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Preparation, characterization and fluorimetric studies of novel photoactive poly(amide-imide) from 1-naphthaldehyde and 2,6-diaminopyridine by microwave-irradiation

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Abstract

Trimellitic anhydride acid chloride (**2**) was obtained by the reaction of trimellitic anhydride (**1**) and excess amount of thionyl chloride. The acid chloride was reacted with 2,6-diamino pyridine (**3**), and produced the monomer **4**. 1-Naphthaldehyde (**5**) was reacted with sulfuryl chloride to produce 1-naphthoyl chloride (**6**) in a quantitative yield. Through the reaction of **6** and 1,3,5-triazine-2,4,6-triamine (**7**), the monomer **8** was produced in high yield. Two monomers were characterized by ^{1}H NMR and FT-IR spectroscopy, and then were used in the polymerization reaction. A new facile and rapid polycondensation reaction of the two monomers was performed by using a domestic microwave oven. The polymerization reaction proceeded rapidly, compared with the conventional solution polycondensation and was completed within 8 min, producing a photoactive poly(amide-imide) in a quantitative yield. The resulting polymer was characterized by IR, ^{1}H NMR and thermal gravimetric analysis (TGA) techniques. Thermogravimetric analysis indicated that polymer **9** was thermally stable in nitrogen atmosphere. In addition the initial decomposition temperature (IDT), 5 and 10% weight loss (T_5, T_{10}) were 265.85 and 292.85 °C. The residual weight percent at 500 °C was 50%, which shows it is moderately thermally stable. Fluorescence properties of polymer **9** were investigated in several solvents. The ideal concentration of each case was determined by fluorescence self-quenching phenomena. Also the self-quenching mechanism was studied according to the specific behavior of the polymer in different solvents.

Keywords: Poly(amide-imide); Polycondensation; Photoactive polymer; Microwave irradiation; Fluorimetric studies

1. 1 Introduction

Aromatic polyimides and heterocyclics are known as high-performance polymer materials for their excellent electrical and mechanical properties, outstanding solvent resistance, high thermal and thermo-oxidative stability [1,2]. Polyimides with the wide variety of chemical structures have been reported that have excellent thermal stability and chemical resistance [3–9]. Classic polyimides synthesized from dianhydrides of aromatic tetracarboxylic acids and diamines, show valuable properties, such as high glass transition temperature (T_g), along with high decomposition temperatures, noncombustibility, and excellent mechanical properties. However, one major drawback was that they were typically insoluble in organic solvents and do not melt, which limits possible practical application. Several efforts have been made to obtain polyimides with good solubility while maintaining the excellent thermal and mechanical properties [10–15]. The synthesis of monomers with polar groups in the diamines or in the dianhydride molecules is one possible way of solving this problem [16,17].

Most fluorescent polymers obtained by polymerization are essentially the copolymers of low molecular weight luminophores, containing vinyl groups, and conventional unsaturated compounds. The derivatives of naphthalene, anthracene, pyrene, other condensed aromatic hydrocarbons, and some heteroaromatic hydrocarbons such as carbazole and pyrazoline are more considerable in the preparation of photoluminescence polymers [18,19]. These polymers have been widely used in several industries. Some of their applications are as: (i) ionizing radiation recording materials, (ii) luminescent solar concentra-

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tors, (iii) materials for lasers, (iv) materials for the paints and varnish industries, (v) luminescent photolayers, and (vi) luminescent probes in fiber-optic sensors [18].

Since 1775, photochemical, catalytic, sonic and high pressure techniques have been added to the chemists' repertoire for accelerating chemical reactions [20]. In this decade a new technique provided an alternative to conventional conductive heating for introducing energy into reactions. The microwave dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions. This in situ mode of energy conversion has many attractions to the chemist, because its magnitude depends on the properties of the molecules [16,17,21–23].

In this article we report a facile method for rapid synthesis of novel photoactive and thermally stable polyimide containing a naphthalenic pendant group with fluorescent property by using a domestic microwave oven and comparing with conventional solution polymerization results.

2. 2 Experimental

2.1 Materials

All chemicals used in this experiment were purchased from Merck Company. 2,6-Diaminopyridine was purified by recrystalisation in benzene. *N*,*N*-Dimethylacetamide (DMAc) was dried over BaO and then distilled under reduced pressure.

2.2. Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance 400 NMR spectrometer. Multiplicities of proton resonance are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). FT-IR spectra were recorded on a Shimadzu FT/IR-4300 spectrophotomer. The spectra of solids were obtained using KBr pellets. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Thermal gravimetric analysis (TGA) for polymer was taken on a Pyris 1 Perkin-Elmer under N_2 atmosphere at a rate of 20 °C/min. The UV absorption spectra were recorded using a Varian Cary-100 Bio UV–Vis spectrophotometer. Measurements of steady state fluorescence were made using a Varian Cary Eclips spectrofluorophotometer.

2.3. Monomer synthesis

*2.3.1. Preparation of trimellitic acid chloride **2***

Into a 50 ml round-bottomed flask 4 g (2.08×10^{-2} mol) of trimellitic anhydride (**1**) and excess amount of thionyl chloride were placed. The mixture was heated on an oil bath up to 79–80 °C. After about 3 h the suspension mixture was converted to a clear solution. The solution was stirred for 1 h at reflux temperature. The unreacted thionyl chloride was removed under reduced pressure to leave 4.14 g (95%) of a white powder. IR (KBr): 3354.0 (w), 3103.2 (m), 1851.5 (s), 1776.3 (s), 1743.5 (s), 1614.3 (sh), 1425.3 (m), 1087.7 (s), 1043.4 (w), 910.3 (s), 833.2 (s), 821.53 (s), 740.6 (m), 416.6 (w) cm^{-1}. ^{1}H NMR: 8.13–8.35 (m, 2H), 8.74 (d, 1H) ppm.

