e-Polymers **2009**, no. 016
http://www.e-polymers.org
ISSN 1618-7229

Photoluminescence and electron migration characteristics of aromatic poly(amide-imide) containing 1-naphthaldehyde and 4,4′-diamino diphenyl ether

Sepideh Khoee, Somayeh Zamani*

*Polymer Laboratory, Chemistry Department, School of Science, University of Tehran, P. O. Box 14155-6455, Tehran, Iran; fax: +98 21 6649 5291; e-mail: Khoee@Khayam.ut.ac.ir

(Received: 23 June, 2008; published: 16 February, 2009)

Abstract: A new photoactive polymer poly(amide-imide), was fabricated by reacting two synthesized monomers, N,N'-(4,4'-oxy-bis(4,1-phenylene))-bis-(1,3-dioxo-1,3-dihydroisobenzofuran-5-carbox amide) and N-(4,6-diamino-1,3,5-triazine-2-yl)-1-naphthamide. Polycondensation reaction of the two monomers was performed under 10 min microwave irradiation in o-cresol as solvent for producing a photoactive poly(amide-imide) in a quantitative yield. The resulting polymer was characterized by FT-IR, ^{1}H-NMR, TGA techniques and its solvatochromic and fluorescence properties were investigated in different solvents. The poly(amide-imide) exhibit broad fluorescent band, and the fluorescence intensity is related to the intermolecular chain-chain or chain-solvent interaction. Also the self-quenching mechanism was studied according to the specific behavior of the polymer in different solvents and the self-quenching rate constant for the association reaction in the excited state (K_q) could be measured from the Stern-Volmer equation. This kind of fused system and diamines show various electron migration mechanisms and photoluminescent properties in the singlet excited states.

Introduction

The application of microwave energy to organic synthesis is known for a long time [1] and in the last decade was successfully applied to radical and condensation polymerization reactions [2, 3]. Since many decades, microwave irradiation has been a useful tool in synthetic polymer chemistry for crosslinking [4], selective decomposition of secondary components [5], and initiating radical polymerization reactions [6]. It has been demonstrated that it is possible to obtain polymers with good yields at short times of reaction under irradiation with microwaves [7, 8]. Although many monomers have been polymerized in these conditions, the effect of microwave irradiation on the rate of chemical reactions is still under debate and many investigators has mentioned the existence of a so-called non-thermal or specific microwave effect, responsible for the acceleration of the reaction rate and for which some theories have been proposed [9, 10].

Aromatic polyimides (APIs), because of their low dielectric constants, low coefficient of thermal expansion, high glass transition temperature, and high radiation resistance have been widely used in aerospace, automotive industries, as alignment layers for liquid crystal displays, and interlayer dielectric insulators in the microelectronics industry. These excellent physical properties result from rigid polymer structures and strong intermolecular interactions. Aromatic polyimides are usually synthesized through a two-step method: preparation of poly(amic acids) (PAAs) and then thermal or chemical imidization. The PAA polymerization rates relate to the electron affinity (Ea) of dianhydrides as an electron-acceptor and the ionization potential of diamines as an electron-donor. This suggests that charge transfer (CT) interaction may occur between the electron-donor and electron-acceptor fragments of the aromatic polyimides [11]. Many previous works reported the relationship between CT and fluorescence in APIs [12-16]. Wachsman and Frank observed a significant increase in the CT fluorescence intensity with increased molecular aggregation resulting from increased imidization temperature [17]. H. Luo et al. reported that an increased concentration of polyimide led to denser packing of the polymer chains then increasing the CT fluorescence [18]. However, aggregation would be one of the main barriers for increasing luminescence quantum yield in the conjugated polymer [19, 20]. This indicates that aromatic polyimides could display a different fluorescence mechanism in comparison with conjugated polymers. Polyimides which contain anthracence, perylene, metal complexes, 2,5-distyrylpyrazine, dibenzofurane, and furyl-substituted biphenylene moieties were used as light-emitting materials [21-27].

Systematic fluorescence studies of polyimidization using microwave energy are scarce. The reaction of 1-naphthaldehyde and 2,6-diaminopyridine was investigated, showing an important acceleration of the reaction rate under microwave conditions in comparison to thermal conditions [28]. Poly(amide-imide) prepared from anthracene-9-carboxaldehyde and 4,4'-diaminodiphenyl ether has particular interest due to its very high thermal and photochemical stability [29]. The aim of the present study was to analyze the effect of the different experimental parameters (polarity of diamines and the length of conjugation systems) on the structure, kinetics of electron migration, absorption and emission wavelengths, thermal stability and solubility properties of poly(amide-imide) obtained under microwave conditions.

