

# Synthesis of and Photodegradation in a Series of Poly(ethylene Terephthalate-co-4,4'-Sulfonyldibenzoate Yarns

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## Synopsis

Phototendering studies of poly(ethylene terephthalate) homopolymer yarn and a series of poly(ethylene terephthalate-co-4,4'-sulfonyldibenzoate) copolymer yarns have shown that photosensitized degradation occurs more readily in the copolymers than in the homopolymer. A photo-oxidative mechanism involving the second monomer, dibutyl 4,4'-sulfonyldibenzoate, has been proposed to account for the photosensitization. The photophysical processes in the second monomer, dibutyl 4,4'-sulfonyldibenzoate, were studied by absorption and luminescence techniques. The lowest excited singlet and triplet in this compound were identified as the  $^1(\pi,\pi^*)$  and  $^3(\pi,\pi^*)$  states, respectively. The energy levels in the second monomer have been assigned as follows:  $^1S_1 \sim 33,000 \text{ cm}^{-1}$ ,  $^1S_2 \sim 42,000 \text{ cm}^{-1}$ , and  $^3T_1 \sim 26,000 \text{ cm}^{-1}$ .

## INTRODUCTION

Terrestrial sunlight has been shown to cause the degradation of many synthetic polymers. Poly(ethylene terephthalate) (PET) fibers lose their tenacity, elongation, and elasticity upon exposure to sunlight.<sup>1,2</sup> The photodegradation of PET has been related to the presence of energy-absorbing groups, the aromatic ester groups, which are inherent in the polymer chain.<sup>3</sup> Photodegradation processes in PET are initiated by the strong absorption in the polymer which occurs below 315 nm.<sup>4</sup> Several factors influence the photodegradation processes in the polymers including radiation wavelength and intensity, radiation atmosphere, and the presence of additives such as dyes and delustrants. Several reports on the photodegradation of PET have been published.<sup>1-14</sup>

Day and Wiles<sup>4,11-13</sup> have performed extensive studies of the photochemical degradation of PET and have postulated mechanisms for the primary photodegradation processes. A clear understanding of these photodegradative mechanisms is necessary when attempting to improve the photostability of the polymer.

Polymers are often protected against photodegradation through the use of photostabilizers. Photostabilizers are generally divided into three groups: light screens, ultraviolet absorbers, and quenchers. A major consideration in these additive-polymer systems is the ability of the additive to remain in the polymer, especially during processing. To prevent the loss attendant with the use of low-molecular-weight additives, the stabilizer may be incorporated into the polymer during polymerization or grafted onto the polymer in a subsequent reaction to form a copolymer.

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The mechanism of energy transfer between an excited polymer molecule and a photostabilizer has been used to explain the quenching effect of photostabilizers. Energy transfer in polymeric systems has seen much study<sup>15-22</sup> and has been recently reviewed by Turro<sup>23</sup> and Guillet.<sup>24</sup> The majority of discussions agree that the resonance energy transfer processes ascribed to small-molecule chemistry also apply to polymer systems.

The photophysical processes of many polymers have been studied extensively.<sup>25-27</sup> Photophysical processes in aromatic esters have not been studied as extensively.

Merrill and Roberts<sup>6</sup> have studied the photophysical processes of PET fiber and film and assigned a  $^1(n,\pi^*)$  transition to the fluorescence emission and a  $^3(\pi,\pi^*)$  transition to the phosphorescence emission. Cheung<sup>28</sup> studied some model esters of PET and arrived at the same transition as did Merrill and Roberts.<sup>6</sup> Takai et al.<sup>29</sup> have observed an emission band at 375 nm and assign this to an excimer emission attributing the formation of the excimer to singlet energy migration in PET.

