

Research Article

Synthesis of New Blue Fluorescent Polymerizable 1,8-Naphthalimides and Their Copolymers with Styrene as Sensors for Fe(III) Cations

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The synthesis, characterization, and functional properties of two new polymerizable 1,8-naphthalimides (MDs) have been described. Their copolymers with styrene designed to act as a fluorescence PET chemosensor have been investigated. The study also reports the influence of different metal cations (Ag^+ , Mg^{2+} , Cu^{2+} , Sr^{2+} , Co^{2+} , Pb^{2+} , and Fe^{3+}) on the fluorescence intensity of both low and high molecular weight fluorophores.

1. Introduction

In the recent years the development of molecular recognition and sensing systems for different analytes has received considerable attention. Fluorescent chemosensors utilised for detection of metal cations and protons in the environment were based on different molecular structures [1, 2]. The fluorescent polymers are very attractive for this purpose. In this case the fluorescent sensor units can be covalently bonded to the polymer chain, thus showing very similar effect to their monomeric sensor units [3]. The functional characteristics of polymer chemosensors can be expressed either by conformational changes of macromolecules or by the collective transport properties.

Recently, new polymerizable 1,8-naphthalimide molecules to sensitive protons or metal cations have been synthesized and their functional properties are investigated. Due to the presence of a polymerizable group they can react with some commercial monomers, allowing copolymers with a green or blue fluorescence to be obtained. It was demonstrated that the copolymers of these polymerizable sensors can be used as homogeneous and heterogeneous photoinduced electron transfer (PET) fluorescent sensors sensitive to metal cations

[4–9]. In all cases 1,8-naphthalimides are enough thermo- and water resistible so the polymers can be used for ion determination in solution without contaminating it. The scientific tasks on development of polymeric systems for detection of environment pollutants will be focused on finding such polymeric systems which have specific chemical, physical, and mechanical properties as transparency, resistance to different environment factor and the harmful chemical substances, flexibility, and so forth.

In this paper we present the synthesis and functional properties of two new polymerizable 1,8-naphthalimides (MDs) and their copolymer with styrene designed to act as fluorescence chemosensors. The influence of different metal cations on the fluorescence intensity of both low and high molecular weight sensors has been investigated and discussed.

2. Experimental Part

2.1. Materials and Methods. 4-Amino-N-allyl-1,8-naphthalimide was synthesized according to the method described previously [10]. Commercial styrene (St) was used after

purification by distillation under reduced pressure. Dibenzoyl peroxide (DBP) (Fluka), crystallized from chloroform to methanol was used as an initiator of the free radical polymerization. Chloroacetyl chloride, piperidine, and dimethylamine were used as obtained from MERCK.

UV/vis spectrophotometric investigations were performed using "Thermo Spectronic Unicam UV 500" spectrophotometer. The fluorescence spectra were taken from a "Cary Eclipse" spectrophotometer. All spectra were recorded using 1 cm path length synthetic quartz glass cells. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using anthracene as reference ($\Phi_{st} = 0.27$ [11]). All absorption and fluorescence measurements were carried out at $1 \times 10^{-5} \text{ mol L}^{-1}$ for MDs. The polymer concentrations in the solutions for all measurements were 5 g L^{-1} .

The effect of the metal cations on fluorescence intensity has been measured by adding a few microliters of stock aqueous solution ($c = 10^{-2} \text{ mol L}^{-1}$) of the metal cations to a known volume of the solution (3 mL) in acetonitrile for monomeric sensors and in aqueous solution for polymeric sensor. This addition was limited to 0.08 mL, so that dilution remained insignificant [12]. For all absorbance and fluorescence measurements the polymer thin film was placed diagonally in the sample quartz cuvette to improve measurement reproducibility. The reproducibility of the results was 99%. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, SrCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AgNO_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were investigated as sources of metal cations.

IR analysis of compounds was carried out using the infrared Fourier transform spectrometer (IRAffinity-1 "Shimadzu") with the diffuse-reflectance attachment (MIRacle Attenuated Total Reflectance Attachment). The NMR spectra were obtained from a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C , respectively, using a dual 5 mm probe head. Deuteriochloroform and tetramethylsilane were used as a solvent and an internal standard.

