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Substituent effect on the fluorescence quenching of polystyrene derivatives by polymeric plasticizers

Khalid E. Al Ani*, Azza M. Suleiman[1]

Department of Chemistry, Faculty of Science, Hashemite University, Zarka, Jordan

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Abstract

The fluorescence quenching of poly (4-methylstyrene), poly (4-methoxystyrene), poly (α-methylstyrene) and poly (4-tert-butylstyrene) by dimethyl terephthalate, diethyl terephthalate, dibutyl phthalate and dioctyl terephthalate has been investigated in solvent of different polarities. Fluorescence spectra of these derivatives reveal the presence of both monomeric and excimeric emissions in all used solvents and were affected by the type of substituent and the polarity of the solvents. Monomeric and excimeric emissions were quenched by the addition of plasticizer as electron donors and quenching efficiency was affected by the polarity of solvents as well as the molar mass of the added plasticizer. As a result of the quenching processes no exciplex emission was observed in all used solvents. Quenching parameters such as quenching rate constants and quenching cross-sections for these quenching processes were calculated in all used solvents.

Keywords: Quenching rate constant; Fluorescence quenching; *Para*-substituted polystyrenes

1. Introduction

Considerable research effort has been devoted to the polymeric fluorescence quenching by polymeric additives, such as dimethyl terephthalate [1–3]. A number of important studies on fluorescence quenching of polystyrene and polystyrene derivatives has been reported [4–7]. The fluorescence spectrum of polystyrene showed a monomeric band at about 283 nm, and an excimeric fluorescence band at 335 nm. The excimeric fluorescence in polystyrene was found to increase by increasing polystyrene concentration and was affected by the change in solvent polarity [8].

The emission spectra of several *para*-substituted polystyrene, such as poly (4-methoxystyrene), poly (4-ethoxystyrens), and poly (4-tert-butylstyrene) were characterized by emission from excimers formed from two neighboring pendant aromatic groups on the same polymer chain [8,9]. It was found that the fluorescence emission of both poly (1-vinylnaphthalene) and poly (*N*-vinylcarbazole) are readily quenched in the presence of small-molecule electron acceptors [3]. The fluorescence emission of poly (4-ethoxystyrene) is greatly reduced when dimethyl terephthalate (DMT) is added to either solid films or solution of the polymer. The quenching process is accompanied by the appearance of a broad, red-shifted, structureless emission. This new emission band has been attributed to the fluorescence from an exciplex that formed between a pendants substituted styrene chromophore and a DMT molecule [8].

Studies on emission of intermolecular excimers [9,10] have shown that perfectly overlapping sandwich geometry is preferred for excimer formation. However, there have been only a few investigations about the geometric requirements of the exciplex and the effects of structural restriction upon the intermolecular exciplex formation [11,12]. The effect of molecular motion on exciplex formation was found to be affected by methylene chain length in {carbazole—$(CH_2)_n$–terephthalic acid ester}. This can be ascribed to the effect of methylene bonds on the rotational motion of the donor and the acceptor residues [13].

In the present study, poly (4-methoxystyrene), poly (4-methylstyrene), poly (4-tert-butylstyrene) and poly (α-methylstyrene) were chosen as electron donors, where dimethyl terephthalate, diethyl terephthalate, dioctyl terephthalate and dibutyl phthalate were electron acceptors. Polystyrene with

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* Corresponding author. Tel.: +962 5 390 3333; fax: +962 5 390 3349.
E-mail address: khalid7@hu.edu.jo (K.E. Al Ani).

[1] This paper is dedicated to Miss Azza Suleiman who died on 27/8/2005.

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various substituents and phthalate and terephthalate plasticizers are employed to investigate how variation of the excited state energy of donors is controlled by various substituents that affect the efficiencies of energy transfer between poly(substituted styrene)–plasticizer complexes. Quenching of the excimeric and monomeric fluorescence by the used plasticizers is expected to reveal the information on the energy transfer processes and the best donor–acceptor pair to accomplish efficient energy transfer.

In solution of doped polymers only a quenching of the monomeric and excimeric fluorescence is noticed. No exciplex emission is observed in all used polymers. From the Stern–Volmer plots, some kinetic parameters such as quenching rate constants and quenching cross-sections are also calculated.

2. Experimental

2.1. Materials

The samples of *para*-substituted polystyrenes were standard with narrow molecular weight distribution and they were purchased from across-organics with high purity. Poly (4-methoxystyrene) ($M_w = 24{,}900$), poly (4-methylstyrene) ($M_w = 72{,}000$), poly (4-tert-butylstyrene) ($M_w = 46{,}000$) and poly (α-methylstyrene) ($M_w = 9000$). Spectroscopic-quality dichloromethane, dichloroethane, tetrahydrofuran, and *N*, *N*-dimethyl formamide were found to give no detectable absorption in range 250–400 nm. These were purchased from Fluka GMBH and used as received. The used plasticizers were dimethyl terephthalate, diethyl terephthalate, dibutyl phthalate and dioctyl terephthalate. Such plasticizers were of high purity of (99.8%), and were found to give no detectable absorption in range 265–400 nm.

