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Effect of Solvent on Fluorescence and Fluorescence Lifetimes of *p*-Substituted Polystyrene

YASER A. YOUSEF*, KHALID E. AL-ANI† and TALAL AKASHEH†
Department of Chemistry, Faculty of Science, Yarmouk University, Irbid, Jordan
E-mail: yhaj@yu.edu.jo

Spectrophtometric measurements for solutions of polystyrene, poly(4-methylstyrene), poly(4-methoxystyrene), poly(α-methylstyrene), poly(4-*tert*-butylstyrene), poly(4-chlorostyrene) and poly(4-bromostyrene), were carried out in dichloromethane, dichloroethane, N,N-dimethyl formamide and tetrahydrofuran solvents. Although insignificant effects could be noticed on the absorption spectra of the polymers in various solvents, the differences in the fluorescence and fluorescence lifetime data were significantly clear. Intense fluorescence could be observed from these polymers when excited at their maximum absorption bands. Highest intensities were found to exist in poly(4-methoxystyrene) as well as in poly(4-*tert*-butylstyrene). The fluorescence lifetime data for any of the polymers could be fitted to a double exponential decay function. The decay included two lifetimes, the shorter lived signal identified as the monomer fluorescence and the longer lived one were assigned as the decay time of the excimer. The fluorescence lifetimes were found to be a function of solvent polarity, *i.e.*, decrease with increasing the solvent polarity. Furthermore, the fluorescence quantum yields for poly(4-methoxy styrene) were measured in four solvents and were found to decrease with increasing solvent polarity.

Key Words: Fluorescence lifetimes, *p*-Substituted polystyrene, Solvent effects.

INTRODUCTION

A number of comprehensive studies on the fluorescence of polystyrene and ring-substituted polystyrene in solution have been reported[1-4]. Nishihara and Kaneko[1] found that the ratio of the intensities of the excimer band to that of the monomer is a function of solvent polarity. The ratio was also found to increase with increasing concentration. This increase was accompanied by a red shift in the excimer band, especially in highly concentrated solutions. Torkelson *et al.*[2] reported the fluorescence intensity dependence on parameters such as solvent polarity and molecular weight. They found that the ratio of excimer to monomer fluorescence intensity increases very slowly and linearly in high concentrations. They, moreover, showed that the intermolecular excimer formation by non-adjacent chromophores were insignificant in dilute solutions of polystyrene[3]. Roots and Nystorm[4] reported the effect of concentration on the fluorescence spectra of polystyrene with different molecular weights. They demonstrated the capability of fluorescence as a technique in determining the critical concentration for transition from dilute to semi-dilute solution behaviour.

The decay lifetimes of excimer and monomer emissions were reported in many

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†Department of Chemistry, Faculty of Arts and Science, Hashemite University, Zarqa, Jordan.

studies[5-8]. However, literature was scarce as related to the influence of solvent nature and time resolved measurements on the photophysics of polystyrene and its para-substituted derivatives[5, 6]. For non-polymeric systems, only two studies have reported the effect of solvent on the fluorescence lifetime values of xanthene dyes[7] and curcumin[8]. It was reported that the fluorescence lifetimes for xanthene dyes increased markedly as the solvent was varied from water to a series of alcohol solvents ranging from methanol to octanol.

The increase in fluorescence lifetime was attributed to the variation in solvent viscosity. The fluorescence lifetime of curcumin was studied in different organic solvents[8]. Inter-system crossing and internal conversion were found to be enhanced when the substitution was fluoro or methyl group and also by the polarity of the solvent. Such finding was in agreement with that obtained for azafluorenone derivatives[9]. The rate of internal conversion increased with increasing solvent polarity to become the major excited state depopulation process for excited polystyrene derivatives in polar media.

Although fluorescence properties of polystyrene polymers were studied several decades ago, to the best of our knowledge no information could be found on the effect of phenyl substitution. The present work reports the fluorescence decay lifetimes of para-substituted polystyrene in solvents of different polarity. The solvents were chosen for their ability to dissolve the above mentioned polymers. Most of the measured decay lifetimes were found to be biexponential decay functions that could be attributed for monomer/excimer conformations. The latter was found to be more stable in polar solvents.

