Synthesis, Photodegradation, and Energy Transfer in a Series of Poly(ethylene Terephthalate–*co*–4,4′-Biphenyldicarboxylate) Copolymers

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Synopsis

Poly(ethylene terephthalate) (PET) filament yarns were photostabilized by addition of 0.5–4.0 mole % dimethyl 4,4′-biphenyldicarboxylate (4,4′-BPDC) to the polymerization feed. The mechanism of photostabilization is proposed to be a triplet–triplet energy transfer from excited terephthalate units to ground-state biphenyldicarboxylate units. The mechanism of transfer is reported to be via an electron exchange mechanism, with the "quenching sphere" calculated to be 14.9 Å. Kinetic studies show the "pseudo" zero-order rate constant of initial photodegradation to decrease from 3.4×10^{-19} for the PET homopolymer to 2.0×10^{-19}% breaking strength loss/quantum exposure/cm^2 for the copolyester containing 4.0 mole % of the 4,4′-biphenyldicarboxyl moieties. The photophysical processes available to the dimethyl 4,4′-biphenyldicarboxylate monomer were characterized by absorption and luminescence studies. In solution, dimethyl 4,4′-biphenyldicarboxylate was shown to emit an intense fluorescence from a $^2(\pi,\pi^*)$ state and a weaker ($\sim 10^{-2}\times$) phosphorescence from a $^1(\pi,\pi^*)$ state derived from the $^1A \rightarrow$supn1L_b absorption. The copolymer yarns were shown to exhibit both fluorescence and phosphorescence from the biphenyldicarboxylate units: the fluorescence from direct excitation, the phosphorescence by sensitized transfer.

INTRODUCTION

All fiber- and film-forming polymers deteriorate to some extent with continued outdoor exposure to solar radiation. In many cases the solar radiation of wavelengths 300–800 nm was readily recognized as the major causative agent in the degradation process. In addition, elements such as water oxygen, atmospheric "pollutants," and substituents in the polymer itself, added for a specific purpose or incurred as an impurity during production, were found to enhance photodegradation.

The initiating species for polymer photodegradation can generally be divided into two groups: impurities incurred during production which absorb radiative energy or recurring groups in the polymer backbone which absorb radiative energy. The polyolefins belong to the first group, with the "impurity" believed to be carbonyl in nature, while the aromatic polyesters belong in the second group, with the aromatic ester being the absorbing species.

Regardless of the initiating species, photodegradation is retarded and the useful lifetime of the polymer is extended by addition of a photostabilizer which can be classified according to activity as a light screen, UV absorber, or quencher. The earliest attempts at photostabilization of polymers were largely empirical in nature; however, in recent years more efforts have been directed toward developing a fundamental understanding of the mechanisms of action of photo-

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stabilizers. In particular, systematic studies incorporating quencher species, acting as energy acceptors, in the polymer backbone have evolved. Representative studies in this area as well as energy transfer processes available to polymeric substrates have been reviewed by Turro.[1]

Poly(ethylene terephthalate) (PET), in comparison to other polymers such as the polyolefins and polyamides, displays more resistance to photodegradation. However, exposure to terrestrial sunlight for extended periods of time leads to a loss of elasticity and tenacity for PET fibers, while under the same conditions PET films become discolored and brittle and develop crazed surfaces. The photodegradative processes and subsequent changes in the physical properties of PET have been studied as a function of many variables including irradiation wavelength, irradiation atmosphere, irradiation time, and polymer additives,[2–15] with the works of Day and Wiles[2–7] generally considered to be the definitive works pertaining to the primary steps in photodegradation.

Even though the primary steps in the photodegradation scheme of PET are believed to be well characterized, there remains some controversy in the literature pertaining to the primary photophysical processes available in PET and related model compounds.[3,8,9,14,16–24] In addition, few studies have attempted to interrelate the primary photophysical processes and the primary steps in photodegradation. Prior reports from our group[8,16,17] have focused on defining the available photophysical processes for PET and, in addition, have delineated methods by which the photophysical properties of PET and PET copolyesters could be used to explain the photodegradative behavior of PET and PET copolymers.

This present work involves the synthesis and characterization of PET copolyesters containing 0–4.0 mole % dimethyl 4,4′-biphenyldicarboxylate (BPDC). The PET copolyesters were spun and drawn into continuous filament yarn. The photophysical properties of the PET copolyesters were examined both as dilute solutions and in yarn form. The photodegradation of the yarns were studied by monitoring loss in tenacity as a function of total exposure to 300 nm radiation. Finally a mechanism for the observed photodegradation behavior (photostabilization) is suggested and supported by the photophysical properties of the PET copolyesters.

EXPERIMENTAL

Analysis and Materials

Ultraviolet absorption spectra were measured on a Varian Associates Cary 118C spectrophotometer. Luminescence measurements were made on a Perkin–Elmer model MPF-3 fluorescence spectrophotometer equipped with a Corrected Spectra Accessory and a Front Surface Accessory. A Tektronix model 5103N storage oscilloscope was used to measure phosphorescence lifetimes. Photolyses were conducted in a Rayonet Type RS model RPR-208 preparative photochemical reactor equipped with a MGR-100 merry-go-round assembly. Yarns were prepared at American Enka Co. Yarn samples were knit on a Lawson Fiber Analysis Knitter (FAK). Yarn tensile testing was performed on an Instron model 1101 (TM-M) constant rate of extension testing machine.

Dimethyl 4,4′-biphenyldicarboxylate (4,4′-BPDC) was purchased from Eastman Organic Chemicals. Dimethyl terephthalate and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were obtained from Eastman Organic Chemicals. Certified ACS-grade acetonitrile, ferric ammonium sulfate, ferrous ammonium sulfate, postassium oxalate, 1,10-phenanthroline (monohydrate), and sodium acetate were obtained from Fisher Scientific Co. USP-grade 95% ethanol, after further purification, was used for luminescence studies. Nuchar granular activated carbon (12 × 40 mesh) was used to remove colored impurities from the dimethyl 4,4′-diphenyldicarboxylate. Distilled in Glass acetonitrile was purchased from Burdick and Jackson.

Purification of Dimethyl 4,4′-Biphenyldicarboxylate

Crude dimethyl 4,4′-biphenyldicarboxylate was recrystallized with decolorization from reagent-grade acetonitrile (1:100). The white crystalline product was recrystallized again from Burdick and Jackson UV-grade acetonitrile (1:100) to give colorless crystals mp 217–219°C.

Synthesis, Characterization and Yarn Properties of Copolyesters

The synthesis, characterization, and spinning into continuous filament yarns were conducted as previously reported.[17] Copolymer properties are listed in Table I, and drawn yarn properties are listed in Table II.

Preparation, Irradiation, and Breaking of Copolyester Yarns

Conditions for preparing, irradiating, and measuring the breaking strength of the copolyester yarns have been described previously.[8]

Actinometry

The modified procedure used to determine the intensity of the 3000-Å irradiating lamps has been previously described.[17] The intensity of the lamps' radiation at the yarn surface was found to decrease from 5.5×10^{14} to 4.0×10^{14} quanta/cm^2/sec during the course of the work.

RESULTS AND DISCUSSION

Photophysical Processes in Dimethyl 4,4′-Biphenyldicarboxylate (4,4′-BPDC)

Absorption and Luminescence Spectra

The ultraviolet absorption spectrum of dimethyl 4,4′-biphenyldicarboxylate was examined in both HFIP (Fig. 1) and 95% ethanol. In each case two distinct absorption maxima were recorded: an intense absorption near 200 nm and a slightly less intense absorption near 280 nm. The band near 200 nm is believed

TABLE I

Characterization of Poly(ethylene Terephthalate) and Poly(ethylene Terephthalate-*co*-4,4′-Biphenyldicarboxylate) Polymer and Copolymers

4,4′-BPDC,[a] mole %	IV[b]	Acid No.[c]	Phosphorous,[d] ppm	T_g[e]	T_{cc}[e]	T_m[e]	T_{rc}[e]	T_{rm}[e]
0.0	0.63	20	47	72	130	252	212	252
0.5	0.67	18	46	72	132	251	204	253
1.0	0.71	16	74	73	132	249	202	251
2.0	0.60	8	41	72	134	249	202	250
4.0	0.61	18	34	77	138	244	204	244

[a] Based on weight of 4,4′-BPDC in polymerization feed.