2.2. Preparation of plasticized polymeric solution

Stock solutions of polymers were prepared by dissolving an appropriate amount of each polymer in a 25 ml volumetric flask to produce a 1×10^{-3} M solution. These solutions were diluted to 1×10^{-4} M concentration in a 10 ml volumetric flask and were used for fluorescence spectra measurements. Furthermore, plasticized polymeric solutions were prepared in the same way mentioned above, and the concentrations of plasticizer were chosen within the range (1×10^{-4} to 1×10^{-5} M).

2.3. Fluorescence measurements

Fluorescence spectra were recorded on JASCO-FP 6500 spectrofluorometer for each of the prepared samples. The parameters used were constant for each one; the excitation wavelength for each polymer was 265 nm, and the emission wavelength range was (270–500 nm). On the other hand, the plasticized and non-plasticized polymer fluorescence spectra were recorded using JASCO FP-6500 fluorescence spectrofluorometer.

3. Results and discussion

3.1. Solvent effect on fluorescence of poly (p-substituted styrene)

The fluorescence spectra of polystyrenes, such as poly (4-methoxystyrene) PMXS, poly (α-methylstyrene) PαMS, poly (4-methylstyrene) PMS and poly (4-tert-butylstyrene) PTBS were measured in solvents of different polarities, such as dichloromethane DCM, dichloroethane DCE and tetrahydrofuran THF. The strong excimeric fluorescence from these polymers was affected by the substituents of the styrene ring and by the increase in solvent polarity. An example of fluorescence spectra of these polymers in DCE and is shown in Fig. 1.

The fluorescence spectrum consists of a short wavelength fluorescence band associated with emission from monomer aromatic moiety in the polymer chain, and a longer wavelength structureless fluorescence band attributed to emission from excimeric sites. Hence, PαMS fluorescence spectrum shows mainly monomer emission, whereas others show mainly excimer emission. The *para* substitution of the phenyl ring along the polymer chromophores resulted in breaking the symmetry of phenyl ring polystyrene and this in turn resulted in an increase of fluorescence intensities, accompanied with a slight shift in peak position toward the red region. It is well known that the excimer formation in many polymeric systems such as poly (*N*-vinylcarbazole), is not possible between adjacent aromatic chromophores due to the steric hindrance, evidence exists that such interaction occurs between adjacent chromophores in polystyrene [14]. In solution of polystyrene, it is clearly established that the singlet excimer formation is an intramolecular process since the ratio of monomer to excimer fluorescence intensities is independent of polystyrene concentration [15]. Moreover, excimer formation usually occurs between neighbor-

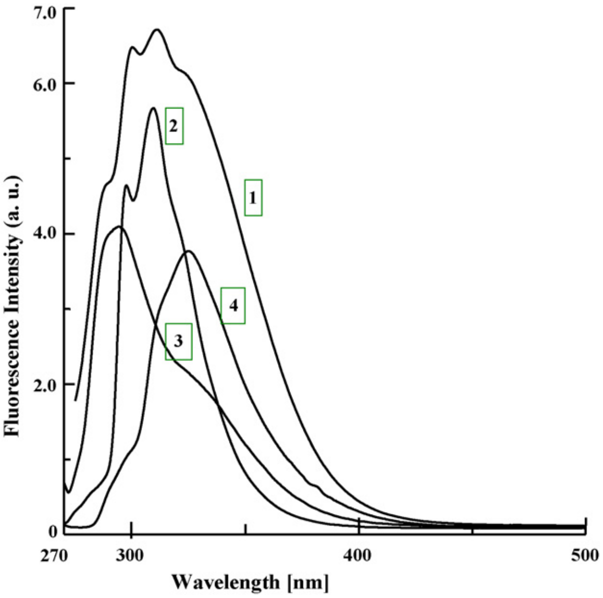

Fig. 1. Fluorescence spectra of SPS of 1×10^{-4} M in DCE solution; (1) PMS and (2) PTBS, and (3) PαMS, (4) PMXS (from top to bottom), at $\lambda_{exc} = 265$ nm.