Thin layer chromatographic (TLC) analysis of the monomeric dyes was followed on silica gel (Fluka F₆₀ 254 20 × 20; 0.2 mm) using the solvent system n-heptane/acetone (1:1) as an eluent.

The molecular characteristics of the poly(St-co-MD) were determined on a GPC Water 244 apparatus. The solvent was THF at a flow rate of 1.0 mL min^{-1} at 45°C . Both a differential refractive index and an UV/vis absorption detector ($\lambda_A = 375 \text{ nm}$) were used. Polystyrene calibration was used for all molecular weight calculations.

2.2. General Procedure for Synthesis of Monomeric Dyes MD1 and MD2 (Scheme 1). 4-Amino-N-allyl-1,8-naphthalimide (0.01 mol) was dissolved in 50 mL of acetic acid and at 50°C 2 mL chloroacetyl chloride was added dropwise. The mixture was stirred at this temperature and after 2 h the product was isolated by pouring it into water and filtrated. After that 0.01 mol of this product was dissolved in dioxane and 0.05 mol of amines was added and stirred at 80°C for 4 h. The final products have been isolated with high yields and purity.

2.2.1. Characterization of MD1

Yield 89%.

FTIR (KBr) cm^{-1} : 3248, 2935, 2818, 1692, 1651, 1614, 1538, 1380, 1235, 781.

$^1\text{H-NMR}$ (CHCl_3) δ (ppm): 10.54 (1H, NH); 8.65–8.44 (dd, 3H, Ar); 8.33–8.29 (d, 1H, Ar); 7.82–7.76 (t, 1H, Ar); 6.08–5.92 (m, 1H, CH=); 5.36–5.17 (dd, 1H, CH=); 4.81–4.79 (d, $\text{CH}_2\text{-CH=}$); 3.49 (s, 2H, $\text{CO-CH}_2\text{-}$); 2.66 (s, 6H, CH_3).

$^{13}\text{C-NMR}$ (CHCl_3) δ (ppm): 171.9, 165.1, 164.9, 140.6, 133.7, 133.0, 132.3, 129.9, 128.0, 125.2, 124, 8, 120.2, 117.6, 64.3, 48.3, 46.2, 39.6.

Analysis: $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_3$ ($337.22 \text{ g mol}^{-1}$): Calc. (%): C-67.67, H 5.63, N 12.46.

Found (%): C-67.44, H 5.69, N 12.39.

2.2.2. Characterization of MD2

Yield 92%.

FTIR (KBr) cm^{-1} : 3223, 2946, 2838, 1693, 1656, 1620, 1532, 1379, 1237, 777.

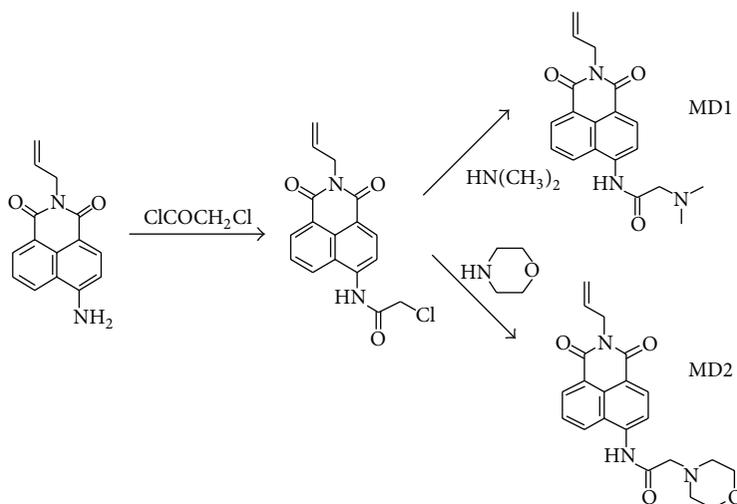
$^1\text{H-NMR}$ (CHCl_3) δ (ppm): s 10.44 (1H, NH); 8.66–8.58 (dd, 3H, Ar); 8.29–8.20 (d, 1H, Ar); 7.85–7.79 (t, 1H, Ar); 6.08–5.92 (m, 1H, CH-CH_2); 5.36–5.20 (dd, 2H, $\text{CH}_2\text{=CH}$); 4.81–4.79 (d, 2H, $\text{CH}_2\text{-CH}$); 3.92 (s, 4H, $\text{CH}_2\text{-N-CH}_2$); 3.42 (s, 2H, $\text{-CH}_2\text{-CO}$); 3.01 (s, 4H, $\text{CH}_2\text{-O-CH}_2$).