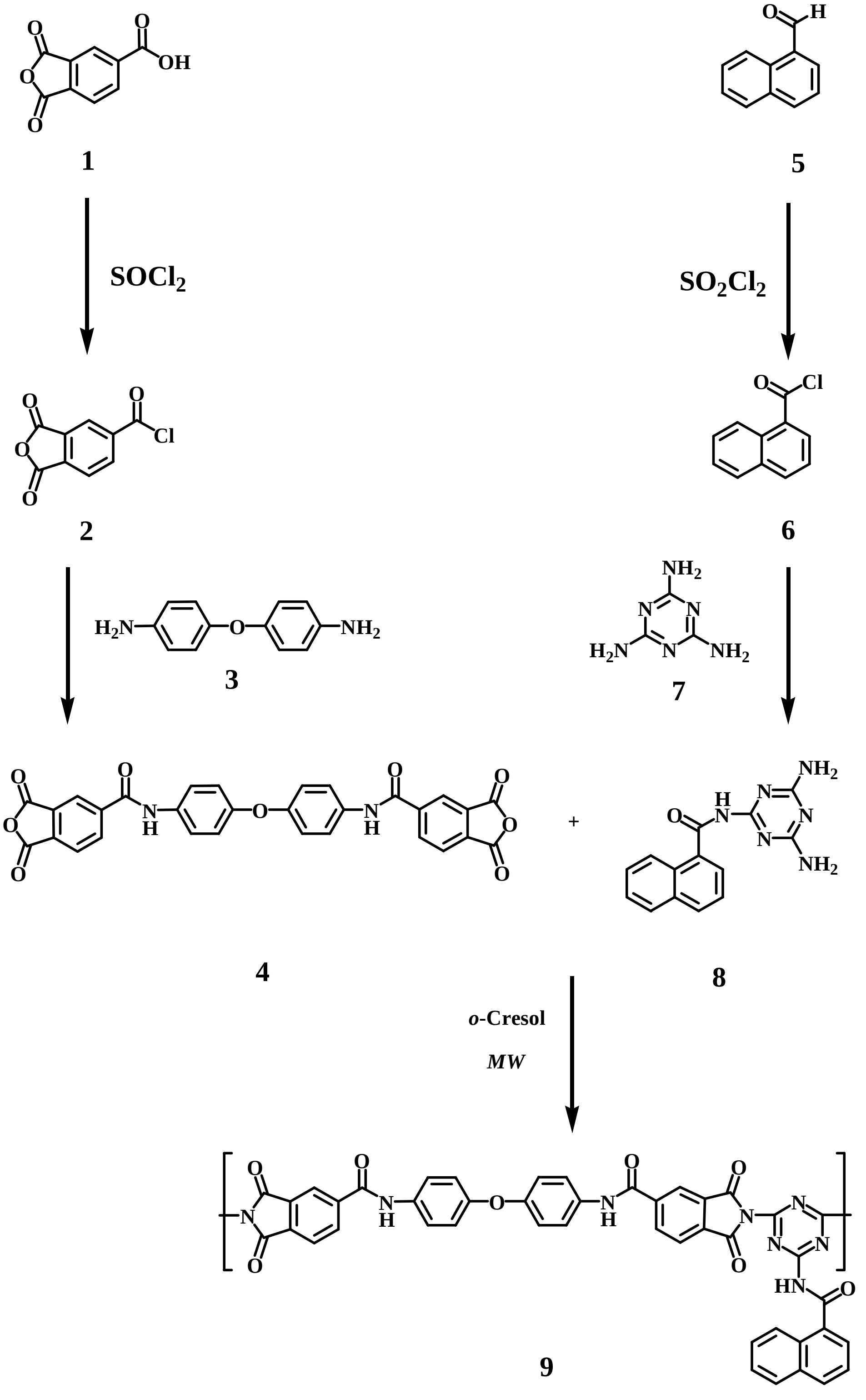
Results and discussion

Polymerization reaction

For the condensation polymerization reaction two monomers **4** and **8** were used. The reaction did not proceed even by applying the long reaction time, higher temperature and removal of 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 use of a small amount of a polar solvent, which is heated when irradiated in a microwave oven, acts as a primary absorber, and as a solvent for both the starting materials and products. Therefore, the solvent induces effective homogeneous heating to convert monomers into polymers. According to our previous works it has been recognized that the appropriate solvent is *o*-cresol [28, 29]. Monomer **4** and monomer **8** were irradiated in *o*-cresol, for 10 minutes. The resulting mixture was precipitated in methanol to obtain polymer **9** with a quantitative yield as shown in Scheme [1].

Polymer characterization

Microwave irradiation is a convenient method for producing 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, ^{1}H-NMR and ^{13}C-NMR spectroscopy.



Scheme 1. Preparation of poly(amide-imide)

As shown in FT-IR spectrum of polymer **9** (Figure 1), all bands of the two monomers are observed. The characteristic bands around 3338 and 1625 cm^{-1} correspond to stretching vibration of amidic N-H and C=O groups. The anhydride bands at 1850 and 1780 cm^{-1} were replaced by imide bands at 1725 and 1785 cm^{-1}.

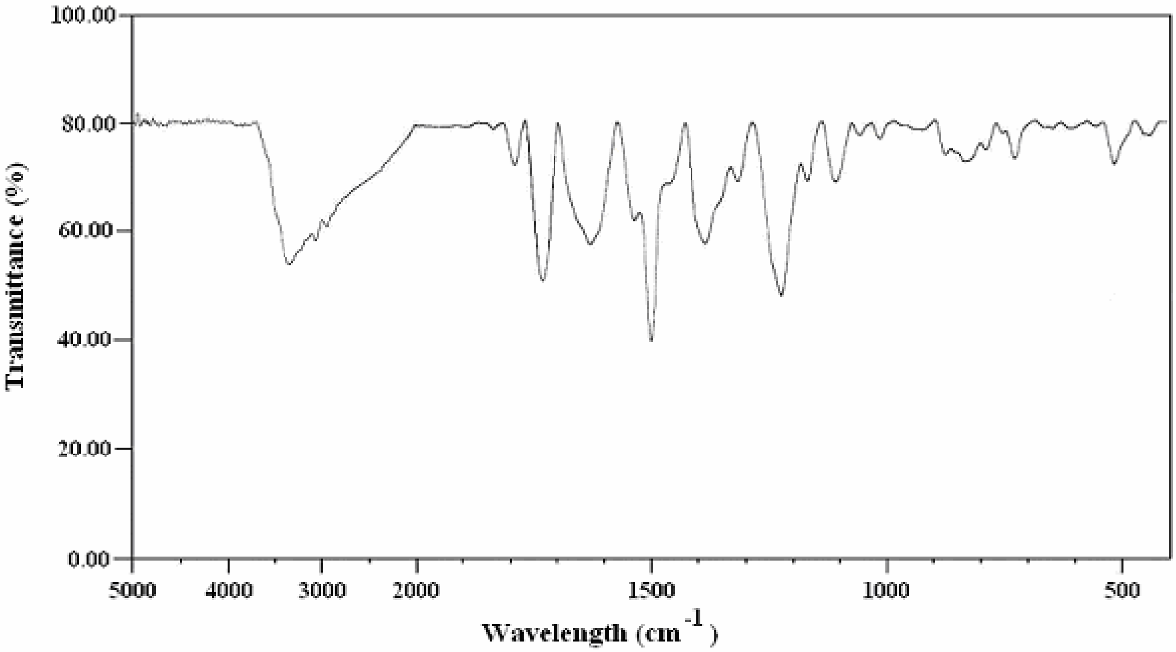


Fig. 1. FT-IR spectrum of polymer **9**.

