

## Research Article

# Irradiation Effect on Stability of Plasticized Poly(Fluorostyrene) Isomers in Solution

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The UV irradiation and blending effects on stability of Poly(Fluorostyrene) isomers in solution were studied at different intervals of irradiation time in presence of air. The increase in irradiation time of these isomers caused an increase in the intensity of the absorption band and an increase in the intensity of the absorption of new broad band at longer wavelength, thus indicating a possibility of photodegradation of polymeric chains. The influence of added dioctyl phthalate and dioctyl terephthalate plasticizers on photooxidative degradation was also investigated and was found to increase the photodegradation processes in polymeric chains. On the other hand, the intensity of excimer and monomer fluorescence bands maxima was also found to decrease with increase in irradiation times. These changes may be attributed to the formation of new photoproducts resulted from the photodegradation of irradiated polymeric chains. The decrease in polarity of used solvents caused a considerable enhancement to the intensity of the polymer fluorescence band and accelerated photodegradation. A proposed mechanism is suggested to account for the effects of added plasticizers, the increase in irradiation time, and polarity of solvents on photodegradation and photooxidation processes in polymeric chains.

## 1. Introduction

The irradiation effects on stability of polystyrene [1–5] and substituted polystyrene [6–10] in solutions have been extensively studied by both theoretical and experimental approaches. The irradiation effect of halogenated polymers received a considerable attention, owing mainly to their industrial importance [11–13]. The photodegradation behavior of halogenated polystyrene has been found to be closely analogous to that of polystyrene [13, 14], and the mechanism of photodegradation of substituted polystyrene depends upon the structure and state of the polymer [15, 16]. Hence, the mechanism of polystyrene degradation in solution depends upon the mobility of free radicals among solvent molecules and is affected by the polarity of the solvent molecules [16, 17].

The photodegradation of polymeric chains can often be attributed to photochemical reactions arising from the

absorption of UV radiation by polymeric chromophores. A number of carbonyl species including aliphatic type ketones, monomer, alcohols, and esters, as well as a drop in molecular weight resulting from the photodegradation, have been identified on the bases of experimental results [17–20], but as yet, there is no general agreement on the nature of the products resulting from photodegradation of polymeric chains.

The study of the photodegradation of poly(*para*-substituted styrene) in different solvents was found to depend on the chemical structure of the substituted group in polymeric chromophores and to decrease by the increase in solvent polarity [7, 8]. It was reported that the photodegradation of poly( $\alpha$ -methylstyrene) in solution occurs with different quantum yields of degradation, and it was found that there is good correlation between solvent polarity and the quantum yield of degradation [21]. In general, the mechanism of photodegradation of polymeric chromophores depends on whether the irradiation of

polymeric solution occurs in the presence or in absence of oxygen [16]. In presence of oxygen, there is a marked increase in the efficiency of photodegradation of poly(substituted styrene).

The photodegradation of poly(*p*-fluorostyrene) in solid films was studied by Weir and Milkie [13]. The obtained results showed that poly(*p*-fluorostyrene) films undergo a yellowish discoloration on irradiation because of the absorption in the UV region. Poly(*p*-fluorostyrene) showed a higher stability in comparison with that for *p*-bromo and *p*-chloro substituent. This was attributed to the strongly withdrawing (inductive) effect of the F-substituent [13]. The aim of this work is to examine the photostability of pure and blended poly(fluorostyrene) isomers in solvents of different polarity, which contain different concentrations of doped dioctyl terephthalate and dioctyl phthalate plasticizers. The present study also seeks to check if plasticization affects the photostability of these isomers and to compare the photostability of poly(*p*-fluorostyrene) with the other two isomers. The polymers used in this study were assigned the following abbreviations: poly(*o*-fluorostyrene), (*o*-PFS); poly(*m*-fluorostyrene), (*m*-PFS); poly(*p*-fluorostyrene), (*p*-PFS). The used plasticizers were assigned the following abbreviations: dioctyl terephthalate, (DOT); dioctyl phthalate, (DOP).

## 2. Experimental

**2.1. Materials.** The samples of *ortho*-fluorostyrene, *meta*-fluorostyrene, and *para*-fluorostyrene monomers were supplied by Across-Organics with high purity. Before polymerization, they were distilled under reduced pressure in the presence of pure nitrogen and stored in the dark at 273 K. Only spectroscopic grade of dichloromethane (DCM), dichloroethane (DCE), dimethyl formamide (DMF), and tetrahydrofuran (THF) solvents was used in preparation of isomers solutions, and they were found to give no detectable absorption in range 250–400 nm. They were purchased from Fluka GMBH and were used as-received. The used plasticizers were dioctyl terephthalate, and dioctyl phthalate. They were of high purity of about 99.8%, were purchased from Across-Organics, and were used without further purifications.

**2.2. Polymerization.** Poly(*p*-fluorostyrene), poly(*m*-fluorostyrene), and poly(*o*-fluorostyrene) were prepared by free radical polymerization. A 1.0 gram of the monomer was dissolved in 25 mL of DCE solvent and was placed in a thick-walled test tube that was necked down near the top. To this tube, 0.04 g azobisisobutyronitrile (AIBN) was introduced. N<sub>2</sub>-gas was pumped into this solution for few minutes to eliminate the dissolved oxygen present in this solution. The sealed tube was placed in a water bath thermostated at 65–70°C for 12 hours. Polymerization took place slowly to give a colorless viscous solution. The tube was broken, and the viscous solution was added with stirring to 250 mL methanol at room temperature, and a white fibrous precipitate was formed of the polymerized monomer. The precipitate was

dissolved in 10 mL DCE and reprecipitated as white fibrous solid by addition of 200 mL methanol. The polymer was collected by filtration and washed repeatedly with methanol. The polymer was further dried under vacuum for 6 hours, at 293 K, to eliminate the presence of solvent molecules. The measured Mw for the prepared PFS isomers by viscosity measurements gave the following values: *o*-PFS (Mw = 21000), *m*-PFS (Mw = 19000), and *p*-PFS (Mw = 16600).

**2.3. Measurements of Absorption and Fluorescence Spectra of Irradiated Polymeric Solutions.** In presence of air, PFS isomers in different solvents were exposed to different intervals of irradiation times (0.0–3 hours). The UV absorption spectra for PFS-isomers solutions were recorded before and immediately after UV irradiation with a Cary 100 Bio UV-visible Spectrophotometer at 293 K.

A JASCO-FP 6500 Spectrofluorometer with a built-in Hydrogen-Xenon lamp (6808-J007A model number ESC-333), and supported with monochromator of holographic grating with 1800 grooves/mm was used for all irradiation processes and for fluorescence spectra measurements. The parameters were constant for all measurements, and the excitation wavelength was 265 nm. The emission wavelength range was 270–500 nm.