$^{13}\text{C-NMR}$ (CHCl_3) δ (ppm): 164.1, 163.2, 162.3, 150.3, 134.1, 130.5, 129.5, 128.3, 127.8, 124.2, 121.9, 120.0, 107.7, 103.3, 55.8, 45.2, 44.4, 39.4, 30.8.

Analysis: $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_4$ ($379.24 \text{ g mol}^{-1}$): Calc. (%): C-66.50, H 5.54, N 11.08.

Found (%): C-66.84, H 5.48, N 11.19.

2.3. Copolymerization. Free radical copolymerization of styrene with MDs was carried out in bulk [13]. 9.80 g styrene, 0.20 g of monomer MD, and 0.05 g DBP were mixed in an ampoule flushed with pure dry nitrogen. The ampoule was sealed and heated at 80°C in a thermostat for 8 h. The side-chain copolymers thus obtained were several times precipitated with ethanol from the chloroform. The precipitated copolymers were repeatedly washed with ethanol, recovered by filtration, and dried in vacuum to constant weight. Transparent fluorescent copolymers of blue emission were obtained. All spectrophotometric measurements were carried out with precipitated coloured polymers. Thin polymeric film used for the fluorescent investigations was obtained from deposition of a 10% solution of the copolymer in chloroform on glass surface. The thickness of the copolymer film was $40 \mu\text{m}$, determined by microscope technique.



SCHEME 1: Synthesis of monomeric MD1 and MD2.

3. Results and Discussions

3.1. Photophysical Characteristics of Monomeric and Polymeric Fluorophores. The photophysical properties of 1,8-naphthalimide are known to depend mainly on the polarization of its chromophore system. In this study the functional properties of MDs were investigated in organic solvents of different polarity. Tables 1 and 2 summarize the basic photophysical characteristics of MDs—absorption (λ_A) and fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$), oscillator strength (f), quantum yield of fluorescence (Φ_F), and energetic yield of fluorescence (E_F).

In all organic solvents under study, the monomeric 1,8-naphthalimides are colourless absorbing in the ultraviolet region at 366–375 nm and emit blue fluorescence at 434–463 nm. The results show that the substituents in C-4 position do not affect the maxima positions significantly.

The Stokes shift is a parameter, which indicates the difference in the properties and structure of the fluorophore between the ground state S_0 and the first excited state S_1 (1). Consider the following:

$$(\nu_A - \nu_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \text{ (cm}^{-1}\text{)}. \quad (1)$$

The Stokes shift values clearly depend strongly on the solvent polarity d . It is seen that the values are higher when alcohols are used as solvents and they were very similar to those of other monomeric 1,8-naphthalimide dyes [14–16]. The Stokes shift of the MD1 has relatively high values when compared to MD2, which is probably due to the conformational changes or electron density redistribution upon excitation.

The ability of the MD molecules to emit absorbed light energy is characterized quantitatively by the quantum yield of fluorescence Φ_F . The quantum fluorescence yield of MDs

in all organic solvents was calculated on the basis of the absorption and fluorescence spectra using

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

where Φ_{st} is the quantum yield of the reference, A_{st} and A_u represent the absorbance of the reference and the sample, respectively, S_{st} and S_u are the integrals of the emission of the reference and the sample, respectively, and n_{Dst} and n_{Du} are the refractive index of the reference and the sample, respectively.