There is a doublet at 6.96 ppm in the ^{1}H-NMR spectrum of polymer **9** (Figure 2). It is related to H_a, which is split through the coupling with H_b (J= 9Hz). H_b coupled with H_a appears as a broad peak at 7.62-7.92 ppm due to the overlap with naphthalenic protons (H_i protons). The reason for such difference in the chemical shifts of H_a and H_b relates to their different chemical environment. H_a is shielded more than H_b because of its vicinity to the nitrogen atom of the amide group. This could be explained by the non-bonding electrons of nitrogen atom in the amide group which are in the stronger resonance with carbonyl group than in with the oxygen atom in the etheric group. H_c is coupled with H_d and split into a doublet (J= 9Hz) at 8.0 ppm. H_d, H_e, H_f and H_g will give a broad peak at 8.35-8.59 ppm according to the anisotropic effect of the carbonyl groups. This anisotropic effect is more pronounced for H_f and will result in deshielding of H_f relative to H_d, H_e and H_g protons (H_f = 9.21 ppm). H_h appears at 10.63 ppm, which corresponds to the amidic NH protons.

The ^{13}C-NMR spectrum of polymer 9 shows that the chemical shifts for the phenylic carbons are similar to that observed in the monomeric form. In general, introducing the naphthalenic ring as a pendent group to the main chain of the polymer complicates the shape of ^{13}C-NMR spectrum. For the etheric carbons, a deshielding of 30 ppm due to the resonance with non-bonding electrons of oxygen atoms was observed in comparison with other aromatic rings. Also all carbonyl groups appear in up-field positions relative to the triazine C=N groups (Figure 3).

The solubility test of polymer **9** has been determined. The polymer is soluble in organic solvents such as DMF, DMAc, *o*-Cresol and *p*-Cresol but is insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, THF, diethyl ether, toluene, water, etc.

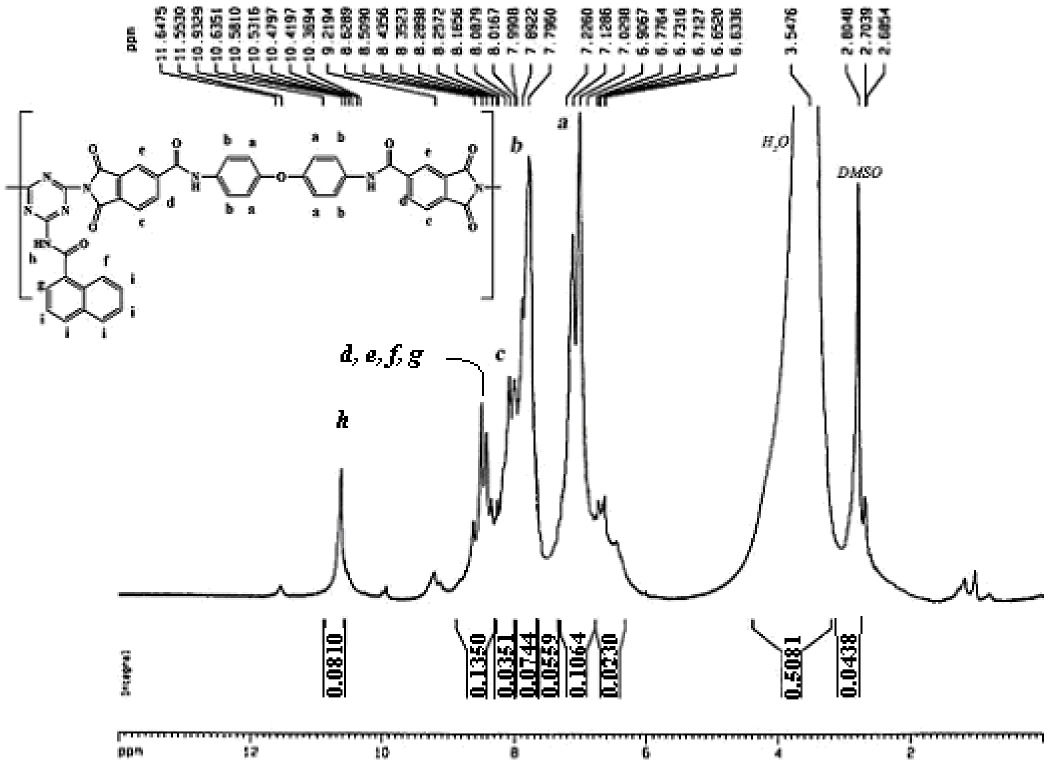


Fig. 2. ^{1}H-NMR spectrum of polymer **9** in $CDCl_3$.