## 3. Results and Discussion

**3.1. Effect of UV Irradiation on the Intensity of Absorption Spectra of Poly(*o*, *m*, and *p*-fluorostyrene) Isomers in (DCE) Solution.** The DCE solution of PFS-isomers was found to absorb radiation in the UV region of 250–280 nm, similar to those of polystyrene and substituted polystyrene. The small changes in the shape of the absorption spectra may be attributed to the chemical structure of the isomers and to the position of substitution in phenyl ring. As in the case of all substituted polystyrenes, the phenyl chromophores are responsible for the absorption of UV energy [6]. The effects of UV irradiation on the absorption spectra of these isomers of ( $1 \times 10^{-4}$  M) solution resulted in a small increase in the absorption intensity of the main band, as well as a small red shift in the absorption band maxima. It is also noticed the formation of new broad absorption band with no clear maxima at longer wavelength that increased its intensity with the increase in irradiation time. These changes become more important when the solutions of these isomers are irradiated in presence of air [21]. The UV absorption spectra of poly(*ortho*, *meta*, and *para*-fluorostyrene) isomers in dichloroethane solvent at concentration of ( $1 \times 10^{-4}$  M) are shown in Figure 1.

It has been reported that irradiation of *para*-substituted polystyrene leads to the generation of aromatic free radicals that can cause chain scission of polymeric chains [22–24], and the formation of new photoproducts resulted from the photodegradation and photooxidation of polymeric chromophores [25].

As can be seen in Figure 1, the increase in the absorption of a new broad band without clear maxima at longer wavelength, with increasing in irradiation time, could be an

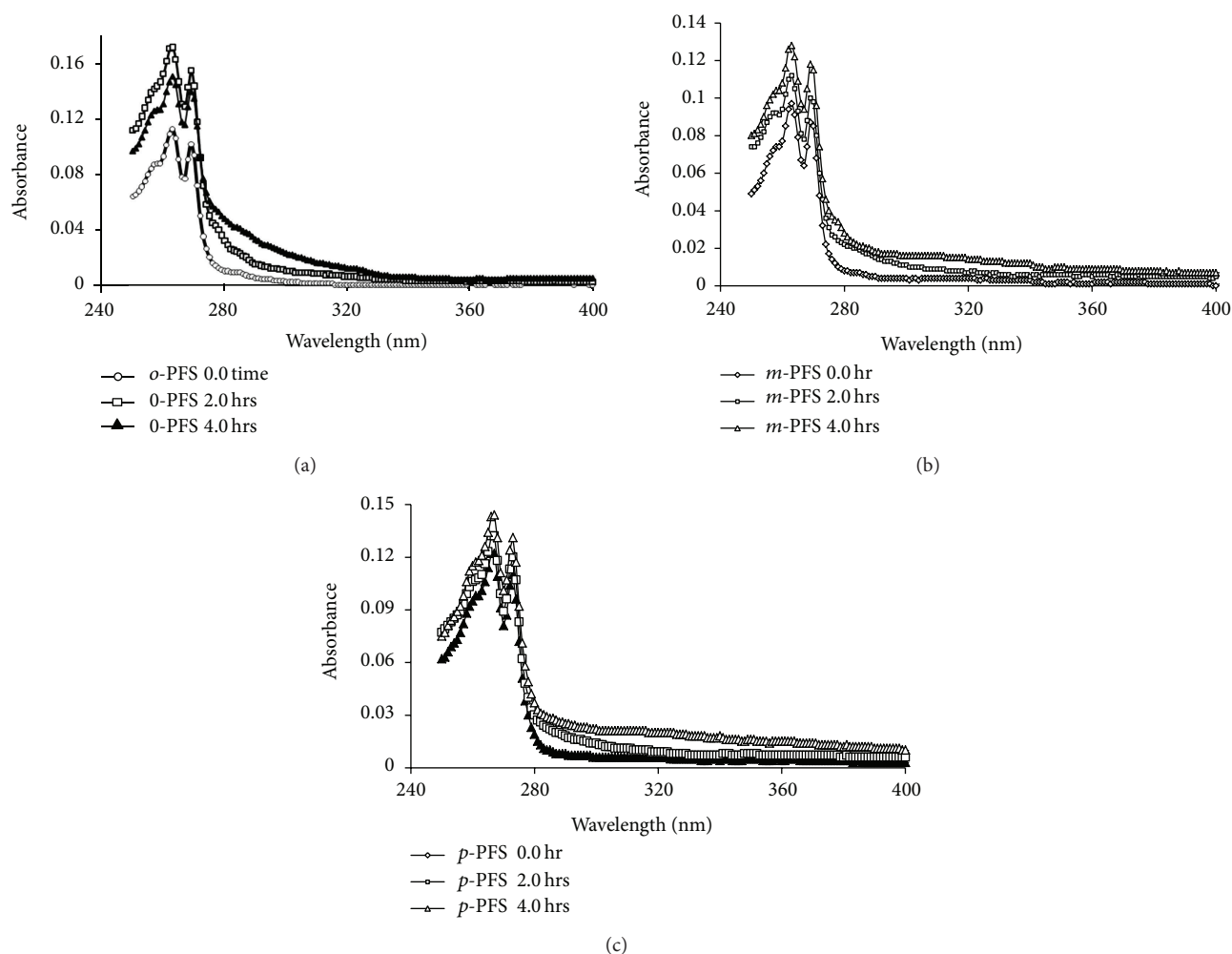


FIGURE 1: UV-absorption spectra of nonirradiated and irradiated poly(fluorostyrene) isomers, for 2 and 4 hrs at, (a) *o*-PFS, (b) *m*-PFS, and (c) *p*-PFS of ( $1 \times 10^{-4}$  M) in DCE solutions.

indication of the photodegradation of the irradiated isomers solutions [16]. The order of photostability of these isomers towards UV-irradiation is *p*-PFS > *m*-PFS > *o*-PFS. As it is expected that *para*-substitution can stabilize the polymeric chromophores in comparison with *meta* or *ortho*-substitution. The high stability of *p*-PFS isomer may be attributed to the stability of the styryl radicals that formed during photodegradation [16]. The lower reactivity of *p*-PFS in relation to polystyrene may be due to the strongly withdrawing-inductive effect of the fluoroatom substitution in *para*-position [7, 13].

**3.2. Effect of UV-Irradiation on the Intensity of Absorption Spectra of Blended Poly(*o*, *m*, and *p*-fluorostyrene) Isomers in DCE Solution.** The effect of UV irradiation on the efficiency of photodegradation processes in blended poly(fluorostyrene) isomers with different percentages of (DOP) and (DOT) plasticizers was studied by their absorption spectra. The absorption spectra of irradiated blended isomers in DCE solution for different exposure time show the following changes: an increase in the intensity of the main

absorption band, the appearance of new absorption broad band at longer wavelength, and a small red shift in the main absorption band. These effects were found to increase with the increase in the amount of blended plasticizers and with the increase in irradiation time. The UV-absorption spectra of nonirradiated and irradiated pure and blended *o*-PFS, *m*-PFS, and *p*-PFS isomers with dioctyl terephthalate (DOT) in dichloroethane solvent are shown in Figure 2.

It was reported that the 265 nm wavelength has sufficient energy to cleave the bonds in polymeric chains with the formation of free radicals. These radicals can initiate further reactions with oxygen molecules, which cause the splitting of polymeric chains and produce new fragments [26, 27]. The same observations were noticed in the irradiation of polystyrene, and blended *para*-substituted polystyrenes [7, 28]. It was noticed that irradiated polystyrene showed absorption by photoproducts at about 350 nm, as well as yellowing during photooxidation processes. The photoproducts resulting from irradiation of polymeric chains involved the benzene ring opening photoreaction in polymer chromophores [29–31].