Cheung<sup>30</sup> has done extensive studies of the luminescence of PET chip, fiber, and film. He assigned a  $^1(\pi,\pi^*)$  transition to the fluorescence emission of PET through correlation of the PET singlet transition to that of DMT in hexafluoroisopropanol (HFIP) solution. The phosphorescence was attributed to a  $^3(\pi,\pi^*)$  transition as in his earlier report.<sup>28</sup>

Copolyesters containing terephthalate and 4,4'-sulfonyldibenzoate (4,4'-SD) moieties were synthesized in this research. The apparent photophysical processes available to the 4,4'-sulfonyldibenzoate monomer, the homopolymer PET, and the copolyesters were determined. The role of the sulfonyl ester in the photodegradation of the copolymers was studied by following the phototendering in the yarns by monitoring the percent loss in breaking strength as a function of the total incident radiation.

## EXPERIMENTAL

### Materials and Analyses

Dibutyl 4,4'-sulfonyldibenzoate (4,4'-SD) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from Eastman Organic Chemicals. Certified ACS-grade ferric ammonium sulfate, ferrous ammonium sulfate, potassium oxalate, 1,10-phenanthroline (monohydrate), and sodium acetate were obtained from Fisher Scientific Co. USP-grade 95% ethanol, after further purification, was used in monomer purification and luminescence studies.

Ultraviolet absorption measurements were performed on a Cary 118C spectrophotometer. A Perkin-Elmer model MPF-3 fluorescence spectrophotometer with corrected spectra, phosphorescence, and front surface accessories was used to obtain luminescence measurements. Luminescence lifetime measurements were obtained from a Tektronix model 5103N storage oscilloscope connected to the MPF-3 spectrophotometer. Photolyses were performed in a Rayonet type RS model RPR-208 preparative photochemical reactor with a MGR-100 merry-go-round assembly. A Lawson Fiber Analysis Knitter (FAK) was used to knit yarn samples. Tensile testing of the yarn samples was carried out on an Instron model 1101 (TM-M) constant rate of extension testing machine.

### Purification of Dibutyl 4,4'-Sulfonyldibenzoate

Crude dibutyl 4,4'-sulfonyldibenzoate was recrystallized twice from purified USP 95% ethanol (1:80). The white, dried crystals had mp 158–160°C.

### Copolyesters Containing Dibutyl 4,4'-Sulfonyldibenzoate

Copolymers were prepared from dimethyl terephthalate containing 0.5, 1, or 2 mole % dibutyl 4,4'-sulfonyldibenzoate and 2.3 mole ethylene glycol using a procedure similar to those reported earlier.<sup>5</sup> The characterization (Tables I and II) and irradiation procedures were carried out as described previously.<sup>5,6</sup>

## RESULTS AND DISCUSSION

### Photophysical Processes in Dibutyl 4,4'-Sulfonyldibenzoate

#### *Absorption and Luminescence Spectra*

The absorption spectra of dibutyl 4,4'-sulfonyldibenzoate (4,4'-SD) in both HFIP and 95% ethanol were measured between 200 and 400 nm. Similar absorptions were displayed in both solvent systems with four bands at about 203, 228, 250, and 285 nm (Table III). The bands at 203, 250, and 285 nm correspond to  $^1A \rightarrow ^1B$ ,  $^1A \rightarrow ^1L_a$ , and  $^1A \rightarrow ^1L_b$  transitions, respectively. Absorption at 228 nm was attributed to a conjugated system across the sulfone group.

The corrected excitation and emission fluorescence spectra of 4,4'-SD in HFIP at 298 K demonstrated a structured excitation spectrum with band maxima at 236, 286, and 294 nm and an emission spectrum with band maxima at 322, 372, and 388 nm.

Figure 1 represents the uncorrected excitation and phosphorescence spectra of 4,4'-SD in a 95% ethanol glass at 77 K. Excitation band maxima were found at 268, 282, and 292 nm. The strong phosphorescence gave a structured emission with band maxima at 382, 398, and 408 nm with a mean lifetime ( $\tau$ ) of 1.2 sec.