As seen from the data in Tables 1 and 2, the MDs quantum yield depends on the solvent polarity also. The quantum yield is considerably higher in nonpolar media. In polar organic solvents, the MDs exhibit much weaker emission. In all cases their fluorescence is not strong which can be explained by the conformation change.

An important characteristic of MDs is the oscillator strength (f); it reveals the effective number of electrons whose transition from the ground state S_0 to the excited S_1 state gives the absorption area in the spectrum. Values of the oscillator strength can be calculated using

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2} \epsilon_{\max}, \quad (3)$$

where the $\Delta\nu_{1/2}$ is the width of the absorption band (in cm^{-1}) at $1/2 \epsilon_{\max}$.

The values obtained for f for MD1 are 0.10 (tetrahydrofuran) and 0.14 (acetonitrile). The higher values in acetonitrile correlate well with the hypsochromic effect of the MD1 in this solvent. The similar behavior has been observed also in the case of MD2.

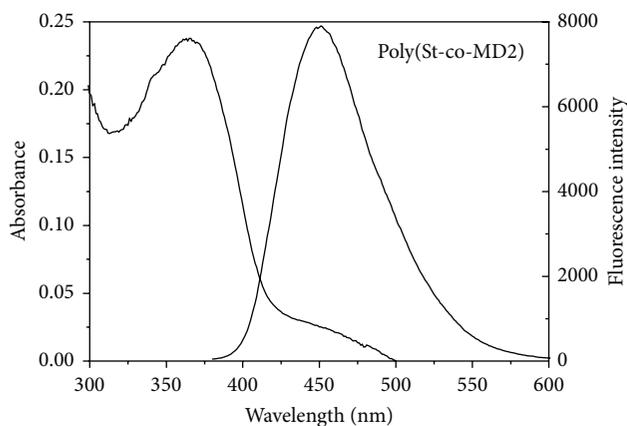
The spectral characteristics of poly(St-co-MD) in the solid state are of interest in order to evaluate this copolymer as a heterogeneous fluorescent sensor. The copolymer was transparent and colourless, emitting blue fluorescence. The absorption and fluorescence spectra of poly(St-co-MD) in the solid state as a thin polymer film ($d = 40 \mu\text{m}$) are presented

TABLE 1: Photophysical characteristics of the MD1 in organic solvents of different polarities (see text).

Solvent	λ_{abs} (nm)	λ_{flu} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	$\nu_A - \nu_F$ (cm ⁻¹)	Φ_F	E_F	f
Dimethyl sulfoxide	375	458	11100	4833	0.03	0.03	0.12
Dimethylformamide	374	452	11900	4614	0.03	0.05	0.12
Acetonitrile	371	452	13000	4830	0.07	0.09	0.14
Methanol	366	463	11900	5724	0.03	0.03	0.15
Ethanol	370	458	12000	5193	0.04	0.04	0.14
Acetone	372	450	12700	4660	0.01	0.02	0.13
Dichloromethane	374	445	13100	4266	0.05	0.09	0.12
Tetrahydrofuran	373	442	11500	4185	0.10	0.18	0.10
Chloroform	374	440	11700	4215	0.08	0.16	0.11

TABLE 2: Photophysical characteristics of the MD2 in organic solvents of different polarities (see text).

Solvent	λ_{abs} (nm)	λ_{flu} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	$\nu_A - \nu_F$ (cm ⁻¹)	Φ_F	E_F	f
Dimethyl sulfoxide	375	451	11400	4494	0.04	0.02	0.11
Dimethylformamide	374	448	12500	4417	0.06	0.03	0.12
Acetonitrile	372	434	13200	3840	0.11	0.05	0.11
Methanol	366	458	12300	5488	0.04	0.03	0.15
Ethanol	370	450	11500	4805	0.05	0.03	0.12
Acetone	372	434	12400	3840	0.02	0.01	0.10
Dichloromethane	375	451	13400	4494	0.10	0.04	0.13
Tetrahydrofuran	373	434	11500	3768	0.20	0.09	0.09
Chloroform	375	445	12400	4195	0.19	0.06	0.11

FIGURE 1: Absorption and fluorescence spectra of poly(St-co-MD2) in solid state as a thin polymer film ($d = 40 \mu\text{m}$).

in Figure 1, from which it is evident that the excitation and fluorescence spectra have bands with a single maximum at 365 nm and 450 nm, respectively. The spectral characteristics of the former reveal that the chemical structure of the chromophoric system does not change its conformation in the solid state.

