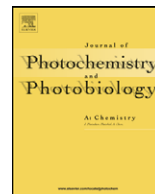




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Fluorescent probes with malononitrile side group in methyl methacrylate copolymers

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ABSTRACT

Fluorescent probes derivated from auramine, 1-aminopyrene, and 9-aminoacridine containing a malononitrile group are copolymerized with methyl methacrylate. These new fluorescent polymeric materials are studied in solution of different solvents by steady-state and time-resolved emission techniques. Their spectroscopic properties and excited state dynamics are driven by charge transfer from the aromatic group to the electron withdrawing CN groups, and this factor is responsible for the non-exponential emission decay behavior.

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1. Introduction

Stationary and time-resolved fluorescence measurements of molecular probes have been used to characterize micelles [1–5], polymers [6–25], and biological systems [26–36]. Several photophysical parameters can be measured for this purpose, like the changes in emission quantum yield [29,32,37], position of the absorption and emission peaks, fluorescence lifetime [6,14], or the formation of probe self-aggregates [29].

When probes are attached to a polymer chain, large changes in their photophysical properties may occur. For instance, when the pseudoisocyanine (PIC⁺) is labeled to poly(methacrylic acid) (PMA), its fluorescence quantum yield increases in a factor 600, and its lifetime changes from a few ps up to 2.7 ns [14]. However, in addition to direct changes in the photophysical properties, the fluorescent polymer can also reveals its segment dynamics in solution when time-resolved fluorescence anisotropy (TRFA) measurements is performed [16–18]. For instance, when dansyl [16], 1-vinylnaphthalene (1-VN) [17], and aminoacridinium derivatives [18] are labeled to PMA, the conformational transition with pH of this polymer can be easier detected with high precision.

On the other hand, there are probes for polymers and biomolecules that do not exhibit intrinsic fluorescence before copolymerization, such as those aromatic probes with maleimide side group [19,30,31]. This class of system, however, turns highly fluorescent when its double bond becomes saturated thought

copolymerization [19], or by reaction with cysteine residues of a given protein [31]. Nevertheless, acrylic polymers marked with fluorescent probes bound to the polymer chain are interesting materials in many applications of optics, colloidal tracers, and photo-electronic devices, because they usually do not undergo probe segregation from the whole material. In a special case, molecules with intramolecular charge transfer (ICT) emission have been suggested as prominent active materials for organic light emitting diodes (OLEDs) [38]. In this work, stationary and time-resolved fluorescence techniques were employed to study the fluorescence kinetics of three different fluorescent probes bound to poly(methyl methacrylate) (PMMA) forming bright copolymer.

2. Experimental

The fluorescent probes auramine, 1-aminopyrene, and 9-aminoacridinium containing malononitrile side group (see structure of compound I, II, and III in Fig. 1) were prepared as described early, and their photophysical and photochemical characterization were reported recently [9,39,40]. The copolymers were synthesized using benzyl peroxide (BP) thermal initiated copolymerization of methyl methacrylate with small amount of the fluorescent probes (0.5% in weight). Reaction was carried out under nitrogen atmosphere at 70 °C in toluene, resulting in the probe labeled copolymers poly(MMA-co-I), poly(MMA-co-II), and poly(MMA-co-III). These materials were purified by multiple precipitations (four to five times) from toluene on addition of methanol and filtration in order to remove unreacted monomers. All samples were dried under vacuum before analysis.

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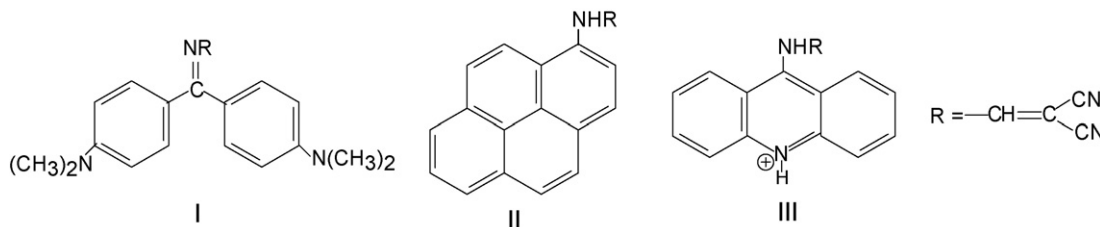


Fig. 1. Molecular structures of the aromatic probes (auramine, 1-aminopyrene, and 9-aminoacridinium) with malononitrile group.