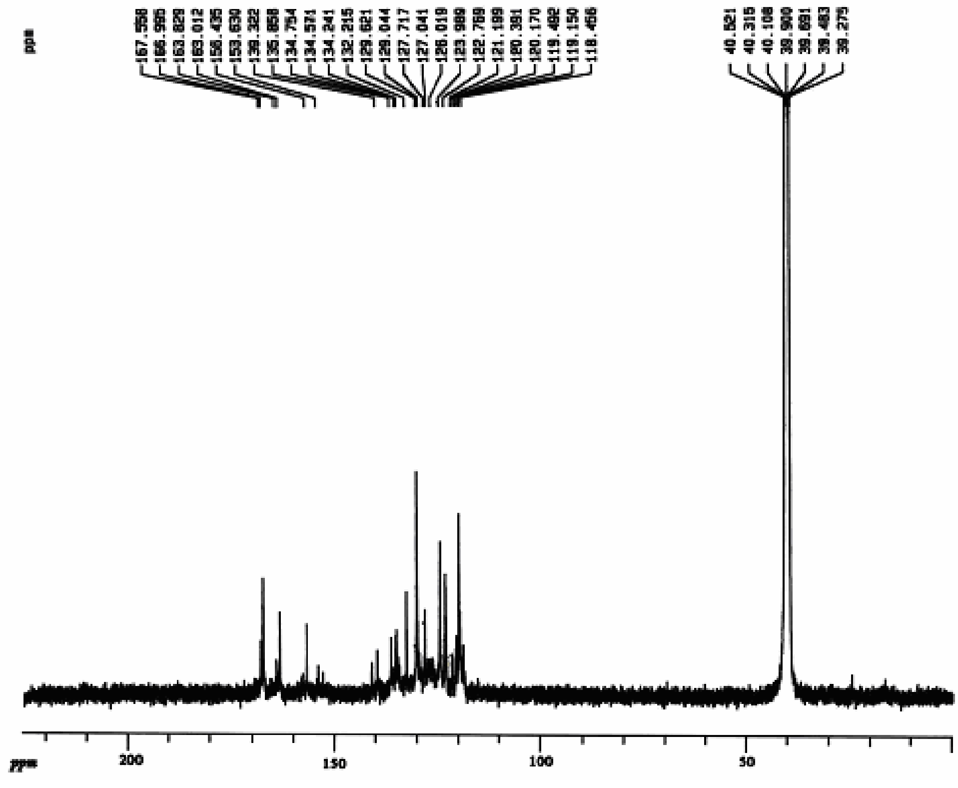


Fig. 3. ^{13}C-NMR spectrum of polymer **9** in $CDCl_3$.

Thermal properties

The thermal behavior of polymer **9** was studied by means of thermal gravimetric analysis (TGA) technique. Figure 4 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 216.3, 230 and 316.3 ^{0}C. The residual weight percent at 500 °C is 65.1% which shows that it is moderately thermally stable.

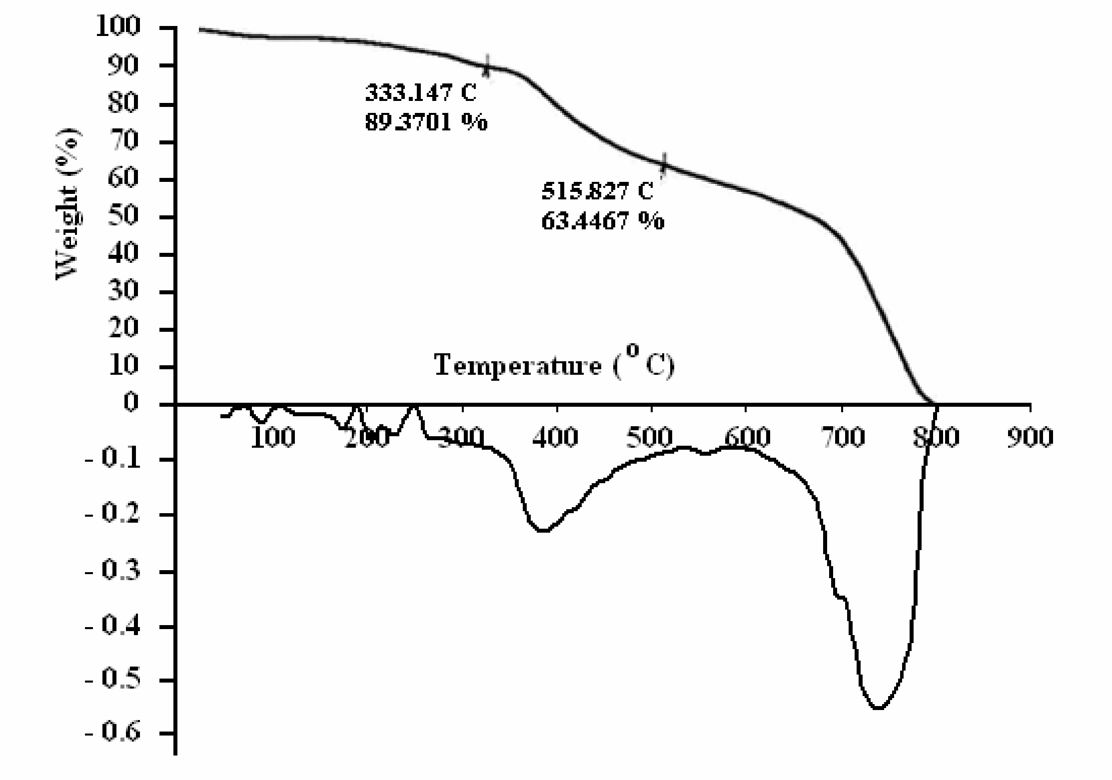


Fig. 4. TGA and DTG thermograms of polymer **9** with a heating rate of 20 ºC min^{-1} under nitrogen atmosphere.

Fluorescence Studies

In our previous works, we prepared some photoactive polymers via polycondensation of different diamines with different dianhydrides [28, 29]. Here, we tried to examine the effect of spacer groups in the dianhydride monomer in combined systems on the mechanism of molecular interaction. UV spectrum of polymer **9** was recorded in DMF, *o*-cresol and *p*-cresol as solvents. A broad peak was observed in the above solvents in which no microstructure was found. The presence of several phenyl groups with different substituents and also naphthalenic moiety is responsible for broadening of the above peaks. Solvent changing causes a displacement of the maximum absorption wavelengths (λ_{max}) and molar extinction coefficient (ε_{max}). The λ_{max} and ε_{max} data of polymer **9** in the above three solvents have been listed in Table 1. The dipole moment of the solvent increases from *o*-cresol to *p*-cresol and in DMF (Table 1).

It was expected to observe the hypsochromic shift to lower wavelength by increasing the solvent polarity. This blue shift is the result of conjugation of carbonyl group with the naphthalenic ring. Increase in the solvent polarity decreases the length of conjugation, which is due to the solvation of oxygen atom in the carbonyl group. Therefore, a hypsochromic shift will be observed because of the difficulty in π→π* transition according to the decreasing length of conjugation. A typical absorption spectrum at given polymer concentration in DMF has been shown in Figure 5.

Tab. 1. UV-Spectroscopic data of polymer **9** in various solvents.

Solvent	μ^a	λ_{max}	ε_{max}
N,N-Dimethyl formamide	3.82	304	8271.8985
p- Cresol	1.48	309	6999.6036
o- Cresol	1.45	335	4443.1232

[a] Dipole moment values of DMF, *p*- and *o*-cresol as solvent at 25 °C [30].