[b] Intrinsic viscosity, measured in 40% phenol/60% tetrachloroethane.

[c] In mequiv/kg of polymer.

[d] Based on weight of polymer.

[e] DTA measurements, point of curve maximum (or minimum); T_{cc} = cold crystallization temperature, T_m = melting temperature, T_{rc} = recrystallization temperature, T_{rm} = remelt temperature.

TABLE II

Characterization of Poly(ethylene Terephthalate) and Poly(ethylene Terephthalate-*co*-4,4′-Biphenyldicarboxylate) Filament Yarns[a]

4,4′-BPDC, mole %	Deniers	Tenacity, g/den	Elongation, %	In. Modulus, g/den
0.0	25.49	4.08	19.4	89.5
0.5	20.89	4.64	22.5	91.9
1.0	25.89	3.88	8.7	88.1
2.0	23.30	3.82	20.9	85.0
4.0	22.00	4.05	25.9	98.2

[a] Data for as-received yarns; yarns were knitted, scoured at 70°C, and deknitted prior to experimental use.

to correspond to the $^1A \rightarrow {}^1B$ transition in benzene. It is believed that both the $^1A \rightarrow {}^1L_a$ and $^1A \rightarrow {}^1L_b$ transitions contribute to the absorption near 280 nm.

The corrected fluorescence excitation and emission spectra of 4,4′-BPDC in HFIP at 298 K are shown in Figure 2. The excitation shows a single broad band centered at 280 nm with a corresponding broad structureless emission band centered at 340 nm. Figure 3 shows the uncorrected fluorescence excitation and emission spectra in a rigid ethanol glass at 77 K; the excitation shows a single broad structureless band centered at 295 nm and a structured emission having maxima at 315, 330, and 342 nm.

The uncorrected phosphorescence spectra were studied in a rigid ethanol glass at 77 K and are shown in Figure 4. The excitation spectrum consists of a broad structureless band centered at 298 nm, and the emission spectrum consists of a structured band having maxima at 472 and 505 nm and a lifetime of 1.2 sec.

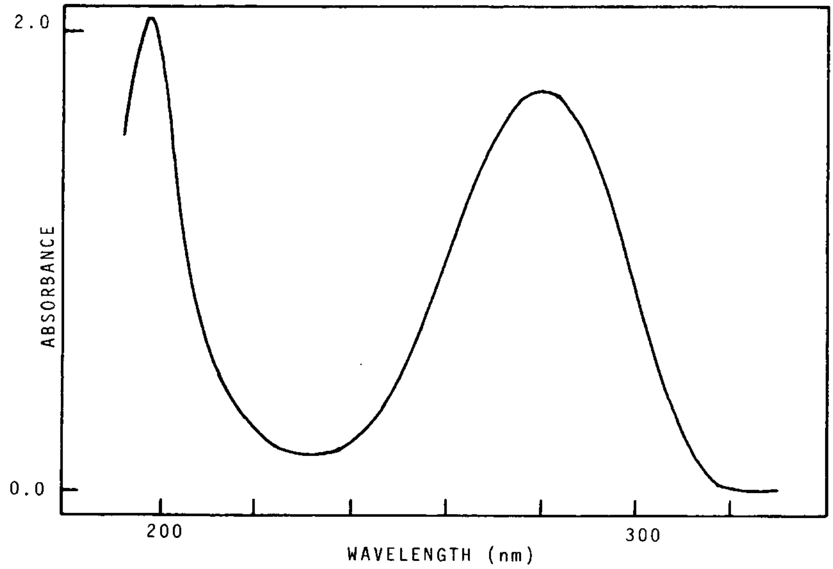

Fig. 1. Absorption spectrum of $4.70 \times 10^{-5} M$ solution of dimethyl 4,4′-biphenyl-dicarboxylate in hexafluoroisopropanol.

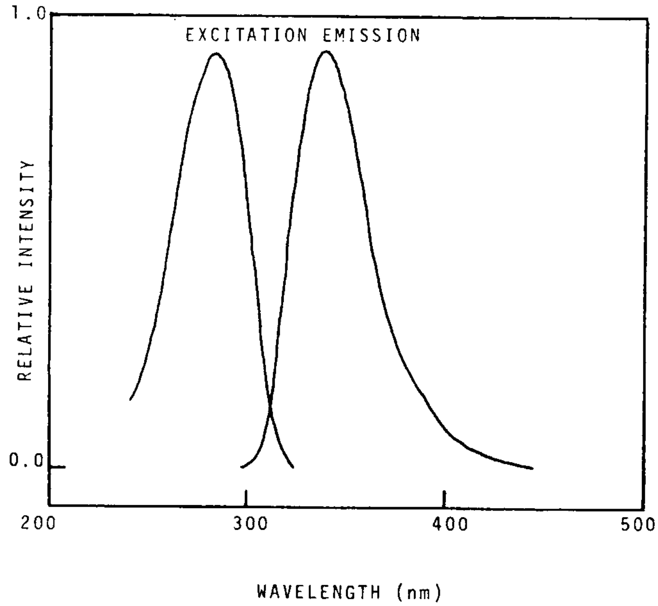

Fig. 2. Corrected fluorescence excitation and emission spectra of dimethyl 4,4′-biphenyldicarboxylate ($4.70 \times 10^{-7}M$) in hexafluoroisopropranol at 298 K. Excitation scan: Em λ 340 nm; emission scan: Ex λ 280 nm.

Interpretation of Absorption and Luminescence Data

Even though the Platt notation of electronic states[25] applies only to benzene and cata-condensed aromatic systems and therefore is not strictly applicable to biphenyl and its derivatives, it has been used for ease of comparison with benzene. For this same reason and, in addition, for comparison with dimethyl terephthalate, the Platt notation will be used in this work.

The UV absorption data for both the parent molecule biphenyl and the 4,4′-BPDC have previously been disclosed in the literature.[26-31] Biphenyl has been reported to have a single structureless absorption centered near 247 nm and a molar extinction coefficient of about 18,000 l./mole·cm. There seems to be little doubt that at least two transitions contribute to this band. Berlman[9] has assigned three transitions to this band; in Platt's notation, they are $^1A \rightarrow {}^1L_b$, $^1A \rightarrow {}^1L_a$, and $^1A \rightarrow {}^1B_b$. The $^1A \rightarrow {}^1L_b$ is a weak transition and has been reported to occur at 275 nm.[27,32] Petelenz[31] has assigned the 247-nm absorption to two nearly degenerate transitions derived from the ^1L_b state. This, however, is unlikely since the extinction coefficient for the 247-nm transition is much larger than expected for the forbidden $^1A \rightarrow {}^1L_b$ transition.