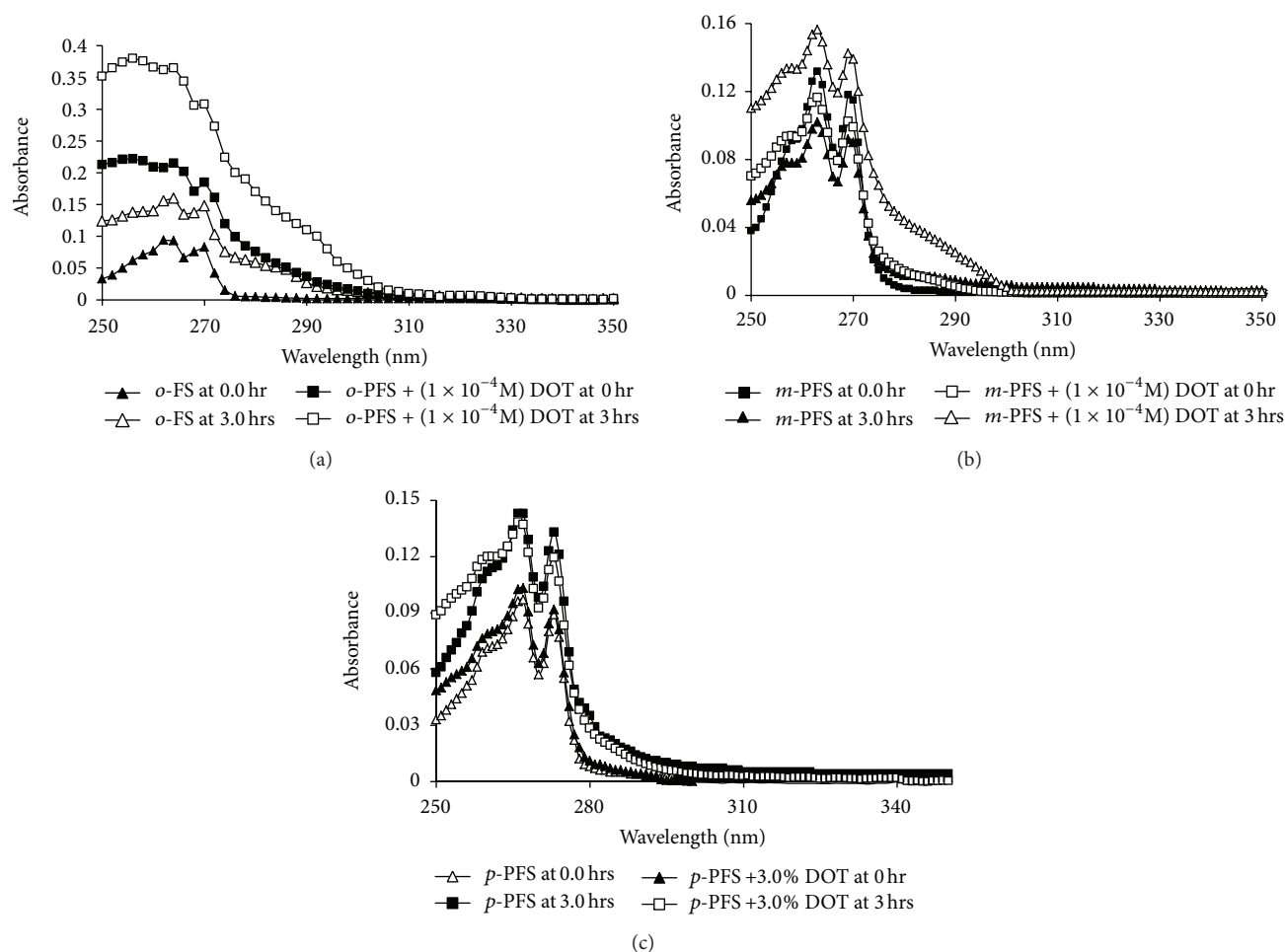


FIGURE 2: UV-absorption spectra of irradiated and nonirradiated (a) *o*-PFS blended with 3% DOT, (b) *m*-PFS blended with 3% DOT, and (c) *p*-PFS blended with 3% DOT at ( $1 \times 10^{-4}$  M) in DCE solutions at ( $\lambda_{\text{ext}} = 265$  nm).

The presence of plasticizer molecules in the polymer backbone also accelerates the photochemical processes in the irradiated polymeric chains. This suggests that added plasticizers may alter both the photochemical stability of these isomers and the process which led to the increase of absorption, such as photodegradation (with scission of bonds in the polymeric chains) and phototransformation (with changes in the conformation of the plasticizer molecules). Moreover, the increase in the absorbance of the main absorption band of the irradiated PFS isomers doped with DOT and the formation of new broad band without clear maxima at longer wavelength (280–330 nm) suggest that photooxidation and photodegradation processes may be the main dominating processes in the irradiated polymer solutions. It was reported that the photostability of substituted polystyrene in solution was found to depend on the bulkiness of the doped plasticizer molecule and on the chemical structure of the *para*-substituted group [32]. The order of increase in the absorption intensity of the irradiated blended isomers with 3.0% DOT was *o*-PFS > *m*-PFS > *p*-PFS. It was reported that the absorption spectra of irradiated polystyrene containing additives displayed an increase in the intensity of absorption

at 310 nm and was chosen as a measure of the photodegradation of polymeric films [33]. According to this, and from the absorption spectra for the irradiated three isomers, one can conclude that pure and blended *p*-PFS isomer show a higher stability towards UV-irradiation in comparison with the *m*-PFS and *o*-PFS.

**3.3. Solvents Polarity Effect on the Intensity of Absorption Spectra of Poly(*o*-fluorostyrene).** The absorption spectra of UV-irradiated poly(*o*-fluorostyrene) in THF, DCM, DCE, and DMF solvents with ( $1 \times 10^{-4}$  M) concentration for 2.0 hours are shown in Figure 3. Irradiation of *o*-PFS solutions causes a noticeable increase in the intensity of the absorption spectrum with that of nonirradiated polymer. The change in the solvent polarity does not change the shape nor the position of the  $\lambda_{\text{max}}$  of the main absorption band (250–280 nm), but an increase in the absorbance of the main band as well as the increase in the absorbance of a new broad band at (280–330 nm). More likely, that the absorption of this new band was due to the formation of fragments that absorb at longer wavelength and resulted from the photodegradation and photooxidation of polymeric chains. A good correlation



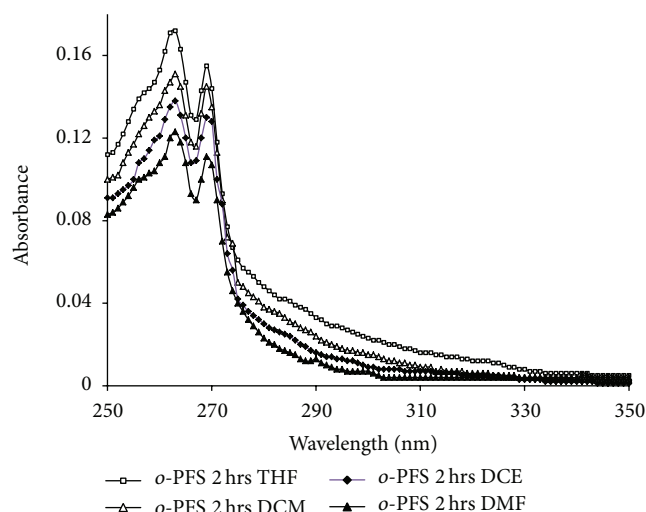


FIGURE 3: UV-absorption spectra of irradiated poly(*ortho*-fluorostyrene) in THF, DCM, DCE, and DMF of ( $1 \times 10^{-4}$  M) solutions for 2 hours, at ( $\lambda_{\text{ext}} = 265$  nm).

was obtained between the increase in solvent polarity and the decrease in the intensity of the new broad band at longer wavelength as shown in Figure 3.