*2.3.2. Reaction of **2** with 2,6-diaminopyridine **3***

2.89 g (1.37×10^{-2} mol) of trimellitic acid chloride **2**, and 15 ml of DMSO was placed into a 100 ml round-bottomed flask. The acid chloride was dissolved quickly and then 0.75 g (6.85×10^{-3} mol) of 2,6-diaminopyridine **3** was added. The solution was stirred at 80 °C for 24 h and then the mixture was added to 100 ml of water. The dianhydride **4** precipitated immediately and was dried under vacuum to give 2.93 g (94%) of deep red powder.

IR (KBr): 3377.1 (m), 3087.8 (m), 1824.2 (w), 1790.9 (m), 1723.2 (s), 1446.5 (m), 1407.9 (w), 1371.3 (w), 1272.9 (sh), 1238.2 (s), 1124.5 (w), 1012.1 (s), 946.9 (s), 869.8 (sh) cm^{-1}. ^{1}H NMR: 6.62 (d, 2H), 7.20 (t, 1H), 7.9–8.7 (m, 4H), 9.98 (d, 2H), 10.60 (s, 2H) ppm.

*2.3.3. Preparation of 1-naphthoyl chloride **6***

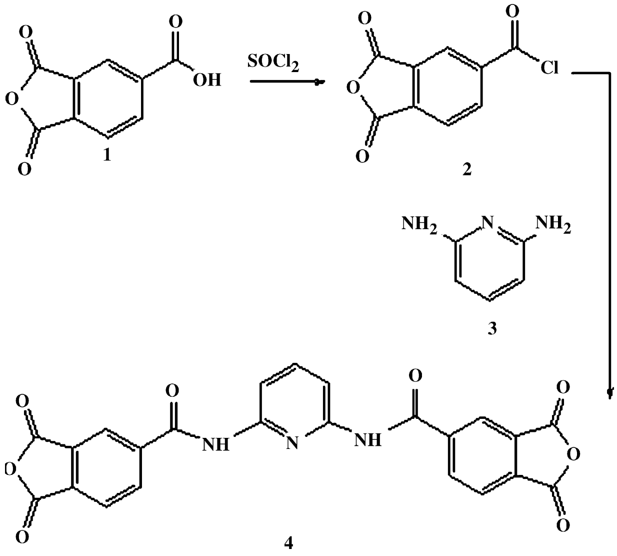
2.0 g (1.28×10^{-2} mol) of 1-naphthaldehyde **5** was placed in a 100 ml round-bottomed flask equipped with a stirrer, a dropping funnel, and a reflux condenser, to which a calcium chloride tube was attached. After the air in the system had been replaced by dry nitrogen, 0.03 g (1.28×10^{-4} mol) of benzoyl peroxide (0.1 wt% of the sulfuryl chloride used), was added to the flask and system was heated to 80 ± 1 °C. When sulfuryl chloride was gradually added through the dropping funnel, the evolution of gas was observed after some induction period. Heating was continued until the gas evolution ceased. After cooling, the hydrogen chloride formed was driven off by heating under vacuum to leave 2.18 g 1-naphtoyl chloride with 90% yield (mp = 26 °C).

*2.3.4. Reaction of **6** and 2,4,6-triamino-2,4,6-triazine **7***

To a solution of 0.99 g (7.85×10^{-3} mol) of 2,4,6-triamino-2,4,6-triazine (**7**) in 8 ml of DMSO, 1.49 g (7.85×10^{-3} mol) of 1-naphthoyl chloride (**6**) was added. The reaction mixture was stirred for an overnight at 85–110 °C. After the completion of the reaction the resulting viscose liquid was poured into distilled water to yield 1.99 g (92%) of *N*-(4,6-diamino-1,3,5-triazin-2-yl)-1-naphthamide (**8**). FT-IR (KBr): 3465.8 (m), 3342.4 (m), 3211.3 (m), 1573.8 (s), 1446.5 (s), 811.9 (m), 779.1 (m) cm^{-1}. ^{1}H NMR: 6.44 (s, 4H), 7.49-8.15 (m, 6H), 9.12-9.14 (dd, 1H), 10.48 (s, 1H) ppm.

2.4. Polymerization reaction

The reaction was performed in a mortar containing 0.25 g of **4** and 0.15 g of **8** and 0.04 ml *o*-cresol. The mixture was well grinded and placed on the center of the turn table in the microwave oven with a power of 2450 MHz that was irradiated for 8 min. The precipitated polymer was washed thoroughly with methanol and filtered to yield 0.36 g polymer **9** (93%). IR (KBr): 3338 (m), 1785 (w), 1728 (s), 1625 (m), 1573 (m), 1352 (m), 1232 (w), 1094 (w), 780 (m), 728 (m) cm^{-1}. ^{1}H NMR: 7.36 (t, 2H), 7.40 (dd, 1H), 7.46–7.98 (br, 4H), 8.05–8.32 (m, 5H), 9.11 (d, 3H), 10.63 (s, 3H).



Scheme 1.