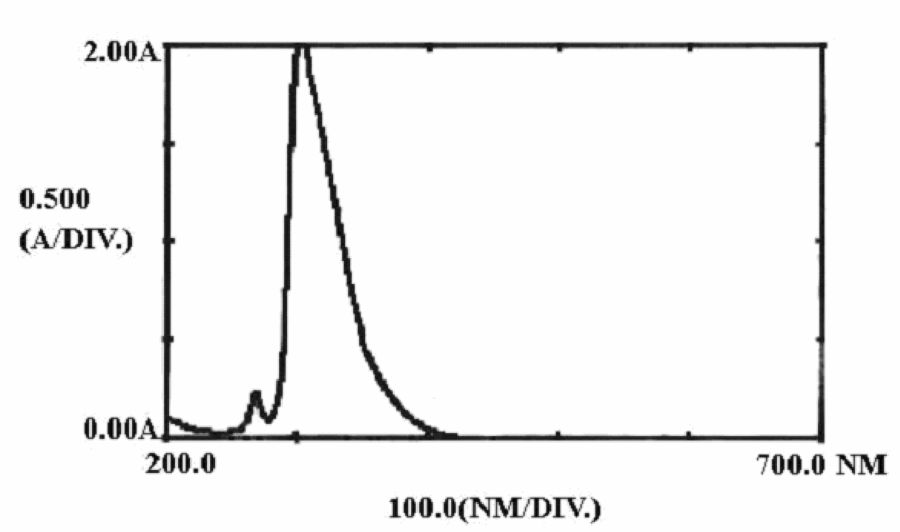


Fig. 5. Absorption spectrum of polymer 9 in DMF at 2.523×10^{-4} M concentration in 1.0 cm optical path.

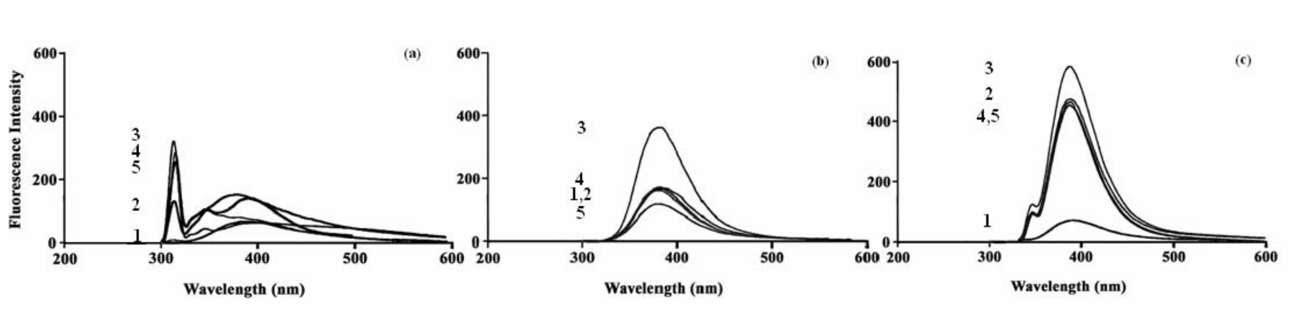


Fig. 6. Fluorescence spectra of polymer **9** in DMF (a) , *p*-cresol (b) and *o*-cresol (c) at **1**: 4.84×10^{-4} M, **2**: 4.84×10^{-5} M, **3**: 4.84×10^{-6} M, **4**: 4.84×10^{-7} M and **5**: 4.84×10^{-8} M of polymer concentrations.

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, *o*- and *p*-cresol by fixing the excitation wavelength at maximum absorption wavelength, *i.e.* at 304, 309 and 335 nm respectively. Consequently, a new band with a maximum around 313-381 nm appears. Figure 6 shows fluorescence spectra of polymer 9 for different polymer concentrations in DMF, *p*-cresol and *o*-cresol.

The solvent nature affects the position and relative fluorescence intensity of the maxima band. Table 2 shows the maximum emission of polymer **9** in different solvents.

Tab. 2. Maximum fluorescence wavelengths and fluorescence intensity of polymer **9** in various solvents.

Solvent	μ^a	ε^b	$\lambda_{max\ em}$	*Fluorescence Intensity*
N,N-Dimethyl formamide	3.82	38.25	313	319.866
p- Cresol	1.48	13.05	376	358.547
o- Cresol	1.45	6.76	381	575.552

[a] Dipole moment values of DMF, *p*- and *o*-cresol as solvent at 25 °C [30].

[b] Dielectric constants of DMF, *p*- and *o*-cresol as solvent at 25°C [30].