It was reported that the mechanism of photodegradation of polymeric chains in substituted polystyrene took place under certain conditions where the formed free radicals were found to be affected by the change in the polarity of the solvent [7]. As a fact, no solvent is inert towards UV-irradiation, because some solvents are photolyzed into free radicals, which have different reactivity towards hydrogen abstracting from polymeric chains [7]. It has been reported that solvent molecules interact with the excited polymer chromophores to produce an activated complex. Although there was no noticeable change in the absorption spectra of the irradiated solvents in comparison with that of nonirradiated solvents, the stability of the irradiated PFS-isomers was affected by the change in solvent polarity.

The increase in the polarity of the solvent may stabilize the formed (PFS-solvent) excited energy transfer complex and decrease the efficiency of photodegradation of polymeric chains. The formation of such energy transfer complex was confirmed in other systems like in [polystyrene- $\text{CCl}_4$ ] [34] and [polystyrene- $\text{CHCl}_3$ ] [35] and was found to be affected by the change in solvent polarity. The primary radicals may also be formed as a result of the interaction of polymer chromophores with solvent radicals. The formation of such radicals may initiate polymer chain scission as well as photooxidation process in presence of oxygen.

**3.4. Effect of UV-Irradiation on the Intensity of Fluorescence Spectra of Pure and Blended Poly(*o*, *m*, and *p*-fluorostyrene) Isomers with DOP and DOT Plasticizers in Solution.** A number of studies have used the fluorescence technique in order to provide information about the photodegradation of irradiated substituted polystyrene [36–40], but none of these studies have dealt with the photodegradation of

poly(fluorostyrene) isomers in solution. Irradiation of solutions containing ( $1 \times 10^{-4}$  M) solution of these isomers at 265 nm and at 293 K for 0.0–180 min resulted in the small decrease of the fluorescence intensity with the increase in irradiation time, as shown in Figure 4.

As shown in Figure 4, the exposures of solutions for these isomers to different intervals of irradiation times were accompanied by slight decrease of both monomer and excimer emissions. Irradiation of those isomers was effectively initiating photochemical reactions as well as quenching of the intensity of fluorescence emission of monomer and excimer bands. Those results correlate well with that obtained in irradiation of poly(*para*-substituted styrene) [7, 8, 26] and polystyrene [4].

The photoquenching of the irradiated *p*-PFS fluorescence in solution shows a lower value than that observed with *o*-PFS and *m*-PFS solutions. It is well known that the formed excimer fluorescence may dissipate its excess energy by giving the fluorescence emission as well as by internal conversion. The latter two processes compete with the photodegradation process and are affected by the position of the fluorosubstitution in phenyl ring. *Para*-substitution seems to stabilize the polymeric chromophores towards UV irradiation in comparison with that for *meta*- and *ortho*-substitutions.

It has been reported that photochemical destruction of the polymeric chains by UV irradiation process resulted in formation of polyene structures, hydroperoxide, carbonyl, and hydroxyl compounds [19, 21]. The formation of polyene (conjugated double bonds) starts with the formation of radicals along the polymer chain by absorbing an energy that leads to the fission of  $\alpha$ -hydrogen from the polymer chain. This process is followed by the attack of the dissociated hydrogen to  $\beta$ -hydrogen in the polymer chain [41]. The formed conjugated double bonds along the polymer backbone are found to be not only having the ability to absorb in the UV region but also fluorescence at this region, so this can explain the red shift of the intensity of the emission band and formation of new fluorescence bands [42, 43].

It was observed that the increase in amount of added terephthalate plasticizer resulted in the increase in the intensity of a broad fluorescence band at longer wavelength. As was observed in many studies of substituted polystyrene, this broad band was attributed to the exciplex fluorescence [6, 44]. Exciplex fluorescence was observed in plasticization of *o*-PFS, *m*-PFS with (DOP), and (DOT) plasticizers as shown in Figure 5. We believe that exciplex emission can be attributed either to the effect of solvent molecules that enhance the intermolecular attraction between the polymer chromophores and the plasticizer molecules or to the increase in the stability of energy transfer complex that formed between PFS-isomers chromophores and plasticizer molecules. On the other hand, exciplex emission at longer wavelength is centered at 376 nm for *o*-PFS and at 381 nm for *m*-PFS and was found to increase in its intensity with the increase in the concentration of added plasticizer. Plasticization of *p*-PFS in DCE solvent did not show the formation of exciplex emission. It is a more common case that we usually observe exciplex conformations