#### *Interpretation of Absorption and Luminescence Spectra*

The UV absorption spectra of conjugated sulfones have been widely studied.<sup>31-40</sup> Closely associated with the sulfone absorption spectrum is the postulated conjugative ability which may exist in the sulfone group.<sup>41-47</sup>

The absorption spectrum of 4,4'-SD can be explained if there is little or no conjugation across the sulfone group.<sup>42-44</sup> This assumption would mean that 4,4'-SD might have a similar absorption spectrum to that of DMT where one carboxyl group on DMT has been replaced by the sulfonyl function. A comparison of the spectra has shown that the transition  $^1A \rightarrow ^1B$ ,  $^1A \rightarrow ^1L_a$ , and  $^1A \rightarrow ^1L_b$  in DMT arise at 191, 244, and 289 nm, respectively. The same proposed transitions in 4,4'-SD are 203.5, 250, and 290 nm, respectively. The absorption band at 228.5 nm in 4,4'-SD is assigned to an excited state in which some  $d-\pi$  conjugative interaction has joined the two aromatic centers.<sup>40</sup> This conjugated excited state possesses a relatively high energy and is a very weak interactor.

Reports of the luminescence behavior of diaryl sulfones are limited.<sup>48</sup> The

TABLE I  
Characterization of Copolyester Polymers<sup>a</sup>

Sample No.	Mole % 4,4'-SD <sup>b</sup>	I.V. <sup>c</sup>	Acid No. <sup>d</sup>	Phosphorus, ppm	$T_g$	$T_{cc}$	$T_m$	$T_{rc}$	$T_{rm}$
1	0.0	0.49	49	42	71	131	255	212	255
2	0.5	0.51	35	41	69	134	255	212	255
3	1.0	0.55	31	49	69	129	253	211	247
4	2.0	0.47	52	66	71	136	249	185	248

<sup>a</sup>  $T_g$  = Glass transition temperature;  $T_{cc}$  = cold crystallization temperature;  $T_m$  = melting temperature;  $T_{rc}$  = recrystallization temperature;  $T_{rm}$  = remelt temperature; from DTA measurements, point of curve maximum (or minimum).

<sup>b</sup> Dibutyl 4,4'-sulfonyldibenzoate based on monomer feed.

<sup>c</sup> Intrinsic viscosity, measured in 40% phenyl/60% tetrachloroethane.

<sup>d</sup> Mequiv/kg of polymer.

<sup>e</sup> Based on weight of polymer.

TABLE II  
Characterization of Copolyester Yarns (30/6)

Sample No.	Mole % 4,4'-SD <sup>a</sup>	Denier	Tenacity g/den	Elongation, %	Modulus
1	0.0	32.29	3.23	43.1	51.1
2	0.5	29.19	3.41	46.4	74.5
3	1.0	28.60	3.14	38.1	78.1
4	2.0	33.49	2.03	73.1	35.8

<sup>a</sup> Dibutyl 4,4'-sulfonyldibenzoate.

low-intensity weak fluorescence of 4,4'-SD in ethanol is analogous to that reported by Cheung<sup>30</sup> for DMT in ethanol solution. The lowest excited singlet state,  $^1S_1$ , possesses  $n, \pi^*$  character.<sup>49,50</sup> The  $n \rightarrow \pi^*$  absorption band associated with this transition is probably hidden by the more intense  $^1A \rightarrow ^1L_b (\pi, \pi^*)$  absorption at 290 nm in 4,4'-SD. The structured strong phosphorescence emission band centered at 398 nm is attributed to a  $^3L_a (\pi, \pi^*)$  state. This assignment arises from the long phosphorescence lifetime, 1.2 sec, and the large  $^1S_1 \rightarrow ^3T_1$  energy splitting,  $7000 \text{ cm}^{-1}$ .<sup>27</sup>