3.2. Molecular Weight and Spectral Characteristics of Poly(St-co-MD). The amount of MDs incorporated into the polymer macromolecules has been determined spectrophotometrically by using a standard curve [17]. The results show that

1.53 wt% for MD1 and 1.45 wt% for MD2 have bonded to the polymer chain. Considering that the value was obtained for repeatedly precipitated copolymer where low molecular weight fractions have been removed during precipitation, the results are rather satisfactory and imply that the MDs are suitable for production of a blue fluorescent copolymer of polystyrene. This fact also demonstrated that some amount from MDs has been bonded to the low molar weight fractions of the polymer chains.

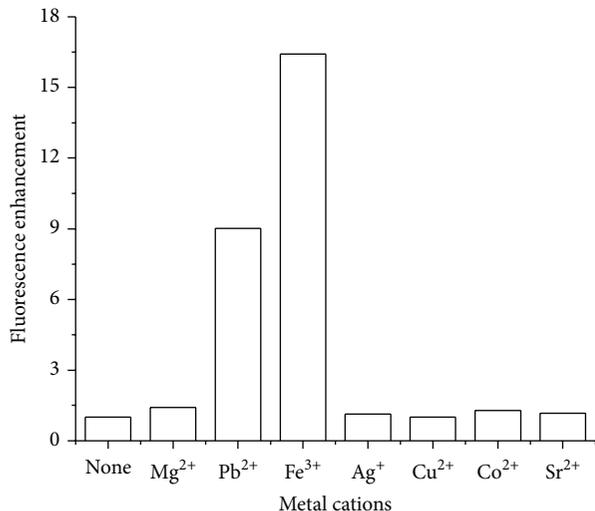
The molecular weight characteristics of the copolymers obtained are collected in Table 3. The molecular weight and molecular weight distribution confirm the formation of high molecular weight polymers. The molecular weights were found to range between $M_w = 1.11$ and 1.34×10^{-5} and $M_n = 0.68 - 0.75 \times 10^{-5}$ for copolymers with polydispersity M_w/M_n 1.63 and 1.78, respectively. The double detection shows close values for the elution time in both chromatograms indicating the presence of copolymers which absorb at about 375 nm in tetrahydrofuran solution.

4. Effect of the Metal Cations on the Fluorescence Intensity of the MDs

The photophysical properties of MDs in the presence of different metal cations (Ag^+ , Mg^{2+} , Cu^{2+} , Sr^{2+} , Co^{2+} , Pb^{2+} , and Fe^{3+}) have been investigated in the view of their potential sensor application. The ability of both MDs to detect metal cations has been tested in acetonitrile solution by monitoring the changes in their absorption and fluorescence spectra in the presence of various metal cations. Acetonitrile

TABLE 3: Molecular weight and spectral characteristics in tetrahydrofuran solution of the copolymers (see text).

	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	λ_A (nm)	λ_F (nm)	$(\nu_E - \nu_F) \text{ cm}^{-1}$
Poly(St-co-MD1)	1.11	0.68	1.63	375	421	2914
Poly(St-co-MD2)	1.34	0.75	1.78	373	428	3446

FIGURE 2: Effect of the metal cations at concentration $c = 10^{-5} \text{ mol L}^{-1}$ on the fluorescence of MD1 in acetonitrile solution.