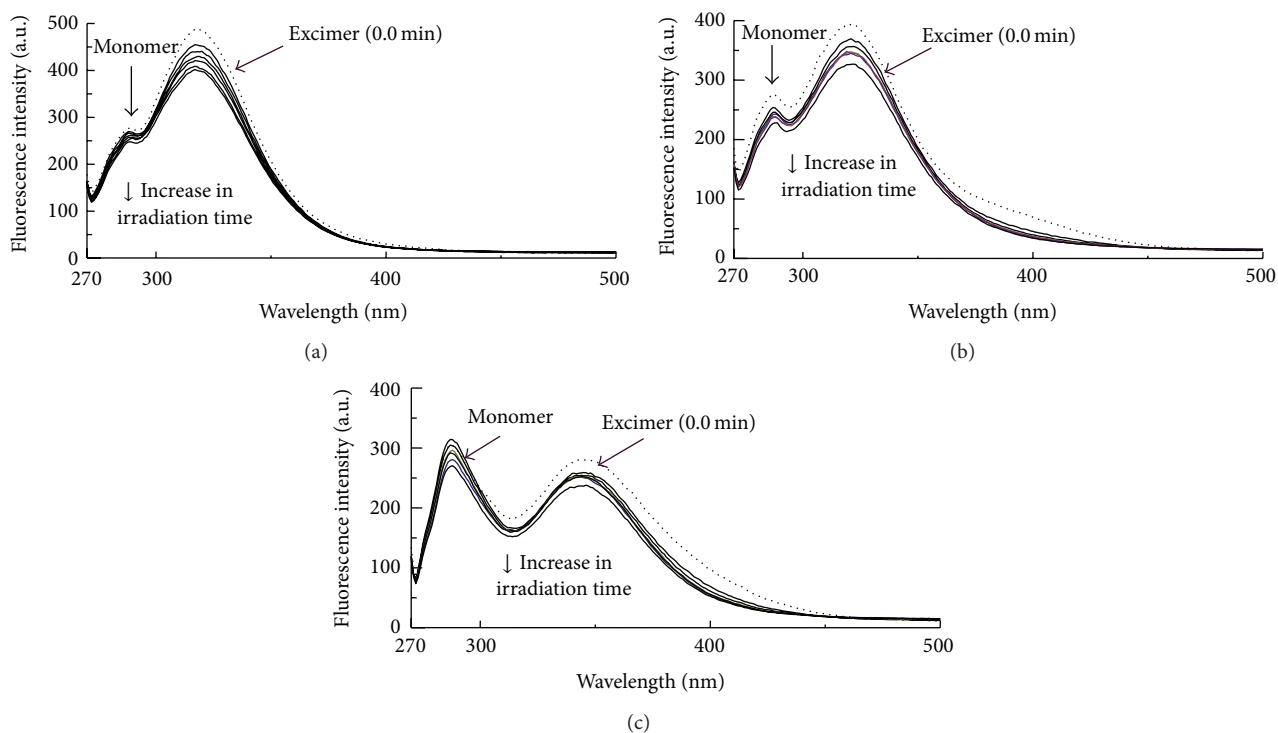


FIGURE 4: Fluorescence spectra of irradiated (a) *o*-PFS, (b) *m*-PFS, and (c) *p*-PFS in DCE solution ( $1 \times 10^{-4}$  M) at different intervals of time (0–180 min). Solid lines: irradiated; dotted line: none irradiated.

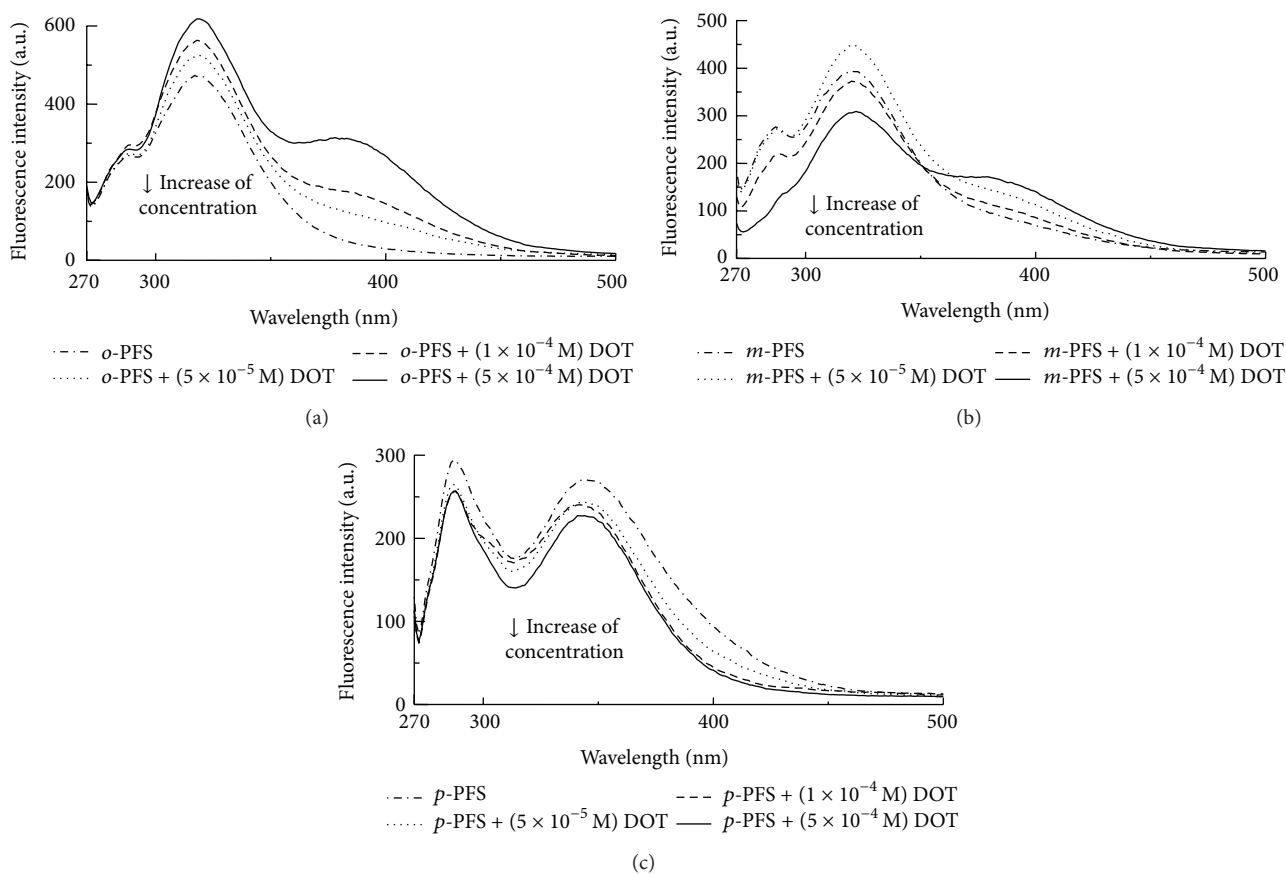


FIGURE 5: Fluorescence spectra of nonirradiated pure and blended polymer; (a) *o*-PFS, (b) *m*-PFS, and (c) *p*-PFS in DCE. All polymer solutions contain (0.0 M), ( $5 \times 10^{-5}$  M), ( $1 \times 10^{-4}$  M), and ( $5 \times 10^{-4}$  M) of DOT plasticizer.