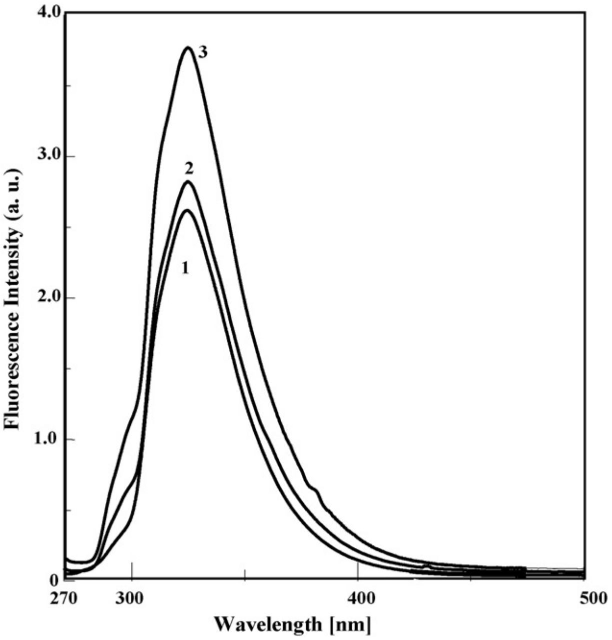

Fig. 2. Fluorescence spectra of PMS of 1 × 10^{-4} M in: (1) DCE, (2) DCM, and (3) THF at $\lambda_{exc} = 265$ nm.

ing chromophores, as well as, two end chromophores in the polymer chain; this has been demonstrated by the study of poly vinyl naphthalene and polystyrene, where the ratio of monomer to excimer fluorescence intensities is proportional to the styrene chromophores pair [16].

Relatively little work has been done on the study of the influence of solvents polarities on the intensity and shift of fluorescence of poly (p-substituted styrene). Fig. 2 shows the effect of change of solvents polarities on the intensities of monomer and excimer emissions of PMS in DCM, DCE and THF solvents at exciting wavelength of ($\lambda_{exc} = 265$ nm).

As can be seen in Fig. 2, the change in solvent polarity does not seem to change the shape of the fluorescence spectrum, or the position of λ_{max}, but there is a decrease in the fluorescence intensities with the increase in solvents polarity. As solvent polarity is increased, and polymer coil contacts, then, other factors become important in sustaining an increase in the ratio of excimer to monomer fluorescence intensities (I_E/I_M). This clearly noticed in Fig. 2, where the calculated ratio gives the values of 3.6 in THF, 4.6 in DCM, and 7.5 in DCE. These values show a significant increase in the ratio with the increase in solvent polarity. This can be attributed to the fact that in polar solvents, internal conversion process to excited monomer chromophores gains more importance with the increase in solvent polarity, and becomes the major excited state depopulation process for substituted polystyrene in polar media. This effect has been ascribed by Gould et al. to a varying degree of charge transfer character in the emitting species and, solvent molecules [17]. If we compare the effect of solvent polarity on excimer emission with that of the electron-donating ability of the solvents, it can be concluded from the data in Tables 1–4 that the dominant factor on the effect on fluorescence quenching is the effect of solvent polarity.

3.2. Effects of added phthalate plasticizers on the efficiency of fluorescence quenching of poly (p-substituted styrene) in solution

Phthalate and terephthalates as fluorescence quenchers were chosen as acceptors, because their lowest lying singlet state falls considerably lower in energy than that of substituted polystyrene. Thus, it can quench SPS fluorescence, and this will be preceded by a bimolecular collisional mechanism involving an excimer moiety, and plasticizer molecule. It was determined, however, that in fluid solutions, DMT, DET, DBP and DOT, quench SPS fluorescence at a rate corresponding to the diffusion limit with mechanism involving a charge transfer interaction between electronically excited SPS and ground state plasticizer molecule. The addition of increasing amount of plasticizer may result in a decrease in the fluorescence intensity of both monomer and excimer emissions. An example of this is the PMXS fluorescence quenching by DBP in DCM solvent, as shown in Fig. 3 below.

Little research work has been devoted to the quenching process of poly (p-substituted styrene) fluorescence by polymeric additives, such as terephthalate and phthalate plasticizers. It was

Table 1
Summary of the rate constants, k_q, K_{SV} and σ_Q^2 for PMXS, PαMS, PTBS and PMS in DCM, DCE, and THE solvents, by the added DET plasticizer

Polymer	Solvent	τ (ns)[a]	K_{SV} (L/mol)	k_q (L s^{-1} mol^{-1}) × 10^{11}	δ_Q^2 (cm^2) × 10^{11}
PMS	DCM	10.7	5,641	5.3	0.1
PMXS	DCM	5.4	10,590	19.6	0.6
PTBS	DCM	7.8	11,380	14.6	0.5
PαMS	DCM	11.4	4,207	5.1	0.1
PMS	DCE	6.6	6,881	10.5	0.3
PMXS	DCE	3.2	6,541	20.4	0.6
PTBS	DCE	5.1	14,254	28.0	0.9
PαMS	DCE	8.3	5,343	6.4	0.2
PMS	THF	10.7	4,519	4.2	0.1
PMXS	THF	5.8	7,023	12.1	0.3
PTBS	THF	7.8	7,276	9.3	0.3
PαMS	THF	8.4	3,227	2.9	0.07

[a] Lifetimes of SPS are from [23].

