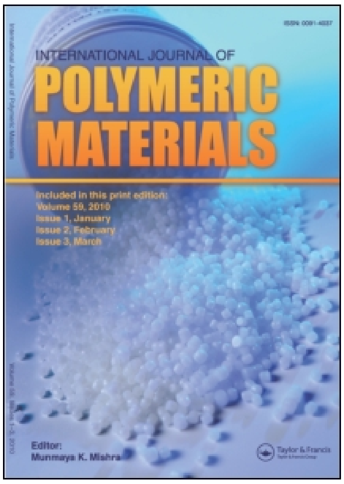

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Decay Lifetimes of Para-Substituted Polystyrene in Solid Films and in Dichloromethane

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*The fluorescence decay times of polystyrene, poly(4-bromostyrene), poly(4-chlorostyrene), poly(4-methylstyrene), poly(α-methylstyrene), poly(4-methoxystyrene), and poly(4-*tert *butylstyrene) were measured in solid films and in dichloromethane solution. A detailed analysis of the emission profile performed by nanosecond time resolved fluorescence spectroscopy confirmed the presence of monomer fluorescence as well as excimer fluorescence in both media. Monomer fluorescence decay times gave shorter times compared with that of excimer decay times in dichloromethane solution. Fluorescence from substituted polystyrene was mainly excimer fluorescence with shift of maximum emission to longer wavelength. The ratio of monomer to excimer contributions was found to be dependent on the emission wavelength, but was not affected by polymer concentration. Both monomer and excimer fluorescence lifetimes as well as excimer intensity increase with increasing emission wavelength. An accompanying decrease in monomer contribution is also observed is solution in comparison with that in solid films.*

Keywords: decay lifetimes, excimer fluorescence, monomer fluorescence, para-substituted polystyrene, solvent effect on decay lifetime

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INTRODUCTION

Polystyrene and its derivatives are extensively used as resins, construction materials, and packaging materials. Because they are susceptible to thermal and photochemical degradation, the measurement of their fluorescence quantum yields and decay lifetimes in solid films can be highly important in an attempt to understand such photochemical and photophysical processes. The chromophores attached to the polymer backbones can undergo electronic energy transfer, thus attracting considerable interest in the photochemical [1] and the photophysical [2] processes that occur. In particular, the prevalence of monomeric and excimeric contributions [2–4] could provide a deep insight for developing a possible approach for the study of the photophysical processes for substituted polystyrenes [4–7].

An earlier study [5] found that ring-substituted polystyrene exhibits excimeric and monomeric fluorescence in both solid films and solution. The ratio of monomer fluorescence intensity to that of excimer fluorescence was found to depend on the molar mass of the polymer [6]. The value of this ratio in solid films is lower than that in solution. Winnik also found that the fluorescence decay time for excimer fluorescence monitored at different wavelengths in pyrene [8] and polystyrene [9–10], showed biexponential decay. The major component resulted from monomeric fluorescence and a minor component was attributed to excimer fluorescence.

The present work reports the fluorescence decay times for polymeric and excimeric conformations in solid films and in dichloromethane solution, as well as the effect of emission wavelengths on decay lifetimes for some para substituted polystyrenes.

EXPERIMENTAL

Materials

Substituted polystyrenes were synthesized by thermal free radical polymerization in solution using α-α'-azobis (iso-butyronitrile) (AIBN), as initiator by a previously described procedure [8]. They were reprecipitated several times into methanol and found to have a viscosity average molecular weights as presented in Table 1. Dimethyl terephthalate (DMT) was purchased from Fluka GMBH; moreover, it was recrystallized several times in benzene and vacuum sublimed. Spectroscopic-quality, dichloromethane (DCM), dichloroethane (DCE), tetrahydrofuran (THF), and benzene were found to give no detectable emission when excited in the range 250–400 nm. These solvents were purchased from Fluka GMBH and were used as received.