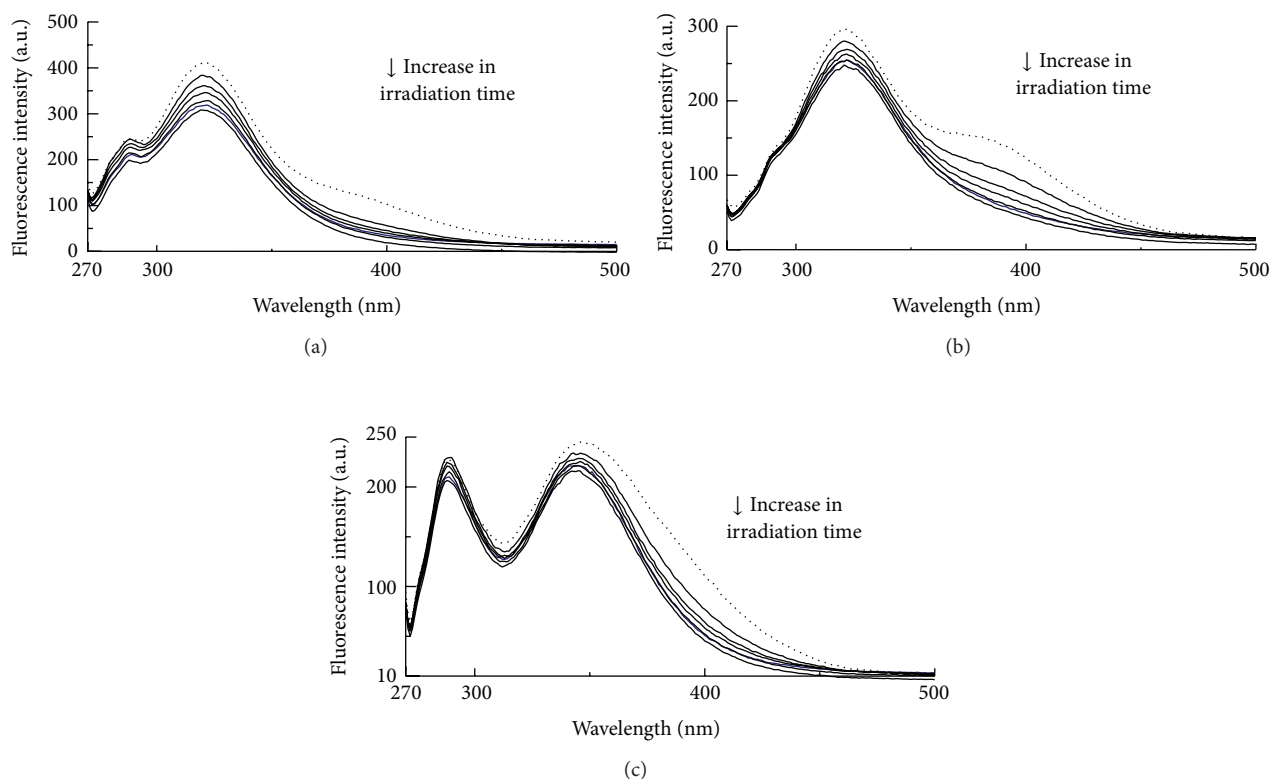


FIGURE 6: Fluorescence spectra of irradiated (a) (*o*-PFS), (b) (*m*-PFS), and (c) (*p*-PFS) in DCE solutions blended with ( $1 \times 10^{-4}$  M) dioctyl phthalate plasticizer (DOP), at different intervals of time (0–180 min).

in blended polymers in solid films rather than in blended polymers in solutions.

Irradiated plasticized PFS isomers in DCE solution showed different behaviors than what was observed with irradiated pure PFS isomers in solution. The *o*-PFS, *m*-PFS, and *p*-PFS isomers were plasticized with ( $5 \times 10^{-4}$  M) concentrations of dioctyl phthalate (DOP) and irradiated for 0.0–180 min as shown in Figure 6.

As can be seen from Figure 6, the increase in exposure time of blended PFS isomers in DCE solution caused a decrease in both the intensity of formed exciplex fluorescence and polymer emission. The increases in exposure time of irradiated solutions accelerate the photooxidation and photodegradation processes that are more likely to be the main processes that caused the decrease in both bands.

**3.5. Kinetics and Mechanism of Photodegradation of Pure and Blended PFS-Isomers in DCE Solutions.** Al Ani and Hawi [45] have formulated a new mathematical relation that can be used to study the kinetic treatments to the decrease of fluorescence quenching of PFS isomers by the increase in the amount of added plasticizers and by the increase in irradiation times.

The fluorescence ratio of  $(I_{[EX]}^o/I_{[EX]})^*$  was found to increase by the increase in irradiation time to polymeric solution.  $(I_{[EX]}^o)^*$  is the intensity of  $(\lambda_{max})$  of excimer fluorescence of pure or doped polymer at zero time of irradiation, whereas  $(I_{EX})^*$  is intensity of  $(\lambda_{max})$  of excimer emission of pure or

doped polymer at different intervals of exposure time, then we can write:

$$\left(\frac{I_{EX}^o}{I_{EX}}\right)^* = 1 + \{(k'_{PQ})(A)\}(t), \quad (1)$$

where  $[A]$  = number of (photons/s) absorbed by polymeric chromophores;  $t$  = time of irradiation in s;  $k'_{PQ}$  = rate constant. And

$$\left(\frac{I_{EX}^o}{I_{EX}}\right)^* = 1 + (k_{PQ})(t), \quad (2)$$

where the quenching rate constant  $k_{PQ}$  is equal to

$$k_{PQ} = \{(k'_{PQ})(A)\}. \quad (3)$$

In the photoquenching processes, if we assume that the number of photons released from the light source and absorbed by polymer chromophores is constant ( $A$ ), then, according to (2),  $(I_{[EX]}^o/I_{[EX]})^*$  values were plotted against time of irradiations ( $t$ ). From the plots, the photoquenching rate constant ( $k_{PQ}$ ) values and  $(I_{[EX]}^o/I_{[EX]})^*$  ratios were calculated and were used to estimate the efficiency of photoquenching and photodegradation processes for pure and blended isomers in solution as shown in Figures 7, 8, and 9, respectively.

From the plots in Figures 7, 8, and 9, and by applying Al Ani-Hawi relation (2), the photoquenching rate constants

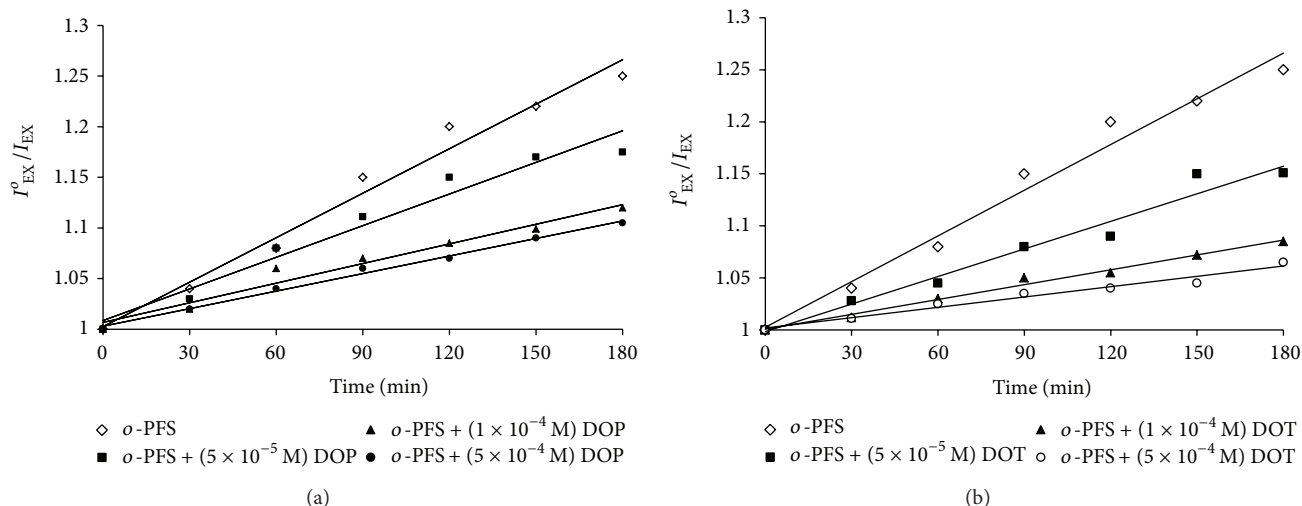


FIGURE 7: Plot of  $(I_{EX}^0/I_{EX})$  fluorescence ratio of nonplasticized and plasticized (*o*-PFS) in DCE solutions at different concentrations of (a) DOP and (b) DOT, plotted against exposure time (0–180) min.