EXPERIMENTAL

Polymers were standard with narrow molecular weight distribution, as indicated in Table-1. All polymers with 99.8% purity were purchased from Aldrich Chem. Co. Polymer solutions used for dissolution were prepared at a concentration of 1×10^{-4} mol/L. Sufficient time was given to obtain complete dissolution before recording the measurements.

Spectroscopic-quality dichloromethane (DCM), N,N-dimethyl formamide (DMF), dichloroethane (DCE) and tetrahydrofuran (THF) were purchased from Fluka GMBH and were used as received. They were tested for emission when excited in the range 250–400 nm and no detectable emission could be observed.

Measurements of absorption and fluorescence

Absorption spectra for polymers in DCM and other used solvents were measured using Cary model 100 Bio UV-Vis spectrophotometer. The corrected fluorescence spectra were recorded using model FS 900 CDT steady state spectrofluorometer from Edinburgh Analytical Instruments (EAI). The spectrometer resolution was set to 2 nm band width by adjusting the inlet and outlet slit width for both excitation and emission monochromators to 200 µm. All solutions were thoroughly degassed by the freeze-pump-thaw technique before they were measured. The relative fluorescence quantum yields for polymers were determined by following the procedure described by Parker[6, 10]. Fluorescence lifetimes (τ_f) were measured using model FL-900 CDT time-correlated single photon counting spectrophotometer from Edinburgh Analytical Instruments[11]. A block diagram for the system is shown in Fig. 1. The most significant features within