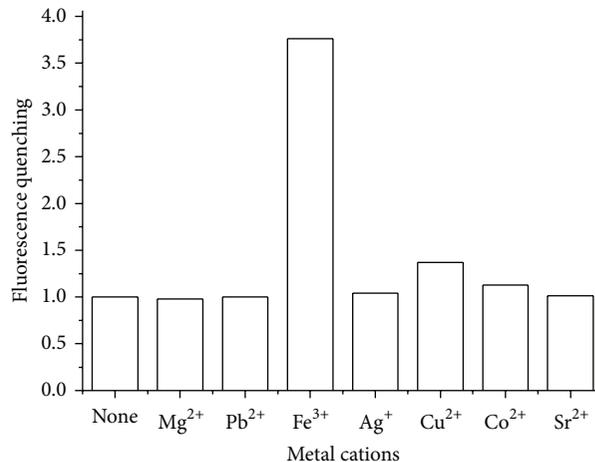
was chosen as solvent for all spectral measurements as it guarantee good solubility of the metal salts, ligands, and the respective complexes. Its ability to mix well with water allows direct usage of aqueous solutions of the metal salts in this study.

In the presence of the guest metal cations an enhancement or quenching of fluorescence intensity was observed. The enhancement (FE) and the quenching (FQ) of the fluorescence emission have been used as a qualitative parameter for the detection of metal cations. $FE = I/I_0$ was determined from the ratio of maximum fluorescence intensity I , after the addition of metal cation, and minimum fluorescence intensity I_0 , before metal cation addition. The $FQ = I_0/I$ has been determined from the ratio between the maximum fluorescence intensity (I_0 , solution free of metal cations) and the fluorescence intensity in the presence of metal cations (I).

Figures 2 and 3 present the calculated FQ and FE results for MD1 and MD2.

The highest enhancement of the monomer fluorescence intensity is observed in the presence of Fe^{3+} cations for compound MD1 ($FE = 16.42$) as can be seen from Figure 2. In the presence of Pb^{2+} cations MD1 increases the fluorescence intensity with the respective $FE = 9.05$. The influence of the other cations under study ($\text{Mg}^{2+} > \text{Co}^{2+} > \text{Sr}^{2+} > \text{Ag}^+ > \text{Cu}^{2+}$) on the fluorescence intensity is negligible.

Figure 3 shows the fluorescence quenching of MD2 upon the addition of cations. As seen the strongest effect is again observed for Fe^{3+} . In this case the complexation with Fe^{3+} cations destabilizes the planarity of the 1,8-naphthalimide molecule and as a result the fluorescence is

FIGURE 3: Fluorescence quenching factor of MD2 in the presence of different metal cations ($c = 2 \times 10^{-5} \text{ mol L}^{-1}$) in acetonitrile solution.

quenched, while Pb^{2+} , Mg^{2+} , Co^{2+} , Sr^{2+} , Cu^{2+} , and Ag^+ cations do not affect the fluorescence intensity of the MD2. Probably MD2 does not form a stable complex with these cations.

5. Effect of the Metal Cations on the Fluorescence of Poly(St-co-MDs)

The presence of the guest metal cations (Cu^{2+} , Sr^{2+} , Co^{2+} , Ni^{2+} , and Fe^{3+}) in poly(St-co-MD) solution in this work is signaled by the quenching of the fluorescence intensity. The changes of the fluorescence intensity of poly(St-co-MD1) in aqueous solution, induced by the metal cations, have been investigated and the respective fluorescence responses of a polymer chromophore are presented in Figure 4. As it can be seen the addition of metal cations leads to a decrease of the polymer fluorescence intensity, different for each metal cation. In the case of Cu^{2+} , Sr^{2+} , Co^{2+} , and Ni^{2+} , the effect of metal cations on the fluorescence intensity is insignificant and the respective alteration of the fluorescent intensity is only 1–5%. The highest effect was observed in the presence of Fe^{3+} cations. In this case the quenching of the fluorescence intensity is 96%. A similar effect has been observed and in the case of poly(St-co-MD2) also. It reveals the good potential of both polymers as effective heterogeneous sensors for detection of Fe^{3+} ions in aqueous solutions even in the presence of other metal ions. These results were in good accordance with our other studies using polymer sensors for detecting metal ions in aqueous media [5–7]. In the form of solid polymer film these heterogeneous sensors can be

