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Dynamics of ESIPT fluorescent methylmethacrylate–benzazole dye copolymers

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Abstract

The dynamics of fluorescent methylmethacrylate–benzazole dye copolymers were investigated in different concentration regimes by dynamic light scattering. In the dilute regime the polymer behaves as typical polydisperse linear chains in good solvent with a dynamics dominated by a single fast mode. In the semidilute regime, the cooperative diffusion coefficient, D_{coop} and the correlation length, ξ could be obtained. Above the semidilute regime the intensity autocorrelation functions show two-step decays, indicating the existence of low range correlations. The dye incorporation, even though small, affects the copolymer dynamics behavior in concentrated solutions if compared to PMMA, which is probably ascribed to a polymer–solvent interaction.

Keywords: Fluorescent polymers; Dynamic light scattering; Concentrated regime

1. Introduction

The synthesis and characterization of polymers containing active structures in its chain has increased significantly only during the last years, since in these materials the macromolecular characteristics and the dye moiety properties can be combined [1]. Applications in nonlinear optical materials [2,3], solid-state laser dyes [4] and fluorescent polymers [5,6] have been reported. Accordingly, molecules as 2-(2′-hydroxyphenyl)benzazoles present an efficient fluorescence emission through an ESIPT mechanism (Fig. 1) with large Stokes shift [7–9].

In the ESIPT mechanism, the UV light absorption through the enol-*cis* (E) produce the excited enol-*cis* (E^*) which is quickly converted to an excited keto tautomer (K^*) by an intramolecular proton transfer [10]. The K^* decays emitting fluorescence to a keto tautomer (K) and the initial enol-*cis* form is regenerated without any photochemical change [11,12].

Since the ESIPT mechanism is quite dependent on the solvent polarity, the incorporation of these dyes in polymeric chains are particularly interesting to discuss hydrophobic/hydrophilic environments, for instance, in systems which use polymers as drug delivery system [13]. In this way, a detailed study about the dynamic of doped polymers is useful, since the dye moiety can affect the polymer behaviour in solution. The information of individual chain characteristics and solvent quality obtained in the dilute regime, as well as, the solution properties in the semidilute regime and higher polymer concentrations are also of interest. The concentrated regime is characterized by a highly entangled network and a screening length comparable to the monomer dimension. Structural or chemical modification at the monomer level could produce some effect in the slow dynamics of concentrated solutions.

The aim of this work is therefore to study the solution properties of methylmethacrylate–benzazole dye

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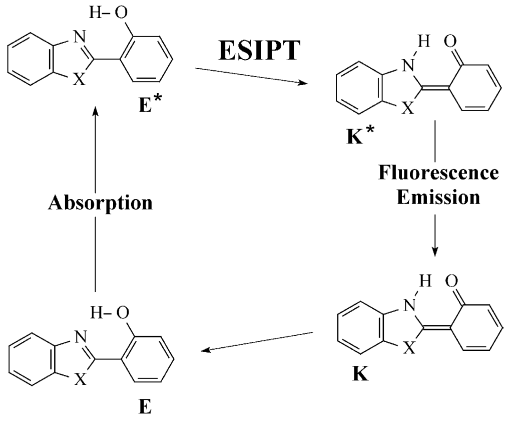


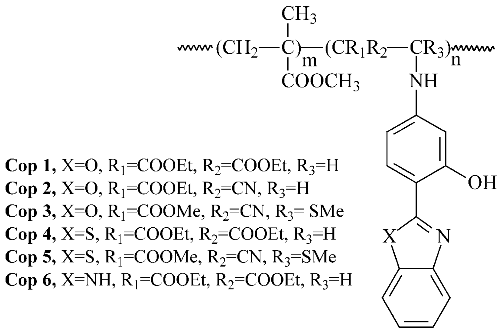
Fig. 1. ESIPT mechanism.

copolymers in THF and chloroform by means of dynamic light scattering. The poly(methylmethacrylate) was used as reference and the dilute, semidilute and concentrated regimes were covered.

2. Experimental part

The synthesis of the investigated copolymers was performed as already described [5,6] and its structures are depicted in Fig. 2. The PMMA and copolymers characterization was already presented [6], where a polidispersity around 1.3 could be obtained for all samples. Values of 170×10^4 g mol^{-1} for the weight average molar mass with a radius of gyration of 65 nm were found to the PMMA and copolymers by means of static light scattering using the same solvents presented in this work. These results allowed to determine the overlap concentration, c^*, which describes the transition among dilute and semi-dilute regime [14]. It was defined in this work as $c^* = 1/A_2\bar{M}_\mathrm{w}$ [15], a good thermodynamic definition of the coil overlap concentration. It was found to be around 3.0 and 2.0 g l^{-1} using THF and chloroform, respectively.