3. 3 Result and discussion

The monomer **4** containing amide groups, was prepared by the two-step procedure as shown in Scheme 1. In the first step, trimellitic anhydride (**1**) was converted into its acid chloride through the reaction with thionyl chloride. In the second step, the symmetric dianhydride **4** was synthesized by the condensation reaction of two equimolar of acid chloride **2** with one equimolar of 2,6-diaminopyridine (**3**) in DMSO (Scheme 1).

The chemical structure of monomer **4** was characterized by FT-IR and ^{1}H NMR spectroscopy. As shown in Fig. 1, the C–Cl group of acid chloride, which appears at about 910 cm^{-1} has been omitted; this confirmed a complete conversion of acid chloride to amide group. Moreover, the amidic N–H and carbonyl groups have been observed at 3377 and 1722 cm^{-1}, respectively. The symmetric and asymmetric stretching vibrations of anhydride ring appeared at 1785 and 1820 cm^{-1}. Aromatic C=C and C–H stretching centered at 1602 and 3126 cm^{-1}.

According to the ^{1}H NMR spectrum (Fig. 2), amidic proton (H$_a$) appeared as a singlet at 10.6 ppm. H$_b$ is observed as a doublet due to its coupling with H$_c$ at meta-position with $J = 3$ Hz. H$_c$ appears as a doublet of doublet due to the coupling with H$_d$ at ortho-position with $J = 9$ Hz and subsequently with H$_b$ by $J = 3$ Hz. H$_d$ couples with H$_c$ with $J = 9$ Hz and overlaps with H$_c$. So the H$_c$ and H$_d$ are appeared in the range of 7.9–8.7 ppm. The environments of protons H$_e$ and H$_f$ are topologically non-equivalent and have different chemical shifts. H$_f$ of the pyridine ring is in meta-position relative to the heterocyclic nitrogen. Therefore, the inductive effect on H$_f$ is less than that of H$_e$ and thus H$_e$ is more deshielded.

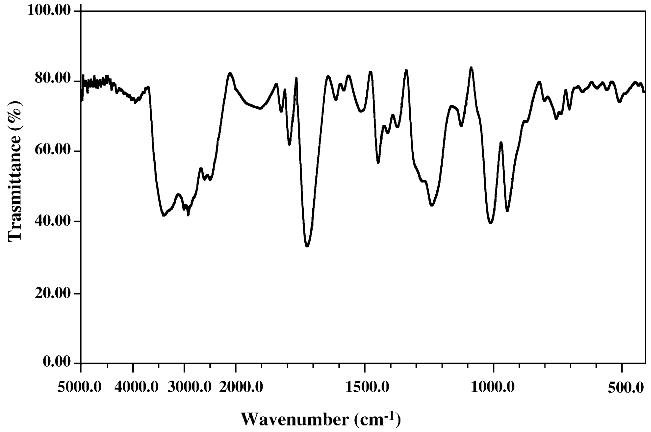


Fig. 1. IR spectrum of monomer **4**.

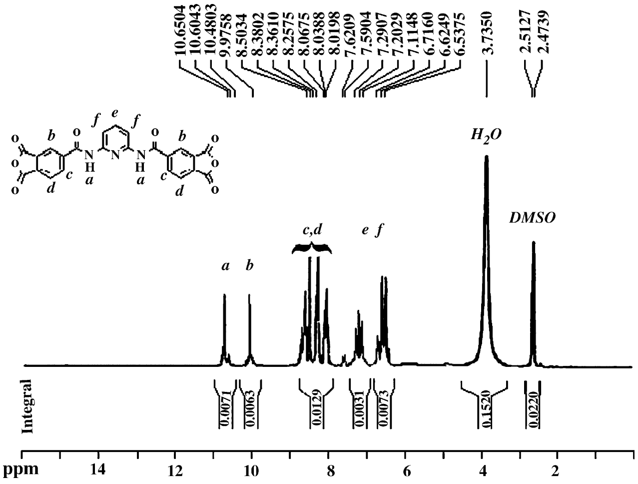
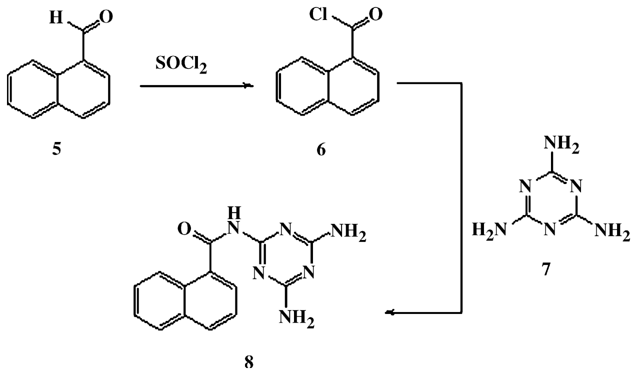


Fig. 2. ^{1}H NMR spectrum of monomer **4**.

The monomer **8** containing a photoactive naphthalenic pendant group was prepared by the reaction of 1-naphthaldehyde (**5**) with sulfuryl chloride, followed by condensation with 2,4,6-triamino-1,3,5-triazine (**7**) (Scheme 2).

The structure of monomer **8** was characterized by FT-IR and ^{1}H NMR spectroscopy. In FT-IR spectrum of compound **8** (Fig. 3), the bands at 1573, 3465 and 1446 cm^{-1} correspond to the stretching vibration of amidic carbonyl group, N–H and aromatic C=N, respectively. Stretching vibration of naphthalenic C–H bonds appears at 3064 cm^{-1}.