Table 2
Summary of the rate constants, k_q, K_{SV} and σ_Q^2 for PMXS, PαMS, PTBS and PMS in DCM, DCE, and THE solvents, by the added DMT plasticizer

Polymer	Solvent	τ (ns)[a]	K_{SV} (L/mol)	k_q (L s^{-1} mol^{-1}) × 10^1	δ_Q^2 (cm^2) × 10^{11}
PMS	DCM	10.7	5,969	5.6	0.1
PMXS	DCM	5.4	6152	11.4	0.3
PTBS	DCM	7.8	7880	10.1	0.3
PαMS	DCM	11.4	1530	1.4	0.03
PMS	DCE	6.57	4138	6.3	0.2
PMXS	DCE	3.2	5931	18.5	0.5
PTBS	DCE	5.1	6955	13.6	0.4
PαMS	DCE	8.3	2288	2.8	0.07
PMS	THF	10.7	3767	3.5	0.1
PMXS	THF	5.8	5033	8.7	0.2
PTBS	THF	7.8	7192	9.2	0.3
PαMS	THF	8.4	1400	1.7	0.04

[a] Lifetimes of SPS are from [23].

Table 3
Summary of the rate constants, k_q, K_{SV} and σ_Q^2 for PMXS, PαMS, PTBS and PMS in DCM, DCE, and THE solvents, by the added DBP plasticizer

Polymer	Solvent	τ (ns)[a]	K_{SV} (L/mol)	k_q (L s^{-1} mol^{-1}) × 10^{11}	δ_Q^2 (cm^2) × 10^{11}
PMS	DCM	10.7	1,350	1.3	0.3
PMXS	DCM	5.4	11,220	20.8	5.8
PTBS	DCM	7.8	13,017	16.7	5.6
PαMS	DCM	11.4	4,720	4.1	1.0
PMS	DCE	6.57	1,245	1.9	0.3
PMXS[b]	DCE	3.2	10,142	31.7	9.1
PTBS[b]	DCE	5.1	7,528	14.7	4.9
PαMS	DCE	8.3	1,012	1.5	0.4
PMS	THF	10.7	1,205	1.2	0.3
PMXS	THF	5.8	1,291	2.2	0.6
PTBS	THF	7.8	1,134	1.4	0.5
PαMS	THF	8.4	601	1.0	0.2

[a] Lifetimes of SPS are from [23].
[b] Data were based on Eq. (5).

reported that the presence of plasticizers in the solid films of poly (4-ethoxystyrene) would result in the quenching of both monomer and excimer emissions and in increasing the fluorescence intensity of a longer range band of the exciplex emission [18]. However, the fluorescence lifetime would remain constant, since only those excited polymer chromophores, which have the plasticizer molecules within some critical interaction radius would be quenched, while those without plasticizer molecules would give fluorescence with their unperturbed lifetime [19]. For all the quenching processes, there was no change in the shape of the fluorescence spectra, or change in the absorption spectra of substituted polystyrenes SPS—quencher system, even

Table 4
Summary of the rate constants, k_q, K_{SV} and σ_Q^2 for PMXS, PαMS, PTBS and PMS in DCM, DCE, and THE solvents, by the added DOT plasticizers

Polymer	Solvent	τ (ns)[a]	K_{SV} (L/mol)	k_q (L s^{-1} mol^{-1}) × 10^{11}	δ_Q^2 (cm^2) × 10^{11}
PMS	DCM	10.7	2,982	2.8	0.7
PMXS	DCM	5.4	5,258	9.7	58.0
PTBS	DCM	7.8	6,448	8.3	53.8
PαMS	DCM	11.4	2,871	2.5	14.0
PMS	DCE	6.6	3,531	3.2	3.0
PMXS[b]	DCE	3.2	12,390	38.7	146.8
PTBS	DCE	5.1	10,766	26.8	139.4
PαMS	DCE	8.3	10,057	16.7	93.3
PMS	THF	10.7	3,099	3.0	2.9
PMXS	THF	5.8	9,044	10.6	53.1
PTBS	THF	7.8	8,126	7.9	41.2
PαMS	THF	8.4	2,771	2.2	13.1

[a] Lifetimes of SPS are from [23].
[b] Data were based on Eq. (5).