The benzazole dye incorporation ($w_\mathrm{dye}/w_\mathrm{MMA}$) was calculated using UV–vis data. Values of 0.051–0.146 were obtained for the copolymers with the copolymer 6 presenting the higher one 0.26. The copolymers presents absorption maximum in the UV region (317–367 nm) with the molar extinction coefficient value on the order of 10^4 l mol^{-1} cm^{-1}, as expected to π–π^* transitions. The fluorescence lies in the violet-blue-green region (412–544 nm) with a Stokes shift of 89–199 nm [6].



Cop 1, X=O, R_1=COOEt, R_2=COOEt, R_3=H
Cop 2, X=O, R_1=COOEt, R_2=CN, R_3=H
Cop 3, X=O, R_1=COOMe, R_2=CN, R_3= SMe
Cop 4, X=S, R_1=COOEt, R_2=COOEt, R_3=H
Cop 5, X=S, R_1=COOMe, R_2=CN, R_3=SMe
Cop 6, X=NH, R_1=COOEt, R_2=COOEt, R_3=H

Fig. 2. Chemical structure of the fluorescent copolymers.

The solutions in THF and chloroform, with concentrations between 0.1 and 30 g l^{-1} were filtered through 0.22 μm pore diameter Durapore® membranes into dust-free cells. The higher concentration (60 g l^{-1}) was obtained by evaporation of a previously filtered diluted solution, inside a laminar flow box. The sample concentration was determined from the weight difference. The measurements were performed at room temperature (20 °C) using a Brookhaven Instruments standard setup (BI200M goniometer, BI9000AT digital correlator) with a He–Ne Laser ($\lambda_0 = 632.8$ nm) as light source. The scattering volume was minimized using a 0.4 mm aperture and an interference filter before detecting the signal on the photomultiplier. The measured homodyne intensity autocorrelation functions, $g_{(2)}(\tau)$, were obtained using an in multi-τ mode with 224 channels. The sample cell was placed in the index-matching liquid decahydronaphthalene (Aldrich) and the scattered light was analyzed in the angular range of 25–145° in steps of 15°. Since the PMMA is a weaker scatter polymer and the light source presented an output power of 25 mW, the run time used for all the DLS experiments were 240 s.

3. Results and discussion

3.1. Dilute regime

Typical normalized intensity autocorrelation functions $g_{(2)}(\tau)$ in the dilute regime (2.0 g l^{-1}) are depicted in Fig. 3 for PMMA and copolymer 6 in dependence of the scattering angle. The inset represents the amplitudes of the relaxation rates Γ (s^{-1}) vs. q^2. The same behaviour could be observed using $\mathrm{CHCl_3}$ as the solvent.

A single exponential decay related to the polymer chain translational dynamics can be observed for the copolymers and PMMA. The same behavior was detected using chloroform as the solvent. The depicted in Fig. 3 are showing a linear dependence on q^2, with zero intercept, as expected for a diffusive dynamics [16].

Since the molecular weight distribution of the samples was determined to be relatively small and the samples have been previously purified, the values of Γ should not be affected by the sample polidispersity. The translational diffusion coefficient D_c is related to Γ through [17]:

$$D_\mathrm{c} = \frac{\Gamma}{q^2} \qquad (1)$$

and the diffusion coefficient at infinite dilution, D_o, was calculated extrapolating D_c to zero concentration according