There are two types of N–H protons as shown in ^{1}H NMR spectrum (Fig. 4). The amidic N–H (H$_a$) appears as a singlet at 10.48 ppm and the N–H of amine group (H$_i$) is observed as a singlet at 6.44 ppm. H$_b$ is coupled with H$_f$ by $J = 9$ Hz and then couples with H$_h$ by $J = 3$ Hz. Thus, H$_b$ appears as a doublet of doublet at 9.13 ppm. The other naph-



Scheme 2.

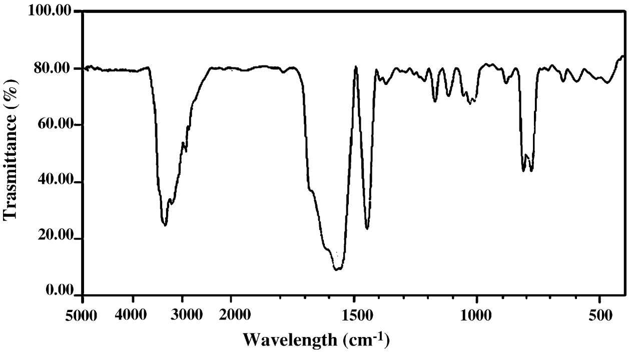


Fig. 3. IR spectrum of monomer **8**.

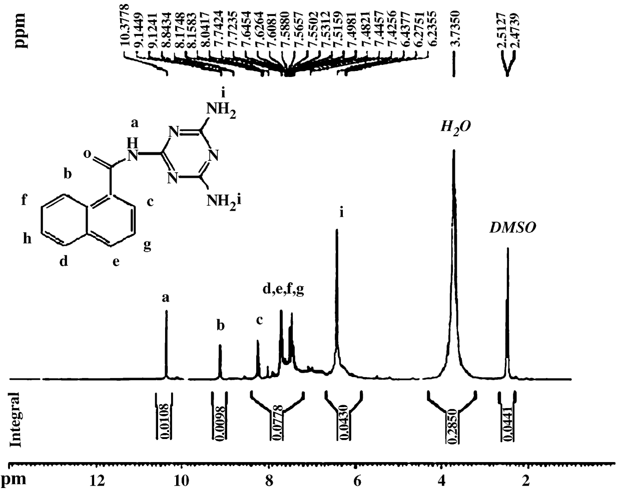


Fig. 4. ^{1}H NMR spectrum of monomer **8**.

thalenic protons are observed as a multiplet peak at 7.42–8.15 ppm.

3.1. Polymerization reaction

Two monomers **4** and **8** were considered for the condensation polymerization reaction. The reaction did not proceed even by applying the long reaction time, higher temperatures and removing the by-product from the reaction media by a Dean-Stark trap. These evidences made us to choose a simple and fast method for performing the polymerization reaction. Microwave radiation energy is very useful for high efficiency utilization of the heat energy. So the application of this technique produces polymers with quantitative yield and high inherent viscosity in a short time. The effective heating utilized in microwave assisted organic transformations is due to dielectric constant (ε) and dielectric loss tangent (δ) of materials. It is particularly convenient that qualitatively, the larger the dielectric constant, the greater the coupling with microwave irradiation. Thus, the use of a small amount of a polar solvent, which is heated when irradiated in a microwave oven, acts: (i) as a primary absorber, and (ii) as a solvent for both the starting and resulting materials. Therefore, the solvent allows induction of effective homogeneous heating to convert monomers into polymers. According to our previous works it has been recognized that the appropriate solvent is *o*-cresol [16,17]. 0.250 g of monomer **4** and one equimolar of monomer **8** were irradiated in 0.04 ml *o*-cresol, for 8 min. The resulting mixture was precipitated in methanol to obtain polymer **9** with a quantitative yield as shown in Scheme 3.

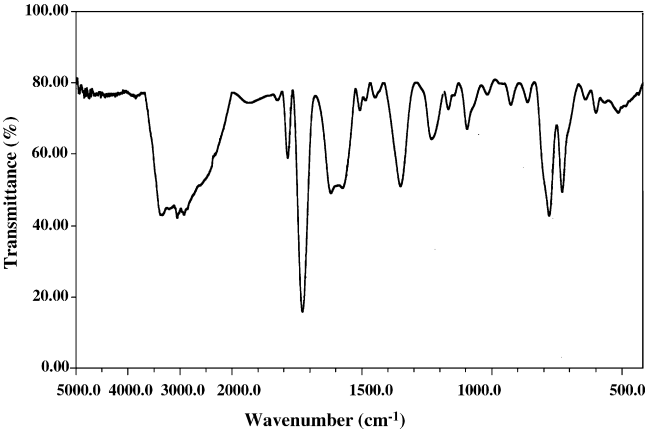
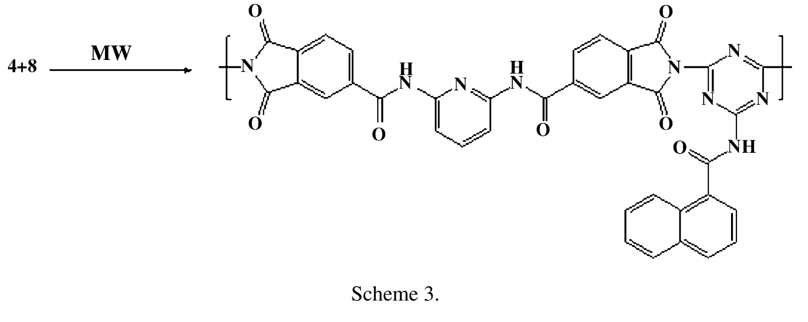


Fig. 5. IR spectrum of polymer **9**.

