Photophysical Properties of Fluorescent Copolymers of Methylmethacrylate for Use in Liquid Crystalline Systems

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The free radical copolymerisation of five fluorescent 4-allylamino-*N*-phenyl-substituted 1,8-naphthalimide dyes (MDs) with methylmethacrylate (MMA) has been investigated. The utility of the copolymers prepared as fluorescent component in polymer/liquid crystal systems has been investigated. The basic photophysical properties of monomeric dyes, poly(MMA-co-MD) and poly(MMA-co-MD)/liquid crystal mixtures are discussed. The influence of poly(MMA-co-MD) on the phase transition temperature from the nematic to the isotropic state of poly(MMA-co-MD)/liquid crystal mixtures have also been investigated.

Key words: Fluorescence Polymers; Polymethylmethacrylate; 1,8-Naphthalimide; Liquid Crystals; Photophysics.

1. Introduction

Copolymers of some monomers with fluorescent dyes can find use as colored polymers resistant to solvents and migration, which have high fluorescence photo- and thermostability [1, 2]. Similar substances are recently reported to have a novel use as luminophores in liquid crystal (LC) systems for displays of the “guest-host” type [3]. In general, guest-host displays are built up of units of nematic LC and dichroic dyes. Their action is based on the so called “guest-host” effect, which consists in the alignment of mesogenic units under an applied voltage accompanied by close alignment of chromophorous units, with a resulting selective absorption by chromophores depending on orientation [4]. Guest-host displays need only one polarizer and have a wide viewing angle [5]. The displays exhibit high image contrast when fluorescent dyes are involved in display systems [6].

In recent years the design of LC displays based on light scattering has been an active research area. The potentials of polymers dispersed in liquid crystals have put this type of studies among the high lights [7]. On the other hand, polymer dispersed liquid crystal systems require no polarizer, they provide increased brightness, larger viewing angle in all directions and higher contrast ratio of the displays. Our first investigations on the behavior of blue and green fluorescent copolymers with 1,8-naphthalimide side-groups in different liquid crystal matrixes have been reported recently [3].

In this article we report on the synthesis and properties of the highly fluorescent side-group copolymers of methylmethacrylate with polymerizable dyes of 4-allyamino-*N*-phenyl-1,8-naphthalimide structures with different substitutes in the phenyl ring. The basic photophysical characteristics of the novel polymeric dyes have been determined in isotropic (solution and solid film) and in anisotropic (liquid crystal) media. Additionally, the effect of the polymeric matrix upon the phase-transitional temperatures and of the liquid crystal ZLI 1840 has been studied, and the utility of the novel materials for liquid crystal displays of the guest-host type is discussed.

2. Experimental

2.1. Materials

Radical suspension copolymerization of methylmethacrylate (MMA) with monomeric dyes (MD) was carried out (Scheme 1).

Commercial MMA was used after purification. Five monomeric dyes of 4-allylamino-*N*-phenyl-1,8-naphthalimide structure with high quantum yield of fluorescence were used. Their synthesis was described in [8]. As initiator of the copolymerization, dibenzoylperoxide (DBP) (Fluka) was used after recrystallization from chloroform.

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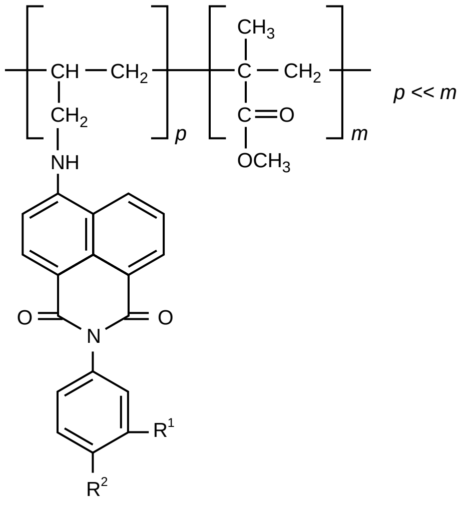

Dye	1	2	3	4	5
R^1	H	H	H	H	OH
R^2	H	CH$_3$	OCH$_3$	Cl	H

Scheme 1. Chemical structure of poly(MMA-co-MD).

The commercial liquid crystal mixture ZLI 1840 (Merck) was used to prepare the binary and ternary guest-host LC systems. It has a wide temperature range of the nematic state (-20 °C ÷ 90 °C [9]). The used LC systems with the copolymers or with the dye/homopolymer of methylmethacrylate mixtures as guests were prepared by the solvent-induced phase separation technique [10]. Films of 20 μm thickness were cast on glass plates at room temperature. An 80 : 20 ratio of LC to polymer was found appropriate to explore the stabilizing effect of the polymeric component upon the LC system. The films obtained were noticeably self-supported, which is most suitable for their application to flexible and large-area displays [11].