From the published work on biphenyl absorption the most reasonable assignment for the 247-nm band seems to be the $^1A \rightarrow {}^1L_a$ transition as the major contribution, with the $^1A \rightarrow {}^1L_b$ submerged and making a smaller contribution to the total absorption. Several workers[28,29] have studied the effects of substitution on the absorption of biphenyl. It has been found that substitution in the para positions causes red shift in the $^1A \rightarrow {}^1L_b$ transition. Williamson and Rodebush[28] reported the absorption spectrum for 4,4′-BPDC as having a single absorption band centered at 280 nm with an extinction coefficient of 30000 l./mole cm. They assigned this band to correspond to the 247-nm absorption band

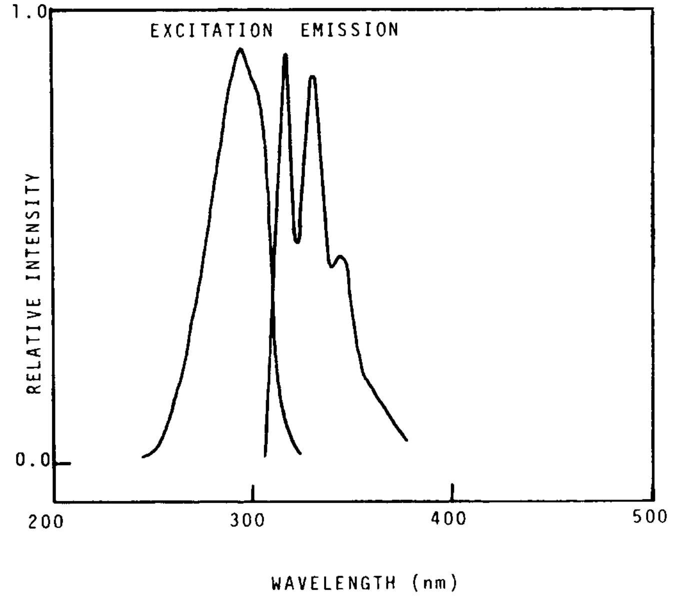

Fig. 3. Uncorrected fluorescence excitation and emission spectra of dimethyl 4,4′-biphenyldicarboxylate (1.0 × $10^{-6}M$) in 95% ethanol at 77 K. Excitation scan: Em λ 330 nm; emission scan: Ex λ 280 nm.

in biphenyl, and they explained the bathochromatic shift as the result of extended conjugation of the π-electron system by the carboxyl functions in the 4- and 4′-positions. Based on these works the band observed near 200 nm is assigned at $^1A \rightarrow {}^1B$, and the band near 280 is assigned as the combined $^1A \rightarrow {}^1L_a$ and $^1A \rightarrow {}^1L_b$ transitions.

In 95% ethanol, 4,4′-BPDC shows a strong fluorescence and relatively weaker

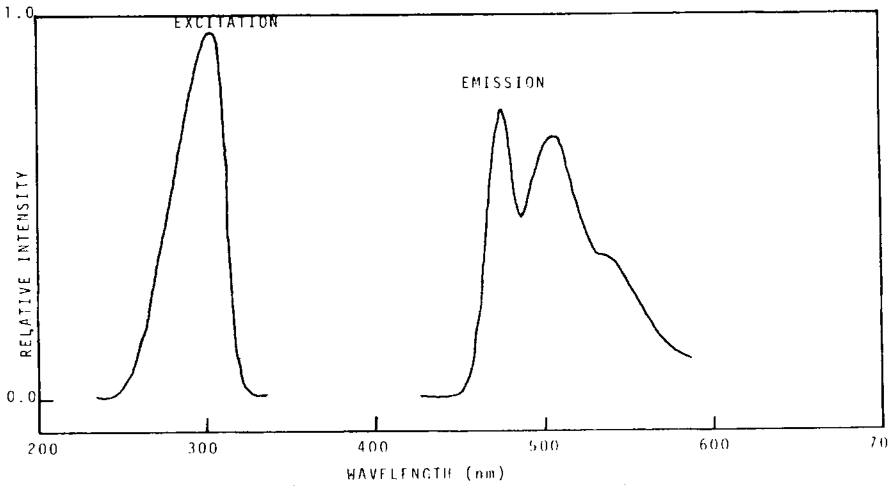

Fig. 4. Uncorrected phosphorescence excitation and emission spectra of dimethyl 4,4′-biphenyldicarboxylate (5.0 × $10^{-5}M$) in 95% ethanol at 77 K; Excitation Scan: Em λ 472 nm; emission scan: Ex λ 298 nm.

phosphorescence (relative intensity) ~10^{-2} times the fluorescence). This indicates, though perhaps unexpected, that the lowest-energy singlet state is a $^1(\pi,\pi^*)$ state rather than a $^1(n,\pi^*)$ state which would produce a weak fluorescence and a relatively intense phosphorescence. Further evidence that the lowest-energy excited singlet state for 4,4′-BPDC is a $^1(\pi,\pi^*)$ state is shown by the slight red shift of the fluorescence in the more polar solvent, HFIP.

From the absorption spectrum it is impossible to determine the energy of the $^1(n,\pi^*)$ transition for 4,4′-BPDC. If, however, it is assumed that the $^1(n,\pi^*)$ state for 4,4′-BPDC is at nearly the same energy level that Cheung[17] has proposed for dimethyl terephthalate (Fig. 5), the strong fluorescence is easily explained. This assumption appears even more valid if it is assumed that replacing the phenyl with a biphenyl nucleus creates a greater $+I$ inductive effect on the carbonyl, thus raising the energy of both the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states. Such effects have been shown to occur for substituted acetophenones.[33]

The above explanation places the $^3(n,\pi^*)$ of 4,4′-BPDC at an energy level above that of the lowest $^1(\pi,\pi^*)$ state. Therefore, for phosphorescence to occur, intersystem crossing must occur from a $^1(\pi,\pi^*)$ to a $^3(\pi,\pi^*)$ state. El-Sayed[34] has shown, to a first-order approximation, that spin-orbit coupling between states of the same configuration is forbidden, yielding a rate of radiationless intersystem crossing that is unable to complete with fluorescence.

The long lifetime of the phosphorescence (1.2 sec) is characteristic of phosphorescence from a $^3(\pi,\pi^*)$ state. This state must be the ^3L_a, in agreement with the generally established concept that the ^3L_a (π,π^*) state is the lowest $^3(\pi,\pi^*)$ state for aromatic molecules.

From the luminescence data, the following electronic state energies have been calculated for 4,4′-BPDC: ^1L_a $(\pi,\pi^*) \sim 35500$ cm^{-1}; ^1L_b $(\pi,\pi^*) \sim 32000$ cm^{-1}; ^3L_a $(\pi,\pi^*) \sim 22000$ cm^{-1}. Figure 5 shows the energy levels schematically.

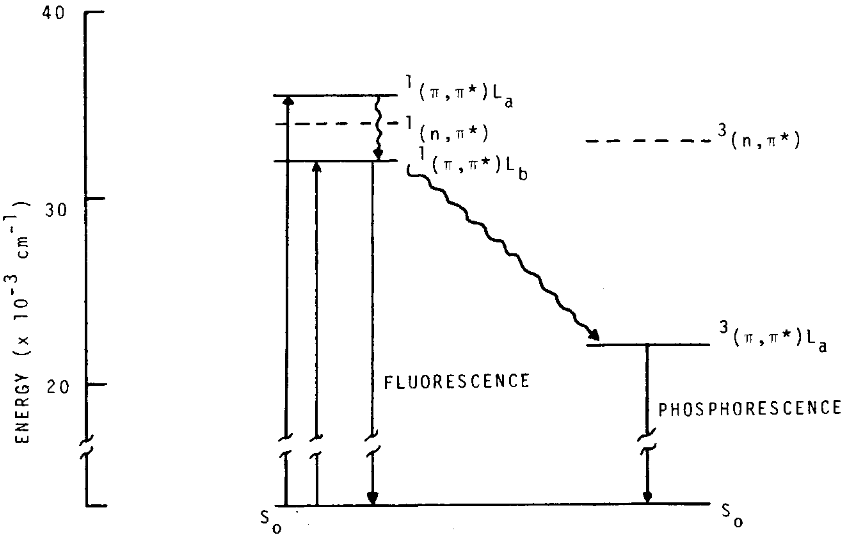

Fig. 5. Electronic energy level diagram and transitions for dimethyl 4,4′-biphenyldicarboxylate. Broken lines represent estimated levels based on dimethyl terephthalate.

Photophysical Processes in Poly(ethylene Terephthalate) (PET) and Poly(ethylene Terephthalate–*co*–4,4′-biphenyldicarboxylate) (PET–*co*–4,4′-BPDC)

Absorption and Luminescence Spectra

The absorption spectrum of PET in HFIP (Fig. 6) is in agreement with the work reported by Cheung.[17] Absorption bands were observed at 193.0, 245.5, and 289.5 nm. The PET–*co*–4,4′-BPDC copolymers, with concentrations of 4,4′-BPDC ranging from 0.5 to 4.0 mole %, showed UV absorption spectra similar to that of PET in HFIP and are summarized in Table III.