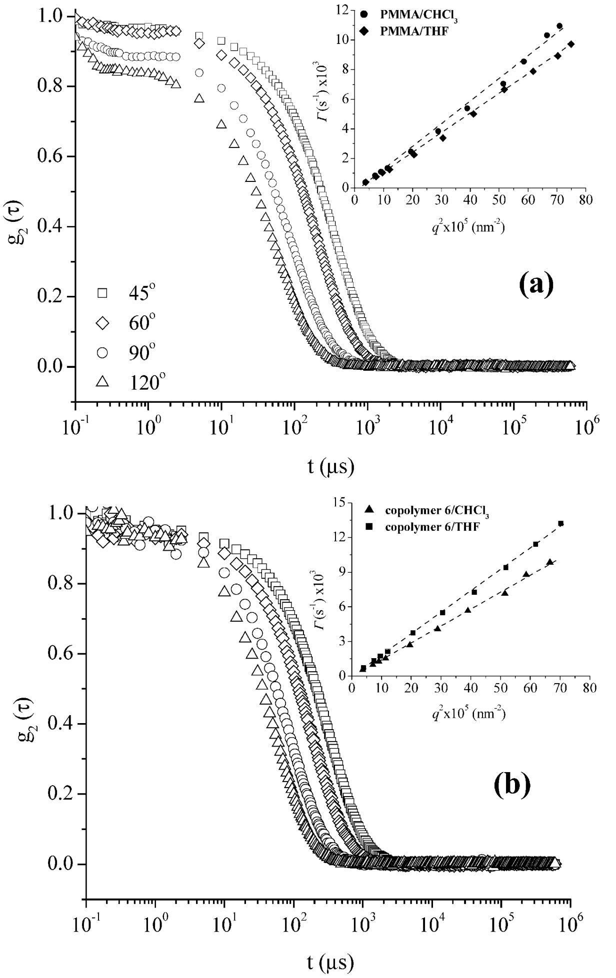


Fig. 3. Normalized intensity autocorrelation functions in dilute regime for the (a) PMMA and (b) copolymer 6 in THF. The inset represents the amplitudes of the relaxation rates Γ (s^{-1}) vs. q^2 in both solvents.

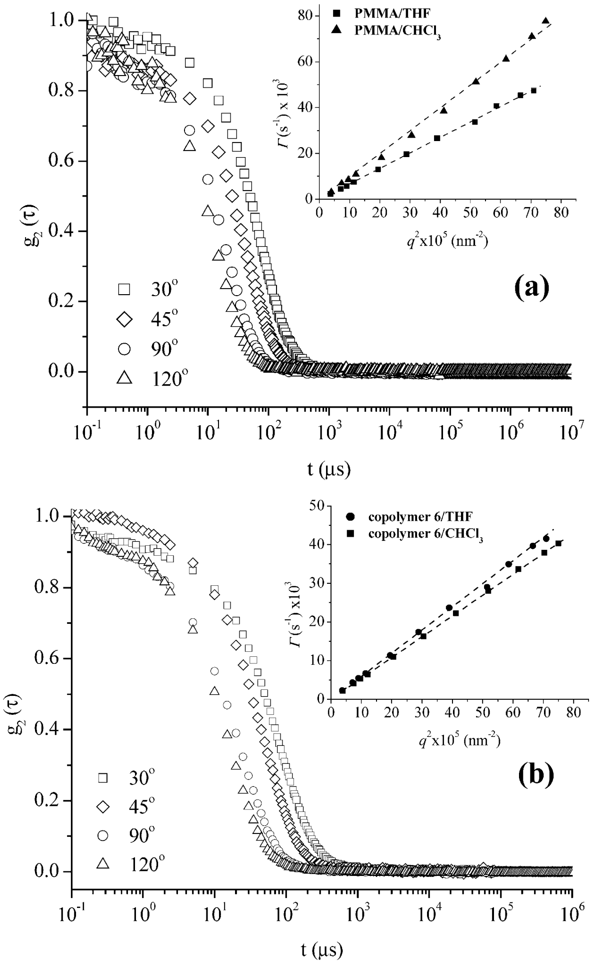


Fig. 4. Normalized intensity autocorrelation functions in semidilute regime for the (a) PMMA and (b) copolymer 6 in THF. The inset represents the amplitudes of the relaxation rates Γ (s^{-1}) vs. q^2 in both solvents.

to [16]:

$$D_c = D_o(1 + k_D c) \tag{2}$$

The concentration coefficient, k_D, gives information about the interaction character and describes the dependence of the translational diffusion coefficient on the concentration. The hydrodynamic radius, R_h, were calculated applying the well-known Stokes–Einstein relationship [17]:

$$D_o = \frac{k_B T}{6\pi\eta_o R_h} \tag{3}$$

with k_B the Boltzmann constant, T the absolute temperature and η_o the solvent viscosity. The results obtained for these parameters are summarized in Table 1.

3.2. Semidilute regime

The PMMA and copolymer 6 were also analyzed in the semidilute regime (from 5 up to 30 g l^{-1}) ($c > c^*$). A single exponential decay characterizes the $g_{(2)}(\tau)$ obtained in solution with THF as depicted in Fig. 4 for PMMA and copolymer 6 in THF to 30 g l^{-1}. The inset represents a linear dependence on q^2, with zero intercept.