3.2. Polymer characterization

Comparing the reaction condition of microwave irradiation technique with the solution method shows that the internal heat generation of both of solvent and monomers under microwave irradiation is much more effective than the conventional external heating. Therefore, the microwave irradiation is a convenient method to produce high molecular weight poly(amide-imide) in a shorter polymerization time during condensation polymerization reaction. The structure of this polymer was found to be a poly(amide-imide) by means of FT-IR and ^{1}H NMR spectroscopy.

As shown in FT-IR spectrum of polymer **9**, all bands of the two monomers are observed. The characteristic bands around



Scheme 3.

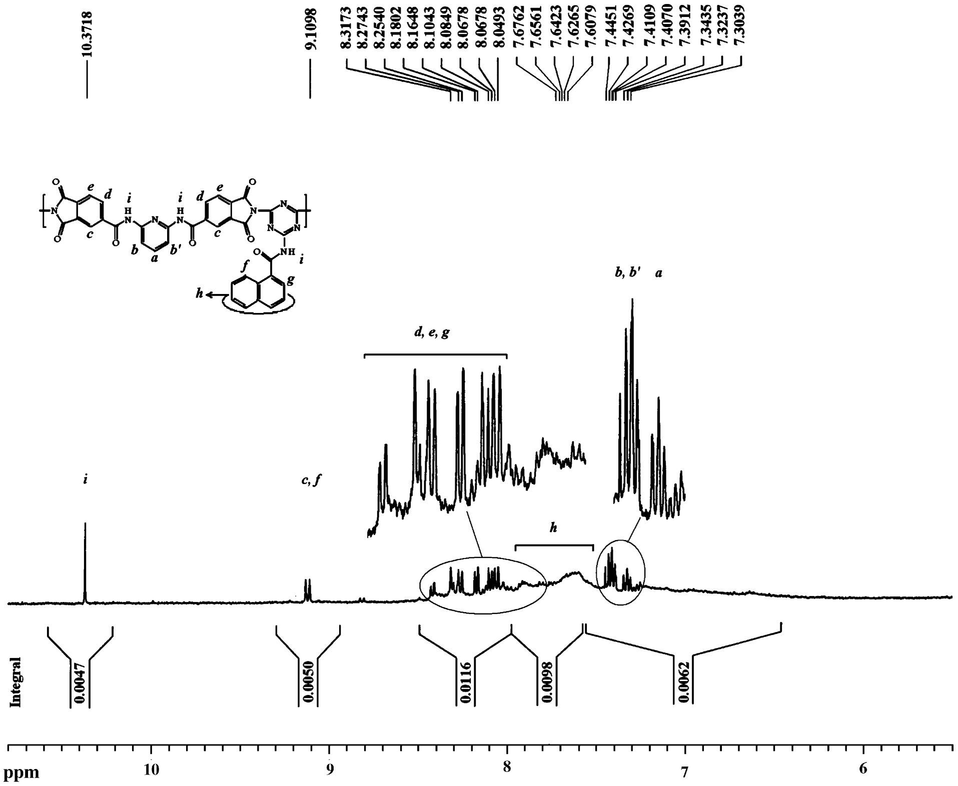


Fig. 6. ^{1}H NMR spectrum of polymer **9**.

3338, 1728 and 1625 cm^{-1} correspond to stretching vibration of amidic N–H, amidic carbonyl groups of pyridine and amidic carbonyl groups of naphthalene, respectively. The anhydride bands at 1820 and 1785 cm^{-1} were placed by imide bands at 1728 and 1785 cm^{-1}(Fig. 5).

There is a triplet (two overlapped doublet) at 7.32 ppm in the ^{1}H NMR spectrum of polymer **9** (Fig. 6). This is related to H_a, which is splitted through the coupling with two H_b and $H_{b'}$ protons. H_b and $H_{b'}$ that couples with H_a appears as two doublet (doublet of doublet) peaks at 7.40 ppm. H_c is coupled with H_d and splits into a doublet ($J = 9$Hz) at 9.11 ppm. H_d, H_e and H_g will give a multiplet peak at 8.05–8.32 ppm according to the anisotropic effect of the carbonyl groups. This anisotropic effect is more sensed for H_f and H_c and will result in deshielding of these protons relative to H_d, H_e and H_g protons ($H_f = 9.11$ ppm). H_i appears at 10.37 ppm, which corresponds to the amidic NH protons. Naphtalenic protons (H_g) that couple together appear as a broad peak at 7.46–7.89 ppm.

The solubility test of polymer **9** has been listed in Table 1. The polymer is soluble in organic solvents such as DMF, DMAc and DMSO and is insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Table 1
Solubility of the polymer **9**

Solvent	Solubility	Solvent	Solubility
H_2SO_4	+	$CHCl_3$	−
Acetic acid	−	CH_2Cl_2	−
DMSO	+	THF	−
DMF	+	Diethyl ether	−
DMAc	+	CCl_4	−
Methanol	−	Toluene	−
Ethanol	−	Cyclohexane	−
Acetone	−	*n*-Hexane	−

+, Soluble at room temperature; −, insoluble.