The molecular mass distribution of the copolymers was determined by size exclusion chromatography (SEC) using a Waters equipment with refractive index detector. The samples and the polystyrene molecular weight standard (Shodex Standard) were eluted with tetrahydrofuran as mobile phase with a flow rate of 1 mL min^{-1} at 40°C .

Absorption measurements were performed on a Cary 5G-Varian spectrophotometer, and the corrected steady-state fluorescence spectra were recorded on a CD-900 Edinburgh spectrofluorimeter at 298 K. Fluorescence quantum yields (Φ_{em}) were calculated using quinine sulfate in $1\text{N H}_2\text{SO}_4$ ($\Phi_{\text{em}} = 0.546$) as standard. The samples (2 g/L) for the time-resolved experiments were conditioned in a $1 \text{ cm} \times 1 \text{ cm}$ quartz cuvette, thermostatted by circulating fluid through a jacketed cuvette-holder, and deaerated with dried N_2 . Fluorescence decays in solution were measured by time-correlated single-photon counting technique using a CD-900 Edinburgh spectrometer equipped a cooled PMT Hamamatsu R955 (fwhm = 700 ps) or using home-made ps spectrometer equipped with Glan-Laser polarizers in magic angle, a Peltier cooled PMT-MCP (Hamamatsu R3809U-50) as photon detector, and Tennelec-Oxford counting electronics. The light pulse was provided by frequency doubling the 200 fs laser pulse of Mira 900 Ti-Sapphire laser pumped by Verdi 5W coherent laser, and the pulse frequency was reduced down to 800 kHz by using a Conoptics pulse picker. The system provides an instrument response function (irf) of about 40 ps (fwhm). Decay traces were collected with 15–50 ps/channel over 1 kB data points. The fluorescence decays were analyzed by reconvolution procedure with multiexponential decay models, and the goodness of the fit was evaluated by the statistical parameters χ^2 . Decays were also analyzed by the global analysis method assuming that the fluorescence decay surface could be represented by a sum of the exponential decay components of the excited species present in the system.

$$I(t) = \sum_i b_i \exp\left[-\frac{t}{\tau_i}\right] \quad (1)$$

In Eq. (1), τ_i and b_i are the decay time and its pre-exponential factor of the i th component, respectively. The decay traces at different emission wavelengths were both individually and globally analyzed by using single, double or triple exponentials fitting routines of the Edinburgh Instruments Level 2 software. Decay times were linked along several decay traces but the b_i parameter was allowed to float independently.

3. Results and discussion

3.1. Copolymers characterization

The molecular weight (M_w), polydispersity (PD), and probe average number per polymer chain of the prepared copolymers are reported in Table 1. The molar mass distribution of the copolymers is illustrated in Fig. 2.

Table 1

Average molecular weight (M_w), polydispersity (DP) and average number of probes per chain of the copolymers

Copolymer	M_w (kg/mol)	DP	$\langle p \rangle$
Poly(MMA-co-I)	100.964	1.562	1.3
Poly(MMA-co-II)	92.308	1.463	0.8
Poly(MMA-co-III)	283.733	1.513	0.7

$\langle p \rangle$ is the concentration ratio [probe]/[copolymer] determined in solution from UV-vis electronic absorption of the aromatic probes and using the values of M_w above.

M_w value of the order of 10^5 g/mol obtained is typical from thermal initiated radical process using benzyl peroxide. The copolymers are labeled by the aromatic probes in dilute condition as indicated by the average number $\langle p \rangle$ reported in Table 1. Such result indicates that bimolecular interaction between probes in the same copolymer chain is practically precluded. The presence of the probes in the copolymers was verified by the FT-IR signal of the CN group at 2230 cm^{-1} .