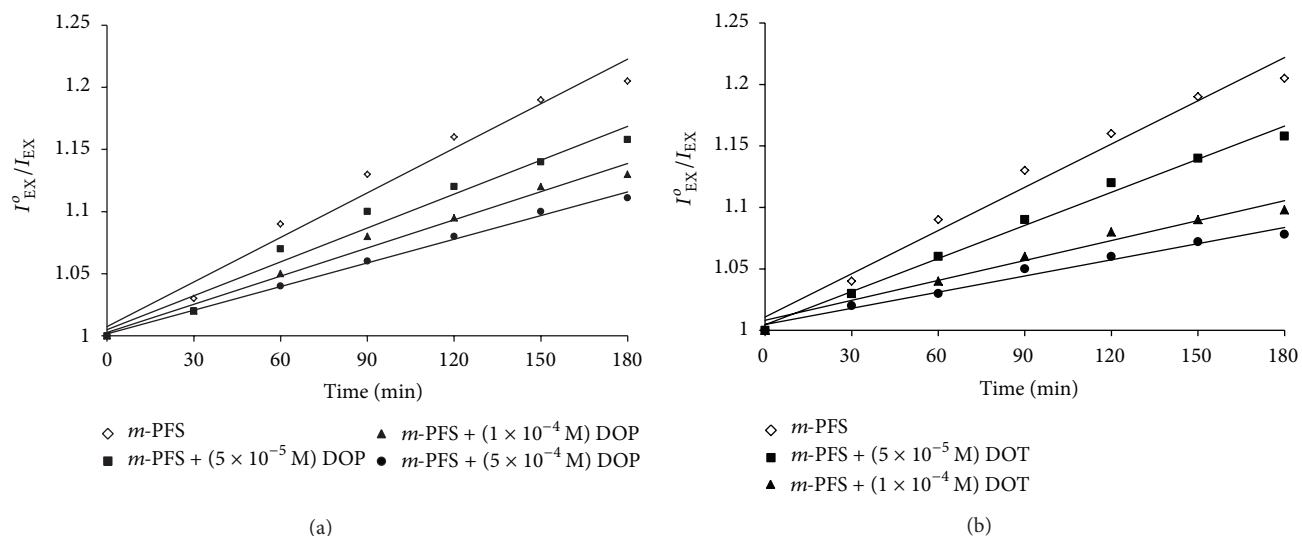


FIGURE 8: Plot of  $(I_{EX}^0/I_{EX})$  fluorescence ratio of nonplasticized and plasticized (*m*-PFS) in DCE solutions at different concentrations of (a) DOP and (b) DOT, plotted against exposure time (0–180) min.

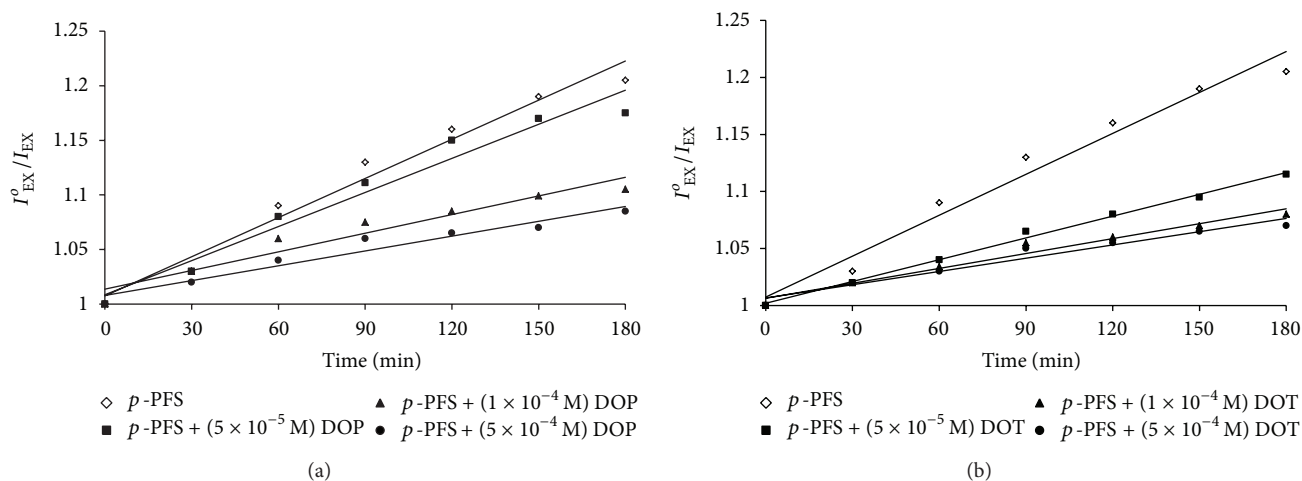


FIGURE 9: Plot of  $(I_{EX}^0/I_{EX})$  fluorescence ratio of nonplasticized and plasticized (*p*-PFS) in DCE solutions at different concentrations of (a) DOP and (b) DOT, plotted against exposure time (0–180) min.



TABLE 1: Relative intensities of the ratio ( $I_{EX}^0/I_{EX}$ )<sup>\*</sup> for intensities of excimer fluorescence bands and excimer fluorescence photoquenching rate constant values ( $k_{PQ}$ ) of irradiated pure and blended (*o*-PFS), (*m*-PFS), and (*p*-PFS) in DCE solutions.

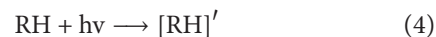
$\lambda_{(emiss.)}$ (nm)	Polymer	Plasticizer (%)	Time (min)	$R^2$	( $I_{EX}^0/I_{EX}$ ) <sup>*</sup>	$k_{PQ}$
320	<i>o</i> -PFS	—	180	0.980	1.352	0.00206
			<i>o</i> -PFS + DOP			
317	<i>o</i> -PFS	$5 \times 10^{-5}$ M	180	0.979	1.183	0.00181
321	<i>o</i> -PFS	$1 \times 10^{-4}$ M	180	0.967	1.172	0.00101
319	<i>o</i> -PFS	$5 \times 10^{-4}$ M	180	0.989	1.160	0.00091
			<i>o</i> -PFS + DOT			
319	<i>o</i> -PFS	$5 \times 10^{-5}$ M	180	0.962	1.172	0.00105
320	<i>o</i> -PFS	$1 \times 10^{-4}$ M	180	0.968	1.148	0.00088
323	<i>o</i> -PFS	$5 \times 10^{-4}$ M	180	0.994	1.125	0.00070
320	<i>m</i> -PFS	—	180	0.978	1.223	0.00122
			<i>m</i> -PFS + DOP			
320	<i>m</i> -PFS	$5 \times 10^{-5}$ M	180	0.976	1.185	0.00098
320	<i>m</i> -PFS	$1 \times 10^{-4}$ M	180	0.985	1.155	0.00078
321	<i>m</i> -PFS	$5 \times 10^{-4}$ M	180	0.988	1.131	0.00069
			<i>m</i> -PFS + DOT			
321	<i>m</i> -PFS	$5 \times 10^{-5}$ M	180	0.992	1.160	0.00081
320	<i>m</i> -PFS	$1 \times 10^{-4}$ M	180	0.974	1.134	0.00068
322	<i>m</i> -PFS	$5 \times 10^{-4}$ M	180	0.979	1.129	0.00060
339	<i>p</i> -PFS	—	165	0.974	1.201	0.00186
			<i>p</i> -PFS + DOP			
351	<i>p</i> -PFS	$5 \times 10^{-5}$ M	180	0.930	1.173	0.0011
346	<i>p</i> -PFS	$1 \times 10^{-4}$ M	180	0.935	1.102	0.00068
348	<i>p</i> -PFS	$5 \times 10^{-4}$ M	180	0.949	1.100	0.00059
			<i>p</i> -PFS + DOT			
344	<i>p</i> -PFS	$5 \times 10^{-5}$ M	180	0.995	1.102	0.00063
345	<i>p</i> -PFS	$1 \times 10^{-4}$ M	180	0.968	1.084	0.00057
345	<i>p</i> -PFS	$5 \times 10^{-4}$ M	180	0.959	1.071	0.00045