3.3. Thermal properties

The thermal behavior of polymer **9** was studied by means of thermal gravimetric analysis technique. Fig. 7 shows TGA thermogram of polymer **9** with a heating rate of 20 °C/min under nitrogen atmosphere. The initial decomposition temperature (IDT), 5 and 10% weight loss (T_5, T_{10}) are 246.7, 268.85 and 291.85 °C. The residual weight percent at 700 °C is 42.9% which shows that it is moderately thermally stable.

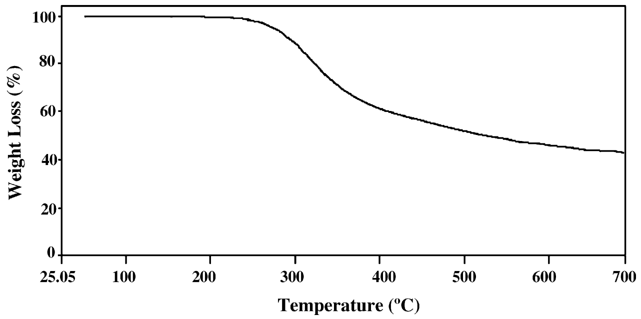


Fig. 7. TGA thermogram of polymer **9** with a heating rate of 20 °C min^{-1} under nitrogen atmosphere.

Table 2
UV-spectroscopic data of polymer **9** in various solvents

Solvent	μ[a]	λ_{max}	ε_{max}
N,*N*-Dimethylacetamide	3.7	275	23243.243
N,*N*-Dimethylformamide	3.82	275	20675.676
N,*N*-Dimethylsulfoxide	3.96	275	20000.000

[a] Dipole moment values of DMAc, DMF and DMSO as solvent at 25 °C [25].

3.4. Fluorimetric studies

UV spectrum of polymer **9** was recorded in DMF, DMAc and DMSO as solvent. A broad peak was observed in the above solvents in which no microstructure was found. The presence of several phenylic groups with different substituents and also naphthalenic moiety are the reasons for broadening of the above peaks. The λ_{max} and ε_{max} data of polymer **9** in the above three solvents have been listed in Table 2. The spectra obtained from the polymer system in different solvents vary in maximum molar extinction coefficient (ε_{max}), but no change is observed in the shape or the position of the band maxima.

The dipole moment amounts of the solvents increase from DMAc to DMF and then DMSO (Table 2). It was expecting to observe the bathochromic shift to lower wavelengths with an increase in ε_{max} by increasing the solvent polarity. This phenomenon is the result of conjugation of carbonyl group with the naphthalenic ring. Increasing the solvent polarity decreases the length of conjugation, which is due to the solvation of oxygen of the carbonyl group. Therefore, the above mentioned shift must be observed because of the difficulty in $\pi \to \pi^*$ transition according to the decreasing in length of conjugation. The difference between solvent dipole moments is so short that changing in solvents only causes a displacement of the maximum molar extinction coefficient (ε_{max}) and do not affect on maximum absorption wavelengths (λ_{max}). A typical spectrum of the molar extinction coefficient versus wavelength at constant polymer concentration in DMF has been shown in Fig. 8.

To investigate the fluorescence behavior of naphthalenic pendent groups, the polymer **9** was excited at λ_{max} of naphthalenic moiety. Emission spectra of polymer **9** were recorded in DMF, DMAc and DMSO by fixing the excitation wavelength at maximum absorption wavelength, i.e. at 275 nm. Consequently, a new band with a maximum around 356 nm appears. Fig. 9 illustrates the relationship between fluorescence intensity of polymer **9** and emission wavelengths at different polymer concentrations in DMF as a solvent.

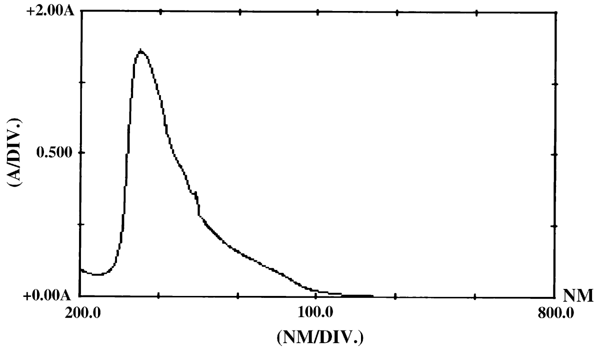


Fig. 8. Absorption spectra of polymer **9** in DMSO at 1.034×10^{-6} M concentration with 1.0 cm optical path.

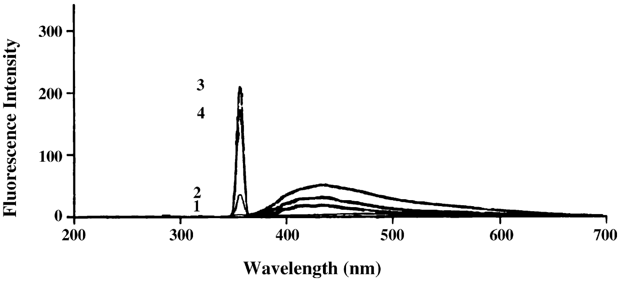


Fig. 9. Self-quenching of polymer **9** in DMF at 1: 4.84×10^{-4} M, 2: 4.84×10^{-5} M, 3: 4.84×10^{-6} M, 4: 4.84×10^{-7} M and 5: 4.84×10^{-8} M of polymer concentrations.

Table 3
Maximum fluorescence wavelengths and fluorescence intensity of polymer **9** in various solvents

Solvent	ε[a]	$\lambda_{max\ em}$	Fluorescence intensity
N,*N*-Dimethylacetamide	38.85	356	223.984
N,*N*-Dimethylformamide	38.25	356	701.458
N,*N*-Dimethylsulfoxide	42.24	356	211.663

[a] Dielectric constants of DMAc, DMF and DMSO as solvent at 25 °C [25].