3.2. Photophysical properties

The poly(MMA-co-I) has a significant increase in fluorescence when compared with free auramine vinyl monomer or with auramine free dye (even when these unbound dyes are dissolved in poly(MMA) solution of similar concentration, data not shown). The increase in fluorescence emission of auramine is usually observed when the dye is in media with high viscosity [37,41]. This behavior is related to the restriction of fast rotation of auramine phenyl rings, inhibiting the formation of a dark or nonemissive state of the dye upon its singlet electronic excitation. The absorption and emission wavelength maxima of poly(MMA-co-I) in different solvents increase with solvent polarity, and the values found are reported in Table 2.

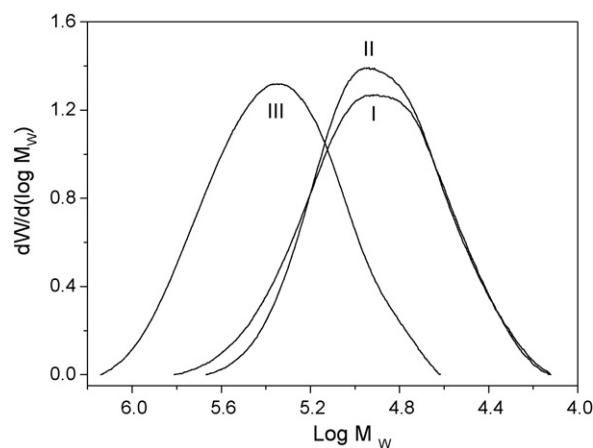


Fig. 2. Molecular weight distribution of the copolymer poly(MMA-co-X), for X = I, II and III obtained from SEC measurements. Average values are reported in Table 1.

Table 2
Absorption and emission maxima (λ_{abs} , λ_{em}), emission quantum yield ϕ of poly(MMA-co-I) in organic solvents

Solvent	λ_{abs} (nm)	λ_{em} (nm)	ϕ (10^{-3})	τ_1 ps (%)	τ_2 ps (%)	τ_3 ns (%)	χ^2
Dioxane	461	542	1.10	16 (98)	144 (1.0)	1.10 (1.0)	1.140
Toluene	460	530	1.14	12 (96)	215 (2.5)	1.60 (1.5)	1.100
Chloroform	471	540	1.47	16 (96)	170 (2.0)	0.95 (2.0)	1.020
Acetone	468	553	0.55	12 (98)	197 (1.0)	1.40 (1.0)	1.130
THF	464	543	0.76	11 (98)	263 (1.0)	1.60 (1.0)	1.103

$\lambda_{\text{exc}} = 400$ nm and $\lambda_{\text{em}} = 530$ nm are the excitation and emission wavelength used in the decay measurements, respectively. $T = 298$ K.

This effect is ascribed to the solvent stabilization of a polar excited state of auramine due to intramolecular charge transfer to the electron withdrawing CN groups. In addition, comparison with the values found for free auramine monomer, indicates a substantial red shift of electronic transitions when auramine is in poly(MMA-co-I) chain. A typical absorption and emission spectra of both free and bound probe (poly(MMA-co-I) and free auramine derivative) in toluene are illustrated in Fig. 3.

The emission quantum yield ϕ of the poly(MMA-co-I) is of the order of 10^{-3} , and although considerable small, it is two-fold higher than the quantum yield of free auramine in solution.

An evidence that poly(MMA-co-I) in solution forms around the probe a microheterogeneous medium of high viscosity is the presence of a triexponential dynamics where the long lived component is in the range of 1–2 ns, although it is in a very small percent when compared to the two fast components in the range of 10–200 ps. The presence of long time decay is only found when auramine is in presence of a high local viscous medium or restricted microenvironment, such as that feel by the probe after binding to DNA [37] or when it is adsorbed in solid matrices [42] like silica particles, and polymer fibers. The fast decay components in poly(MMA-co-I), where the shorter one dominates the whole excited state dynamic (from 11 to 16 ps and more than 96% in weighted contribution, see Table 2), is related to the auramine excited state which deactivates by crossing to the dark state with an intramolecular charge transfer character. Another interesting point of this system is the increase of the percent of the long-lived component τ_3 in the red part of the emission spectrum. The decays of poly(MMA-co-I) in dioxane are illustrated in Fig. 4. The percent of τ_3 changes from 1% at $\lambda_{\text{em}} = 500$ nm, 2% at $\lambda_{\text{em}} = 530$ nm, 2.8% at $\lambda_{\text{em}} = 550$ nm, 4.2% at $\lambda_{\text{em}} = 620$ nm, and finally 7.4% at $\lambda_{\text{em}} = 650$ nm.