The corrected fluorescence excitation and emission spectra of PET in HFIP (Fig. 7) at room temperature showed excitation maxima at 255 and 290 nm with a corresponding emission at 324 nm and are consistent with spectra previously reported by Cheung.[17] The corrected fluorescence spectra of the copolymers (Fig. 8) in HFIP exhibited excitation maxima at 255 and 290 nm. The emission spectrum displayed emission from the terephthalate portion of the polymer when excited by 255 nm radiation and emission from the 4,4′-biphenydicarboxylate portion of the polymer when excited with 290-nm radiation. A list of the corrected fluorescence spectra of the copolymers in HFIP is given in Table IV.

Examination of the corrected room temperature fluorescence properties of PET yarns (Fig. 9) revealed an excitation maximum at 388 nm. At 77 K, in the uncorrected mode, the fluorescence spectra of PET yarns exhibited a structured excitation having maxima of 342 and 360 nm and a shoulder at 320 nm. At 77 K, PET yarns displayed a structured emission with maxima at 368 and 388 nm (Fig. 9). As they also do in solution, the copolymer yarns showed both fluorescence from the terephthalate portion of the polymer and the 4,4′-biphenyldicarboxylate portion of the polymer. Excitation at 342 nm produced an emission

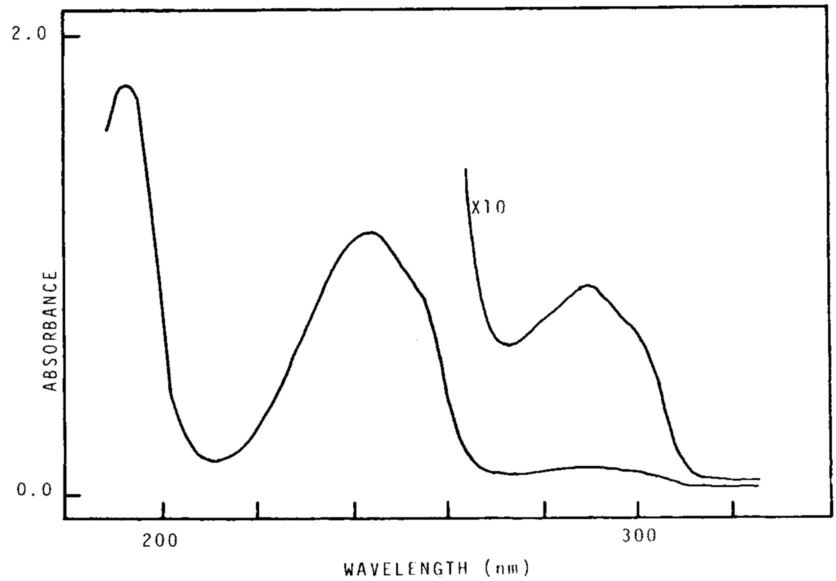

Fig. 6. Absorption spectrum of 9.37×10^{-3} g/l. poly(ethylene terephthalate) in hexafluoroisopropanol.

TABLE III
Absorption of Poly(ethylene Terephthalate) and Poly(ethylene Terephthalate-*co*-4,4'-Biphenyldicarboxylate) Polymer and Copolymers in Hexafluoroisopropanol

4,4'-BPDC, mole %	λ, nm	$A^{1\%}_{1\,\mathrm{cm}}$
0.0	193.0	1782
	245.5	1137
	289.5	88.6
0.5	191.4	1840
	245.5	1077
	289.5	95.7
1.0	193.0	1718
	244.5	1110
	289.5	104.1
2.0	194.5	1731
	244.5	1112
	289.5	121.0
4.0	194.5	1592
	244.5	1021
	289.5	154.6

band centered at 388 nm. This excitation and the emission correspond to the PET homopolymer emission. Excitation with about 325 nm radiation produced an emission with a maximum near 348 nm from the 4,4'-biphenyldicarboxylate

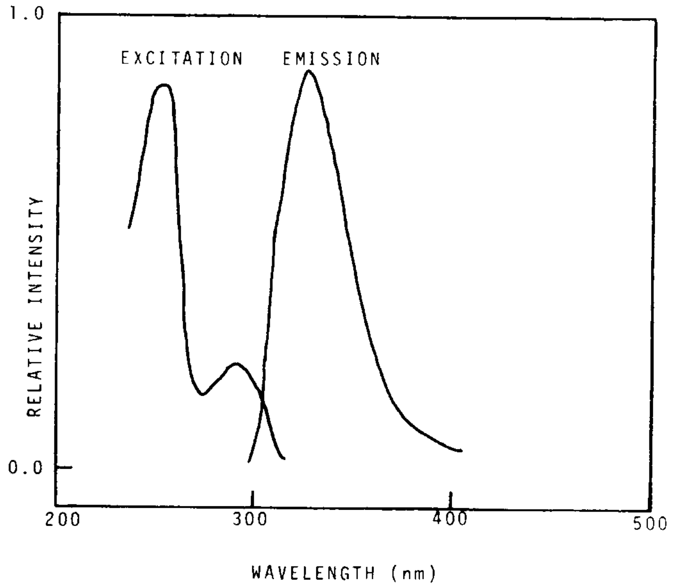

Fig. 7. Corrected fluorescence excitation and emission spectra of poly(ethylene terephthalate) in hexafluoroisopropranol (9.37×10^{-3} g/l.) at 298 K. Excitation scan: Em λ 324 nm; emission scan: Ex λ 255 nm.

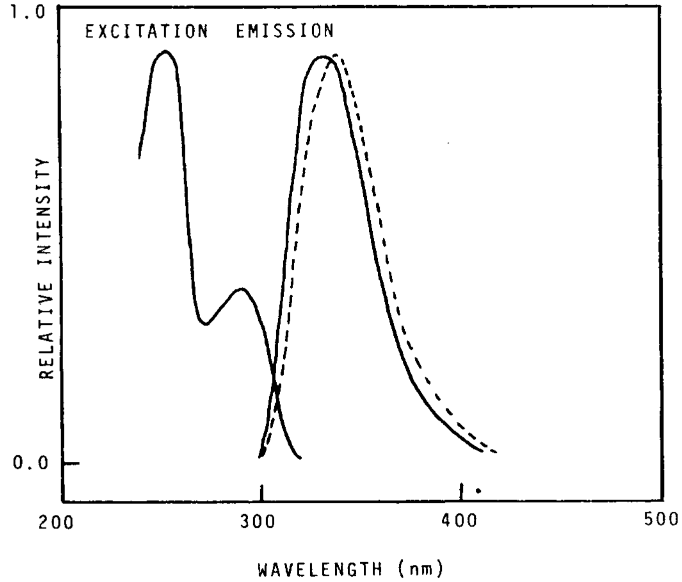

Fig. 8. Corrected fluorescence excitation and emission spectra of poly(ethylene terephthalate–*co*–4,4′-biphenyldicarboxylate), containing 1.0 mole % 4,4′-BPDC, in hexafluoroisopropanol (9.11 $\times 10^{-3}$ g/l.) at 298 K. Excitation scan: Em λ 388 nm; emission scan: Ex λ (——) 255 nm (- - -) 290 nm.

portions of the polymer. Figure 10 shows the 77 K uncorrected fluorescence spectra for the copolymer yarn containing 1.0 mole % 4,4′-BPDC. Table V summarizes the uncorrected fluorescence spectra at 77 K for PET and the copolymer yarns.