The solvent nature affects on the position and relative fluorescence intensity of the maxima band. Table 3 shows the maximum emission of polymer **9** in different solvents.

The dependency of fluorescence intensity on polymer concentration illustrates the self-quenching phenomenon. By decreasing the polymer concentration to a specific concentration (ideal concentration), the fluorescence intensity increases and after that, by decreasing the polymer concentration the fluorescence intensity decreases too. The spectra obtained from the polymer systems vary in the intensity, shape and position of the maxima band. The diagram of the relative fluorescence intensity versus polymer concentration in different solvents has been shown in Fig. 10.

In all above plots, the relationship between relative fluorescence intensity and polymer concentration before and after ideal concentration were linear. In polymer **9**, the maximum fluorescence intensity was observed in DMF. All intensities in DMAc were less than DMF and also in DMSO were less than DMAc.

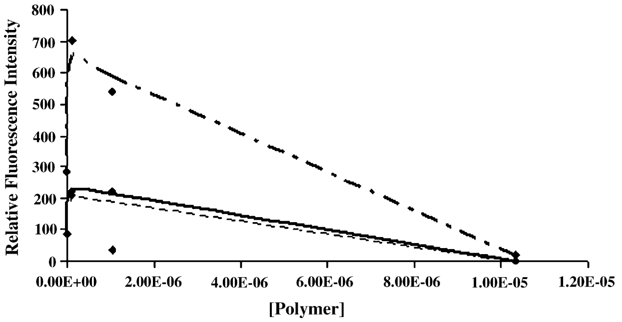


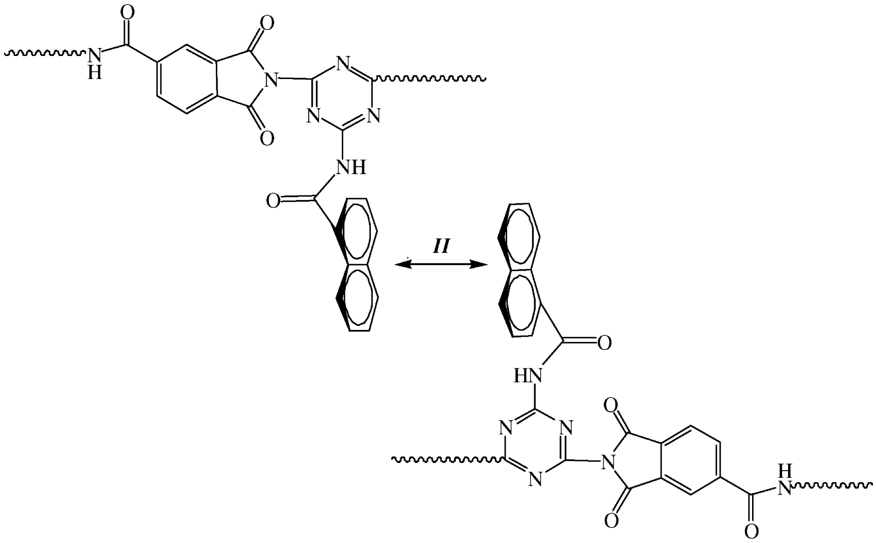
Fig. 10. Plots of relative fluorescence intensity vs. polymer **9** concentration in: DMAc (—), DMSO (– –) and DMF (– – –).

Table 4
τ-Values and singlet state properties of polymer **9** in various solvents

Solvent	τ	$K_q\tau$	K_q	η[a]
N,*N*-Dimethylacetamide	5.0000×10^{-9}	1.7948×10^{7}	3.5896×10^{15}	0.927
N,*N*-Dimethylformamide	4.8366×10^{-9}	3.7611×10^{6}	8.3953×10^{14}	0.794
N,*N*-Dimethylsulfoxide	4.3023×10^{-9}	2.1298×10^{7}	4.9530×10^{15}	1.987

[a] Viscosity values of DMAc, DMF and DMSO as solvent at 50 °C [25].

The fluorescence intensities trends are due to the intermolecular interaction between aromatic systems of the polymer side group as shown below:



II = Intermolecular Interaction

By increasing the dielectric constant of the solvent, separation between these molecules is increased and consequently self-quenching of a polymer with another one will be decreased. Therefore, the relative fluorescence intensity must increase. According to this hypothesis, it is expected that the relative fluorescence intensities will follow the trend based on dielectric constant, i.e. DMSO > DMAc > DMF, whereas, the observed trend is in contrast with above one. Hence, another parameter, which is the effect of viscosity on intermolecular separation, should be considered. With increasing the viscosity of solvent, the quenching of polymer with solvent will rise up whereas, the self-quenching is decreased. Consequently, the results of these two opposite phenomena promote the relative fluorescence intensity. Due to the viscosity mentioned in Table 4, it is expecting that the relative fluorescence intensity in DMSO is less than DMAc and in DMAc is also less than DMF. This was experimentally observed too (Table 3). At constant temperature, the diffusion rate constant has reciprocal relationship with viscosity. So, the following trend is expectable for self-quenching phenomena in different solvents: DMF < DMAc < DMSO (Table 4). This behavior might come from the mechanism of molecular interactions. Exchange and columbic interactions are two spin-allowed mechanisms for singlet–singlet energy transfer (Eq. (1)).