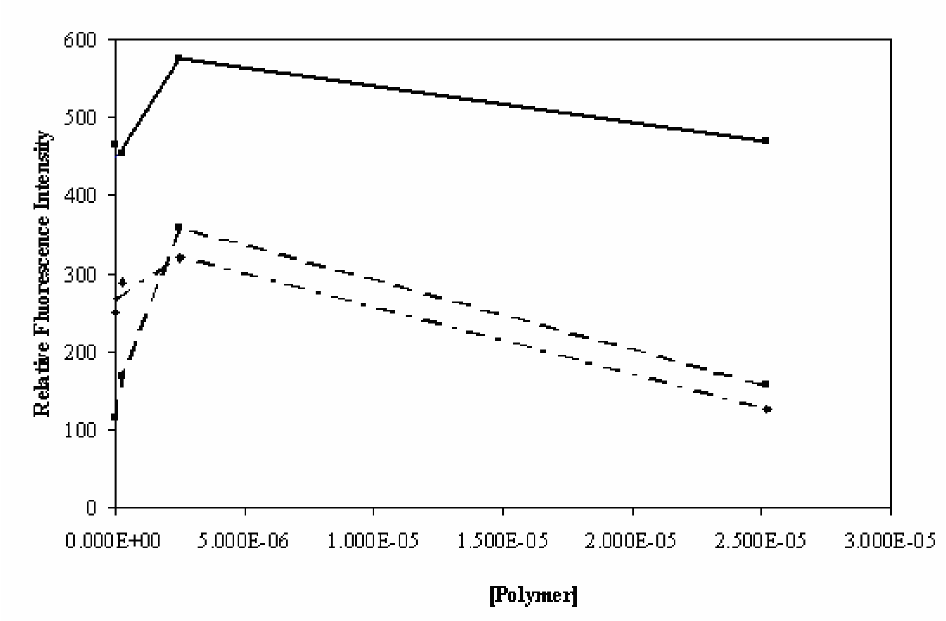
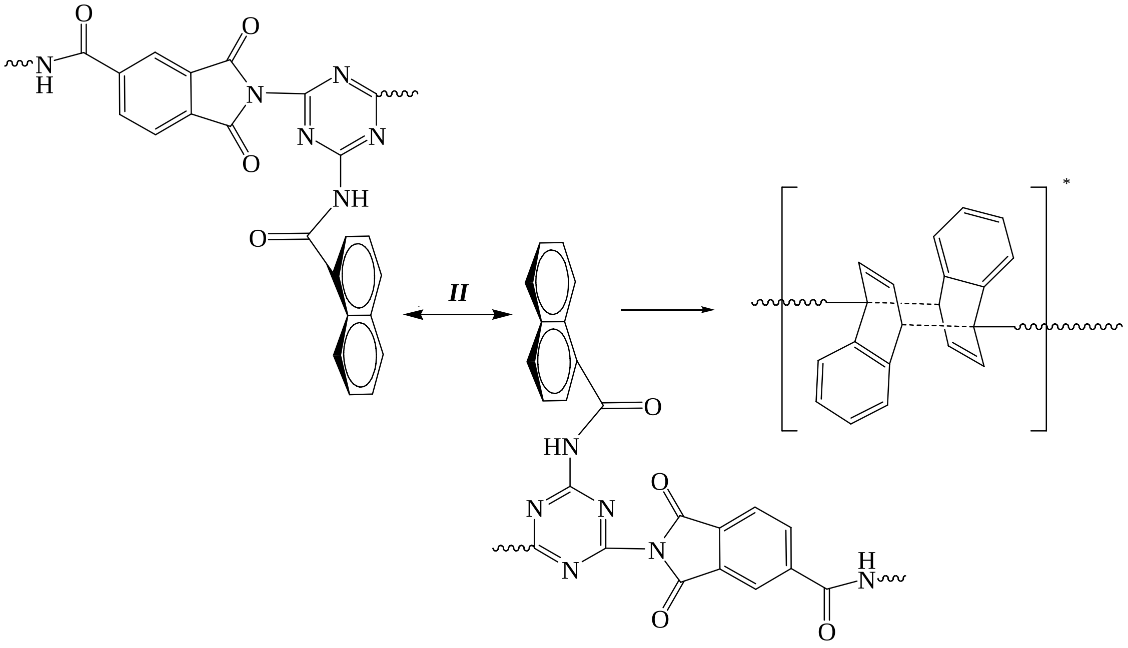


Fig. 7. Plots of relative fluorescence intensity versus polymer (**9**) concentration in: *o*-cresol (——), *p*-cresol (——) and DMF (— – —).

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 Figure 7.

In the 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 o-cresol. All intensities in *p*-cresol were less than o-cresol and also in DMF were less than *p*-cresol. The fluorescence intensities trends are due to the intermolecular interactions between aromatic systems of the polymer pendant group as shown in scheme 2:



II = Intermolecular Interaction

Scheme 2. The intermolecular interactions between aromatic systems of the polymer pendant group.

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. DMF> *p*-cresol> *o*-cresol, whereas, the observed trend is in contrast with above one. Hence, another parameter, which is the effect of dipole moment on intermolecular separation, should be considered. With increasing the dipole moment of solvent, the quenching of polymer with solvent will rise up. Due to the dipole moment mentioned in Table 1, it is expected that the relative fluorescence intensity in DMF is less than *p*-cresol and in *p*-cresol is also less than *o*-cresol, this was experimentally observed as well (Table 2). In our system, the magnitude of bimolecular quenching rate constant (Kq) corresponds to the following equation:

$M^* (S_1) + M (S_0) \xrightarrow{Kq} 2M$ Self-quenching of M* by M (1)

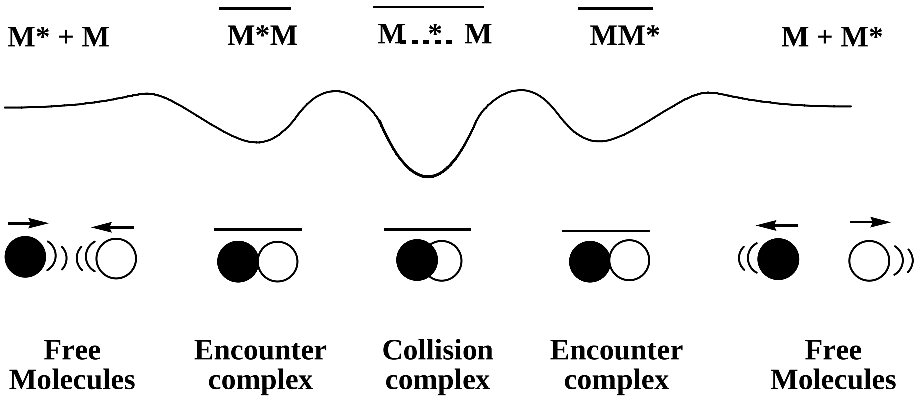
It is possible to visualize a competitive electronic energy transfer process as below:

$M^* (S_1) + M (S_0) \longrightarrow M (S_0) + M^* (S_1)$ (2)

Exchange and columbic interactions are two spin-allowed mechanisms for singlet-singlet energy transfer. 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.

In self-quenching (eq. 1) and electron transfer (eq. 2) path, M and M* molecules approach each other in solution and undergo a number of collisions with one another. Consequently each parameter, which controls self-quenching phenomena, must control the electron transfer process as well. If the observed self-quenching is relative to the diffusion rate, it can be concluded that the predominant mechanism for electron transfer is based upon the exchange interaction. Whereas, if an inverse trend is observed in self-quenching process, the columbic energy transfer will be the predominant mechanism.

At constant temperature, the diffusion rate constant has reciprocal relationship with viscosity. So, when the diffusion rate is included in the process, following trend will be expected for self-quenching phenomena in different solvents: *p*-cresol < *o*-cresol < DMF (Table 3). The inverse trend must be observed while columbic energy transfer is occurred. 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. M and M* molecules come close each other until they are within each other's sphere of influence and surrounded by a solvent cage (Scheme 3). It means that by each collision the peripheries of the electron clouds of M and M* overlap and interpenetrate with one another.