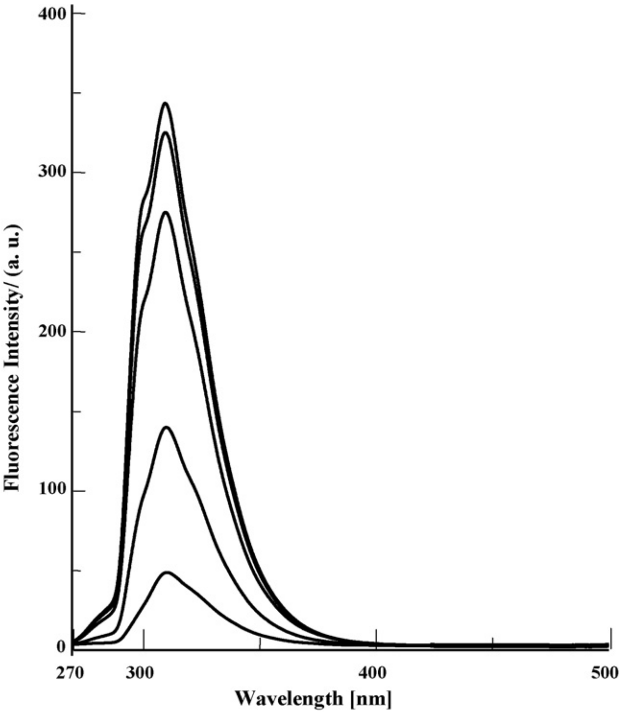

Fig. 3. Steady-state fluorescence quenching of PMXS by DBP in DCM. The DBP concentrations (from top to bottom) are: (1) 0.0 M, (2) 1×10^{-5} M, (3) 4×10^{-5} M, (4) 2×10^{-4} M and (5) 5×10^{-4} M, at $\lambda_{exc} = 265$ nm.

with high concentrations of the added plasticizers [18]. Thus no exciplex formation was observed in the present system, which indicates that the formed energy transfer complex between the excited polymer chromophore and plasticizer molecule is not stable enough to give exciplex emission or the other possibility is no ground state complex formation. In order to support this possibility, absorption spectra for PMXS containing a verity of DOT concentration in DCE solution, is shown in Fig. 4 below. Excitation was performed at 265 nm, where DOT molecules do not absorb and only the PMXS chromophores are excited. As can be seen, no change in the position of the absorption spectra or formation of a new absorption band at longer wavelength, indicating the absence of a ground state complex formation.

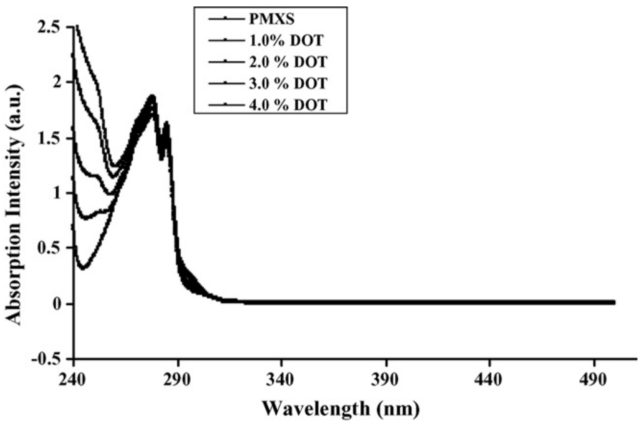

Fig. 4. The absorption spectra of PMXS with varying concentration of DOT in DCE. The concentration of PMXS is 1×10^{-4} M. The DOT concentrations (from bottom to top) are: 0.0, 1.0, 2.0, 3.0, and 4.0%.

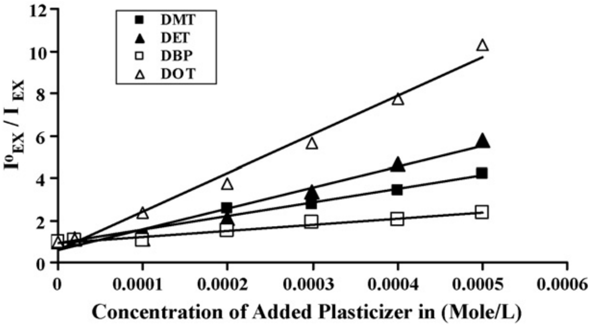

Fig. 5. Stern–Volmer plots for the fluorescence quenching of excimer emission band of PMXS by the added plasticizers, (DBP, DOT, DET, and DMT) in DCE solution. (Polymer concentration is 1×10^{-4} M solution, $\lambda_{exc} = 265$ nm.)

The fluorescence quenching processes of PMXS, PMS, PαMS and PTBS by DMT, DET, DBP and DOT in DCM, DCE, and THF solvents were achieved in this work. DOT plasticizer is the most efficient quencher where as DBP is the least efficient quencher. This trend of quenching efficiencies was found to be the same in PMS, PαMS and PTBS. Typical steady-state fluorescence quenching of PMXS by DMT, DET, DBP and DOT plasticizers in DCE solvent is shown in Fig. 5 below.