2.2. Synthesis and Characterization of Fluorescent Copolymers

The copolymerization of 10 g MMA with the dyes MD1 – MD5 was carried out in 60 ml water at 70 °C for 6 h in the presence of 1.0 wt% dye, 1.0 wt% DBP and 0.34 g poly(vinylalcohol) as emulsifier [12]. Transparent side-group copolymers of intense green fluorescence were obtained. They retain their colour and fluorescence after multiple precipitations from chloroform solutions with ethanol. The precipitated copolymers were repeatedly washed with ethanol, recovered by filtration and dried in vacuum to constant weight.

The quantity of blinded dye was determined by means of UV-Vis spectrophotometry, using the method of the standard line and calibrating with the maxima of the absorption spectra of monomeric dyes.

The molecular weights and polydispersity of the copolymers were determined by GPC in THF solvent at 45 °C and a flow rate of 1.0 ml/min on a Waters 244 apparatus, equipped with an universal linear Ultrastyragel column. Both differential refractive index and UV-Vis absorption detectors ($\lambda_A = 420$ nm) were used. Calibration was performed with polystyrene standards.

UV-Vis absorption spectra were recorded with a Hewlett Packard 8254 A spectrophotometer, for the copolymers both in chloroform and on solid films and for the MDs only in chloroform. The films were 40 μm thick and absorb in the range of validity of the Lambert-Beer law.

Fluorescence spectra of the monomeric and polymeric dyes were recorded on a Kontron spectrophotometer. For the excitation, monochromatic light of $\lambda = 420$ nm was used. The spectra of the dyes in LC were taken on surface-stabilized display cells. The latter consisted of two glasses covered from inside with oriented polymer layers where the LC systems doped by monomeric or polymeric dyes (in ratio 80 : 20) were sandwiched [3b].

The quantum fluorescence yield (Φ_F) was determined on the basis of the absorption and fluorescence spectra of all the dyes in chloroform at concentrations of $1 \cdot 10^{-5}$ M for MDs and of 5 g/l for the copolymers, using Rhodamine 6G as standard ($\Phi_o = 0.85$ [13]).

The temperatures of the nematic-isotropic phase transition of the pure LC and of the polymer/LC systems were determined by a polarizing microscope, equipped with a heating stage, with 0.1 K accuracy.

3. Results and Discussion

3.1. Copolymers and Composition

By means of thin-layer chromatography (TLC) and UV/Vis- and fluorescence spectroscopy, the presence of a covalent bond between the MD units and the polymethylmethacrylate (PMMA) main chain was proved. Two types of systems were analyzed by conventional TLC analysis, both a mixture of the homopolymer of MMA with a dye and the relevant copolymer of MMA and the dye. It was observed that in the first case the

Copolymer	Yield (%)	Incorporated dyes (%)	M_w	M_n	M_w/M_n
Poly(MMA-co-MD1)	89	0.80	255 300	157 100	1.62
Poly(MMA-co-MD2)	84	0.80	274 800	161 600	1.70
Poly(MMA-co-MD3)	84	0.79	393 400	195 800	2.01
Poly(MMA-co-MD4)	92	0.78	423 200	209 900	2.01
Poly(MMA-co-MD5)	87	0.75	136 100	64 500	2.11

Table 1. Yield, quantity of bonded MD and molecular weight characteristics of side-group copolymers poly(MMA-co-MD).

homopolymer remained at the start, but the dye moved while in the second case (the copolymer), the dye did not move and remained at the start with the polymer. This obviously implies that the dye is covalently bound to the polymer chain.

The precipitated copolymers were found to have the same absorption maxima as the monomeric dyes (Table 1), showing that the basic chromophore of the dye has not changed neither during the polymerization, nor as result of its binding to the polymer chain. This fact allows the use of the method of the standard curve when determining the percentage of chemically bonded dye to the polymer chain. It was found that over 80% of the initially introduced dyes (1%) were chemically bound (Table 1). Considering that the values are obtained for repeatedly precipitated copolymers where low molecular fractions have been removed during the precipitation, the results are rather satisfactory and imply that the MD dyes are suitable for the production of fluorescent copolymers in good yield.