It is known that in the semi-dilute regime the weak hydrodynamic interactions are exceeded by the strong cooperative interaction due to a more effective overlap between the polymer chains [16]. The length between two points of entanglement, so-called correlation length ξ, is dependent on the polymer concentration and is associated to the cooperative diffusion coefficient, D_{coop}, by the relation [16]:

$$D_{coop} = \frac{k_B T}{6\pi\eta\xi} \tag{4}$$

Since the characteristic decay time ($1/e$) is lower than the observed in the dilute regime, the dynamics may be now related to the cooperative diffusion due to the entanglements in the network. Analysis of the $CHCl_3$ solutions shows the same behavior. The values of ξ as a function of the polymer concentration in the limit of $q \rightarrow 0$ are depicted in Fig. 5, as well as the linear fit ($R^2 > 0.998$) for concentrations of 5, 6, 7, 8, 15, 20 and 30 g l^{-1}.

Table 1
Diffusion coefficient at infinite dilution D_o, hydrodynamic radius R_h, and dynamic interaction parameter k_D, in the dilute regime

	THF			$CHCl_3$		
	$D_o \times 10^8$ (cm^2 s^{-1})	R_h (nm)	k_D (cm^3 g^{-1})	$D_o \times 10^8$ (cm^2 s^{-1})	R_h (nm)	k_D (cm^3 g^{-1})
PMMA	6.04	64.6	397.4	4.15	89.1	875.9
Copolymer 1	5.78	67.5	354.7	3.73	99.2	874.0
Copolymer 2	5.83	66.9	418.5	4.22	87.6	824.6
Copolymer 3	5.79	67.4	394.6	4.10	90.2	814.0
Copolymer 4	5.67	68.8	370.4	3.87	95.6	878.6
Copolymer 5	5.53	70.5	409.1	3.50	105.7	828.6
Copolymer 6	6.04	64.6	372.5	4.13	89.5	836.4

Positive k_D values mean that THF and chloroform are good solvents for the PMMA and copolymers [18]. The increase in k_D for the copolymers in chloroform if compared to THF, indicates the chloroform as a better solvent for the polymer chains.

In both solvents the correlation length decreases by the increase in the polymer concentration. However, it is worth to mention, that the correlation length becomes shorter for copolymer 6 in $CHCl_3$ if compared to the values obtained for PMMA in the same solvent. According to the literature [19], in entangled polymeric solutions, where only one dynamic should be detected, the relaxation mode is connected to the concentration fluctuations of the polymer subsystem. Therefore, the benzazole dye bounded to the PMMA in the copolymer structure affects the entanglements in the semidilute regime. The same behaviour is not observed when THF is used as the solvent, probably because of $CHCl_3$ is a better solvent for the studied samples than THF [6].

3.3. Concentrated regime

In this concentration regime, solutions of 60 g l^{-1} were studied. The normalized intensity autocorrelation functions for PMMA and copolymer 6 in THF are depicted in Fig. 6, respectively, where two exponential decays can be seen. The same behaviour could be observed in similar systems [19,20]. The slow mode is pronounced q-dependent in both systems. At low angle, the dynamic of the slow mode overcome the system dynamics, and is associated to a self-diffusion of the polymer network. Even at higher scattering angles (60 and 90°) the slow mode can be detected. Increasing the scattering angle, the fast mode overcomes the system dynamics, as expected. This mode is related to the swelling-deswelling of the network [20] described through a gel diffusion coefficient (D_{gel}) [20].

To evaluate the dynamics processes observed in the Fig. 6, the fast and slow mode relaxation rate were analyzed as function of q^2, as depicted in Fig. 8.

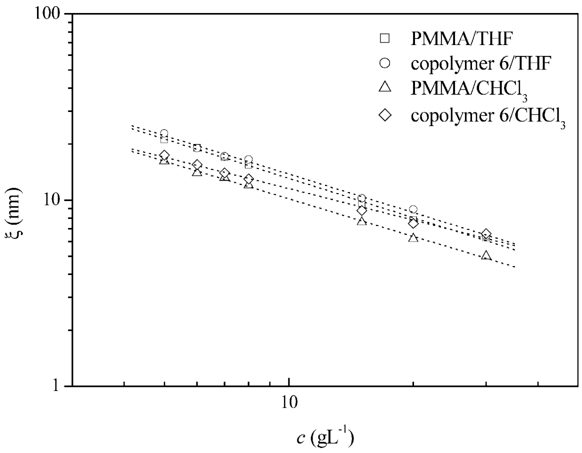


Fig. 5. Double logarithmic plot relating ξ vs. solution concentration in the semidilute regime.