Fluorescence quenching experiments for a variety of SPS, containing various electron-donating (α-methyl, *para*-methyl, *para*-tert-butyl and *para*-methoxy) substituents with increasing the concentration of added plasticizers have been conducted. As can be seen in Fig. 6, the fluorescence emissions of PMXS, PMS, PαMS and PTBS are quenched efficiently by the addition of DBP plasticizer. PαMS showed a small quenching efficiency, whereas PTBS showed the highest efficiency of fluorescence quenching. The efficiency of fluorescence quenching is of the order PTBS > PMXS > PMS > PαMS. Such an order follows the combination of the electron-donating ability, and the bulkiness of the substituents of polystyrenes. The major part of the fluorescence from these polymers was excimer fluorescence, and the bimolecular collisions between the excimer chromophores and added plasticizer molecules resulted in the deactivation of

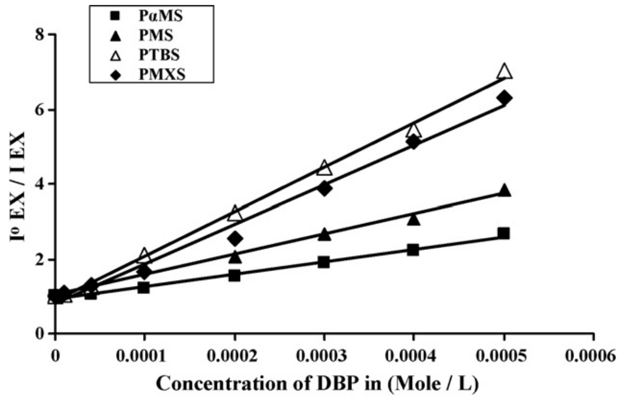

Fig. 6. Stern–Volmer plots for the fluorescence quenching of excimer emission band of PMXS, PMS, PαMS and PTBS by the added DBP in DCE solution. (Polymer concentration is 1×10^{-4} M solution, $\lambda_{exc} = 265$ nm.)

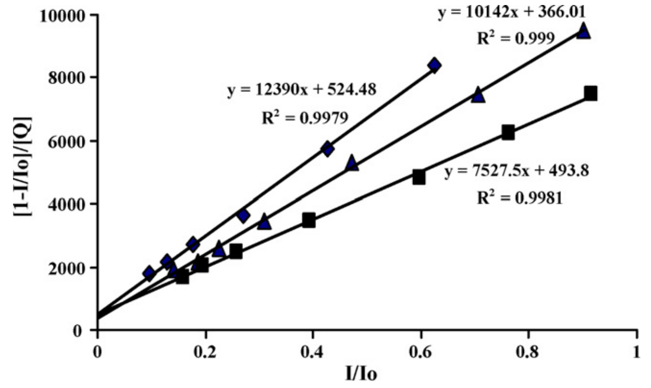

Fig. 7. Plot of $[1 - I/I^{o}]/[Q]$ against I/I^{o} for PMXS and PTBS quenched by DOT and DBP in DCE solvent ((■) PMXS quenched by DOT, (▲) PMXS quenched by DBP, and (◆) PTBS quenched by DBP).

the excimer fluorescence, without the appearance of the exciplex emission. This indicates that the formed energy transfer complex is not stable enough to give fluorescence emission.

To understand the effect of the polarity of solvents on the quenching rate constants, it is necessary to consider the electron acceptor ability of the excited singlet state of SPS. In most of these used solvents, the excited chromophores interact with solvent molecules, and form a complex with varying degree of charge transfer character [20]. As can be noted in Fig. 7 the quenching efficiencies of PTBS fluorescence by DOT in the solvents, DCE, DCM and THF showed a reasonable difference in quenching parameters. This can be indicative that quenching process is mediated by the complex SPS–DOT and the effectiveness of quenching process is reduced due to the competition with the solvent molecules, as the charge transfer interaction with the solvent increases [17,21].

Similar results were obtained from the fluorescence quenching of PMXS, PMS and PαMS with the other plasticizers in DCE, DCM and THF solvents. According to the Stern–Volmer scheme [22], the intensities of the unquenched $[I^{o}]$ and partially quenched $[I]$ emissions are given by Eqs. (1) and (2), where K_{SV} is the Stern–Volmer constant, k_{q} is the bimolecular quenching rate constant, τ is the excited state lifetime of SPS, and $[Q]$ is the quencher molar concentration of added terephthalate plasticizers.

$$\frac{I^{o}}{I} = 1 + K_{\mathrm{SV}}[Q] \quad (1)$$

$$K_{\mathrm{SV}} = k_{\mathrm{q}}\,\tau \quad (2)$$

Therefore, the bimolecular quenching rate constants (k_{q}) and the excited state lifetimes (τ), can be used to express the quenching efficiencies of these photo-physical processes. Collision cross-sections (σ_{Q}^{2}) values were calculated according to Eq. (3):

$$k_{\mathrm{Q}} = \sigma_{\mathrm{Q}}^{2}\left[\frac{8\pi RT}{\mu}\right]^{1/2} \quad (3)$$

where μ is the reduced mass.