1-Aminopyrene malononitrile free monomer (compound II) has a weak emission in most organic solvents and in CCl_4 and CHCl_3 it practically does not fluoresce [39]. However, poly(MMA-co-II) has

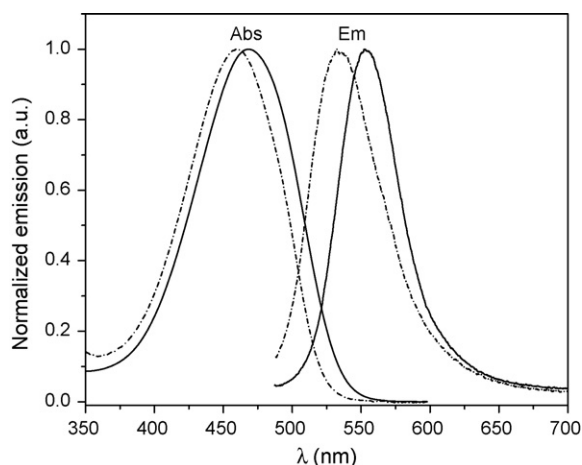


Fig. 3. Normalized absorption and emission spectra of the auramine monomer I (---) and poly(MMA-co-I) (—) in acetone.

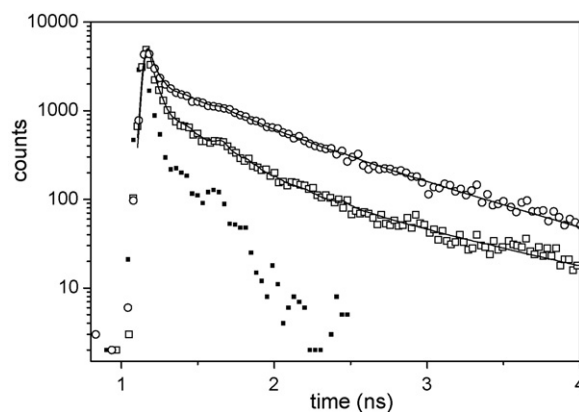


Fig. 4. Fluorescence decays of poly(MMA-co-I) in dioxane at 530 nm (□), and 620 nm (○) emission wavelengths. irf (■). $\lambda_{\text{exc}} = 400$ nm, $T = 298$ K.

fluorescence in solution of the cited apolar solvents. Absorption and emission spectra of poly(MMA-co-II) are slightly structured in UV region as illustrated in Fig. 5.

Band shape is similar to that of 1-aminopyrene spectra in polar solvents, which may indicate a $\pi\pi^*$ transition. In the red region of the emission spectrum, however, a weak broad band at about 500 nm is observed (see Fig. 5). This band could be ascribed to intramolecular charge transfer of the pyrene donor to the CN acceptor groups, or a sort of excimer formation due to a small percent of copolymer chains with double pyrene occupancy (considering the low number of probes per copolymer chain of 0.8, the fraction with double occupancy should be 0.14 in an ideal Poisson distribution). But this last assumption may be rule out because the weak red band does not increase in intensity in apolar solvents as would be expected for excimer formation. Moreover, the time resolved emission of the red band does not present the classical growing with negative amplitude as usually found in pyrene excimer dynamics. The total emission quantum yield of poly(MMA-co-II) in different

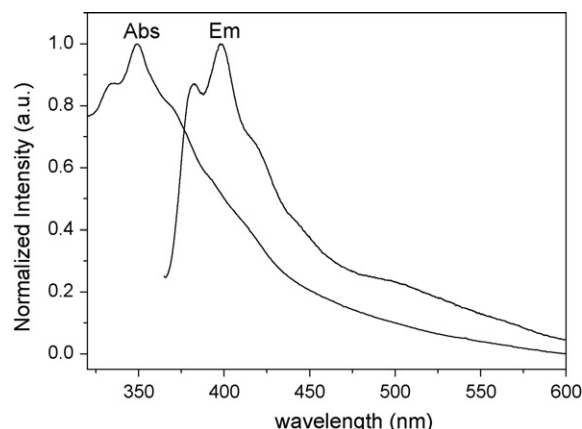


Fig. 5. Absorption and emission spectra of poly(MMA-co-II) in CHCl_3 .

