Synthesis of a fluorescent dye for preparing of self-colored polymer based on naphthalimide

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Abstract— **A novel fluorescent dye based on naphthalimide has been synthesized from 4-bromo-1,8-naphthalic anhydride. This compound was reacted with N-ethylglycinate and buthylenediamine, respectively. Purification of products was carried out through recrystalization and characterized by means of FTIR, ^{1}HNMR and ^{13}CNMR spectroscopic techniques. The maximum absorption wavelength, extinction coefficient and fluorescent spectra of the dye together with quantum yield have been evaluated in DMF and toluene solvents. Results showed that the synthesized dye has positive solvatochromism effect and good color strength in yellow hue. This dye was grafted to the chain of a polymer leading to colored fluorescent polymer. In this study novel polymer with naphthalimide pendant group were prepared. The ability of the dye for grafting to polymer chain was demonstrated that 95% dye incorporated in to the polymer chain.**

Keywords — Synthesis, Dye, Fluorescent, 1,8-Naphthalimide, Self-colored polymer.

I. Introduction

In the last three decades 1,8-naphthalimides and their 4-substituted derivatives have been the subject of many scientific investigations [1]. Derivatives of 1,8-naphthalimide usually exhibit strong fluorescent properties. Generally, the excellent fluorescent properties of commercial 1,8-naphthalimide compounds depend largely on the presence of strong electron donating groups, as alkoxy and alkylamine, at the C-4 position [2]. For example 4-aminonaphthalimide compounds tend to show fluorescent properties due to having amino derivatives as donor groups, and two carbonyl groups as the acceptor groups. The acceptor and donor behavior of these substituents should bring about a considerable bathochromic effect.

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Fluorescent dyes are currently of great interest in various application fields [3], so the 1,8-naphthalimide derivatives, because of their strong fluorescence and good photo-stability were used in different scientific areas including laser active media [4], potential photosensitive biologically active unites [5], fluorescent markers in biology [6], analgetics in medicine [7], dyeing of fibers [8-10], photo-induced electron transfer sensors[11], organic light-emitting diodes[12], as well as "guest-host" liquid-crystal systems [13].

During recent years many researchers have synthesized fluorescent polymerisable compounds from derivatives of 1,8-naphthalimide [14] to investigate their ability to copolymerize with styrene, methylmethacrylate or acrylonitrile, obtaining copolymers with remarkable fluorescence [15] . Copolymers of 1,8-naphthalimide with vinyl monomers have been obtained using free radical mass polymerization [16], cation solution polymerization [17] and condensation polymerization [18]. However, there is a little published works concern the preparation of fluorescent polymers using a polymer and chain-grafting a naphthalimide fluorescent dye to it.

In this research, the photo-physical and photochemical properties of a novel 1,8-naphthalimide dye are reported. The chain-grafting process of a new fluorescent 4-(4-aminobutyl) amino-N-ethylglycinate-1,8-naphthalimide dye to an acrylic polymer, in toluene solution, yielding colored polymer has been investigated with some of their properties such as fluorescence and absorbance considered. Therefore, novel dye was used for grafting an acrylic polymer with side chain carboxylic groups. Thus, a fluorescent intrinsically colored polymer were obtained and the synthesis of this colored polymer and their intermediates are showed in Fig 1.
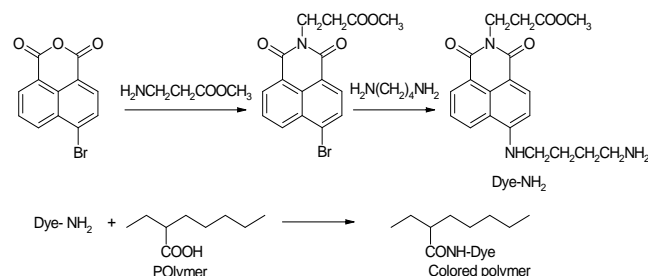

Figure 1. Synthesis of dye and colored polymer

II. Experimental

All organic solvents and materials used in this study were purchased from Merck and Aldrich Companies. These materials were pure and used as received. UV-Vis absorption spectra of dye and colored polymer were performed on a Double beam CECIL 9200 spectrophotometer in DMF and

toluene solutions. The fluorescence excitation and emission spectra were recorded with Osean Optics Usb2000flg Fluorometer. Fluorescence quantum yield was calculated on the basis of the absorption and fluorescence spectra of fluorescein as standard (Φ=0.95). To determine fluorescent properties of dye, a solution with concentration of 10^{-4} M of the synthesized dye was prepared in toluene. ^{1}HNMR and ^{13}CNMR measurements were performed on a Bruker, 500 MHz instruments, in DMSO-d6 solution at ambient conditions. FTIR spectra were evaluated by a NICOLET IR 100/ FTIR spectrophotometer, using KBr pellets. Melting points and glass transition temperature of colored polymer were obtained using a Perkin-Elmer Pyris 6 differential scanning calorimeter.