TABLE 1 Absorption and Emission Maxima of Poly(Para-Substituted Styrene) in Solid Films, and in DCM Solution at (1.0×10^{-4} M)

Polymer	Mw	$\lambda_{\text{max. abs.}}$ (nm) (solid films)	$\lambda_{\text{max. emis.}}$ (nm) (DCM[†])	$\lambda_{\text{max. emis.}}$ (nm) (solid films)
PS	210 000	269, 261, 252	283, 335	309, 335
PMS	72 000	275, 265, 261	291, 318	345
PαMS	11 000	269, 261, 259	290, 319	312, 336
PMXS	50 000	286, 279, 262	295, 330	345
PTBS	24 000	272, 264, 256	290, 318	310, 322
PCS	65 000	278, 271, 263	289, 322	312, 336
PBS	75 000	279, 271, 263	290, 318	309, 334

[†] Fluorescence bands in DCM were obtained from Reference [12].

Solid Films Preparation

For the purpose of obtaining polymer solid films, a 10–20 mg sample of the polymer was prepared and dissolved in a certain amount of dichloroethane solvent. The carefully mixed solutions were poured onto leveled quartz plates. After a slow evaporation of solvent, the resulting thin films (about 50 μm thick) were carefully dried at room temperature for 2 h to allow slow evaporation of the solvent. Films were further dried under vacuum at 20°C for 6 h in order to evaporate any residual solvent present in the polymer film by obtaining a constant weight. The resulting films appeared to be of uniform thickness and were optically clear. No effort was made to determine film thickness or to keep a constant thickness, because this parameter had no apparent effect on the experimental results after removal from the plate [7].

Absorption and Fluorescence Measurements

Absorption spectra for polymers in DCM were measured using a Cary 100 Bio UV-Visible spectrophotometer. The spectra for solid films were recorded by using a solid sample cell. To record the corrected fluorescence spectra of the polymers in DCM or solid films, samples were excited at (260–280 nm) and measuredon an FS 900 CDT steady state spectrofluorometer from Edinburgh Analytical Instruments (EAI).

Fluorescence Decay Time Measurements

Fluorescence decay times were measured using a FL 900 CDT nanosecond time correlated single photon counting spectrophotometer [11], from Edinburgh Analytical Instruments.

The poly(para-substituted) styrene used in this study were assigned the following abbreviations: polystyrene PS; poly(4-methylstyrene) PMS; poly(4-methoxystyrene) PMXS; poly(α-methylstyrene) PAMS; poly(4-chlorostyrene) PCS; poly(4-bromostyrene) PBS, and poly (4-*tert*-butylstyrene) PTBS.

RESULTS AND DISCUSSION

Steady State Absorption and Emission Spectra

All the studied polymers were found to absorb in the UV-region, in DCM and in solid films [10]. The absorption spectra for polystyrene and para-substituted polystyrene in solid films are shown in Figure 1. All spectra show three absorption bands that are red shifted and more intense compared to polystyrene. The electron-donating groups introduced on the phenyl ring such as OMe in PMXS induce a large bathochromic shift of about 17 nm. The increase in extinction coefficient results from the change in symmetry in going from poly [styrene] to the para substituted compounds. The absorption spectra also shows a small red shift compared to that in DCM solution as was reported in previous work [12]. Figure 2 shows the steady state of fluorescence spectra for PS and poly(para-substituted styrene) in solid films. The absorption and emission maxima are summarized in Table 1.