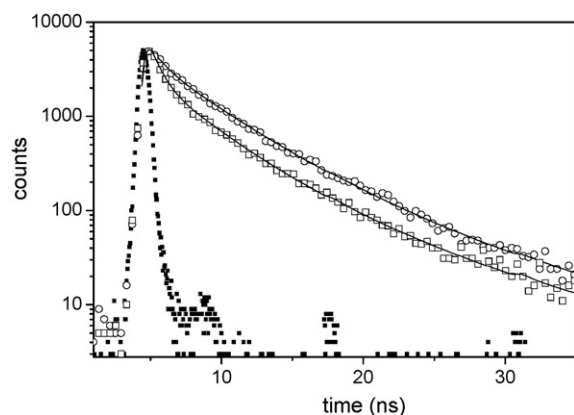


Fig. 6. Fluorescence decays of poly(MMA-co-II) in dioxane at 450 nm (○), and 490 nm (□) emission wavelengths. Instrument response function (■). $\lambda_{\text{exc}} = 380$ nm, $T = 298$ K.

solvents is listed in Table 3. The measured values are in the range of 0.02–0.11. In more polar solvent, which favors the ICT formation, emission quantum yield decreases due to nonradiative deactivation of this low energy state.

Fluorescence decay of poly(MMA-co-II) is complex (see Fig. 6). It shows three exponential decay components of about 8, 3, and 0.8 ns, where the two short ones have together about 90% of weight contribution (see Table 3). The long lived component may be ascribed to 1-aminopyrene in a restricted medium provided by the compact coil region of poly(MMA-co-II). This assumption is based on previous observation of long lived decay of 1-aminopyrene adsorbed on silica with lifetime of 11.3 ns [43,44]. Previous study has also shown that the free 1-aminopyrene monomer has a lifetime of 10.8 ns when it is adsorbed onto poly(methyl methacrylate) [25].

In some way, the fluorescence decay of poly(MMA-co-II) resembles the photophysics of amino aromatics like amino naphthalene in solution of different viscosity as reported in the early work of Meech et al. [45]. These probes with amino group have interplay of two relaxation mechanism in excited state. The first one is related with intramolecular charge reorganization, forming possible charge-transfer emitting states, and the second one is the solvent dipole relaxation about the formed excited state dipole moment. In poly(MMA-co-II), the solvent polarity seems to play minor effect in the dynamics of excited state because the three decay components remain practically similar along the change in solvent from toluene to acetone (see values in Table 3). However, an unusual behavior is found in most solvents concerning the weight percent of the decay components. For instance, in dioxane the global analysis of four decay traces at $\lambda_{\text{em}} = 420, 460, 490,$ and 540 nm with linked decay components result in a very good global fitting with $\chi_{\text{global}} = 1.089$, and decay components of $\tau_1 = 8.2$ ns, $\tau_2 = 2.8$ ns, and $\tau_3 = 0.70$ ns. The weight of τ_1 is 13% at 420 nm, and it decreases to 7% at 540 nm. But the larger change occurs in the contribution of τ_3 that starts with 39% and goes to 63% at the longer wavelength. If this low energy excited state has a charge transfer