A. *Synthesis of 4-bromo-N-ethylglycinate - 1,8-naphthalimide*

4-Bromo-1,8-naphthalic anhydride (5.6 g, 20 mmol) was dispersed in 100 mL ethanol and ethylglycinate hydrochloride (29 mmol, 4 g) was added to it at 70ºC. The solution was refluxed for 10 h and a solution of 20% wt NaOH used to adjust pH between 5 and 6. After that, the liquor was cooled, poured onto 100 mL distilled water, remained for 2 h, filtered, washed and dried in oven at 50-60 ºC. Then the precipitate was recrystallised from ethanol[20]. Yield: 56%; m.p: 146 ºC; FTIR (KBr, cm^{-1}): 3080 (C–H str. Ar), 2968 (C–H str. Aliphatic), 1648 and 1688 (C=O str. Carbonyl), 1513 (C=C str. Ar), 426 (C-Br); ^{1}HNMR (500 MHz, DMSO): 1.20-1.23 (t, 3H, J=7.53 Hz,CH_3), 4.02 (s, 2H, N-CH_2), 4.09–4.13 (q, 2H, J=7.8 Hz, CH_2CH_3), 7.96–8.00 (t,1H, J=7.8 Hz, C-6), 8.21–8.22 (d, 1H, J=7.6 Hz, C-3), 8.31–8.33 (d,1H, J=7.9 Hz, C-2),8.51-8.52 (d, J=8.0 Hz, 1H, C-7), 8.85–8.86 (d, J=7.1 Hz, 1H, C-5); 1[3]CNMR (125 MHz, DMSO): 14.1, 44.2, 66.0, 124.2, 125.1, 125.4, 129.2, 130.5, 132.4, 132.5, 136.7, 137.2, 137.8, 159.6, 159.6, 167.5.

B. *Synthesis of 4-(4-aminobutyl) amino-N-ethylglycinate-1,8-naphthalimide*

0.1 g of CuSO$_4$.5H$_2$O was added to a solution of butylenediamine (7.93 g, 90 mmol) and 4-bromo-N-ethylglycinate-1,8-naphthalimide (1.2 g, 3 mmol) in 15 mL of DMF. The resulting mixture was stirring under reflux for 5 h. After cooling down to room temperature, the solution was poured onto 100 mL of water, and the precipitate was collected by filtration, washed with water and dried. Recrystallization from toluene leaded pure main product [21]. Yield: 53%; m.p: 117ºC; FTIR (KBr, cm^{-1}): 3387-3395 (N-H Str. amine), 3040 (C–H str. Ar), 2931 (C–H str. Aliphatic), 1640, 1690 (C=O str. Carbonyl), 1539 (C=C str. Aromatic ring); ^{1}HNMR (500 MHz, DMSO): 1.10-1.14 (t, 3H, J=7.24 Hz, CH$_3$),1.45-1.50 (m , 2H, J=7.70, -NH-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$), 1.52-1.56 (m , 2H, J=7.67, -NH-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$), 2.64-2.69 (m , 2H, J=8.34, -NH-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$), 3.35-3.40 (q, 2H, J=7.80, -NH-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$), 4.00-4.03 (t, 1H, J=7.88, -NH-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$), 4.18 (s, 2H, N-CH$_2$), 4.27-4.32 (q, 2H, J=8.41, CH$_2$CH$_3$), 5.10–5.13 (t, 2H, J=7.86 Hz, -NH-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$), 7.21–7.22 (d, 1H, J=7.85 Hz, C-3), 7.75–7.78 (t,

1H, J=7.36 Hz, C-6), 8.23-8.25(d, 1H, J=7.87 Hz, C-2), 8.33–8.34(d, 1H, J=8.51 Hz, C-7), 8.39–8.40 (d, 1H, J=7.51 Hz, C-5); 13CNMR (125 MHz, DMSO): 9.4, 25.9, 26.2, 41.7, 47.3, 51.5, 70.7, 112.0, 116.5, 121.7, 124.1, 126.1, 128.4, 130.5, 132.5, 137.2, 137.4, 159.6, 159.6, 172.7.

C. *Grafting dye into the polymer chain*

Acrylic resin (5 g) was added to 20 ml of a solution of dye in toluene (1 M). The mixture was refluxed for 1 h. Afterwards, the produced water of reaction was collected for 30 min and a thin film of polymer's solution was prepared. After 24 h a transparent colored polymer with obvious fluorescence was obtained.