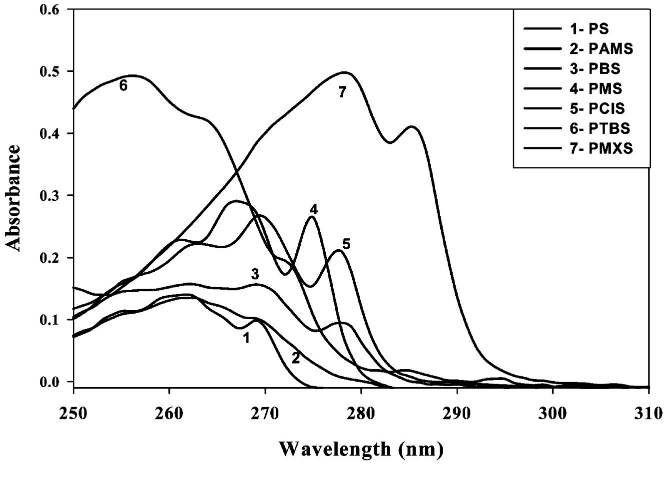

FIGURE 1 UV-absorption spectrum of para-substituted polystyrene in solid films at 25°C.

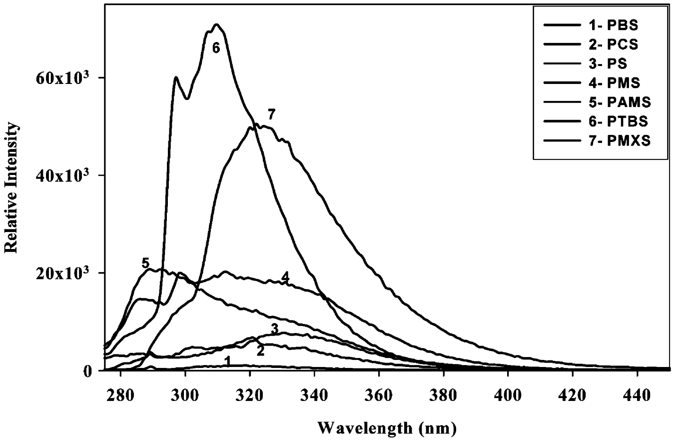

FIGURE 2 Normalized fluorescence spectra for para-substituted polystyrene in solid films at an excitation wavelength of 265 nm.

Table 1 and Figure 2 show that the fluorescence spectrum consists of a slightly structured short wavelength fluorescence band associated with emission from the monomeric aromatic moiety in the polymer chain. They also show a longer wavelength structureless fluorescence band attributed to emission from excimeric sites. Apart from PMS and PMXS, only excimeric fluorescence was observed, and all other polymers showed both bands. In comparison with PS, the fluorescence intensities are higher and affect the peak position; suggesting that breaking the symmetry of PS by para-substitution results in an increase of fluorescence intensities, with a slight shift in peak positions.

Fluorescence Decay Times

Figure 3 shows the fluorescence decay time for all polymers in DCM at concentrations of 1×10^{-3} M. Biexponential decay is observed, thus indicating that the decay curves have contributions from both monomer fluorescence and excimer fluorescence in solution and in solid films (Figure 4). Experimental results showed that the lifetimes of the monomer and excimer are entirely independent of polymer concentration. The data correlate very well to the biexponential decay obtained by Phillips *et al.* for polystyrene in DCM [13]. The short-lived component was assigned to the monomer fluorescence; the other was assigned to the excimer fluorescence [14–15]. The biexponential decay times and the ratio of excimer conformations to that of monomer conformations (B_2/B_1) in dichloromethane solution and in solid films