If it is assumed that the  $^3(n, \pi^*)$  state is located below the  $^1L_b$  state, the high rate of intersystem crossing which occurs because of the effective spin-orbit coupling between  $(\pi, \pi^*)$  and  $^3(n, \pi^*)$  states can account for the high phosphorescence yield and low fluorescence intensity in 4,4'-SD.<sup>51</sup> The polar solvent (HFIP) raises the energy level of the  $^1(\pi, \pi^*)$  and  $^3(n, \pi^*)$  states because of stronger hydrogen bonding. This places the  $^3(n, \pi^*)$  state at a higher energy than the  $^1L_b$  state. The inefficient spin-orbit coupling between  $^1(\pi, \pi^*)$  and  $^3(\pi, \pi^*)$ <sup>51</sup> states decreases the rate of intersystem crossing leading to enhanced fluorescence in HFIP solution.

The 0-0 transition bands exhibited in the fluorescence and phosphorescence spectra of 4,4'-SD give the following electronic state energies:  $^1S_1 \sim 33,000 \text{ cm}^{-1}$ ,  $^1S_2 \sim 42,000 \text{ cm}^{-1}$ , and  $^3T_1 \sim 26,000 \text{ cm}^{-1}$ . These energies are identical to those found in DMT,<sup>30</sup> which lends support to the postulate that there is little or no through-conjugation across the sulfone group. The electronic energy diagram and band assignments of dibutyl 4,4'-sulfonyldibenzoate are shown in Figure 2.

TABLE III  
Absorption Characteristics of Dibutyl 4,4'-Sulfonyldibenzoate

Solvent	$\lambda$ , nm	$\epsilon$ , l./cm mole
Hexafluoro-2-propanol	228.5	22,020
	250.0	28,940
	280(s) <sup>a</sup>	6,851
	290(s) <sup>a</sup>	3,999
95% Ethanol	203.5	26,208
	227.5	17,322
	252.0	23,753
	279.0	4,581
	289(s) <sup>a</sup>	2,766

<sup>a</sup> Shoulder.

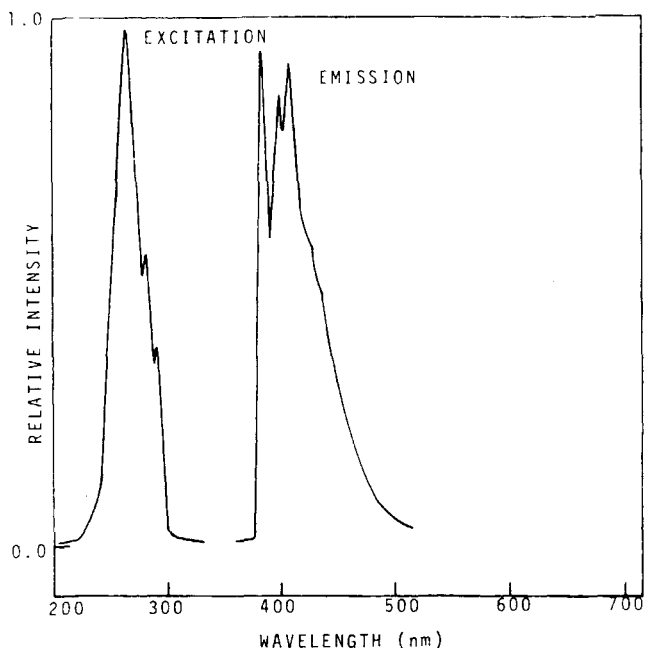


Fig. 1. Uncorrected phosphorescence excitation and emission spectra of dibutyl 4,4'-sulfonyldibenzoate ( $5 \times 10^{-5}M$ ) in 95% ethanol at 77 K. Excitation scan:  $Em \lambda 408 \text{ nm}$ ; emission scan:  $Ex \lambda 268 \text{ nm}$ .