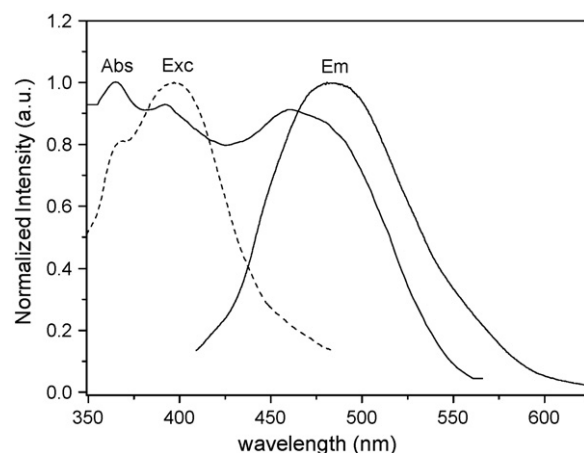


Fig. 7. Absorption, excitation (with emission at 480) and emission spectra of poly(MMA-co-III) in toluene.

character, then the environment of poly(MMA-co-II) chain is somewhat stabilizing the charge separation, even when the copolymer is in apolar solvents.

Similar to 1-aminopyrene derivative (compound II), 9-aminoacridinium malononitrile (compound III) has no fluorescence in apolar solvents like CCl_4 , and dioxane, but only very weak signal in chloroform [40]. However, labeled in poly(MMA-co-III) chain, the system becomes fluorescent in apolar and polar solvents used. Contrasting with the previous two labeled copolymers, poly(MMA-co-III) has a broad absorption band in the visible region with maximum about 460 nm (see Fig. 7).

This band has been assigned to an optical intramolecular charge transfer through the alternated double bonds of the heterocycle and malononitrile group toward the CN electron withdrawing groups [40]. Therefore, a fraction of 9-aminoacridine is bound in poly(MMA-co-III) retaining its malononitrile double bond. It means that a fraction of this monomer is adding to the chain or is terminating the chain propagation by H transfer, probably from its exocyclic amino group of the 9-amino acridinium. Once a fraction of chains still has a malononitrile end group, its further reaction with a macro radical will increase the polymer mass and this would explain the larger M_w value of poly(MMA-co-III) compared with the two other copolymers (see Table 1). The emission spectrum of poly(MMA-co-III) has a broad band centered on 480 nm ascribed to a major ICT emission. The excitation spectrum (see Fig. 7) differs from the absorption spectrum, which again is a strong indication that the acridine probe is bound to the polymer chain in different forms as discussed. The emission quantum yield of poly(MMA-co-III) is practically solvent independent and the average value found is 0.035. Comparing to the quantum yield of free amino-acridinium of 0.54 [46], it is clear that the ICT process opens a channel of nonradiative deactivation of the electronic excited state, and therefore, reduces the emission quantum yield.

The decay of poly(MMA-co-III) is triexponential with one component of about 12 ns, a second one in between 2.9 and 4.8 ns, and

Table 3

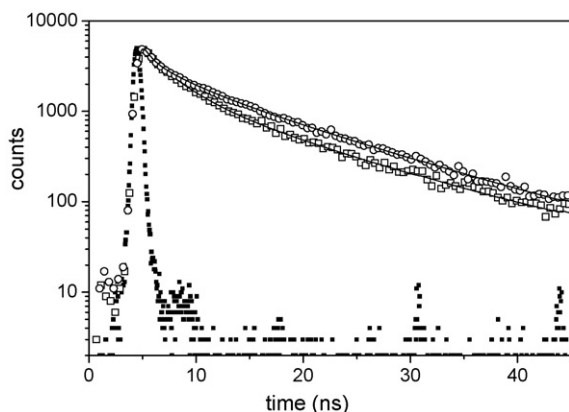
Absorption and emission maxima ($\lambda_{\text{abs}}, \lambda_{\text{em}}$), emission quantum yield ϕ and fluorescence decay time components of poly(MMA-co-II)

Solvent	λ_{abs} (nm)	λ_{em} (nm)	ϕ (10^{-3})	τ_1 ns (%)	τ_2 ns (%)	τ_3 ns (%)	χ^2
Dioxane	345	415	40	9.15 (10)	3.20 (45)	0.76 (45)	0.992
Toluene	347	416	50	7.30 (14)	3.60 (48)	0.87 (38)	1.150
Chloroform	347	380, 404	20	8.00 (7.0)	2.92 (40)	0.98 (53)	1.050
Acetone	348	429	30	7.60 (11)	3.40 (35)	0.60 (55)	1.110
THF	344	430	110	7.20 (8.0)	2.90 (58)	0.74 (34)	1.094

$\lambda_{\text{exc}} = 380$ nm and $\lambda_{\text{em}} = 420$ nm are the excitation and emission wavelength of the decay measurements, respectively. $T = 298$ K.