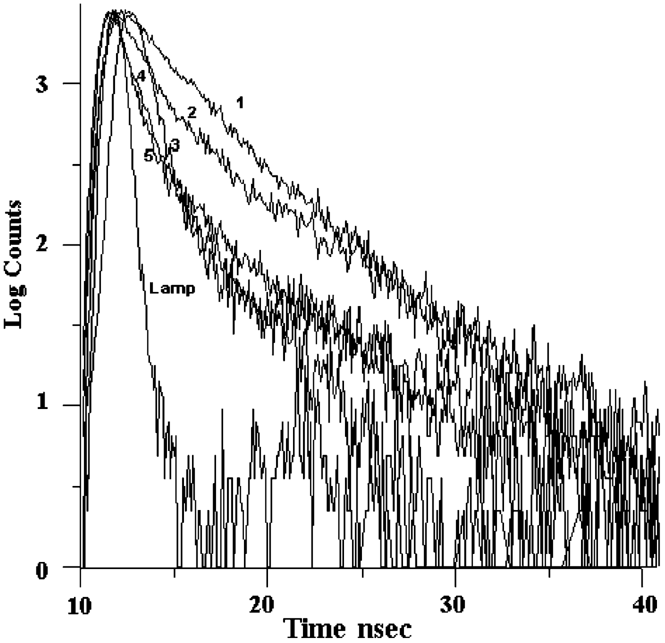

FIGURE 3 Fluorescence decay times for para-substituted polystyrene in DCM, 1-PAMS, 2-PMS, 3-PMXS, 4-PS, 5-PTBS at an excitation wavelength 265 nm, emission wavelength of 300 nm and 0.0001 M concentration.

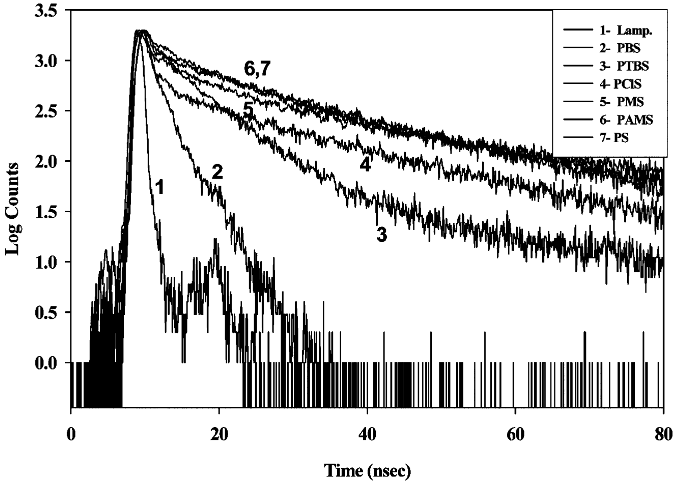

FIGURE 4 Fluorescence decay time curves of para-substituted polystyrene in solid films at an excitation wavelength of 265 nm and emission wavelength of 300 nm.

TABLE 2 Fluorescence Decay Times for Poly(Para-Substituted Styrene) in Solid Films and in DCM† Solution, at λ_{exc} of 265 nm, and at (1.0×10^{-4} M) Concentration

Polymer	λ_{emis} nm	χ^2	τ_1 ns	τ_2 ns	B_2/B_1
PS†	300	1.00	1.50	12.9	7.77
PMS†	280	0.98	3.60	10.7	3.85
PMXS†	300	0.99	0.70	5.40	1.38
PTBS†	300	0.94	2.30	7.80	3.18
PαMS†	300	0.95	2.90	11.4	4.10
PCS†	300	0.99	0.79	8.60	1.93
PBS†	320	0.97	2.00	4.50	1.36
PS	300	0.93	1.08	12.9	8.90
PMS	280	1.00	5.87	8.60	2.34
PMXS	300	0.98	3.06	10.5	2.54
PTBS	300	0.90	2.70	4.08	3.69
PαMS	300	0.94	4.0	7.70	5.59
PCS	300	0.99	1.35	12.0	8.80
PBS	320	0.91	0.76	4.40	3.22

†All decay lifetimes for DCM solution were obtained from Reference [12].

are shown in Table 2. B_1 represents the percent of monomer emission; B_2 represents the percent of excimer emission; and both were obtained as intensities at $t = 0$ from the biexponential curve fitting. From the experimental data for τ_{f1} and τ_{f2} in Table 2, it can be seen that τ_{f2} values in solid films are higher than those in DCM. The B_1/B_2 ratios for solid films are also higher than those in DCM solution, indicating that in solid films, there is an enhancement in excimer formation [16].