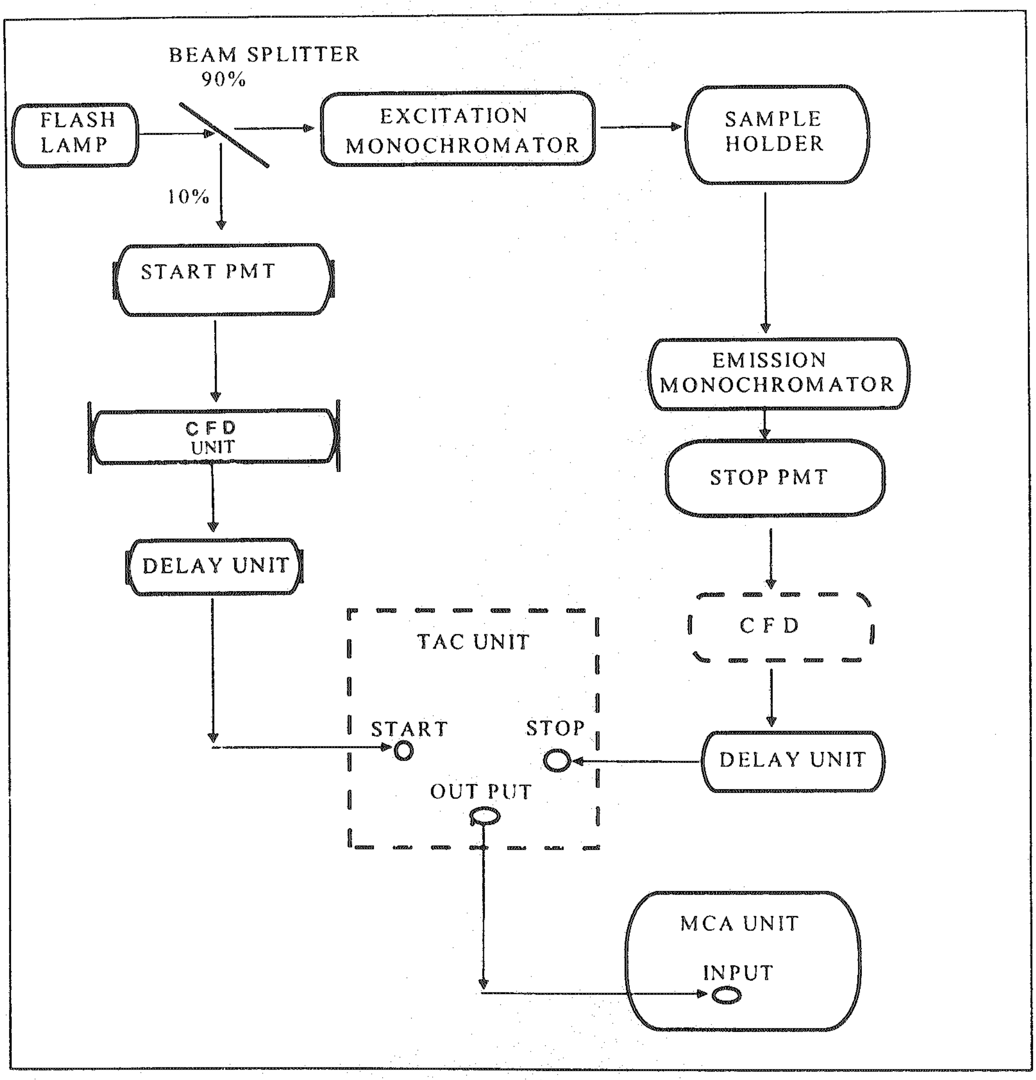

Fig. 1. Block diagram for the time correlated single photon counting system

the scheme are the lamp, the time-to-analogue converter (TAC) unit, and the multi channel analyzer (MCA) unit. Hydrogen flash lamp operating at 20 kHz is normally used as the UV light source in the wavelength range 200–300 nm. The lamp operating conditions are adjusted for a minimum pulse width of 2 nsec. Lamp intensity and pulse width are continuously monitored for any changes using special electronic units. Excitation and emission monochromators are adjusted for a spectral resolution of 5 nm. The TAC range was set to 50 nsec as the decay profiles for all samples are expected to fall within this time range. The TAC output is connected to the MCA, which is set to operate in pulse height analysis (PHA) mode. A set of 1024 channels corresponding to 50 nsec time range was used to represent the decay profile. The decay profile for the lamp and the combined lamp/sample profile are transferred to a computer that uses deconvolution software to extract the sample fluorescence decay time. The deconvolution software enables the determination of the number of decay times in the decay profile as well as their corresponding ratios.

TABLE-1
ABSORPTION AND FLUORESCENCE PARAMETERS FOR POLYSTYRENE AND PARA-SUBSTITUTED POLYSTYRENE IN DCM[a] AT $\lambda_{ext.}$ = 265 nm

Polymer	m.w.	Mn	Absorption peak (nm)	Fluorescence band (nm)	Φ_f^b	Stoke shifts (cm^{-1})	τ_{f2} (ns)^c	τ_0 (ns)
PS	212000	155000	269, 262, 254	283, 335	0.041	1839	12.9	322
PMXS	50000	24000	285, 274, 267	295, 330	0.122	1187	5.4	48
PMS	72000	40000	284.8, 275, 267	291, 318	0.104	748	10.8	104
PTBS	24000	10000	284.2, 271, 263	290, 318	0.227	763	7.8	34
Pα MS	9000	4000	277.9, 269, 262	290, 319	0.075	1502	8.3	111
PCS	65000	31000	277, 268.5, 261	289, 322	0.030	1499	5.2	173
PBS	75000	33000	277, 268, 261.6	290, 318	0.013	1619	5.6	430

[a] The concentrations of substituted polystyrene are 1 × 10^{-4} M.
[b] All Φ_f values were based on PS-value from Ref. 6 and 8.
[c] Fluorescence lifetime of excimer conformations.

RESULTS AND DISCUSSION

Steady state absorption spectra

The absorption spectra for polystyrene and para-substituted polystyrenes in dichloromethane at room temperature are shown in Fig. 2. Three different peaks can characterize the absorption spectrum for polystyrene with values around 269, 262 and 254 nm. The effect of substitution is found to enhance the extinction coefficient for all solutions. Moreover, a band red shifts with values dependent on the type of the substituent. PMXS, PMS and PTBS show three peaks at around 285, 275 and 261 nm, while PCS, PBS and PαMS show three peaks at around 275, 266 and 261 nm. It is clear that the para-substituted groups in phenyl chromophore along the polymer chain exhibit a red shift in their absorption band positions, implying that the electronic transitions in PS are enhanced by the presence of the para-substituents, owing to the reduction of the HOMO-LOMO gap. The electron-donating groups such as —OCH_3, —CH_3 and —$C(CH_3)_3$ show a bathochromic effect of 16.0 nm, compared with about 9.0 nm for Cl, Br and —αCH_3. The peak shifts indicate that the transition of the styrene moiety is influenced by an inductive effect of the first group and mesomeric effects in the second group of substituents. These results are in complete agreement with those obtained in functionalized fullerene[12]. Fig. 2 indicates that there are variations in the absorption coefficients of these substituents, although the polymers have different molecular weights.