### Photophysical Processes in Poly(ethylene Terephthalate-co-4,4'-Sulfonyldibenzoate) (PET-4,4'-SD)

#### *Absorption and Luminescence Spectra*

PET-4,4'-SD copolymers have UV absorption spectra similar to that of PET homopolymer in HFIP solution. Band maxima were exhibited at about 290, 245, and 191 nm in the homo- and copolymers.

The corrected excitation and fluorescence spectra of PET-4,4'-SD copolymers in HFIP solution are identical to the spectra of PET homopolymer. The band maxima for the excitation spectra of all the samples were at 246 and 290 nm, with the fluorescence emission occurring at 325 nm.

The corrected excitation and emission spectra of PET-4,4'-SD copolymer yarns were identical to that of PET homopolymer yarn. A structured excitation spectra exhibited band maxima at 326, 342, and 358 nm. The structured fluorescence spectra had band maxima at 369, 390, and 418 nm.

The uncorrected phosphorescence excitation and emission spectra of PET-4,4'-SD copolymer yarns were also identical to that of the PET homopolymer yarn. An excitation band maximum was found at 312 nm with a broad, structureless band centered at 452 nm found in the emission spectra. The phosphorescence mean lifetime ( $\tau$ ) was found to be 1.2 sec.

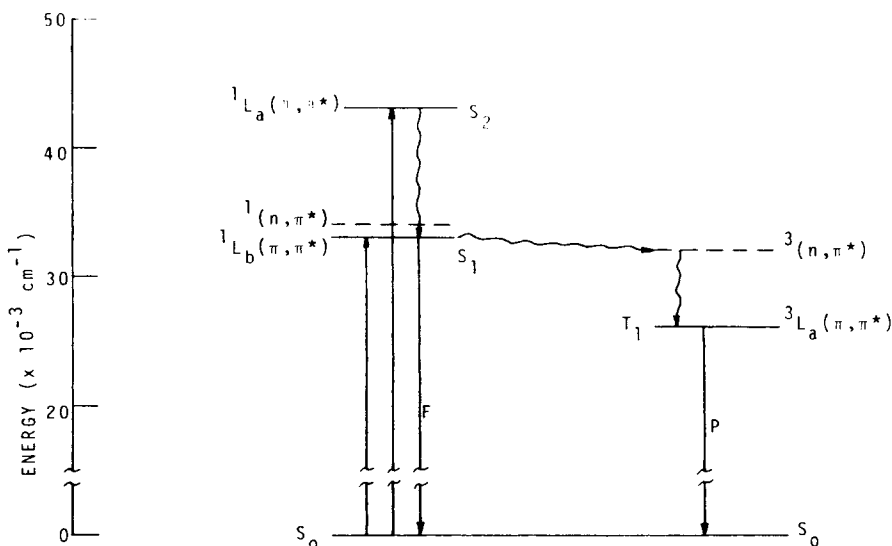


Fig. 2. Electronic energy level diagram and transitions for dibutyl 4,4'-sulfonyldibenzoate; estimated levels are represented by broken lines.

### *Interpretation of Absorption and Luminescence Data*

The absorption and luminescence properties of polysulfones and poly(ether sulfone) have been studied.<sup>48,52</sup> Studies of the same type processes involving aromatic sulfones in other polymer systems are not readily available.

The structures of the copolymer absorption spectra are identical to that found for PET, but all the copolymers show some increased absorption over all the regions. Band assignments for the copolymers simply correspond to those of the homopolymer PET and the second monomer, 4,4'-SD.

The solution fluorescence and yarn fluorescence and phosphorescence give no indication of the presence of the second monomer, 4,4'-SD. By again applying the assumption that 4,4'-SD behaves much like DMT, one arrives at the conclusion that the excitation and emission of 4,4'-SD are hidden under the strong excitation and emission bands of the dominant PET absorbing species.