The fluorescence decay of PMXS was monitored at wavelength range of (290–350 nm) as shown in Figure 5 and Table 3, where it can be noticed that emission at longer wavelength decays more slowly. The presence of long-lived component in the monomer fluorescence at 300 nm reveals that dissociation of the excimer into an excited and ground state monomer does occur. According to Birks two-state mechanism for excimer formation and decay [17], the following two equations can describe the time profile of the monomer decay and the growth as well as the decay of the excimer for a δ-pulse excitation.

$$I_{m(t)} = B_1 \mathbf{e}^{-t/\tau 1} + B_2 \mathbf{e}^{-t/\tau 2} \tag{1}$$

$$I_{D(t)} = B_2 [\mathbf{e}^{-t/\tau 1} - \mathbf{e}^{-t/\tau 2}] \tag{2}$$

It is apparent that if the excimer dissociation cannot be ignored, then monomer decay, given in Eq. 1, will be the sum of two exponential

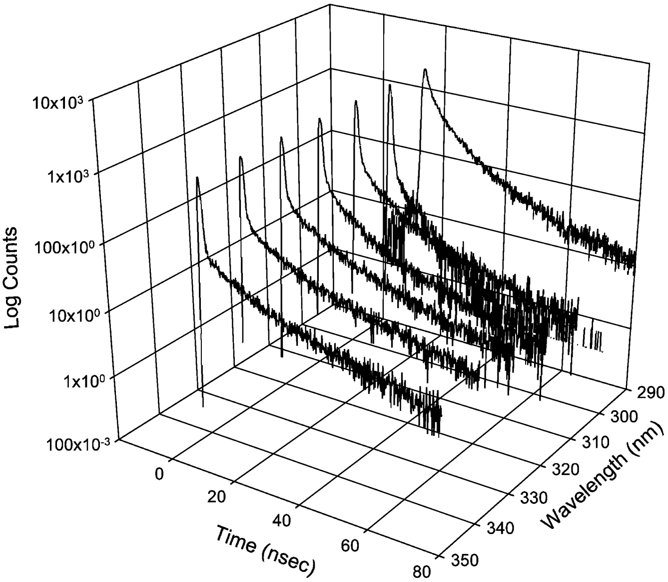

FIGURE 5 Fluorescence decay curves of poly(4-methoxystyrene) at emission wavelengths of 320 nm, 336 nm, 350 nm, 380 nm, in solid films.

decays. A short decay corresponding to initially excited monomer decay and a longer decay corresponding to monomer would be produced by reverse dissociation of the excimer. The excimer decay would have a grow-in corresponding to the monomer decay. The kinetics of excimer decay in Eq. 2 will be given by the difference of two exponential components.

TABLE 3 Effect of Emission Wavelength on Fluorescence Decay Time of Poly(4-Methoxy Styrene) in DCM, at $\lambda_{exc.}$ of 265 nm and Emission Wavelength of 300 nm

λ_{emis} (nm)	χ^2	τ_{f1} monomer (ns)	τ_{f2} excimer (ns)	B_2/B_2	$I_{Monomer}$ τ_{f1}/B_1	$I_{Excimer}$ τ_{f2}/B_2
290	0.98	1.38	5.01	1.15	1.38/0.465	5.01/0.535
300	0.96	1.40	5.43	1.38	1.40/0.421	5.43/0.579
310	1.09	1.44	7.03	1.68	1.44/0.373	7.03/0.627
320	0.99	1.65	8.21	2.56	1.65/0.281	8.21/0.719
330	0.94	1.80	8.86	4.81	1.80/0.172	8.86/0.828
340	0.96	2.31	9.31	7.55	2.31/0.117	9.31/0.883
350	0.99	2.99	9.55	10.0	2.99/0.091	9.55/0.909