Scheme 3. The mechanism of self quenching phenomena.

Association of a singlet excited state (M*) with a ground state molecule (M) forms an unstable dimer named "excimer" (Eq. 3).

$$M + M^* \rightarrow (M M^*) \tag{3}$$

Excimers play an important role in the migration of electronic excitation energy in polymers. The fluorescence spectrum of an excimer is a structure less band with the maximum red shift relative to that of monomeric emission by 90-100 nm. Excimer emission is quite typical of solid or concentrated polymers (Figure 6 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 2.

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

$$I^{o}/I = 1 + Kq\,\tau\,[Q] \tag{4}$$

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 313-381 nm for the polymer **9** solutions in DMF, *o*-cresol and *p*-cresol as solvents, were used for plotting the results. Plots of I^{O}/I vs. polymer concentration gave straight lines with good accordance with the theoretical equation and supporting the simple nature of self-quenching of the polymer fluorescence phenomena (Figure 8).

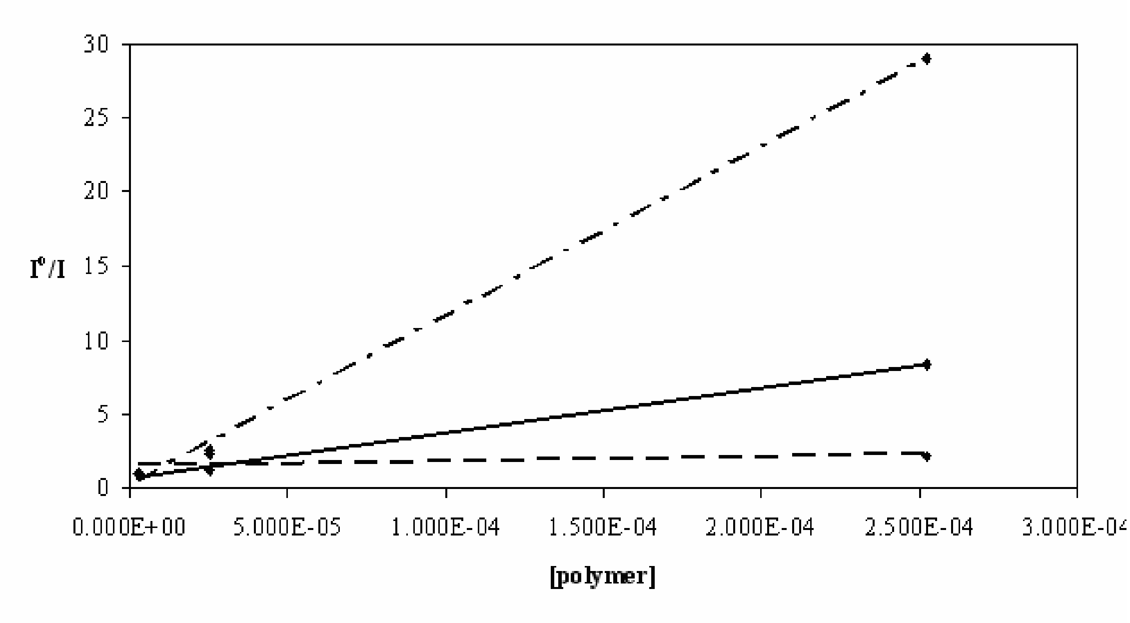


Fig. 8. Plots of I^{O}/I versus polymer (**9**) concentration in: *o*-cresol (——), *p*-cresol (——) and DMF (— – –—).

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 [30]. With this modified formula, the τ values were calculated and the obtained results are given in Table 3.

Tab. 3. τ-values and singlet state properties of polymer **9** in various solvents.

Solvent	τ	$K_q\,\tau$	K_q	η^{a}
N,N-Dimethyl formamide	1.21×10^{-8}	1.13×10^{5}	9.34×10^{12}	0.62
p- Cresol	1.43×10^{-8}	2.60×10^{3}	1.82×10^{11}	4.48
o- Cresol	2.25×10^{-8}	2.93×10^{4}	1.30×10^{12}	3.03

[a] viscosity values of DMF, *p*- and *o*-cresol as solvent at 50°C [30, 31].

No significant changes in the value of τ were investigated. The self quenching rate constant for the association reaction in the excited state (Kq) could be measured from the slope of the lines by knowing τ values (Table 3). In our system, the calculated value for Kq corresponds to the value of bimolecular rate constant for the diffusion-controlled process of quenching (Eq. 1).

Conclusions

Monomer **4** and monomer **8** react very fast with each other 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 properties. To investigate the fluorescence behavior of the polymer, its emission spectra was recorded in several solvents. The poly(amide-imide) solutions exhibit obvious fluorescent behavior and the fluorescent intensity relates to physical characteristics of the solvent and polymer. The dependency of fluorescence intensity on polymer concentration illustrates the self-quenching phenomenon, which has been discussed here. It is suggested that low diamine polarity decreases the population of face-to-face stacking of the naphthalenic rings, so the CT interactions would be reduced and the fluorescent mechanism would be changed. It was shown that by changing the fused systems from naphthalene to anthracene, the maximum absorption and emission wavelengths varied but no change was observed in the mechanism of molecular interaction. In the above mentioned polymer chains, the exchange energy transfer mechanism was the predominant spin-allowed energy transfer mechanism.

Experimental Part

Materials

All chemicals used in experiments were purchased from Merck Company. 4,4′-diaminodiphenyl ether (or 4,4′-oxydianiline; ODA) was purified by sublimation before use. N,N-dimethylacetamide (DMAc) was dried over BaO and then distilled under reduced pressure. Trimellitic acid chloride (**2**), N,N'-(4,4'-oxy bis(4,1-phenylene))-bis-(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxamide) (**4**), 1-naphthoyl chloride (**6**) and N-(4,6-diamino-1,3,5-triazine-2-yl)-1-naphthamide (**8)** were prepared according to the previously reported procedures (Khoee et al, 2007; Khoee and Zamani, 2007).