The molecular characteristics of the copolymers obtained are listed in Table 1. The determinations of the molecular the weight and molecular weight distribution confirm the formation of high molecular weight polymers. The molecular weights found are in the range $(64.5 \div 209.9) \cdot 10^3$. The double detection shows close values for the elution time in both chromatograms, indicating that copolymers are present which absorb at about 420 nm. The polydispersity coefficient M_w/M_n is in the range $1.62 \div 2.11$ (Table 1), which is a common width of the molecular weight distribution at suspension polymerization. The most unfavourable molecular weight and M_w/M_n values are found for the copolymer with MD5, which may be due to possible dye-water interactions terminating the copolymerization process.

3.2. Spectral Characteristics of Monomeric Fluorescent Dyes and their Copolymers with Methylmethacrylate

Table 2 presents the basic photophysical characteristics of the dyes MD1 – MD5 measured in chloroform solution: the values of the absorption maximum (λ_A), molecular extinction coefficient (ε), fluorescence maximum (λ_F), Stokes shift ($\nu_A - \nu_F$), energy of the first singlet state (E_{S1}) and the quantum yield of fluorescence (Φ_F).

Table 2. Photophysical characteristics of low molar 1,8-naphthalimide dyes in chloroform.

	Dye				
	MD1	MD2	MD3	MD4	MD5
λ_A [nm]	423	422	423	424	423
	280	274	279	280	280
ε [l mol^{-1} cm^{-1}]	13 700	10 500	12 900	15 200	11 100
	17 200	15 200	19 400	18 000	15 400
λ_F [nm]	500	500	500	500	502
$(\nu_A - \nu_F)$ [cm^{-1}]	3640	3696	3640	3585	3720
E_{S1} [kJ mol^{-1}]	257	258	257	257	256
Φ_F	0.86	0.85	0.84	0.85	0.80

The MD1 – MD5 exhibit in chloroform a yellow-green colour and intense fluorescence, with $\lambda_A = 422$ – 424 nm and $\lambda_F = 500$ – 502 nm (Table 2). Figure 1 displays the absorption and fluorescence spectra of MD1 as a typical example of all spectra. The absorption and fluorescence spectra of the monomeric dyes are similar with each other. In comparison to the polar proton-donating ethanol, the absorption maxima in chloroform are hypsochromically shifted ($\Delta\lambda_A = 14$ – 15 nm) [8a]. This may be related to the different polarity of the solvents and to the specific dye-solvent interactions causing a change in dye polarization. The fluorescence curve is an approximate mirror image of the absorption curve in the visible region, which indicates the molecular structure of the dyes in the excited state and prevailing fluorescence emission [14].

The Stokes shift indicates the difference in the properties and structure of the fluorophores in the ground state S_0 and the first exited state S_1. The Stokes shift is given by

$$(\nu_A - \nu_F) = (1/\lambda_A - 1/\lambda_F) \cdot 10^7 \text{ cm}^{-1}. \qquad (1)$$

The Stokes shift values are in the region 3585 – 3720 cm^{-1} that is common for the dyes of this class. On excitation, the MD1 – MD5 pass from the ground state S_0 basically to the first excited singlet state S_1,

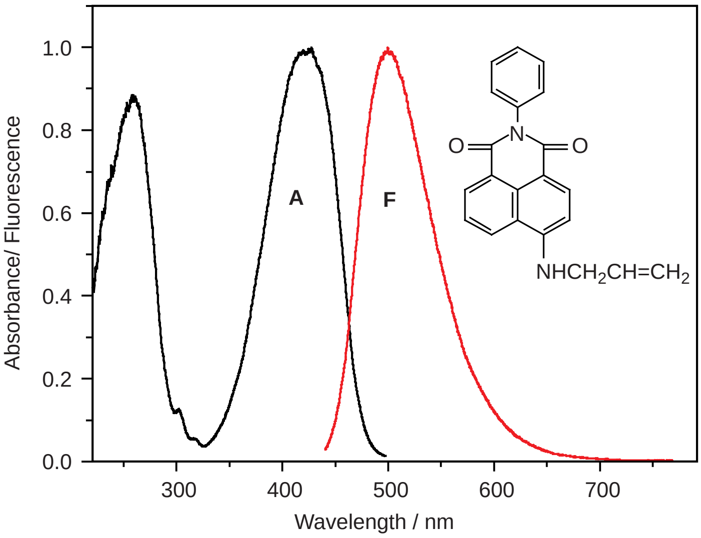

Fig. 1. Normalized absorption (A) and fluorescence (F) spectra of MD1 in chloroform solution.

the energy of the first excited state E_{S1} being 256–258 kJ mol^{-1}. On emission, dye molecules deactivate and pass back to the ground state.

