3
1	O	CO_2Et	CO_2Et	H
2	O	CO_2Et	CN	H
3	O	CO_2Me	CN	SMe
4	S	CO_2Et	CO_2Et	H
5	S	CO_2Me	CN	SMe
6	NH	CO_2Et	CO_2Et	H

FIGURE 1 Chemical structure of the copolymers MMA-Benzazole dyes.

For the SLS experiments solutions of PMMA and copolymers in THF and $CHCl_3$, with concentrations ranging between 0.1 and 30 g·L^{-1}, were prepared. They were filtered using a 0.22 μm Durapore® membrane into dust-free scattering cells. Measurements were made at 20 °C using a Brookhaven Instruments Goniometer BI200M/v2.0 coupled to a 35 mW Spectra Physics He-Ne Laser and a BI9863 detection system. The scattered light was analyzed between $\theta=25°$ and $\theta=145°$.

RESULTS AND DISCUSSION

The Benzazoles dyes incorporation was calculated using *UV-vis* data and is given in Table 1. It is assumed that the coefficients do not change by Benzazoles incorporation to the PMMA.

TABLE 1 Benzazoles dyes incorporation percentage in the PMMA *I*(%).

Sample	Cop.1	Cop.2	Cop.3	Cop.4	Cop.5	Cop.6
$I^{a)}$ (%)	36.0	29.5	24.3	49.7	26.3	61.7

a) Taking the initial mass of the Benzazole dyes into account.

TABLE 2 Weight average molecular weight $\overline{M}_w$ (g·mol^{-1}), second virial coefficient A_2 (cm^3·mol·g^{-2}) and radius of gyration R_g (nm) for PMMA and copolymers.

	THF			CHCl$_3$		
Sample	$\overline{M}_w$ $x10^3$	$A_2\,x10^{-4}$	R_g	$\overline{M}_w$ $x10^3$	$A_2\,x10^{-4}$	R_g
PMMA	166	1.79	62.3	171	2.49	69.8
Cop. 1	171	1.70	66.1	173	2.54	67.0
Cop. 2	164	1.91	63.3	175	2.52	66.9
Cop. 3	166	1.79	66.2	177	2.48	67.2
Cop. 4	169	1.77	67.4	178	2.40	73.2
Cop. 5	163	1.79	65.4	178	2.67	65.5
Cop. 6	179	1.78	66.7	175	2.69	67.5

The scattered light intensities I_s are measured at several angles (θ) for each solution concentration (c) and extrapolated to $\theta=0$ and $c=0$. Subtraction of the solvent scattering from the solution scattering yield the excess polymer scattering I_s^P and according to the Berry equation [9,10]:

$$\left[\frac{Kc}{R_\theta}\right]^{0,5} = \left[\frac{1}{\overline{M}_w}\right]^{0,5}\left[1+\frac{16\pi^2 n_o^2}{6\lambda_o^2}\left\langle R_g^2\right\rangle \operatorname{sen}^2\left(\frac{\theta}{2}\right)\right]\left[1+A_2\overline{M}_w c\right] \quad . \quad (1)$$

where R_θ is the Rayleigh ratio at scattering angle θ, related to I_s^P, and K the solution optical contrast. The parameters obtained are shown in Table 2.

The second virial coefficient is found to be positive in both solvents indicating a good polymer-solvent interaction. Since the values in $CHCl_3$ are higher than those in THF, chloroform is taken as a better solvent for the copolymers studied.

Information related to the polymer architecture (*g*-parameter) can be extracted from SLS measurements in the forward scattering ($R_{\theta=0}$) as shown in equation (2). The parameter *X*, given as $A_2\overline{M}_w c \sim c/c^*$, is a scaling one, dependent on the overlap concentration c*:

$$\frac{A_2 R_{\theta=0}}{K} = \left(\frac{X}{1+2X+3gX^2}\right). \quad \textbf{(2)}$$

A plot of $A_2R_{\theta=0}/K$ *as a function of* X *for the samples in this work is given in Figure 2. The curve-maximum is related to the* g-*parameter by [12]:*

$$g=\frac{1}{3}\left[\frac{(1-2y_{\max})}{(2y_{\max})}\right]^2 . \quad \textbf{(3)}$$

The shape of the experimental curves are similar to that expected for flexible linear chains. The obtained *g*-values for the polymer and copolymer using THF as solvent were 0.34 and 0.30 respectively and are close to the theoretical values for flexible linear chains (0.29) [11]. The higher values of *g*-parameter obtained for PMMA and Cop.6 using chloroform as being 1.53 and 1.45 respectively, are due to the strong solvent scattering.

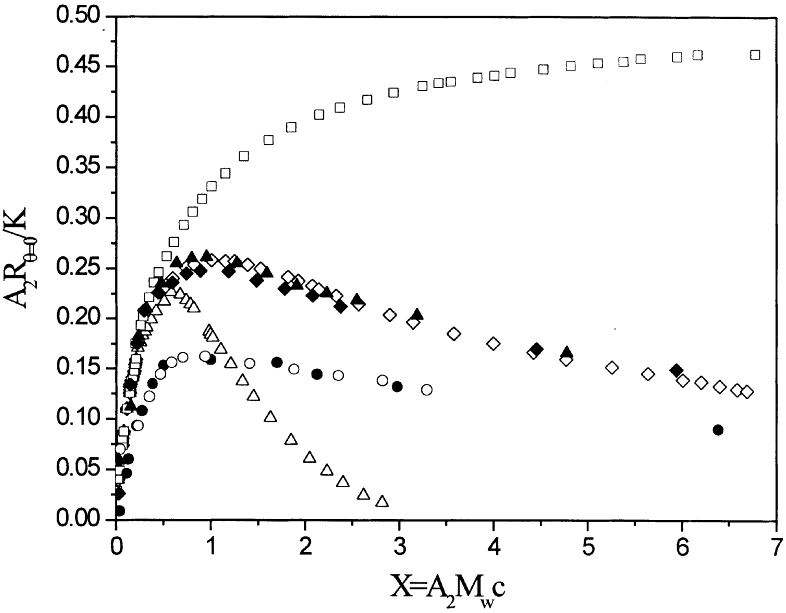


FIGURE 2 $A_2R_{\theta=0}$ / K versus $X = A_2M_wc$ for (◆) PMMA/THF, (▲) Copolymer 6/THF, (●) PMMA/CHCl3 and (O) Copolymer 6/CHCl3. Theoretical curves for (Δ) spheres, (◊) flexible chains and ( ) stiff chains.

CONCLUSIONS

The SLS technique can be taken as a suitable method in order to determine the polymer average molar weight of the copolymers. Chloroform and THF can be taken as good solvents for PMMA and copolymers with chloroform being the better one for all studied samples. The obtained *g*-parameter is showing that the macromolecular parameters and architectures for the copolymers in solution are not changing in relation to those of PMMA. It can be concluded that Benzazole dyes incorporation in PMMA does not affect the final polymer properties and conformations.

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