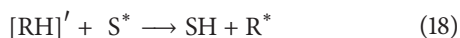
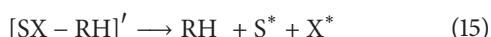
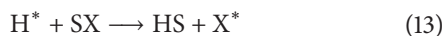
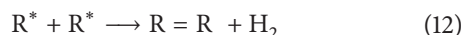
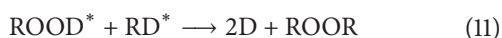
( $k_{PQ}$ ) values of the excimer fluorescence as function of increase in irradiation time for pure and blended isomers were calculated and are presented in Table 1, for *o*-PFS, *m*-PFS, and *p*-PFS isomers, respectively.

As can be seen from Table 1, the photoquenching efficiency ratio ( $I_{EX}^0/I_{EX}$ )<sup>\*</sup> and the photoquenching rate constant ( $k_{PQ}$ ) values were found to decrease with the increase of the amount of added plasticizers and to decrease with the increase of exposure time. The trend of increase in the efficiency of fluorescence quenching is DOP > DOT. This behavior may indicate that there is high stability for the [terephthalate-PFS]<sup>\*</sup> excited complex than that of [phthalate-PFS]<sup>\*</sup> excited complex [46]. Phthalate plasticizers, on the other hand, displayed a higher efficiency of photoquenching than that of terephthalate plasticizers. Numerous mechanisms for polystyrene photodegradation under UV irradiation have been proposed by many authors [40–43], but a totally consistent theory is yet to be agreed upon due to the complexity of the kinetics and the formation of different photodegradation products. The mechanism of photodegradation of PFS isomers was prepared in a similar basis and according to the results obtained from the changes in the

intensities of UV-vis absorption bands and changes in the intensities of fluorescence spectra of irradiated pure and blended PFS-isomers.

A more detailed discussion on the processes involved in the oxidative degradation in polymer films has been reported by Rabek [47]. The following proposed reaction scheme will summarize the possible photochemical processes resulting from the irradiation of blended PFS isomers solutions. The proposed mechanism involves the photodegradation of polymeric chromophores of PFS isomers [RH] through a hydrogen radical abstraction ( $H^*$ ), followed by the interaction of both radicals ( $R^*$  and  $H^*$ ) with solvent molecules (SX) and plasticizer molecules (D), in presence of oxygen molecules ( $O_2$ ). The photodegradation processes in the irradiated PFS-isomers solutions can be summarize by the following mechanism:





According to the above mechanism, the absorption of light quantum by polymeric chromophores produces an excited state chromophore  $[\text{RH}]'$ . The latter photodegrades to produce hydrogen radicals  $\text{H}^*$  and polymer radicals  $(\text{R})^*$  (5). The polymer radicals  $(\text{R})^*$  either react with plasticizer molecules (D) to produce  $\text{RD}^*$  radical or react with molecular oxygen to produce proxy radicals  $\text{ROO}^*$  ((6), (9)). Proxy radicals initiate free radical reactions with polymer radical to produce peroxide structure  $\text{ROOR}$  (8) and hydroperoxide  $\text{ROOH}$  (7) or react with the plasticizer molecules to produce  $\text{ROOD}^*$  radical. The latter reacts with  $\text{RD}^*$  radical to produce  $\text{ROOR}$  (11). Also, the excited state chromophores produce with solvent molecules an activated complex that degraded into solvent radicals  $(\text{S})^*$  and halogen radicals  $(\text{X})^*$  (15).  $\text{S}^*$  radicals and  $\text{R}^*$  radicals may be involved in the formation of proxy radicals that react with  $[\text{RH}]'$  excited state (18) to produce a new radical that can accelerate photodegradation processes.  $\text{R}^*$ -radicals may combine to produce polyene structure compound as well as hydrogen abstraction process. The decrease in the polarity of solvent molecules may destabilize the formation of  $[\text{SX} - \text{RH}]^*$  (14), which increases the rate of formation of  $\text{S}^*$  and  $\text{X}^*$  radicals that enhance photodegradation and photooxidation processes ((16), (18)). The possibility of these reactions is also supported by the results obtained by Tagawa et al. [35], relevant to the formation of solvent radical in  $[\text{polystyrene-CHCl}_3]$  system. However, the rapid transformation of solvent radicals in polymeric solution in presence of oxygen molecules into peroxide radicals suggests that degradation of polymer chromophores with peroxide radical is one of the important processes in polymer photodegradation in solution.

#### 4. Conclusions

Based on the obtained results of absorption and fluorescence spectra of pure and blended PFS isomers, the conclusions can be summarized as follows.

- (1) Irradiation of pure and blended PFS isomers that absorbs by polymeric chromophores in presence of air resulted in small increase in the intensity of the absorption band, with increase in exposure time. On other hand, irradiation of plasticized PFS isomers caused the formation of a broad band with no clear maxima at longer wavelength, indicating possibility of photodegradation of polymer chains.
- (2) It was found that blending of poly(*m*-fluorostyrene) and poly(*o*-fluorostyrene) with DOT and DOP plasticizers resulted in the formation of exciplex emission band and the latter was found to increase with the increase in the amount of added plasticizer. Irradiation of blended PFS isomers resulted in a decrease in the intensities of both excimer and exciplex emissions. This indicates that there is a possibility of photodegradation in the polymeric chains.
- (3) Poly(*p*-fluorostyrene) shows higher stability towards UV irradiation in comparison with that for poly(*m*-fluorostyrene) and poly(*o*-fluorostyrene) in solvents of different polarity. This is possibly due to the strongly withdrawing and inductive effects are caused by the *para*-substitution of fluoro atom. The order of photostability was found to follow the order *P*-PFS > *m*-PFS > *o*-PFS.
- (4) The increase in the polarity of the used solvent caused a decrease in the photoquenching of monomer and excimer emission bands without change in the shape or position of the fluorescence bands.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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