The fluorescence efficiency of the MD1–MD5 is estimated by measuring their fluorescent quantum yield Φ_F using (2) on the basis of the absorption and fluorescence spectra taken in chloroform using Rhodamine 6G as a standard.

$$\Phi_F = \Phi_{st} \frac{S_u}{S_{st}} \frac{A_{st}}{A_u} \frac{n_{Du}^2}{n_{Dst}^2}, \qquad (2)$$

where Φ_F is the emission quantum yield of the sample, Φ_{st} the standard emission quantum yield, A_{st} and A_u represent the absorbance of the standard and sample at the excited wavelength, respectively, while S_{st} and S_u are the integrated emission band areas of the standard and sample, respectively, and n_{Dst} and n_{Du} is the solvent refractive index of the standard and sample, respectively.

The MD1–5 exhibit a very high quantum yield of fluorescence $\Phi_F = 0.80–0.86$ in chloroform, which is larger than that in ethanol ($\Phi_F = 0.32–0.75$ [8a]) and methanol ($\Phi_F = 0.36–0.60$ [8b]). This accords with previous data on other 1,8-naphthalimide dyes [15]: Φ_F decreases with the increased values of the absorption maxima in more polar solvents. It is noteworthy that this finding is very rough; it was not valid with the dyes under study in a single solvent. The difference in Φ_F for the MD1–MD5 in chloroform is not large, therefore the Φ_F dependence on the solvent has been ascribed to possible solute-solvent interactions [8a, 8b] or/and the conformation effect.

Table 3. Photophysical characteristics of poly(MMA-co-MD) in chloroform.

	Poly(MMA-co-MD)				
	MD1	MD2	MD3	MD4	MD5
λ_A [nm]	420	422	422	422	423
ε [l g^{-1} cm^{-1}]	0.022	0.047	0.054	0.023	0.023
λ_F [nm]	502	500	500	500	500
$(\nu_A - \nu_F)$ [cm^{-1}]	3889	3696	3696	3696	3640
E_{S1} [kJ mol^{-1}]	258	257	257	259	262
Φ_F	0.85	0.90	0.90	0.85	0.90

The copolymers poly(MMA-co-MD) are yellow-green. All the copolymers are soluble in the solvents common for the homopolymer of PMMA. Table 3 presents the data obtained from the absorption and fluorescence spectra of the side-group copolymers poly(MMA-co-MD) in chloroform. The absorption maxima of the copolymers are in the range 420–423 nm being very close to those of the monomeric dyes.

The fluorescence spectra of the copolymers in chloroform solution show maxima at $\lambda_F = 500–502$ nm. The Stokes shift values are 3640–3889 cm^{-1}, being rather large they are the main cause [16] for the brilliant yellow-green colour of the copolymers obtained. The absorption and fluorescence maxima of the copolymers in chloroform are very similar with those of the monomeric dyes in the same solution, indicating further the preservation of the chromophore system during the copolymerization.

Table 4. Absorption and fluorescence characteristics of the copolymers poly(MMA-co-MD) in the form of solid films.

Copolymer	λ_A [nm]	λ_F [nm]	$\nu_A - \nu_F$ [cm^{-1}]	E_{S1} [kJ mol^{-1}]
Poly(MMA-co-MD1)	419	515	4449	251
Poly(MMA-co-MD2)	424	520	4354	252
Poly(MMA-co-MD3)	424	520	4354	253
Poly(MMA-co-MD4)	420	502	3889	254
Poly(MMA-co-MD5)	420	507	4085	254

The UV-Vis absorption spectra of the copolymers in the solid state are similar to those in chloroform solution, the maxima being in the range $\lambda_A = 419$–424 nm (Table 4). The fluorescence maxima of the thin polymer films are in the region 502 – 520 nm in dependence on the chemical structure of the MDs. For the MD1 – MD3, the fluorescence maxima are at 515 – 520 nm, while for the MD4 and MD5 they are at 502 – 507 nm probably due to conformational effects in the solid film. There is almost no difference in the energy of the first excited state E_{S1} which is in the range 251 – 254 kJ/mol, being of slightly larger in chloroform solution, 257 – 262 kJ/mol.

The quantum yield of fluorescence of the copolymers is with $\Phi_F = 0.85 \div 0.89$ higher than for the MDs themselves. This is obviously related to the binding of the chromophore to the polymer chain.