$$M^*(S_1) + M(S_0) \rightarrow M(S_0) + M^*(S_1) \qquad (1)$$

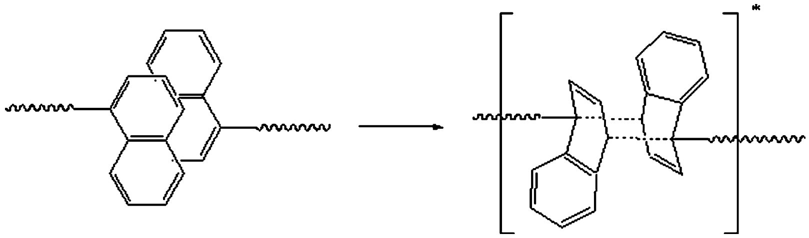
This energy transfer occurs for columbic interactions when M^* and M are far from each other and for exchange interactions if M^* and M are near to each other. As the observed trend is relative to the diffusion rate, it could be concluded that the predominant mechanism is based upon the exchange interaction in which the diffusion rate has been included.

One of the factors determining the efficiency of energy transfer in polymers is the migration of energy, i.e. the energy transfer between identical chromophores. Association of a singlet excited state with a ground state molecule forms an unstable dimer named “excimer” (Eq. (2)).

$$M_0 + M^* \rightarrow (M_0M^*) \qquad (2)$$

Excimers play an important role in the migration of electronic excitation energy in polymers. The fluorescence spectrum of an excimer is a structureless band with the maximum red shift relative to that of monomeric emission by 70–80 nm. Excimer emission is quite typical of solid or concentrated polymers (Fig. 9, entry 1). The formation of excimers in polymers is determined by the conformation of polymer chain and occurs with a parallel (sandwich) arrangement of the chromophoric groups as shown in Scheme 4.

To investigate the self-quenching phenomena in polymer systems, the equation for determination of the relative fluorescence yields can be written as below:



Scheme 4.

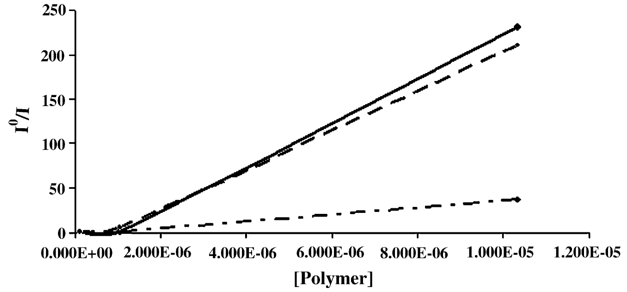


Fig. 11. Plots of I^o/I vs. polymer **9** concentration in: DMAc (—), DMSO (– –) and DMF (– - –).

$$\frac{I^o}{I} = 1 + K_q\tau[Q] \tag{3}$$

where I^o and I are the fluorescence intensities in an ideal and a typical sample of polymer with definite concentration respectively, [Q] is the quencher concentration for the polymer **9** and τ is the fluorescence lifetime of the excited polymer. The relative fluorescence intensity data, measured at 356 nm for the polymer **9** solutions in DMF, DMSO and DMAc as solvents, were used for plotting the results. Plots of I^o/I versus polymer concentration do not gave straight lines with good accordance with the theoretical equation and supporting the completed nature of self-quenching of the polymer fluorescence phenomena (Fig. 11).

As well as, the intercept values close to unity were found in all cases. Strickler–Berg equation usually gives the relationship between fluorescence lifetime (τ) to absorption intensity with some approximation [24]. With this modified formula, the τ-values were calculated and the obtained results are given in Table 4.

No significant changes in the value of τ were investigated. The self-quenching rate constant for the association reaction in the excited state (K_q) could be measured from the slope of the lines by knowing τ-values (Table 4). In our system, the calculated value for K_q corresponds to the value of bimolecular rate constant for the diffusion-controlled process of quenching (Eq. (4)).

$$\mathrm{M}^* + \mathrm{M} \xrightarrow{K_q} 2\mathrm{M} \quad (\text{Self-quenching of } \mathrm{M}^* \text{ by } \mathrm{M}) \tag{4}$$

Rate of unimolecular deactivation of the excited species (Eq. (5)) is comparable with the rate of Eq. (4).

$$\mathrm{M}^* \xrightarrow{K_1} \text{product} \quad (\text{Unimolecular decay of } \mathrm{M}^*) \tag{5}$$

At constant temperature, the diffusion rate constant has reciprocal relationship with viscosity. So, the following trend is expectable for self-quenching phenomena in different solvents: DMF < DMAc < DMSO (Table 4). Fluorescence lifetime of polymer **9** in several solvents obeyed the above trend.

4. 4 Conclusion

Novel photoactive monomer **8** has been synthesized by the reaction of 1-naphthoyl chloride (**6**) with 2,4,6-triamino-1,3,5-triazine (**7**). Monomer **4** was prepared through reaction of one equimolar trimellitic acid chloride (**2**) and 2 mol ODI (**3**). This monomer reacts very fast with the first monomer in the presence of a small amount of *o*-cresol as solvent by using of microwave irradiation technique and gives a novel photoactive polymer in high yield. The resulting polymer is thermally stable and shows fluorescence emission phenomena. To investigate the fluorescence behavior of the polymer, its emission spectra was recorded in several solvents by fixing the excitation wavelength at maximum absorption wavelengths. The dependency of fluorescence intensity on polymer concentration illustrates the self-quenching phenomenon, which has been discussed here.

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