D. *Spectral characteristics of dye and colored polymer*

The absorption properties of the synthesized dye were evaluated in DMF and toluene solvents. The concentrations of solutions were 5×10^{-6}, 1×10^{-5}, 1.5×10^{-5} and 2.5×10^{-5} M.

Fluorescent spectrum of dye is assessed by a 10^{-5} M solution of dye in toluene, but for measuring fluorescence spectrum of polymer a 5 g/l solution of polymer was prepared.

III. **Results and discussion**

The main intermediate was 4-bromo-N-ethylglycinate-1,8-naphthalimide which obtained by imidation reaction. The imidation of aromatic cyclic anhydride is a nucleophilic displacement reaction in which the amino group in ethylglycinate is the attacks the carbonyl groups in naphthalic anhydride. In this reaction, bromo group on naphthalene ring is not replaced. In order to obtain colored polymers from 4-(4-aminobutyl)amino-N-ethylglycinate-1,8-naphthalimide, the bromine atom in the intermediate of 4-bromo-N-ethyl glycinate-1,8-naphthalimide is substituted by the nucleophilic reaction of 1,4-diaminobutane (synthesized dye).

In the next step, the amino group of dye was reacted with the carboxylic acid groups of selected polymer chain and converted into amide group. This reaction was characterized by spectrophotometer, acid number and FTIR techniques. In spectrophotometric method, the colored polymer was dissolved in toluene and its absorbance (A1) was measured by UV-Vis spectrophotometer. Afterwards polymer solution was precipitated in methanol solution. Since the dye is soluble in both solvents, methanol and toluene, the unreacted dye remain in the solution above the precipitation. After evaporation of the solvent the residue was dissolved in toluene and its absorbance was measured at maximum wavelength (A2). Then the percentage of reacted dye (P%) was determined according to equation (1). The results indicated that 95% of the dye was incorporated into the polymer chains[19].

$$P(\%)=(A1-A2)/A1 \cdot 100 \qquad (1)$$

In Acid Number (χ), at first solid percent of the resin was measured. Then 5 g of resin was dissolved in a 100 mL mixture of toluene (30 mL) and isopropyl alcohol (70 mL) with 1 mL of phenolphthalein as indicator. KOH solution (0.1

N) was poured into a burette, and added to the resin solution during stirring. The end point of the reaction was determined when a steady purple color for 30 seconds emerged. Acid number was calculated by equation (2).

$$\chi=(\nu*N*56.1)/\alpha*\beta \qquad (2)$$

In which, ν is the volume of used KOH solution, N is the normality of KOH solution. α and β are weights of resin sample and its solid percent, respectively.

The reduction of carboxylic acid groups shows the grafting reaction between acrylic resin and synthesized dye which is demonstrated with the amount of acid number. For this purpose, acid number of resin and final product was measured according to equation 2. The acid number of plain resin was in the range of 18-24 .The acid number of colored polymer solution were 8-11. The decline in the acid number of resin sample showed that the carboxylic acid groups have been converted into the amide groups, and this is a factor determining the reaction between NH_2 groups of dye and COOH groups of resin.

FTIR data of polymer and colored polymer were evaluated. Since there is no amide groups in the resin structure and dye, so it could be concluded that the amide groups peaks are related to the spectra of colored polymers. This shows that the resin has successfully reacted with dye. It is obvious from polymer FTIR spectra; the range of 1640-1670 cm^{-1} is attributed to the formation of amide groups.

A. *Spectral characteristics of dye and colored polymers*

The absorption properties were evaluated in two organic solvents with different polarities to investigate their solvatochromic effects. Recently in different projects it has been shown that the photo-physical properties of 1,8-naphthalimide derivatives are sensitive to the polarization of dye molecules and the solvents [22]. The polarization of 1,8-naphthalimide molecule is basically related to the electron donor-acceptor interaction between the substituents at C-4 position and the carbonyl groups from the imide structure of the naphthalimide. Absorption maximum wavelengths and extinction coefficient of dye in DMF as a polar solvent and toluene as a non-polar solvent are demonstrated in Table I.

Table I. The photophysical characteristics of the dye

Solvent	ε_{max} (Lmol^{-1} cm^{-1})	λ_{max} (nm)
Toluene	18518	425
DMF	18675	438

The intermediate of 4-bromo-N-ethyglycinate-1,8-naphthalimide which has a bromine atom as a substituent at C-4 position is a colorless compound and shows absorption maximum wavelength in the UV region at 335 nm and 337 nm in toluene and DMF solutions, respectively. Substitution of bromine atom of 4-bromo-N-ethylglycinate-1,8-naphthalimide with 1,4-diaminobutane which is an electron donating group results in a bathochromic shift of absorption maximum

wavelength, due to the naphthalimide fluorophore is polarized, and the absorption maximum wavelength of dye is 425 nm. The absorption wavelength maxima of 1,8-naphthalimide derivatives are clearly altered with a change in solvents polarity. It could be concluded that dye has positive solvatochromic effect (Table 1), which is due to the increasing polarity of the solvent.