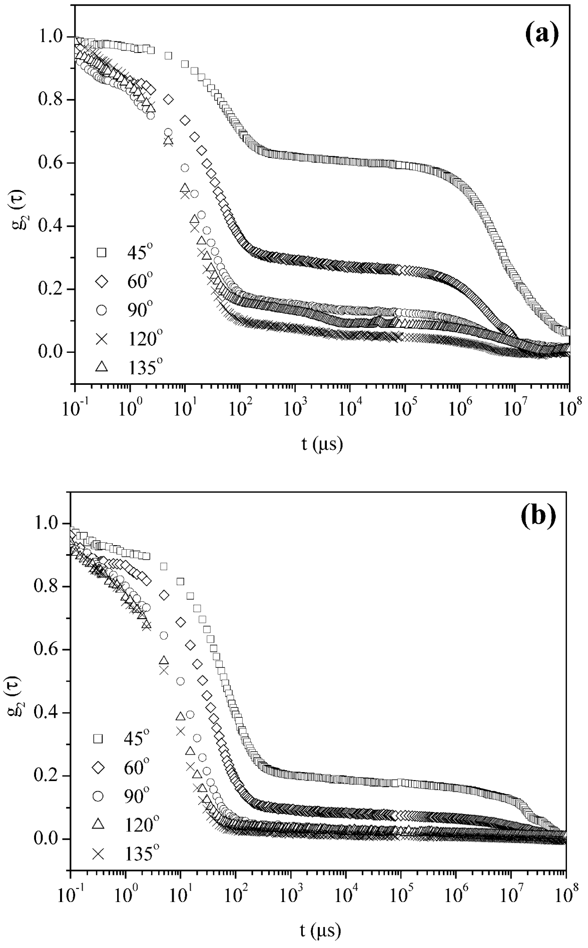


Fig. 6. Normalized intensity autocorrelation functions for (a) PMMA/THF and (b) copolymer 6/THF.

The fast dynamics in Fig. 7 shows a linear dependence on q^2, with zero intercept, as expected for a diffusive process [16]. The slow dynamics shows a linearity deviation as a function of q^2, typical from nondiffusive dynamical processes, associated to the dimensions of the network formed by the entanglements of the polymer chains in solution. The slow mode observed in the PMMA and copolymer 6 in THF at 60 g l^{-1} allowed to analyze the sample fraction $a_2(q)$ contributing to the network formation in each system through the slow mode plateau in the autocorrelation functions, as can be seem in Fig. 8.

In both systems PMMA/THF and copolymer 6/THF, an increasing of $a_2(q)$ with a decrease in the scattering angle can be observed, with the slow modes overcoming the autocorrelation functions at low angles. A higher contribution of the slow mode was detected to the solutions containing PMMA. The benzazole dye incorporated in the copolymer chain contributes in a decisive way to the difference observed in the $a_2(q)$ values, if compared to the PMMA.

The analysis of the fast and slow modes in the correlation functions gives the gel diffusion coefficient (D_{gel}), the network self-diffusion (D_s) and its correlation length, named the gel (ξ_{gel}) and network correlation length (ξ_s), respectively (Table 2).