The uncorrected phosphorescence excitation and emission spectra of PET yarn at 77 K are shown in Figure 11. An excitation maximum at 310 nm and emission at 452 nm with a lifetime τ equal to 1.2 sec agree with previous reports.[17]

TABLE IV
Corrected Fluorescence Spectra of Poly(ethylene Terephthalate) and Poly(ethylene Terephthalate–*co*–4,4′-Biphenyldicarboxylate) Polymer and Copolymers in Hexafluoroisopropanol

4,4′-BPDC, mole %	Excitation $\lambda_{\max}$, nm	Emission $\lambda_{\max}$, nm
0.0	255	324
	290	324
0.5	255	326
	290	335
1.0	255	228
	290	335
2.0	255	336
	290	339
4.0	255	338
	290	340

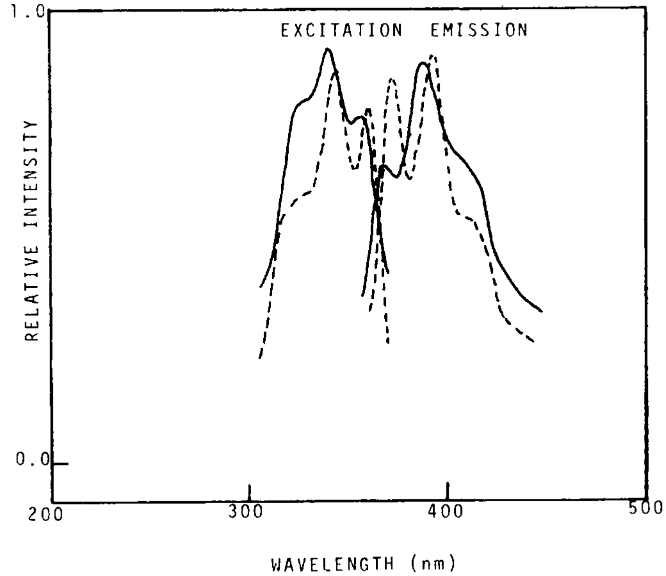

Fig. 9. Fluorescence spectra of poly(ethylene terephthalate) yarn; (——) corrected at 298 K; (- - -) uncorrected at 77 K. Excitation scans: Em λ 388 nm; emission scans: Ex λ 342 nm.

The phosphorescence spectra of the copolymer yarns (Fig. 11) showed excitation in the 305- to 310-nm range, with corresponding emission maxima at 480 and about 515 nm and corresponding lifetimes of 1.2 sec. In the copolymer yarns containing 0.5–2.0 mole % 4,4′-BPDC, a small shoulder was observed at 452 corresponding to the PET homopolymer phosphorescence. A summary of the phosphorescence data for PET and the copolymer yarns is given in Table VI.

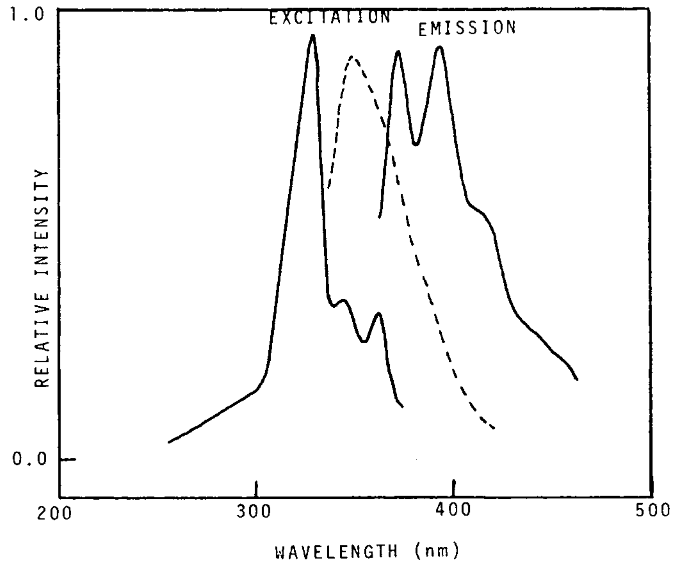

Fig. 10. Uncorrected fluorescence excitation and emission spectra of poly(ethylene terephthalate-*co*-4,4′-biphenyldicarboxylate), containing 1.0 mole % 4,4′-BPDC, yarn at 77 K. Excitation scan: Em λ 388 nm; emission scans: Ex λ (——) 342 nm, (- - -) 324 nm.

TABLE V
Uncorrected Fluorescence Spectra of Poly(ethylene Terephthalate) and Poly(ethylene Terephthalate-*co*-4,4′-Biphenyldicarboxylate) Yarns at 77 K

4,4′-BPDC, mole %	Excitation λ_{max}, nm	Emission λ_{max}, nm
0.0	342, 360	368, 688, 410[a]
0.5	323	350
	342	370, 390, 410
	362	390, 410
1.0	324	345
	342	369, 390
	360	
2.0	326	346
	342	368, 390
	360	
4.0	326	352
	342	370, 388
	362	

[a] From Day and Wiles.[5]

Interpretation of Absorption and Luminescence Data

The bands at 193.0, 245.5, and 289.5 nm in the absorption spectrum of PET in HFIP have been assigned as the $^1A \rightarrow {}^1B$, $^1A \rightarrow {}^1L_a$, and $^1A \rightarrow {}^1L_b$ transitions of DMT, respectively. These bands predominate in the absorption spectra of the copolymers. As the concentration of 4,4′-BPDC increases, an increase in the intensity of the band at 289.5 nm is observed. This is the result in the increased intensity of the $^1A \rightarrow {}^1L_a$ transition of the 4,4′-BPDC in this region.

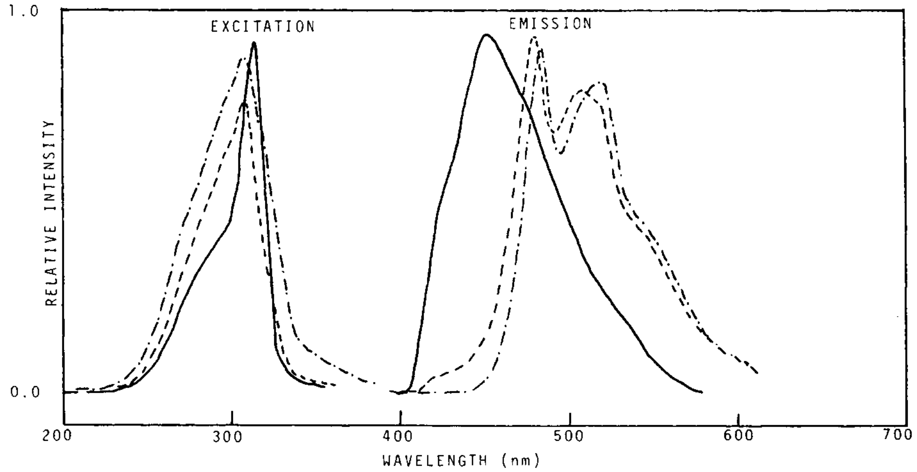

Fig. 11. Uncorrected phosphorescence spectra of poly(ethylene terephthalate) (——) and poly(ethylene terephthalate-*co*-4,4′-biphenyldicarboxylate), containing 0.5 mole % (- - -) and 2.0 mole % (-·-) 4,4′-BPDC. Excitation scans: Em λ (——) 452 nm, (- - -) 480 nm, (-·-) 480 nm; emission scans: Ex λ (——) 310 nm, (- - -) 305 nm, (-·-) 305 nm.

TABLE VI
Uncorrected Phosphorescence Spectra of Poly(ethylene Terephthalate) and Poly(ethylene Terephthalate-*co*-4,4′-Biphenyldicarboxylate) Yarns at 77 K

4,4′-BPDC, mole %	Excitation λ_{max}, nm	Emission λ_{max}, nm	τ, sec
0.0	310	452	1.2
0.5	305	480, 510	1.2
1.0	305	480, 515	1.2
2.0	305	480, 515	1.2
4.0	310	480, 520	1.2

Although the presence of the 4,4′-BPDC in low concentrations makes only a small difference in the absorption characteristics of the copolymers, its existence is quite obvious in the emission spectra. In dilute HFIP solutions, the copolymers show a fluorescence emission in the 336- to 338-nm range when excited with 255-nm radiation. This emission corresponds to emission from the terephthalate units of the copolymer. However, excitation with 290-nm radiation produces an emission that is red shifted relative to the terephthalate emission. This emission originates from the 4,4′-biphenyldicarboxylate units in the copolymer. From the data in Table IV, the relative increase in 4,4′-BPDC emission intensity can be observed. In the copolymer containing 0.5 mole % 4,4′-BPDC, a slight red shift in the terephthalate emission is observed as a result of the presence of the longer-wavelength emission of the 4,4′-BPDC. Similarly, the emission of the 4,4′-biphenyldicarboxylate is blue shifted from the expected 340 nm because of the presence of emission from the terephthalate unit. At 4.0 mole % 4,4′-BPDC in the copolymer, the 4,4′-biphenyldicarboxylate emission is observed at the expected 340-nm wavelength. This indicates that at 4.0 mole % concentration of 4,4′-BPDC the fluorescence emission intensity of the 4,4′-BPDC uit is greater than the fluorescence emission of the terephthalate unit of the copolymer.