On the whole, solvent effects on absorption maxima of the polymer results from a non-specific salvation, which depends only on bulk solvent parameters such as dielectric constant (ε). These also result from non-specific solute-solvent interactions[13]. In the absence of any specific solvent-solute interactions, the energy of electronic transition increases with increasing solvent polarity, which is the function of solvent polarization $[(\varepsilon - 1)/(2\varepsilon + 1)]$ (Kirkwood function) as shown in Table-2. The different polarity of the solvents used shows minor effects on absorption coefficients of these para-substituted polystyrenes.

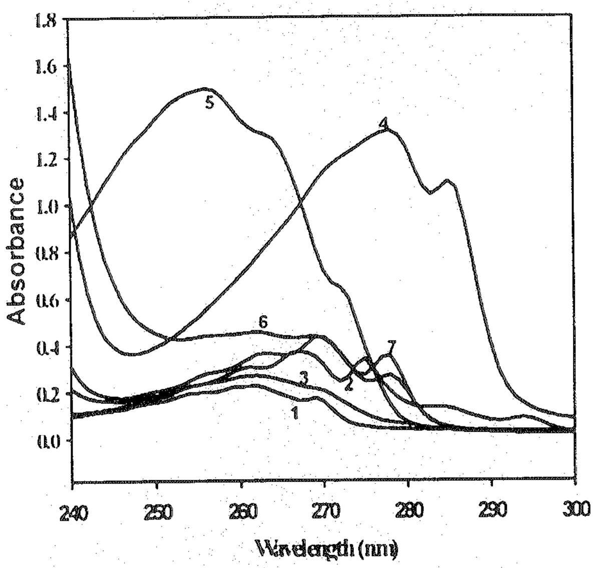

Fig. 2. Absorption spectra of *p*-substituted polystyrene in DCM. The concentration is 1 × 10^{-4} mol/L, at 25°C, 1-PS, 2-PMS, 3-PAMS, 4-PMXS, 5-PTBS, 6 PCS and 7-PBS

TABLE-2

EFFECT OF SOLVENT POLARITIES ON (I_E/I_M) AND DECAY LIFETIME FOR POLY(4-METHOXYSTYRENE) SOLUTIONS[a], $\lambda_{emis.}$ = 300 nm and $\lambda_{ext.}$ = 265 nm

Solvent	$\lambda_{max\ abs}$ (nm)	Φ_f	I_E/I_M	τ_1 (ns)	τ_2 (ns)	Dielectric constant (ε)[b]	$(\varepsilon - 1)/(2\varepsilon + 1)$
THF	273.0	0.112	3.80	1.10	5.80	7.6	0.384
DCM	274.5	0.122	3.38	0.94	5.40	8.9	0.401
DCE	275.0	0.204	3.30	1.04	3.93	10.4	0.411
DMF	277.0	0.215	3.26	1.06	3.40	36.7	0.473

[a]The concentration is 1 × 10^{-4} M.

[b]Dielectric constant values (ε) from Ref. 2.

Steady state fluorescence spectra

The fluorescence spectra for polystyrene and *p*-substituted polystyrenes in dichloromethane are shown in Fig. 3. Except for PCS and PBS, all used substituents show higher fluorescence intensities than in PS. The increase in fluorescence intensity can be ascribed to the break of symmetry of the phenyl ring leading to an increase in transition probability. The high rate of radiationless processes in PCS and PBS can be said to be the main reason for the drop in their fluorescence intensity. Two distinctive bands characterize the fluorescence spectra for all polymers. The short wavelength band is normally attributed to monomer florescence, whereas the band at higher wavelength is normally attributed to excimer fluorescence[2]. This concurs with the data reported by Hiarayama[14], where the fluorescence emission of PS was excimeric in nature. The mechanism of excimer formation in polystyrene involves initial excitation of the aromatic chromophore followed by singlet excitation migration along the polymer chain until the excitation is competitively trapped at a chain conformation. This condition is suitable for excimer