If the 4,4'-SD could be seen in any spectra, it would be reasonable to assume that it would appear in the phosphorescence spectra of the copolymer yarns. No distinct bands appear to indicate the presence of 4,4'-SD in the copolymers. Allen and McKellar<sup>52</sup> found that excitation for a poly(ether sulfone) film occurred around 315 nm, with phosphorescence at about 450 nm. They attribute this luminescence to the phenyl sulfone units within the polymer. The similarities of the absorbing group in the poly(ether sulfone) polymer and in PET-4,4'-SD copolymers would also support the conclusion that the excitation and phosphorescence spectra of the 4,4'-SD comonomer are hidden under the PET spectra. The phosphorescence mean lifetimes ( $\tau$ ) of the PET homopolymer and the PET-4,4'-SD copolymers are identical and therefore give no indication of the presence of the comonomer in the copolymer yarns.

Microanalysis of the three PET-4,4'-SD copolymer yarns for sulfur yielded concentrations very close to the theoretical values (Table IV). Since the 4,4'-SD comonomer was definitely incorporated into the three copolymer yarns, the

TABLE IV  
Sulfur Analysis of Poly(ethylene Terephthalate-co-4,4'-Sulfonyldibenzoate) Copolymer Yarns

Mole % 4,4'-SD	% S (Theory)	% S (Analysis)
0.5	0.08	0.10
1.0	0.17	0.19
2.0	0.33	0.32

absorption and luminescence characteristics of the copolymers suggest a "co-absorption" process between 4,4'-SD and PET rather than an electronic energy transfer process.

Electronic energy levels for PET have been calculated by Cheung<sup>30</sup> and show a slight decrease in energy as compared to the model compound, DMT. The electronic energy levels of 4,4'-SD can experience this same decrease in energy due to incorporation within the polymer matrix.

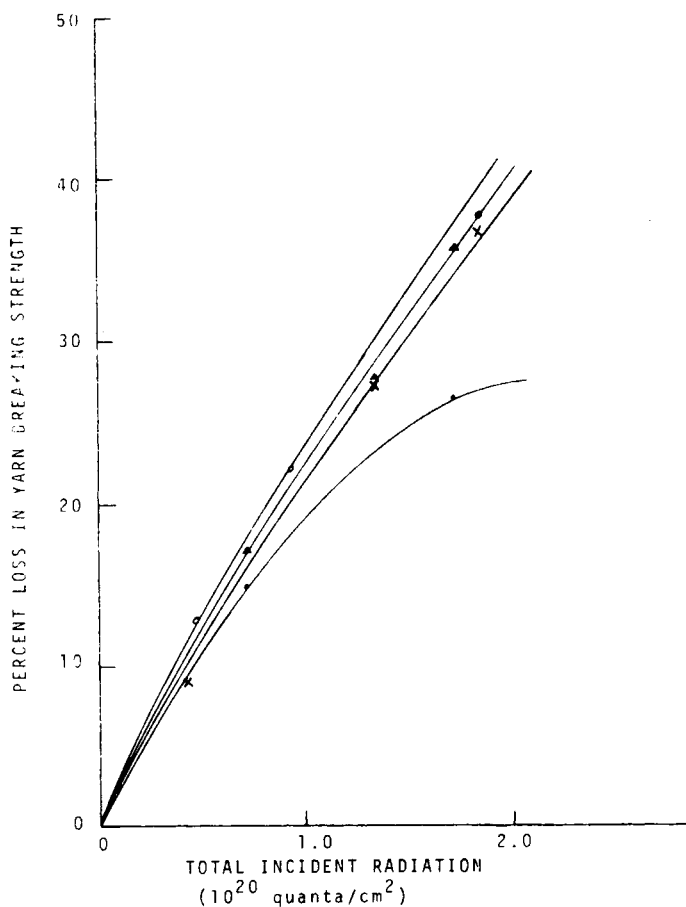


Fig. 3. Effect of radiation on poly(ethylene terephthalate-co-4,4'-sulfonyldibenzoate) yarns; mole % 4,4'-SD: (●) 0.0; (×) 0.5; (▲) 1.0; (○) 2.0.