In the yarns, as would be predicted, the fluorescence of the 4,4′-biphenyldicarboxylate unit is distinct and predominates both at 298 and 77 K. This can be seen from Table V and Figure 10. This is expected because it has been shown that the monomer DMT exhibits a weak fluorescence and a relatively much larger phosphorescence, while the 4,4′-BPDC monomer exhibits a strong fluorescence and a relatively much weaker phosphorescence. Extrapolating this to the copolymer yarns, it is predicted that the emission of the 4,4′-biphenyldicarboxylate unit will predominate in the fluorescence spectra and the emission from the terephthalate unit will predominate in the phosphorescence spectra.

Examination of the phosphorescence spectra of the PET and PET-*co*-4,4′-BPDC yarns revealed three emission maxima. In the PET homopolymer, excitation with 310-nm radiation produced an emission at 452 nm which has been assigned as phosphorescence from the terephthalate chromophore.[17] In the copolymer yarn, excitation with either 305- or 310-nm radiation produced emission spectra with distinct maxima at 480 and ~515 nm (τ = 1.2 sec) and a shoulder near 452 nm (τ = 1.2 sec). The maxima in the phosphorescence spectra were assigned as emissions from the 4,4′-biphenyldicarboxylate units of the copolymer. The observed emissions are bathochromatically shifted from the emission of the present 4,4′-BPDC in a glassed solvent. This red shift is believed to be caused by the 4,4′-biphenyldicarboxylate being more coplanar in the polymer matrix, thereby allowing better electronic interactions between the phenyl rings. This hypothesis is supported by the observed emissions from solid 4,4′-BPDC at 520 and 560 nm ($\tau = 0.3$ sec) when excited with 340- or 356-nm radiation.

The phosphorescence characteristics of the copolymer yarns are somewhat unexpected. It has been shown previously that the terephthalate emission should predominate in the phosphorescence spectra. However, in the copolymer yarn containing only 0.5 mole % 4,4′-BPDC, phosphorescence emission from the 4,4′-biphenyldicarboxylate units predominates, and at 4.0 mole % 4,4′-BPDC, the terephthalate emission is completely quenched.

The observed luminescence properties of the copolymer yarns can be explained if an energy transfer mechanism is assumed to be operating. Triplet–triplet energy transfer from the terephthalate units to the 4,4′-biphenyldicarboxylate units explains both the dual fluorescent/phosphorescent emissions from the 4,4′-biphenyldicarboxylate units as well as the quenched phosphorescence from the terephthalate units.

To prove unequivocally that radiationless triplet–triplet energy transfer is occurring, the expected donor chromophore should be selectively excited and the phosphorescence spectrum monitored for emission from the expected acceptor chromophore. Since the absorption/excitation energies overlap for the terephthalate and 4,4′-biphenyldicarboxylate units, such an experiment was impossible. However, it seems reasonable, with the terephthalate chromophore present in a concentration at least 24 times the concentration of 4,4′-biphenyldicarboxylate, that irradiation with 310-nm light (the most probable wavelength to produce terephthalate phosphorescence), in the absence of an energy transfer mechanism operating, a significantly greater phosphorescent emission should be observed from the terephthalate unit in comparison to the phosphorescent emission from the 4,4′-biphenyldicarboxylate chromophore.

The observed luminescent characteristics of the copolymer yarns are explained by the following reaction sequence:

$$^{1}\mathrm{PET} + h\nu \rightarrow {}^{1}\mathrm{PET}^{*} \quad \text{(absorption)}$$

$$^{1}(4,4'\text{-BPDC} + h\nu \rightarrow {}^{1}(4,4'\text{-BPDC})^{*} \quad \text{(absorption)}$$

$$^{1}(4,4'\text{-BPDC})^{*} \rightarrow {}^{1}(4,4'\text{-BPDC}) + h\nu' \quad \text{(fluorescence)}$$

$$^{1}\mathrm{PET}^{*} \rightarrow {}^{3}\mathrm{PET}^{*} \quad \text{(intersystem crossing)}$$

$$^{3}\mathrm{PET}^{*} + {}^{1}(4,4'\text{-BPDC}) \rightarrow {}^{1}\mathrm{PET} + {}^{3}(4,4'\text{-BPDC})^{*} \quad (T\text{–}T \text{ energy transfer})$$

$$^{3}(4,4'\text{-BPDC})^{*} \rightarrow {}^{1}(4,4'\text{-BPDC}) + h\nu'' \quad \text{(4,4'-BPDC sensitized phosphorescence)}$$

Triplet–triplet energy transfer is spin forbidden by the long-range dipole–dipole radiationless transfer mechanism, but it is spin allowed for the electron exchange mechanism. The constant lifetime (1.2 sec) of the 452-nm emission indicates that the quenching mechanism involved fits the Perrin model[35] described by the following equation:

$$\ln \phi_0/\phi = NV[\mathrm{A}]$$

where ϕ_0 and ϕ are the unquenched and quenched phosphorescence intensities, respectively; N is Avagadro's number; V is the volume of the quenching sphere; and [A] is the concentration of quencher molecules. As predicted by the Perrin model, a plot in $\ln \phi_0/\phi$ versus concentration of 4,4′-BPDC yielded a straight line (Fig. 12), the slope of which was identified with NV. The radius R_0 of the active volume or quenching sphere was calculated by the following equation:

$$R_0 = (3V/4\pi)^{1/3}$$

Using a least-squares analysis, the slope was determined to equal 8.43 l./mole, which yielded a value of R_0 equal to 14.9 Å. This value for the transfer radius is within the 15 Å required for electron exchange to occur.

Figure 13 shows the electronic transitions and possible energy transfer processes available to the PET–*co*–4,4′-BPDC copolymers.

Phototendering of PET and PET–co–4,4′-BPDC Filament Yarns

Both PET homopolymer and PET–*co*–4,4′-BPDC copolymer yarns, after being knitted, scoured at 70°C, and deknitted, were irradiated from 20 to 80 hr in the photolysis chamber. Irradiation energy was supplied by eight high-intensity, low-pressure mercury and phosphor conversion lamps (RUL 3000 Å, Southern New England Ultraviolet Co.), which have a high-intensity output at 300 nm.

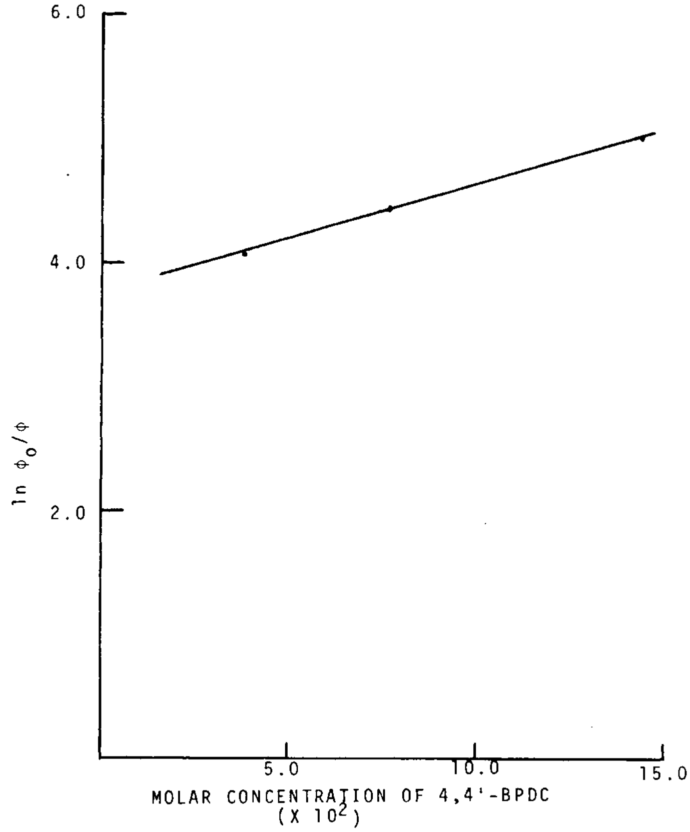

Fig. 12. Relative phosphorescence yield at 352 nm in poly(ethylene terephthalate–*co*–4,4′-biphenyldicarboxylate) yarns at 77 K.