The fluorescent properties of dye could be evaluated with different parameters such as fluorescence maxima, fluorescence quantum yield, and Stokes shift. These fluorescent characteristics of dye and colored polymer are summarized in Table II. The dye show vivid yellow-green fluorescence in toluene solution due to the charge transfer in the naphthalimide units from the electron donating amino group at C-4 position to the accepting carbonyl groups [22]. In this research, it could be concluded that the presence of electron amino donating groups in C-4 position of naphthalimide derivatives result in a red shift.

Table II. Fluorescence data of dye and colored polymer

Compound	λ_s (nm)	ν_A-ν_F (cm^{-1})	Φ_F (%)
Dye	487	2995	51
Coloured polymer	487	3036	-

The emission maxima of dye and colored polymer reveal the similar polarization of the chromophoric system in the dye molecule and the colored polymer, so it could be deduced that the grafting process has no effect on the fluorescent properties [23]. The efficiency of the fluorescence process is quantitavely characterized by the fluorescence quantum yield (Φ_Γ). As a matter of fact, quantum yield is the ratio of the number of photons emitted to the number of photons absorbed, so it could be estimated from the absorption and fluorescence spectra of the samples by equation (3) [24]. For calculating the quantum yield of fluorescent compound fluoroscein was used ($\Phi_\tau = 0.95$) as a standard.

$$\Phi_\Gamma = \Phi_\tau(\varsigma_I/\varsigma_{II})(A_{II}/A_I)(\eta_{II}^2/\eta_I^2) \qquad (3)$$

Where Φ_Γ is the emission quantum yield of the sample, Φ_τ is the emission quantum yield of the fluorescein (standard) and A_I and A_{II} are the absorbances of the sample and the fluorescein, respectively. ς_I and ς_{II} represent the integrated respective emission band areas of the sample and the fluorescein as a standard agent. Here η_{II} is the solvent refractive index of the sample and η_I is the solvent refractive index of the standard agent (water).

Both quantum yield and Stokes shift are important parameters for evaluating the fluorescent properties of the synthesized dye. The Stokes shift is a parameter which indicates the difference in properties and structure of the dyes between the ground state S_0 and the first excited state S_1. The Stokes shift was calculated according to the absorption maximum wavelength and fluorescence maximum wavelength by equation (4) [25].

$$\nu_A-\nu_B = (1/\lambda_A - 1/\lambda_B)* 10^7 \qquad (4)$$

Where λ_A is absorption maximum wavelength and λ_B is fluorescence maximum wavelength.

A collection of fluorescent compounds based on 1,8-naphthalimide were synthesized and their fluorescent properties reported by other researchers. The reported quantum yields of naphthalimides by other researchers were around 50-60% [23-28].

The spectral characteristics of colored polymer were also investigated. The colored polymer has demonstrated considerable fluorescence in toluene solution. The absorption and fluorescence maxima of the colored polymer in toluene was similar to the dye in the same solution. So it could be inferred that during the grafting process, there is no change in the chemical structure of the dye's chromophoric system [25].

IV. Conclusion

A novel naphthalimide dye has been prepared based on naphthalic anhydride by imidation and amination processes. The characterization of the synthesized dye has been carried out by utilizing FTIR, DSC, ^{1}HNMR and ^{13}CNMR techniques which confirmed their chemical structure.

The synthesized dye was employed to produce self-colored polymer from reaction between carboxylic acid containing polymer and aforementioned dye. The results denoted that the dye was covalently bonded to the chain of an acrylic polymer containing carboxylic acid groups giving self-colored fluorescent polymer i.e. polymer with naphthalimide groups. The ability of the dye for covalently bonding to polymer chain was examined, and percentage of the covalently bound dye into the polymer chain was% 95.

The absorption spectra of dye in both toluene and DMF solvents with different polarity were appraised and the results obviously showed its solvatochromism properties. Although with respect of absorption results, it could be judged that the substitution of bromine atom of 4-bromo-N-ethyglycinate-1,8-naphthalimide with electron donating groups of diaminobutane in dye leads to a bathochromic shift.

The fluorescence excitation and emission spectra for dye and colored polymer were recorded in toluene solution. Results revealed that the amino group in C-4 position of 1,8-naphthalimide dye can affect their fluorescent properties. It could be deduced that the presence of electron amino donating group in C-4 position of naphthalimide derivatives result in a red shift.

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