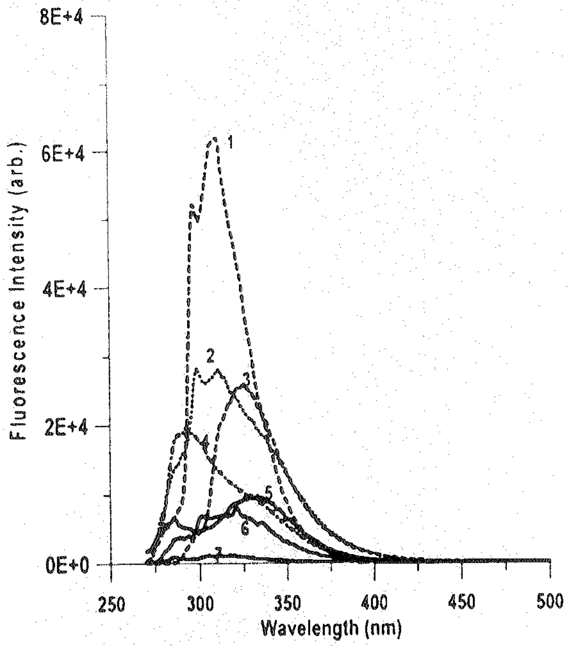

Fig. 3. Corrected fluorescence spectra for para-substitutedpolystyrene in DCM solution at (1×10^{-4} mol/L), 1-PTBS, 2-PMS, 3-PMXS, 4-PAMS, 5-PS, 6-PCS and 7-PBS, at $\lambda_{ext.}$ = 265 nm

formation[15]. Upon substitution, the electrondonating groups cause red shifts in the monomer fluorescence maxima compared with PS. On the other hand, excimer fluorescence band shows a blue shift compared to that for PS. The shift in fluorescence bands is attributed to the electron-donating groups which is affected by the electronic potential curves in the ground and excited states[12, 16].

Polar solvents cause considerable effects on both monomer and excimer fluorescence bands, as can be seen for PMXS in various solvents as shown in Fig. 4 and Table-2. It is obvious that the increase in fluorescence intensity is related to the increase in solvent polarity. This effect has been ascribed by Gould *et al.*[17] to a varying degree of charge transfer interactions of the singlet-excited state of para-substituted polystyrene and solvent molecules. Fig. 4 shows the correlation between the polarity of the solvent (ε) and the magnitude of the fluorescence intensities. This suggests that the behaviour is a consequence of a general polarity effect of the solvent molecules and the excited singlet state polymer chromophores. For PMXS the better-resolved fluorescence peak at 274 nm in DCM showed a small red shift in other solvents of higher polarity. In DCM the stoke shifts caused by para-substitution which is compared with polystyrene indicates that electron-donating groups affect the electronic potential energy curves in the excited and ground states. Absorption and emission maxima are summarized in Table-1.

The dependence of the intensities of excimer to monomer emission bands on solvent polarity is presented in Table-2. The values of (I_E/I_M) were corrected for the absorption of the monomer fluorescence as described by Matsuyama *et al.*[18] The (I_E/E_M) ratios in solvents of different polarities are in agreement with those of Torkelson *et al.*[3] on polystyrene. As the solvent polarity is reduced, other factors may be important in sustaining an increase in the (I_E/I_M) values. Thus, we have

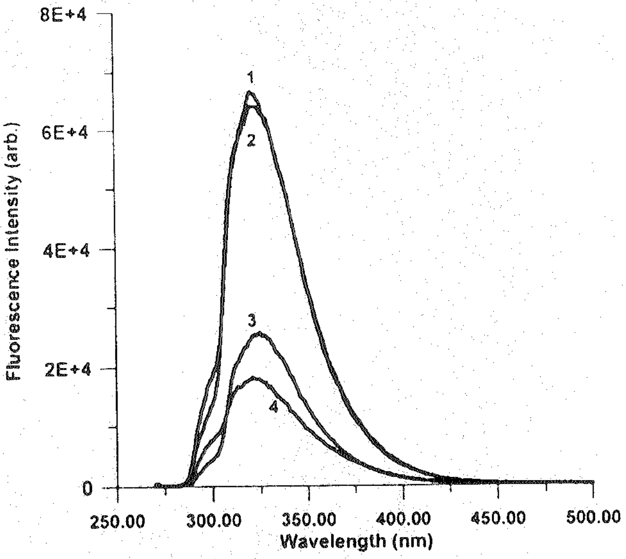

Fig. 4. Corrected fluorescence spectra for poly(4-methoxystyrene) in: 1-THF, 2-DCM, 3-DCE and 4-DMF at $\lambda_{ext.}$ = 265 nm and at (1×10^{-4} mol/L) concentration

considered one possibility that poly-substituted styrene-solvent interaction stabilizes the lowest excited singlet state to a greater extent than the ground state for solvent of higher polarity. This interaction tends to stabilize the formation of the energy transfer-excimer conformations[17].