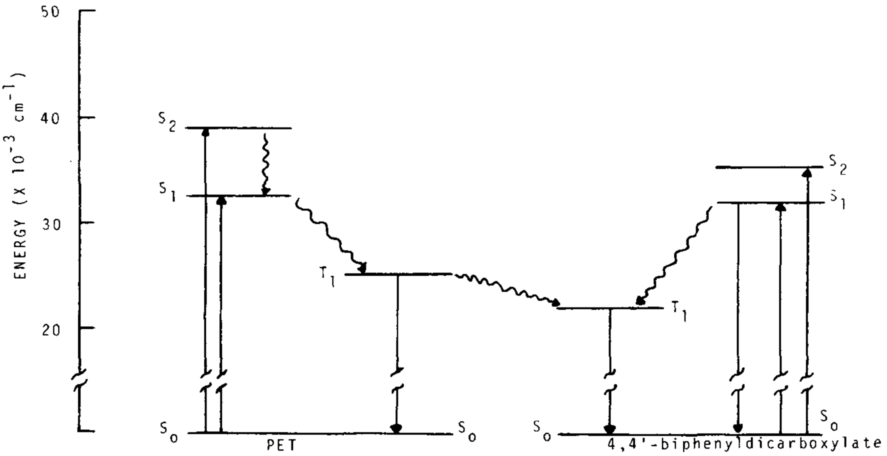

Fig. 13. Electronic energy level diagram and transitions for poly(ethylene terephthalate–*co*–4,4′-biphenyldicarboxylate) yarn.

In order to account for the lamp aging, the phototendering rate curves were plotted as percent loss in tenacity versus total quanta/cm^2 of exposure, rather than irradiation time (Fig. 14). All the samples became weaker as total quanta/cm^2 of exposure was increased. The phototendering curves show an initial period with a relatively linear relationship between percent loss in tenacity and total quanta/cm^2 of exposure, then a flatting of the curve. Merrill and Roberts[8] have also observed this effect. They point out that since most photooxidation of PET occurs at the surface, this reduction in the rate of degradation may be the result of a "skin" layer of photooxidized polymer acting as a radiation-absorbing barrier.

Assuming a zero-order rate of phototendering of the yarn samples during the initial stage of photolysis and using a least-squares analysis gave a rate constant for phototendering of PET homopolymer, k_{PET}, equal to 3.4×10^{-19}% breaking strength loss/quantum exposure/cm^2. Similar treatment of the phototendering data for the copolymers showed a decrease in the rate of phototendering with increasing concentration of 4,4′-BPDC in the copolymer to give the following phototendering rate constants: $k_{0.5} = 3.0 \times 10^{-19}$, $k_{1.0} = 2.6 \times 10^{-19}$, $k_{2.0} = 2.6 \times 10^{-19}$, $k_{4.0} = 2.0 \times 10^{-19}$% breaking strength loss/quantum exposure/cm^2, where the subscript on the rate constant equals the mole % 4,4′-BPDC in the copolymer.

The kinetic analyses showed that the rate of phototendering for the copolymer containing 4.0 mole % 4,4′-BPDC decreased to about 59% of the rate of PET homopolymer phototendering. Tensile rates revealed after 80 hr of exposure ($\sim 1.3 \times 10^{20}$ quanta/cm^2), where the rate of degradation appears to be approaching zero in all cases, that the percent loss in breaking strength of the copolymer yarn containing 4.0 mole % 4,4′-BPDC was about 54% of the loss incurred by the PET homopolymer.

The relationship between the radius of the active spherical volume around each molecule and the molar concentration has been shown to be related by the following expression[36,37]:

$$C = 3000/4\pi N R^3$$

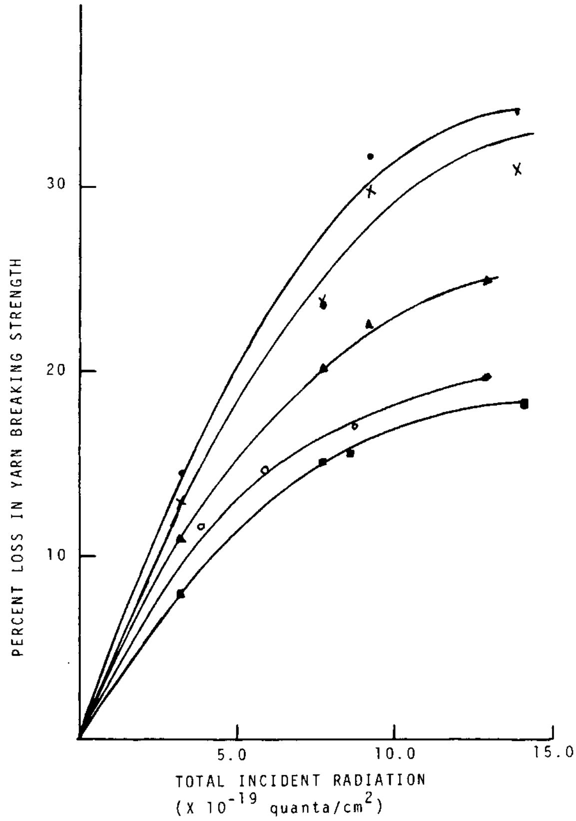

Fig. 14. Effect of radiation on the poly(ethylene terephthalate-*co*-4,4′-biphenyldicarboxylate) yarns. 4,4′-BPDC mole % (●) 0.0; (X) 0.5; (▲) 1.0; (O) 2.0; (■) 4.0.

where C is the concentration in mole/l., N is Avogadro's number, and R is the radius of the volume in cm. From this relationship, the concentration needed to have a 4,4′-biphenyldicarboxylate unit within the 14.9 Å (calculated from the Perrin model) of each terephthalate unit can be calculated. Assuming a totally random distribution of 4,4′-biphenyldicarboxylate units in the polymer matrix, a value of 1.6 mole % 4,4′-BPDC is needed in the polymerization reaction feed.

If a totally random distribution is achieved in the polymerization, one would predict that the copolymer yarns containing 2.0 and 4.0 mole % 4,4′-BPDC would behave almost identically under identical photooxidative environments. Reviewing Figure 14, one recognizes that even though the rates of degradation are not equal, the differences between the copolymer yarns containing 2.0 and 4.0 mole % 4,4′-BPDC are not as large as the differences between the copolymers containing 1.0 and 2.0 mole % 4,4′-BPDC.

Day and Wiles[5] have shown the importance of the Norrish-type II intramolecular rearrangement in PET photolysis. Based on their quantum yield measurements for formation of –COOH endgroups in both oxidative and inert environments, they report the Norrish type II rearrangement to be the predominate chain scission reaction in PET photolysis at wavelengths of 300 nm and greater Other workers[38,39] have shown that in some systems the Norrish type II rearrangement proceeds via both the lowest excited singlet and triplet states. Doughterty[39] has implied that when excitation occurs to the lower-level excited states, intersystem crossing is more efficient thus allowing the triplet state to have a greater participation in the rearrangement reaction. In the case of PET photolysis, using an excitation source with a maximum output at 300 nm, the excitation process must occur to the lower-level excited states (see Fig. 6 for absorption spectrum of PET). If the intersystem crossing process is efficient at this excitation, then the Norrish type II rearrangement must occur from the triplet state. This is further substantiated by a reduction in loss of tenacity with increasing concentration of triplet-state quencher. The reduction in loss of tenacity may be equated with interruptions of the chain scission process(es). Since previous work[5] has established the Norrish type II process as the predominate chain scission for PET, one can conclude that the Norrish type II rearrangement in PET proceeds, for the most part, via the lowest triplet state.