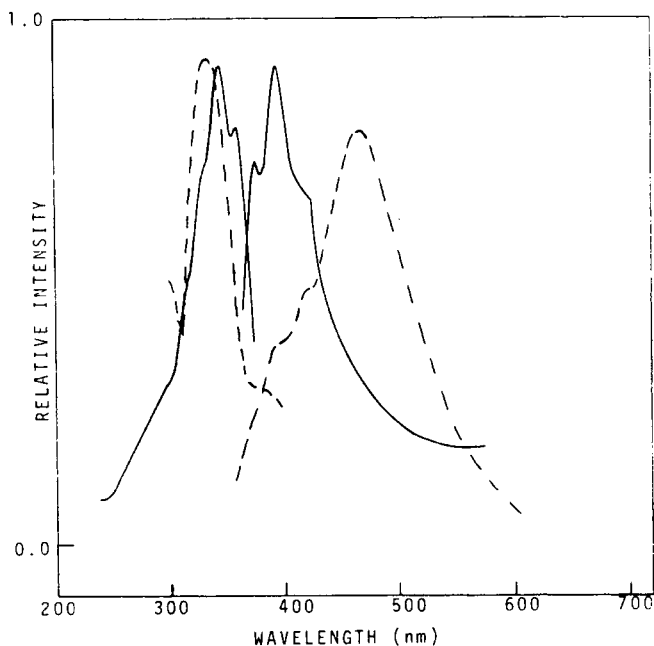


Fig. 4. Corrected fluorescence excitation and emission spectra of poly(ethylene terephthalate-co-4,4'-sulfonyldibenzoate) yarn containing 2 mole % 4,4'-SD; (—) 0 hr of irradiation; excitation scan:  $Em \lambda$  418 nm; emission scan:  $Ex \lambda$  326 nm; (- - -) 144 hr of irradiation; excitation scan:  $Em \lambda$  468 nm; emission scan:  $Ex \lambda$  342 nm.

### Phototendering of PET and PET-4,4'-SD Filament Yarns

Samples of PET-4,4'-SD copolymer filament yarns containing 0.5–2.0 mole % 4,4'-SD as the second monomer along with PET homopolymer filament yarns were irradiated in the photoreactor from 20 to 80 hr. The variation in lamp intensity was considered in order to normalize the phototendering curves. The percent loss in breaking strength was expressed as a function of the total incident radiation rather than as a function of irradiation time.

Figure 3 shows the phototendering rate curves for PET homopolymer and the PET-4,4'-SD copolymer yarns; the curves show that the samples become weaker with increase in irradiation time. It was also observed that the samples became more brittle and had lower elongation at break with increasing irradiation time. The curves show that the copolymer yarns degrade more quickly than does the PET homopolymer yarn. Increasing the concentration of the 4,4'-SD comonomer increased the rate of yarn phototendering.

### Fluorescence Analysis of Irradiated PET and PET-4,4'-SD Yarns

A blue-green fluorescent material has been observed in irradiated PET polymer.<sup>2,9</sup> The fluorescence emission at 460 nm has been attributed to the hydroxyterephthaloyl component.<sup>9</sup> The fluorescence spectra of irradiated PET homopolymer yarns and PET-4,4'-SD copolymer yarns are identical (Fig. 4). The curves agree with that obtained by Day and Wiles for PET film.<sup>2</sup>

A study of the relative fluorescence intensities at 460 nm of PET and PET-4,4'-SD yarns after receiving identical irradiation intensities reveals an increase