The intensities of SPS fluorescence in different solvents in presence of terephthalate plasticizers were fitted according to Eq. (1), yielding values of K_{SV}. Using the measured values of the fluorescence lifetimes of SPS in the used solvents [23], the quenching rate constants (k_{q}) and quenching cross-sections (σ_{Q}^{2}) values for SPS in DCE, DCM and THF solvents by DET and DMT quenchers were calculated and are presented in Tables 1 and 2, below.

From Table 1, it can be observed that Stern–Volmer quenching constant is increased as the substituents of SPS have more electron-donating ability. This indicates that polystyrene derivatives containing more electron-donating substituents, such as PMXS and PTBS undergo probably faster photoinduced energy transfer amongst various SPS-plasticizer pairs. The Stern–Volmer plots of the excimer emission quenched by the used plasticizers are found to be linear for most of the used polymers in DCE, DCM and THF solvents, as shown in Figs. 4 and 5. These results support the fact that the quenching of excimer emission by the used plasticizer takes place through a dynamic mechanism. The dynamic quenching constants (k_{q}), in all cases are determined by the least square fit method using Eq. (1) and Figs. 6 and 7.

In the case of highly efficient quenching, the Stern–Volmer plots of the excimer quenching are deviated from linearity, and show positive deviation. An example of these are the fluorescence quenching of PMXS by DOT in DCE and the fluorescence quenching of both PMXS and PTBS by DBP in DCE solvent, and are shown in Figs. 4 and 5, respectively. Thus, positive deviation from linearity suggests that quenching is not purely collisional, and reveals the role of static quenching process. This can be explained by the fact that only a certain fraction (W), of the excited state is quenched by the collisional mechanism. Other chromophores in the excited state, the fraction of which is $(1 - W)$ are deactivated almost instantaneously after being formed. Several models were employed to describe this static quenching process [24,25], all of which leading to modification form of the Stern–Volmer equation.

$$\frac{I^{o}}{I} = \frac{\{1 + K_{\mathrm{SV}}[Q]\}}{W} \quad (4)$$

as W depends on the quencher concentration $[Q]$, the Stern–Volmer plots for a quencher of high quenching ability generally deviate from linearity, and then Eq. (4) is modified as follows:

$$\frac{[1 - I/I^{o}]}{[Q]} + K_{\mathrm{SV}}\left[\frac{I}{I^{o}}\right] + \frac{[1 - W]}{[Q]} \quad (5)$$

Fig. 8 below, shows the plots of $[1 - I/I^{o}]/[Q]$ against $[I/I^{o}]$ for PMXS quenched by DOT and DBP, and PTBS quenched by DBP, which are both linear according to Eq. (5).

The dynamic quenching constant K_{SV} is determined by the least square fit method, using Eq. (5). k_{q} and σ_{Q}^{2} values are also calculated and shown in Tables 3 and 4.

Fluorescence of SPS can be quenched through either energy transfer or electron transfer. To obtain information on the energetic for energy transfer and electron transfer processes, and examine which one is favorable quenching pathway, solvent effect on fluorescence quenching was investigated. In less polar solvent (THF, $\varepsilon = 7.8$), fluorescence of SPS proved to be much less efficiently quenched with adding DOT, DBP, DET and DMT

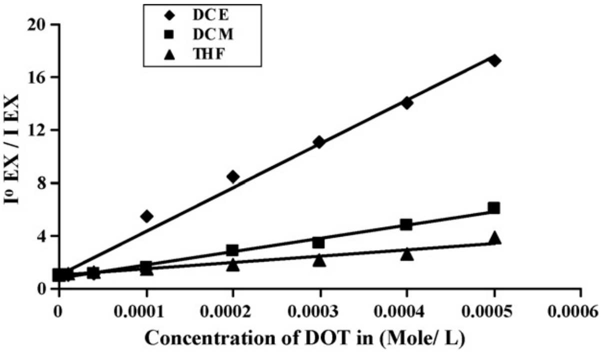

Fig. 8. Stern–Volmer plots of quenching of PTBS fluorescence with DOT plasticizer in DCE, DCM and THF solvents. (Polymer concentration is 1×10^{-4} M solution, $\lambda_{exc} = 265$ nm.)