Fluorescence Analysis of Irradiated PET and PET-co-4,4′-BPDC Yarns

The presence of a material that emits a blue-green fluorescence on photooxidized PET has been reported previously.[3,19] This fluorescent material, which emits at 460 nm when excited by 342-nm energy, has been proved to be the hydroxyterephthaloyl moiety.

Figure 15 shows the fluorescence spectra of PET yarns, one of which has not been irradiated and the other which has had 100 hr of exposure in the photolysis chamber. Figure 16 shows a similar comparison of fluorescent emissions for the PET-*co*-4,4′-BPDC copolymer containing 4.0% 4,4′-BPDC. The emission spectrum of the irradiated PET yarn when excited by 342-nm energy (Fig. 15) is totally dominated by the 460-nm emission, which has been attributed to the presence of hydroxyterephthalate, with only a shoulder as evidence of the residual fluorescence from the terephthalate units. On the other hand, the exposed copolymer yarn containing 4.0 mole % 4,4′-BPDC still exhibits the normal ter-

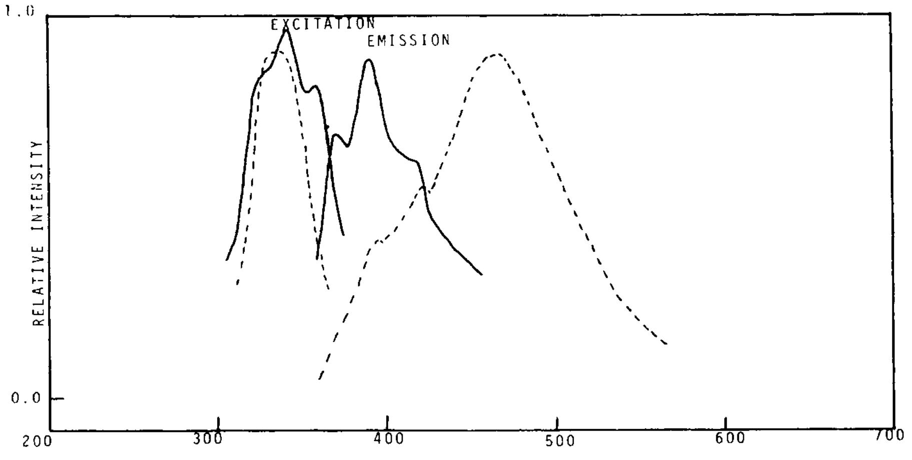

Fig. 15. Uncorrected fluorescence spectra of poly(ethylene terephthalate) yarn. (——) 0 hr Exposure: excitation scan Em λ 388 nm; emission scan Ex λ 342 nm. (- - -) 100 hr Exposure to RUL 3000 Å lamps; excitation scan Em λ 460 nm; emission scan Ex λ 342 nm.

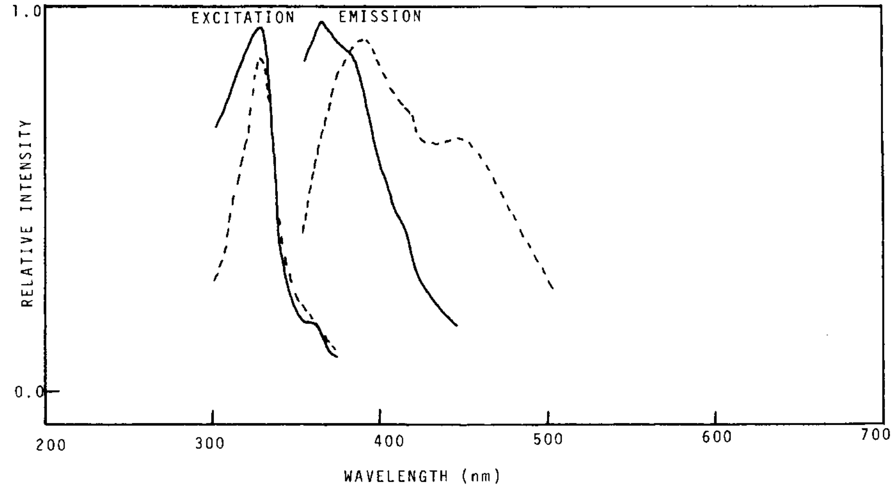

Fig. 16. Corrected fluorescence excitation and emission spectra of poly(ethylene terephthalate–*co*–4,4′-biphenyldicarboxylate) yarn (4% comer). (——) 0 hr Exposure: excitation scan Em 388 nm; emission scan Ex λ 342 nm. (---) 100 hr Exposure to RUL 3000 Å lamps: excitation scan Em λ 388 nm; emission scan Ex λ 342 nm.

ephthalate fluorescence (388 nm emission) as the major band in the emission spectrum when excited with 342-nm energy. A less intense second band was also observed in the emission spectrum centered at 460 nm. This band is also assigned as emission from the hydroxyterephthalate units.

In the previous section it was shown that stabilization by triplet–triplet energy transfer interrupted the sequence leading to chain scission, hence a reduction in loss of tenacity. From these facts it can be assumed that the presence of the 4,4′-biphenyldicarboxylate units in the polymer also inhibits the rate of formation of the hydroxyterephthalate. Several mechanisms have been proposed for the formation of hydroxyterephthalate.[5,15] At this time it is impossible to conclusively determine the mechanism of inhibition of hydroxyterephthalate.

CONCLUSIONS

Studies of the luminescence properties of 4,4′-BPDC monomer in solution have revealed an intense fluorescence from a $^1(\pi,\pi^*)$ state and a relatively weak phosphorescence from a $^3(\pi,\pi^*)$ state.

The luminescence properties of poly(ethylene terephthalate–*co*–4,4′-biphenyldicarboxylate) copolymers readily showed the presence of the 4,4′-BPDC in both solution and drawn fiber. The phosphorescence spectra revealed a quenching of the PET triplet state with a concomitant sensitized population of the 4,4′-biphenyldicarboxylate triplet state. This is concluded to be the result of triplet–triplet energy transfer occurring by electron exchange. Kinetic analysis, by the Perrin model, yielded a critical transfer distance of 14.9 Å, in agreement with the expected limitations for electron exchange.

Phototendering studies revealed zero-order rate constants of $3.4 \times 10^{-19}\%$ breaking strength loss/quantum exposure/cm^2 for the homopolymer PET and $2.0 \times 10^{-19}\%$ breaking strength loss/quantum exposure/cm^2 for the copolymer containing 4.0 mole % 4,4′-BPDC. The reduction in rate of loss in tenacity by quenching of the PET triplet state implies that the major chain scission reaction proceeds via a triplet. The major chain scission reaction for PET has been proposed to proceed by a Norrish type II mechanism. Therefore, it is concluded that the Norrish type II rearrangement for PET occurs mainly via a triplet state. Also, the phototendering studies show that after 80 hr of exposure ($\sim 1.3 \times 10^{20}$ quanta/cm^2), a decrease in the percent loss in tenacity was observed with increasing concentration of 4,4′-BPDC. At 4.0 mole % 4,4′-BPDC, the ultimate tenacity loss was only 54% of the loss of the PET homopolymer under the same conditions.

Fluorescence measurements on fibers after 100 hr of exposure (3000 Å) showed that the incorporation of 4,4′-BPDC slowed down the rate of formation of hydroxyterephthalate (evidenced by a decrease in the 460-nm fluorescent emission) as the concentration of 4,4′-BPDC in the copolymer was increased.

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