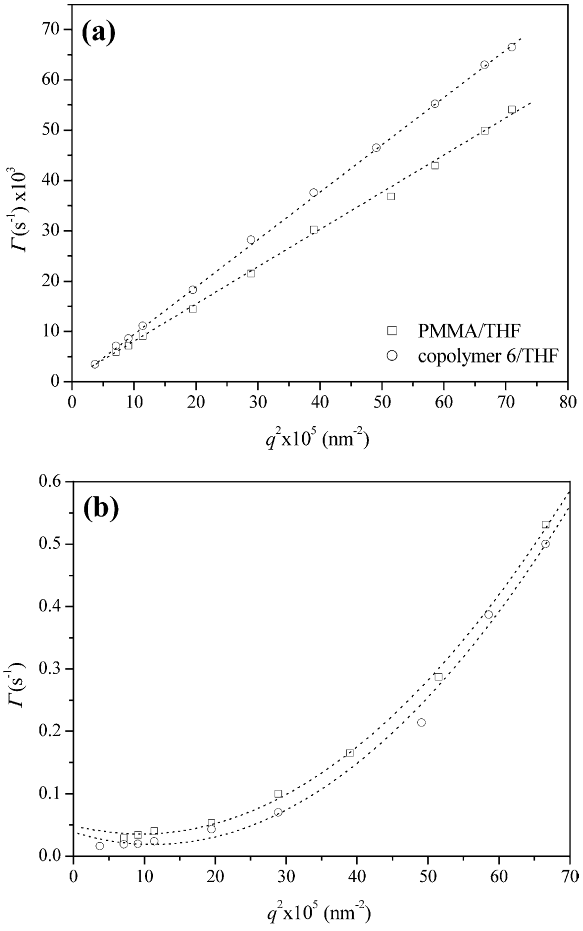


Fig. 7. (a) Fast mode and (b) slow mode relaxation rate (Γ) vs. q^2.

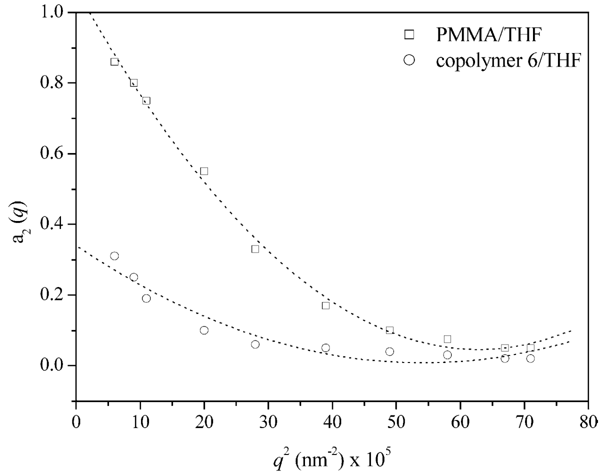


Fig. 8. $a_2(q)$ vs. q^2.

The network self-diffusion and its correlation length show that PMMA/THF and copolymer 6/THF behave as a continuous network in solution. Otherwise, the values of the gel diffusion coefficient and the gel correlation length are different for the solutions PMMA and copolymer 6 in THF. The benzazole dye incorporation makes easier the swelling-deswelling process in the network formed by the copolymer in relation to the system PMMA/THF.

The same behavior was not observed in the solution with chloroform in the same concentration, which is probably ascribed to a polymer–solvent interaction. Since the $CHCl_3$ showed to be a better solvent than THF, it was expected to observe this behaviour at higher concentrations.

4. Conclusions

The autocorrelation functions from poly(methylmethacrylate) and copolymer 6, obtained by dynamic light scattering in the dilute and semidilute regimes, show a single exponential decay. In the dilute solution the dynamics is related to a translational diffusion of the polymer chains and in the semidilute regime is probably connected to a cooperative diffusion coefficient of the entanglements. The interaction parameter values obtained in dilute regime indicate the tetrahydrofuran and chloroform as good solvents for poly(methylmethacrylate) and copolymers,

Table 2
Gel diffusion coefficient D_{gel}, network self-diffusion D_s, gel correlation length ξ_{gel} and network correlation length ξ_s

	Fast mode		Slow mode	
	$D_{gel}\times10^7$ (cm^2 s^{-1})	ξ_{gel} (nm)	$D_s\times10^{12}$ (cm^2 s^{-1})	$\xi_s\times10^{-6}$ (nm)
PMMA	7.9	4.9	5.5	7.1
Copolymer 6	9.5	4.1	5.4	7.2

with chloroform being the better one. In the semidilute regime, a distinct behavior between poly(methylmethacrylate) and copolymer 6 was observed in chloroform, by increase in the polymer concentration. The entanglements relaxation mode is affected by the benzazole dye incorporation in the polymer chain and the correlation length is higher in the solutions of copolymer if compared to those containing only poly(methylmethacrylate). Therefore, the benzazole dye affects the chains entanglement phenomenon. In concentrated regime, the existence of a long time contribution in the autocorrelation functions together with fast diffusive modes was observed. The network formed with poly(methylmethacrylate) presents a higher contribution to the slow modes than if prepared with the copolymer. The results, obtained in a wide range of scattering angles and different concentration regimes, are showing that dye incorporation, even though small, affects the copolymer dynamics behavior if compared to poly(methylmethacrylate), by means of the copolymer–solvent interaction in concentrated solution.

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