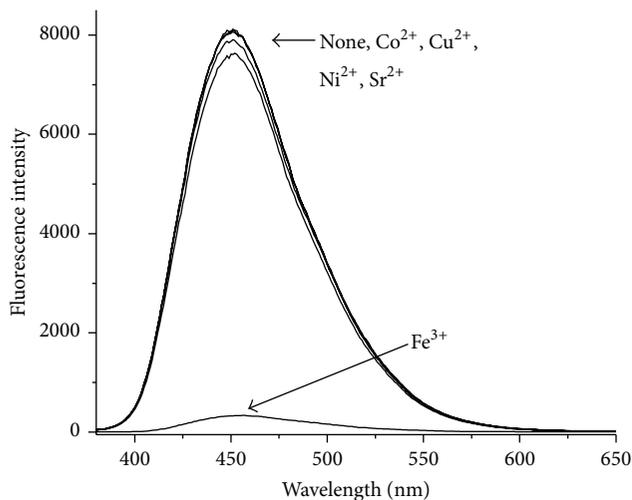


FIGURE 4: Effect of the metal cations at concentration $c = 2 \times 10^{-4} \text{ mol L}^{-1}$ on the fluorescence of poly(St-co-MD1) in aqueous solution.

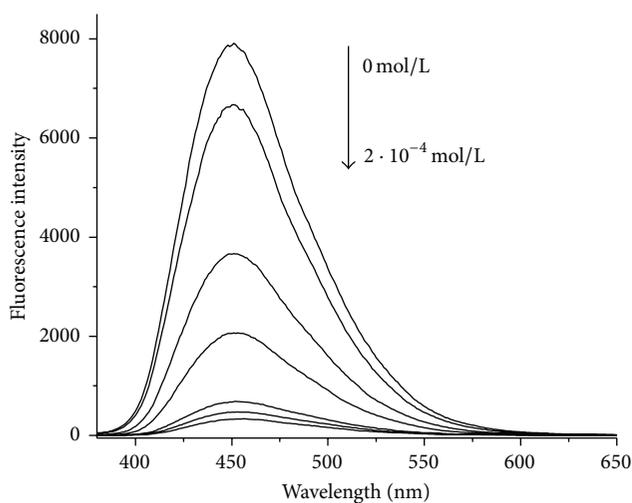


FIGURE 5: The influence of Fe^{3+} cations on the fluorescence intensity of the poly(St-co-MD1) at different concentrations of Fe^{3+} in aqueous solution.

used repeatedly for detection in aqueous solutions after prior removal of the coordinated metal ions.

The typical change in the fluorescence intensity of the copolymer induced by Fe^{3+} cations has been presented in Figure 5. The decrease of fluorescence intensity occurs after the addition of Fe^{3+} cations up to $2 \times 10^{-4} \text{ M}$. It is seen that the initial addition of the Fe^{3+} cations ($5 \times 10^{-5} \text{ M}$) to the polymer leads to a decrease of the fluorescent intensity and the respective quenching effect is 31% which indicates very good sensor sensitivity. Further addition of the Fe^{3+} cations into the polymer solution decreases the fluorescence intensity more as can be seen in Figure 5. At high metal concentrations the fluorescence quenching is not full, which is probably due to a competition between the metal cations and

the respective counterions from the solution for coordination with the chromophore site.

6. Conclusion

In this paper we discuss the synthesis and some functional properties of two new blue fluorescent polymerizable 1,8-naphthalimides and their copolymers with styrene. The photophysical characteristics of both low and high molecular weight fluorophores have been investigated. The influence of various metal cations (Ag^+ , Mg^{2+} , Cu^{2+} , Sr^{2+} , Co^{2+} , Pb^{2+} , and Fe^{3+}) on the fluorescence intensity of the new 1,8-naphthalimides has been studied with regard to their potential application as fluorescent sensors for metal ions. It has been shown that the fluorescence intensity depends strongly on the nature of metal cations. The new monomer compounds can detect Pb^{2+} and Fe^{3+} . It has been shown that the blue fluorescent polymer films possess properties allowing their use as sensors for Fe^{3+} cations. On the basis of the present investigation it can be assumed that the new monomers and fluorescent copolymers are suitable for the selective detection of Fe^{3+} cations.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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