Instrumentation

Proton (^{1}H- NMR) and carbon (^{13}C-NMR) nuclear magnetic resonance spectra were recorded on a **Bruker** Avance 400 NMR spectrometer. FT-IR spectra were recorded on a Shimadzu FT/IR-4300 spectrometer. The spectra of solids were obtained using KBr pellets. An LG domestic microwave oven (2450MHz, 900W) was used for polycondensation. 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 Eclipse spectrofluorophotometer.

Polymerization reaction

The reaction was performed in a mortar containing 0.1 g of **4**, 0.05 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 and then irradiated for 10 min. The precipitated polymer was washed thoroughly with methanol and filtered off to yield 0.13 g of polymer **9** (90%). FT-IR (KBr): 3338 (m), 1785 (w), 1728 (s), 1625 (m), 1498 (s), 1222 (m), 829 (w) cm^{-1}. ^{1}H- NMR: 6.90-7.02 (dd, 4H), 7.62-7.92 (br, 9H), 7.99-8.01 (d, 2H), 8.35-8.59 (br, 5H), 9.21 (d, 1H), 10.63 (s, 3H) ppm. ^{13}C-NMR: 118-

139 ppm (phenylic and naphthalenic carbons), 156 ppm (C-O-C), 163-167 ppm (amidic and imidic carbonyl groups, and triazine C=N).

Acknowledgements

We wish to express our gratitude to the Iran National Science Foundation (grant number 84076/1), Tehran, for financial support. We also thank Dr. Mahdavian and his group in Iran Polymer and Petrochemical Institute (IPPI), Tehran, Iran, for performing ^{1}H-NMR, ^{13}C-NMR and TGA analysis.

References

[1] Strauss, C. R.; Trainor, R. W. *Aust. J. Chem.*, **1995**, *48*, 1665.
[2] Bogdal, D.; Penczek, P.; Pielichowski, J.; Prociak, A. *Adv. Polym. Sci.*, **2003**, 163, 194.
[3] Wiesbrock, F.; Hoogenboom, R.; Schubert, U.S. (2004) *Macromol. Rap. Commun.*, **2004**, *25*, 1739.
[4] Kurtz, S. M.; Muratoglu, O. K.; Evans, M.; Edidin, A. A. *Biomaterials*, **1999**, *20*, 1659.
[5] Abdallah, J.; Silver, M.; Allen, S.A.B.; Kohl, P.A. *J. Mater. Chem.*, **2007**, *17*, 873.
[6] Machi, S.; Hagiwara, M.; Gotoda, M.; Kagiya, T. *J. Polym. Sci. Part A: Polym. Chem.*, **1966**, *4*, 1517-1524.
[7] Jacob, J.; Chia, L.H.L.; Boey, F.Y.C. *Polym. Testing*, **1995**, *14*, 343.
[8] Cortizo, M.S. *J. Appl. Polym. Sci.*, **2007**, *103*, 3785.
[9] Perreux, L., Loupy, A. *Tetrahedron*, **2001**, *57*, 9199.
[10] Jacob, J., Chia, L. H. L., Boey, F. Y. C. *J. Mater. Sci.*, **1995**, *30*, 5321.
[11] Ghosh, M.K.; Mittal, K.L. *Polyimides: Fundamentals and Applications.* Marcel Dekker, New York, **1997**.
[12] Ghassemi, H. ; Zhu, J. H. *J. Polym. Sci. Part B: Polym. Phys.*, **1995**, 33, 1639.
[13] Qinghua, L.; Takashi, Y.; Kazutuki, H.; Hiroshi, Y. J. Polym. Sci. Part *A: Polym. Chem.*, **1998**, *36*, 1329.
[14] Masatoshi, H.; Ishii, J.; Shindo, Y. *Macromolecules*, **1999**, *32*, 6111.
[15] Hasegawa, M.; Horie, K. *Prog. Polym. Sci.*, **2001**, *26*, 259.
[16] Yu, J.W.; Sung, C.S.P. *Macromolecules,* **1997**, *30*, 1845.
[17] Wachsman, E.D.; Frank, C.W. *Polymer*, **1988**, *29*, 1191.
[18] Lu, W.; Gao, J.P.; Wang, Z.Y.; Sacripante, G.G. *Macromolecules*, **1999**, 32, 8880.
[19] Jakubiak, R.; Collison, C.J.; Wan, W.C. *J. Phys. Chem.*, A, **1999**, *103*, 2394.
[20] Setayesh, S.; Grimsdale, A.C.; Weil, T.F. *J. Am. Chem. Soc.*, **2001**, *123*, 946.
[21] Maltsev, E.I.;Berendyaev, V. I.; Brusentseva, M.A. *Polym. Int.*, **1997**, *42*, 404.
[22] Wu, A.P.; Akagi, T.; Jikei, M.; Kakimoto, M. *Thin Solid Films*, **1996**, *273*, 214.
[23] Spiliopoulos, I.K. ; Mikroyannidis, J.A. *Macromolecules*, **1998**, *31*, 515.
[24] Pyo, S.M.; Kim, S.I.; Shin, T.J. *Macromolecules*, **1998**, *31*, 4777.
[25] Kim, Y.; Cho, W.J.; Ha, C.S. *Mol. Cryst. Liq. Cryst.*, **1997**, *295*, 31.
[26] Matsumoto, T.; Nishimura, K.; Kurosaki, T. *Eur. Polym. J.*, **1999**, *35*, 1529.
[27] Luo, H.; Dong, L.; Tang, H.; Teng, F. *Macromol. Chem. Phy.*, **1999**, *200*, 629.
[28] Khoee, S.; Sadeghi, F.; Zamani, S. *J. Photchem. Photobiol. A- Chem.*, **2007**, *189*, 30.
[29] Khoee, S.; Zamani, S. *Eur. Polym. J.*, **2007**, *43*, 2096.
[30] Lide, D. R. Handbook of chemistry and physics; CRC press, 85th ed., **2004-2005.**

[31] Rosal, R.; Medina, I.; Forster, E.; MacInnes, J. *J. Fluid Phase Equilibria*, **2003**, *211*,143.
[32] Strickler, S.J.; Berg, R.A. *J. Chem. Phys.*, **1962**, 37, 814.