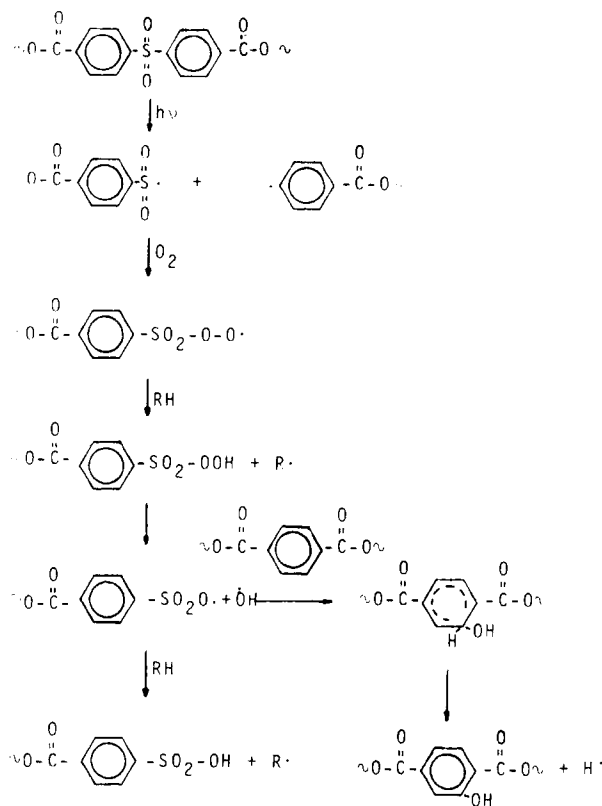


Fig. 5. Possible photo-oxidative mechanism occurring in poly(ethylene terephthalate-co-4,4'-sulfonyldibenzoate) yarns.

in the formation of the hydroxyterephthaloyl moiety with increasing amounts of 4,4'-SD. This indicates that a photo-oxidative mechanism involving the second monomer is the source of increasing degradation rates.

Several studies have been performed on the photodecomposition of diaryl sulfones and polysulfones.<sup>48,52-55</sup> Khodair et al.<sup>55</sup> demonstrated that the photodecomposition of diaryl sulfones proceeds by a free-radical mechanism with initial carbon-sulfur bond cleavage. This yields an aryl radical and an aromatic sulfonyl radical. The latter radical can react with oxygen and a hydrogen donor to eventually form the hydroxy radical. The hydroxy radical attacks the aromatic nucleus in PET and forms the hydroxyterephthaloyl radical.

Figure 5 shows a photo-oxidative mechanism which may account for the increased formation of hydroxyterephthaloyl within the presence of 4,4'-SD.<sup>53</sup>

## CONCLUSIONS

The fluorescence and phosphorescence properties of dibutyl 4,4'-sulfonyldibenzoate have been studied. The results indicate that there is little through-conjugation across the sulfone group. The lowest excited singlet and triplet in the monomer are assigned as the  $^1(\pi, \pi^*)$  and  $^3(\pi, \pi^*)$  types, respectively. The electronic energy levels have been characterized as follows:  $^1S_1 \sim 33,000 \text{ cm}^{-1}$ ,  $^1S_1 \sim 42,000 \text{ cm}^{-1}$ ,  $^3T_1 \sim 26,000 \text{ cm}^{-1}$ .

The luminescence properties of poly(ethylene terephthalate) and a series of poly(ethylene terephthalate-co-4,4'-sulfonyl dibenzoate) copolymer yarns show that no energy transfer occurs. The absence of any detectable luminescence from the 4,4'-sulfonyldibenzoyl moieties in the copolymers points toward similar absorption-emission processes occurring in the copolymers.

The phototendering studies of poly(ethylene terephthalate) and poly(ethylene terephthalate-co-4,4'-sulfonyldibenzoate) yarns demonstrate that the inclusion of the second monomer photosensitizes the degradation of the polymer. The enhanced rate of formation of the hydroxyterephthaloyl units with increasing concentrations of 4,4'-SD indicates that the photosensitization proceeds by a photo-oxidative mechanism involving the initial dissociation of the C—S bond.

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