Fluorescence quantum yield

The fluorescence quantum yields for para-substituted polystyrene in DCM solution were determined by using a comparative method[19]. The fluorescence quantum yield of polystyrene in DCM was used as a reference with a value of 0.04 at 265 nm excitation[6, 10]. If the differences in absorption coefficient values of these substituents were considered, then para-substitution of the styrene causes an increase in the fluorescence intensity and quantum yields. In DCM, the fluorescence quantum yields for the polymers were 0.227, 0.122 and 0.03 for PTBS, PMXS and PCS, respectively. The fluorescence quantum yields of PMXS in various solvents are reported in Table-2. The quantum yields are relatively high; the fluorescence intensities and quantum yield (Φ_f) of the para-substituted polystyrene decreases markedly with an increase in solvent polarity, as shown in Fig. 4 and Table-2, which suggests that an extra deactivation pathway competes with the radiative path[20]. The fluorescence lifetime data (τ_f) could be related to the natural lifetime (τ_0) *via* the fluorescence quantum yield (Φ_f):

$$\tau_0 = \tau_f/\Phi_f$$

Using this expression, the natural lifetimes of PS and poly-para-substituted styrene in DCM were calculated (Table-1). The Φ_f values for PMXS in various solvents were found to be very sensitive to solvent polarity (Table-2). The Φ_f values are relatively high in THF (0.215) and DCE (0.204), but lower in DMF (0.088). These observations are in agreement with the data obtained for Curcumin[8, 21]. In conclusion, although fluorescence for these polymers exists as monomer and excimer, the excimeric fluorescence is the dominant. Thus, the

Φ_f values represent the excimeric fluorescence quantum yield. Therefore, charge transfer-excimer conformations were destabilized in polar solvents; they are reduced due to a more non-radiative interaction in polar solvents.

Fluorescence decay time

The time dependence of fluorescence intensities of polystyrene and its para-substituted derivatives is biexponential in solvents of different polarities as illustrated in Table-3.

The fluorescence decay profiles for the polymers are shown in Fig. 5. Phillips *et al.*[6] obtained similar results for polystyrene in DCM. The decay was biexponential with τ_1 of 1.02 ns and τ_2 of 18.9 ns, respectively. Our study on these four solutions employs solvents of different dielectric constants indicating that the amount of excimer conformations is more than that of monomer conformations. The study also shows that the amount of excimer conformation increases with increasing solvent polarity. The effect of para-substitution of styrene on the lifetimes in solvents of different polarity, as in THF, DCM, DCE, and DMF solvents, is shown in Fig. 5 and Table-3. There is an increase in the decay time of the excimer and decrease in that of the monomer. This effect becomes clearer by increasing solvent polarity[22, 23]. The effects of decreasing solvent polarity on the decay lifetimes of PMXS have increased the lifetime of monomer conformations and decreased the lifetime of excimer conformations. This behaviour could be caused by the stabilization of the monomer conformations by forming a stable energy transfer complexation with solvent molecules.

TABLE-3

FLUORESCENCE DECAY TIMES FOR (EXCIMER τ_2) AND (MONOMER τ_1) OF PARA-SUBSTITUTED POLYSTYRENE AT CONCENTRATION OF (1×10^{-4} M) AT λ_{emis} = 300 nm AND AT λ_{ext} = 265 nm