Effect of Emission Wavelength on Fluorescence Lifetime

As shown in Table 3, at different emission wavelengths the fluorescence decay time becomes much longer by increasing emission wavelength for both excimer and monomer conformations. In a solid film of PMXS, the fluorescence decay time is changed upon changing emission wavelength as in Figure 5. The ratio of monomeric to excimeric contributions changes too. Increase of emission wavelength causes an increase in excimeric contribution and decreases the monomeric contribution. The effect of emission wavelength on excimer/monomer onomer conformation ratio for PMXS in solid film and in solutions is shown in Figure 6. The B_2/B_1 ratio in solid films is found to be higher than in dichloromethane solution and to increase with the increase in solvent polarities, indicating that in polar solvent there is an enhancement in excimer formation. From Table 3, the decay curve of PMXS in DCM can be fitted to biexponential decay. The decay curve monitored

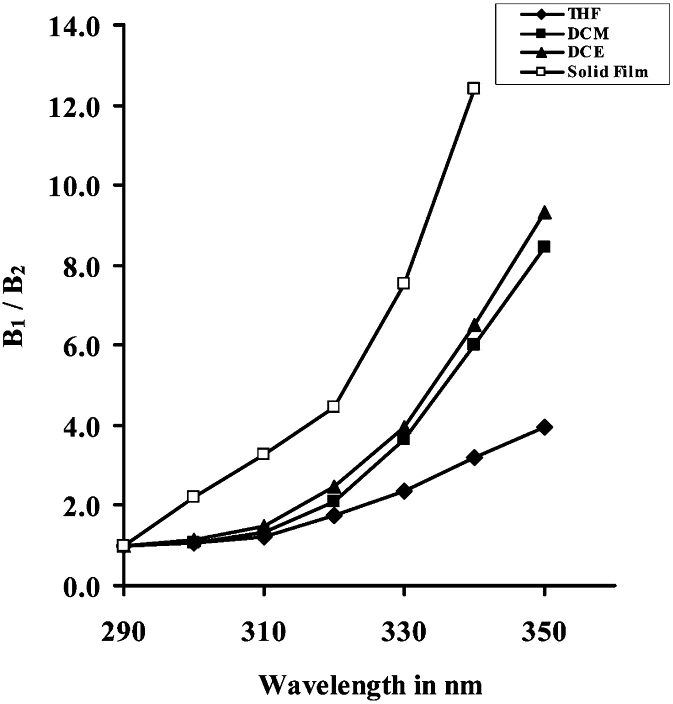

FIGURE 6 Effect of emission wavelength on excimer/monomer conformation ratio for poly(4-methoxystyrene) in solid film and in solutions at an excitation wavelength 265 nm.

at 290 nm is analyzed with a biexponential fit with almost equal components for the monomer with a lifetime of ($\tau_{f1} = 1.38 \pm 0.18$ ns), and the excimer with a lifetime of ($\tau_{f2} = 5.0 \pm 0.21$ ns). The decay curve monitored at 350 nm consisted of a biexponential decay with a major excimer component with a lifetime of ($\tau_{f2} = 9.55 \pm 0.23$ ns) and a minor monomer component of a lifetime ($\tau_{f1} = 2.99 \pm 0.23$ ns). This indicates that at longer wavelengths, the monomer fluorescence quenching occurs on trap sites of the polymer ground state near the excited polymer chromophore.

CONCLUSION

The fluorescence decay lifetimes for polystyrene and para-substituted polystyrene showed biexponential decay with minor component of monomer fluorescence and a major component of excimer fluorescence. In comparison with polystyrene, an increase in fluorescence intensities for both components was observed for para-substituted polystyrenes in solid films and DCM. This indicates that the symmetry reduction in polystyrene enhances the radiative processes from excited singlet states. The ratio of emission intensities of polymer compared to that of excimer conformations B_2/B_1 was found to increase with increase in emission wavelength.

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