3.3. Poly(MMA-co-MD)/LC Bi-component Systems

The polymer dispersed liquid crystals (PDLC) are composite materials comprising a rather small amount of a liquid crystal embedded into a continuous polymer matrix (usually in the form of LC droplets of several micrometers in diameter). The properties of PDLC films depend on the nature of both the LC and the polymer matrix. Dispersing the coloured copolymers in LCs leads to bright yellow-green colour. The mixtures exhibit intense green fluorescence with maxima at 502 – 508 nm. The fluorescence intensity of the copolymers is higher in LC than in chloroform. The fluorescence maxima tend to be bathochromical by shifted in LC ($\Delta\lambda = 2$ – 6 nm) with respect to the maxima in chloroform but are hypsochromically shifted ($\Delta\lambda$ = 13 – 18 nm) with respect to the maxima of the solid copolymer films. On the other hand, the fluorescence intensity of the bi-component poly(MMA-co-MD)/LC systems is higher than that in the respective dye/LC mixtures. This fact can be explained by the bonding of the dyes into the polymer macromolecules, leading to a decrease of the non-radiative processes taking place in the rigid polymeric matrix.

3.4. Phase-transitional Behaviour of the Systems Polymer/Liquid Crystal

It is well-known that addition of a non-mesogenic solute to a nematic LC changes its nematic-isotropic phase transition temperature, in most cases causing its decrease. Another specific feature of the phase transition is the appearance of two-phase regions predicted by the theory and observed many times experimentally [17].

The effect that polymeric dyes and MD/PMMA homopolymer mixtures have upon the phase transitional behaviour of LC was studied by means of a polarizing microscope with a heating stage. The results of temperature investigations on pure LCs, binary (copolymer/LC) and ternary (MD/PMMA/LC) mixtures are given in Table 5. The following characteristic temperatures of the nematic-isotropic phase transition are determined: T_N, at which the first drop of the isotropic liquid appears, and T_I, at which the last drop of the nematic disappears. Their difference ($T_I - T_N$) is the range of the two-phase region, and ΔT_N and ΔT_I are the shifts of T_N and T_I with respect to the relevant temperatures of pure LC. $T_{NI} = 1/2(T_N + T_I)$ is the average temperature of the nematic-isotropic transition of guest/LC mixtures and ΔT_{NI} is its shift with respect to the pure LC.

The temperature investigations on the binary systems (copolymer/LC) show that the copolymers decrease both phase transition temperatures T_N (2.6 – 3.1 K) and T_I (4.8 – 5.3 K) of pure LC. The depression is enhanced when PMMA and MD are introduced into the system being within 6.2 – 7.3 K for T_N and 6.3 – 7.3 K for T_I. Thus, the destructive influence upon the mesophase of the three types of guests (making use of data for the MDs in [8]) increases in the row: low molar dyes, colour copolymers, MD/PMMA homopolymer mixtures.

This behaviour accords with theoretical predictions (based on Helfand's lattice model) describing the effect which flexible polymer guests have upon the nematic-isotropic phase transition of low molar LCs [18]. Along these lines, a comparison of the temperature behaviour observed here with earlier results on side-group copolymers of styrene with 1,8-naphthalimide units [3b] is of interest. The higher flexibility of the PMMA chain in comparison to polystyrene chain leads to larger depressions of the phase transition temperatures and widening of the bi-phase temperature intervals.

Systems	T_N	T_I	$T_I - T_N$	ΔT_N	ΔT_I	T_{NI}	ΔT_{NI}
LC	362.5	368.5	6.0	–	–	365.5	–
Poly(MMA-co-MD1) + LC	359.7	363.4	3.7	−2.8	−5.1	361.6	−3.9
Poly(MMA-co-MD2) + LC	359.4	363.2	3.8	−3.1	−5.3	361.3	−4.2
Poly(MMA-co-MD3) + LC	359.6	363.5	3.9	−2.9	−5.0	361.6	−3.9
Poly(MMA-co-MD4) + LC	359.9	363.7	3.8	−2.6	−4.8	361.8	−3.7
Poly(MMA-co-MD5) + LC	359.8	363.5	3.7	−2.7	−5.0	361.7	−3.8
PMMA + MD1 + LC	355.8	362.2	6.4	−6.7	−6.3	359.0	−6.5
PMMA + MD2 + LC	356.3	361.5	5.2	−6.2	−7.0	358.9	−6.6
PMMA + MD3 + LC	355.8	361.8	6.0	−6.7	−6.7	358.8	−6.7
PMMA + MD4 + LC	356.3	361.2	4.9	−6.2	−7.3	358.8	−6.7
PMMA + MD5 + LC	355.2	361.5	6.3	−7.3	−7.0	358.4	−7.1

Table 5. Phase-transition temperature data for the pure liquid crystal ZLI 1840 and for binary and ternary systems of the copolymers of poly(MMA-co-MD) with MD1 – MD5 and of mixtures comprising homopolymer PMMA with the monomeric dyes dispersed in the liquid crystal (in K).

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