Polymer	χ^2	τ_1 (ns)	τ_2 (ns)	B_1	B_2	B_2/B_1
PS[a]	1.06	1.90	12.90	11.0	89.0	8.09
PMS[a]	1.12	3.60	10.70	10.0	90.0	9.00
PMXS[a]	0.98	1.10	5.80	46.0	54.0	1.17
PTBS[a]	0.99	—	7.80	—	100.0	—
PαMS[a]	1.10	2.90	8.40	49.0	51.0	1.02
PCS[a]	1.05	0.80	10.50	50.1	49.9	1.00
PBS[a]	0.97	2.03	7.50	42.0	58.0	1.38
PS[b]	1.02	1.90	12.80	3.6	96.4	28.40
PMS[b]	1.12	3.60	10.70	10.6	89.4	8.43
PMXS[b]	1.09	0.94	5.40	38.0	62.0	1.63
PTBS[b]	1.10	2.30	7.70	19.6	80.4	4.12
PαMS[b]	1.05	2.90	8.40	7.6	92.4	12.15
PCS[b]	1.11	0.70	8.60	49.0	51.0	1.02
PBS[b]	0.97	2.00	6.50	42.4	57.6	1.36

Polymer	χ^2	τ_1 (ns)	τ_2 (ns)	B_1	B_2	B_2/B_1
PS[c]	0.98	1.70	10.20	44.0	56.0	1.27
PMS[c]	1.00	2.20	6.57	42.0	58.0	1.38
PMXS[c]	1.10	1.04	3.93	44.0	56.0	1.27
PTBS[c]	0.99	2.30	7.10	19.5	80.5	4.13
PαMS[c]	1.10	1.85	8.30	48.0	52.0	1.08
PCS[c]	1.05	0.55	8.20	35.0	65.0	1.86
PBS[c]	1.04	1.00	5.60	29.0	71.0	2.45
PS[d]	1.00	1.60	12.00	40.0	60.0	1.50
PMS[d]	1.01	1.50	6.30	83.0	17.0	0.20
PMXS[d]	1.01	1.06	3.40	65.0	35.0	0.54
PTBS[d]	1.07	—	7.00	—	100	—
PαMS[d]	0.98	2.80	8.30	37.0	63.0	1.70
PCS[d]	1.10	0.81	7.40	85.9	14.1	0.16
PBS[d]	1.01	1.10	5.50	56.3	43.7	0.77

a = THF; b = DCM; c = DCE and d = DMF.

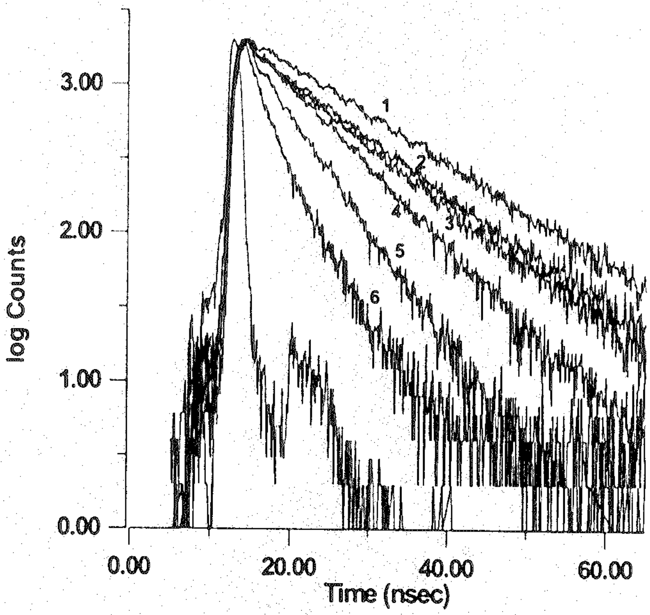

Fig. 5. Fluorescence lifetime of para-substituted polystyrene in DCE solution at $\lambda_{ext.}$ = 265 nm, λ_{emis} = 300 nm and at (1 × 10^{-4} mol/L), 1-PS, 2-PAMS, 3-PMS, 4-PTBS and 5-PMXS

Conclusions

The photophysical behaviour of PSS is strongly dependent on the solvent. The position and intensity of the fluorescence and the fluorescence quantum yield of PMXS shows a dependence on solvent polarization, while the ground state absorption spectra show less solvent sensitivity. In general, these effects can be attributed to the ability of PSS to participate in charge transfer interactions. Thus, the fluorescence quantum yield (Φ_f) was found to decrease with the increase of dielectric constant values of solvents. The decay times of PSS monomers were found to increase with increasing solvent polarity; on the other hand, the decay time of the excimer fluorescence is found to decrease. This may be attributed to the stabilization of the monomer, by forming a stable energy transfer complexation with solvent molecules.

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