Table 4Absorption and emission maxima (λ_{abs} , λ_{em}), emission quantum yield ϕ , and decay times of poly(MMA-co-III) in different solvents

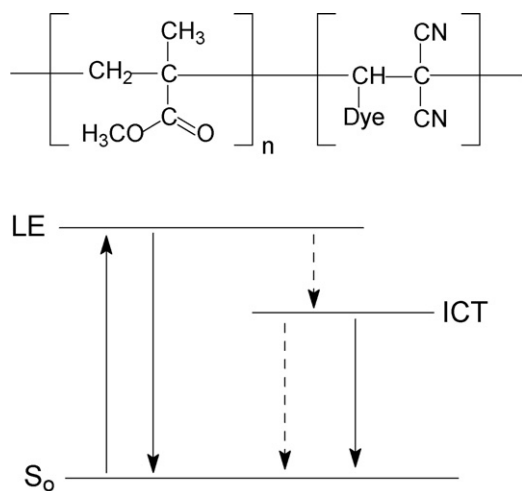
Solvent	λ_{abs} (nm)	λ_{em} (nm)	ϕ (10^{-3})	τ_1 ns (%)	τ_2 ns (%)	τ_3 ns (%)	χ^2
Dioxane	365, 392, 460 ^a	480	34	11.5 (37)	3.24 (25)	0.70 (38)	1.037
Toluene	362, 385, 470 ^a	480	45	11.5 (8.0)	3.46 (58)	1.13 (34)	1.006
Chloroform	362, 386, 470 ^a	480	36	12.7 (10)	3.70 (51)	1.52 (39)	1.091
Acetone	365, 400, 476 ^a	430, 455	39	12.1 (36)	4.80 (32)	0.95 (32)	1.091
THF	361, 387, 470 ^a	470	20	11.5 (30)	2.90 (25)	0.50 (45)	1.040

Reported decay parameters with excitation wavelength at 400 nm and emission wavelength at λ_{em} .^a Refers to the maxima of the broad absorption band.**Fig. 8.** Fluorescence decays of poly(MMA-co-III) in dioxane at 450 nm (○), and 490 nm (□) emission wavelengths. irf (■). $\lambda_{\text{exc}} = 390$ nm, $T = 298$ K.

a fast decay component with 0.5–1.5 ns (see data listed in Table 4) for different solvents.

The long lived decay component is assigned mainly to the $\pi\pi^*$ deactivation of the 9-aminoacridinium chromophore, and the other two components arise from the interplay of this high energy locally excited (LE) state with low energy relaxed intramolecular charge transfer (ICT) state.

Similar to poly(MMA-co-II), the short lived component τ_3 increases its weight % in the red part of the emission spectrum which may support the assumption of a low energy ICT state with fast decay to electronic ground state. This decay behavior is illustrated in Fig. 8 with traces at 450 and 490 nm.

**Fig. 9.** Poly(MMA-co-malononitrile dye) and electronic energy diagram with ground (S_0), locally excited (LE) and intramolecular charge transfer (ICT) states. The structures of the dye or probe used are represented in Fig. 1.

Concerning the copolymers prepared, their photophysics may be represented by a simple scheme of deactivation paths as represented in Fig. 9.

4. Conclusions

Aromatic probes with malononitrile group are copolymerized with MMA to form new fluorescent materials with possible applications as polymeric emission marker with photo induced charge transfer character. The nonexponential fluorescence decay of the copolymer in solution arises from interplay between the prompt singlet excited state of the chromophore (LE state) and intramolecular charge transfer (ICT) state in addition to charge reorganization and solvent relaxation owing the presence of amino and aromatic electron donor and CN electron withdrawing groups in the copolymer chain.

Acknowledgments

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