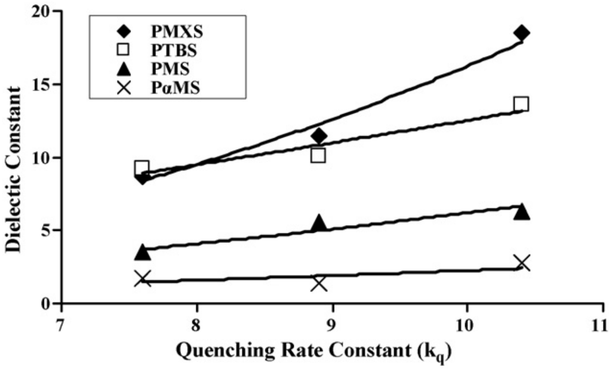

Fig. 9. Variation of k_q as function of dielectric constant of used solvents for fluorescence quenching of SPS by DMT.

than in more polar solvents such as (DCM, $\varepsilon = 8.9$ and DCE, $\varepsilon = 10.4$). These results support the fact that the fluorescence quenching may be attributed to the photoinduced electron transfer processes. We can be sure of that if we have the data of the redox potentials of SPS and the various plasticizers, then from the calculated free energy changes (ΔG_{OX}) for the photoinduced oxidative process, we can predict the type of fluorescence quenching process.

In case of low efficiency of quenching, a linear Stern–Volmer plots were obtained, the data for the quenching parameters, K_{SV}, k_q and σ_Q^2 for SPS in different solvents by DBP, and DOT plasticizer are included in Tables 3 and 4, respectively.

From the Stern–Volmer quenching constants $K_{SV} = k_q\tau$ and k_q for the fluorescence quenching of SPS that are listed in Tables 1–4. These constants are increased as the substituents of SPS have more electron-donating ability. This indicates that the SPS derivatives containing more electron-donating substituents, such as PMXS and PTBS undergo probably faster photoinduced electron transfer among other SPS derivatives. The order of increase in fluorescence quenching efficiencies in the three used solvents is PMXS > PTBS > PMS > PαMS. In addition, the increase in the K_{SV} and k_q values are attributed to two factors, first; the effect of solvent polarity, and second, the structure of the plasticized molecules. These quenching processes are accompanied by a fast photoinduced electron transfer and to enhancement of the non-radiative processes. To confirm the electron transfer quenching, solvent effect on fluorescence quenching was investigated. As evident in Tables 1–4, the fluorescence quenching constants, increase by the increase in dielectric constant of the used solvent. This may be attributed to the fact that the interaction between solvent molecules and excimer chromophores is affected by the change in solvent polarity. This effect of dielectric constant suggests the charge transfer character in the formed (SPS-plasticizer) complex. The high value of quenching rat constant (k_q), in polar solvent (DMF), compared to less polar solvent (THF), may also be explained by the greater charge transfer character of the excited complex in polar solvent [26]. Fluorescence quenching constants also increase by the increase in the molar mass of the plasticizer molecule. The order of increase in fluorescence quenching efficiencies in the three terephthalate plasticizers is DOT > DET > DMT, where dibutyl phthalate gave the less efficiency of fluorescence quenching. This may also be accounted for the less polarity of the phthalate molecule compared to that of terephthalate molecule.

We observed that the value of k_q increases as the dielectric constant of the solvent increases. This indicates that the character of the formed complex is of the type of charge transfer character. As can be noticed in Fig. 9 below, the effect of dielectric constant of the solvent used on the fluorescence quenching rate constant of SPS using DMT as a quencher molecule, showed an increase in quenching efficiency by the increase in the dielectric constant of the used solvents.

PMXS shows a large effect of increase in k_q value with the increase in the dielectric constant of the solvent, where PαMS shows the smallest effect. This indicates the combination of increase in the donating ability of the solvent and using a strong electron donor such as PMXS and PTBS can accelerate the excimer quenching efficiency.

4. Conclusion

In the present contribution, the effects of added plasticizers and solvents on fluorescence quenching efficiencies of SPS were investigated. From the calculated quenching rate constants for PMXS, PαMS, PMS and PTBS that were plasticized with DMT, DET, DBP and DOT in THF, DCM and DCE solvents; we can summarize the conclusions by:

- The Stern–Volmer plots showed a positive value of the slopes, leading to high values of quenching rate constants.
- K_{SV} and k_q values were found to increase with the increase in the polarity of the used solvents. This shows the possibility of different solvent molecules interaction around the solvated charge transfer complex (SPS–plasticizer).
- The fluorescence quenching efficiencies for these derivatives were affected by both the polarity of the solvents, and the molar mass of the added plasticizers. The quenching processes were accompanied by the decrease in both excimer and monomer fluorescence, without the appearance of the exciplex emission. Increasing the polarity of the used solvent caused an increase in the efficiency of quenching; this may

be attributed to the charge transfer nature of the quenching process.

- Terephthalate increased the efficiency of quenching by the increase in their molar masses. Hence, DOT was the most efficient quencher, and DMT was of the less efficiency of quenching ability. The increase in the polarity of the additive molecule may cause a destabilizing to the charge transfer complex formed during the quenching processes. Phthalate additive, DBP, showed a poor efficiency of quenching, and of course can be attributed to the small polarity compared with that for terephthalate.

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