

Photophysical Processes and Interactions Between Poly(ethylene Terephthalate) and 1-Amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-Anthraquinone

ROBERT G. MERRILL and CARLETON W. ROBERTS, *Textile Department, Clemson University, Clemson, South Carolina 29631*

Synopsis

The effect of 1-amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-anthraquinone (C. I. Disperse Red 59) on the phototendering of poly(ethylene terephthalate) (PET) was assessed. The photophysical processes occurring in the polymer, the dye, and the dyed polymer² were determined. The energy and nature of the dye and polymer electronic excited states were assigned on the basis of absorption and luminescence properties. Irradiation failed to produce dye-sensitized phototendering of PET; however, the titanium dioxide delusterant in commercial PET did function as a sensitizer in the presence of moist air. The phototendering of blank-dyed PET yarn was found to obey (pseudo-) zero-order kinetics $k = 1.69 \times 10^{-19}$ per cent breaking strength loss/quantum absorbed/cm². The dye exhibited fluorescence from a lowest, ~51.5 kcal/mole, singlet charge-transfer (C-T) excited state but did not phosphoresce. The PET possessed a complex fluorescence spectrum attributed to similar $^1(n, \pi^*)_1$ excited states, ~78.1 kcal/mole, while its phosphorescence derives from a proposed $^3(\pi, \pi^*)$ state, ~69.8 kcal/mole, populated by intersystem crossing from a $^1(\pi, \pi^*)$ state, ~92.3 kcal/mole. The dyed polymer exhibited a PET-sensitized delayed fluorescence from the dyestuff involving triplet-singlet transfer by a dipole-dipole (Coulombic) long-range resonance excitation mechanism. The transfer process was characterized by an experimentally determined critical transfer distance, R_0 , of approximately 40 Å.

INTRODUCTION

For most textile products, actinic exposure initiates photodegradation reactions that result in a general weakening of the polymer, commonly referred to as phototendering. In addition to their inherent phototendering tendency, many polymers undergo more rapid photodegradation in the presence of certain substances which act as photosensitizers for the polymer degradation. A complete study of polymer phototendering and the effects of photosensitizers on the tendering process requires, first of all, that the general mechanism of photochemical degradation be determined for the polymer in the absence of sensitizers. The sensitized phototendering process is characterized by analysis of the effects of the sensitizer on the molecular weight and/or mechanical properties of the irradiated polymer. Determination of the manner in which a sensitizer enhances the normal polymer phototendering process requires a knowledge of the polymer and sensitizer electronic energy states (most photochemical and photophysical processes occur from the lowest excited states for organic molecules).

A sensitizing substance may function as a direct or indirect photosensitizer,

a photo-initiator, or a photo-optical sensitizer of polymer degradation. Direct (photophysical) sensitization requires a donor-acceptor electronic energy transfer process in which the polymer plays the part of the acceptor. Indirect (photo-physical) sensitization employs a third species as the acceptor. Photo-initiators, on the other hand, react directly with the polymer or undergo photochemical decomposition first, with the photochemical products then initiating degradation reactions of the polymer. Photo-optical sensitizers require the formation of a polymer-sensitizer complex resulting in a new absorbing chromophore.

The photochemical aspects of the degradation of poly(ethylene terephthalate) (PET) have recently been investigated extensively by Day and Wiles¹⁻⁶; however, to our knowledge, no previous studies of PET photophysical processes or the effects of possible sensitizing phototenderers on PET photodegradation have been published except for the preliminary work with model phthalate esters by Cheung.⁷

Cheung examined the photophysical processes of dibutyl terephthalate, bis(2-ethoxyethyl) terephthalate, and bis[2-(2-ethoxyethoxy)ethyl] terephthalate, and the dyestuff C. I. Disperse Red 59 [1-amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-anthraquinone] (structure obtained through courtesy of E. I. du Pont de Nemours & Co., Wilmington, Del., 1973). The model esters exhibited fluorescence at room temperature and phosphorescence when cooled to 77°K. The electronic absorption leading to the observed luminescence was tentatively assigned as a $^1(n,\pi^*)$ transition of the ester chromophore. Cheung proposed that in solution, the dye fluoresced from a $^1(n,\pi^*)$ electronic state. The fact that no phosphorescence was detected for the dyestuff, under any conditions, indicated that it should be a poor sensitizer for photosensitized oxidation.⁸ Solutions of the dye in the model compounds exhibited no evidence of intermolecular electronic energy transfer or complex formation.

This research involved the accelerated phototendering of C. I. Disperse Red 59-dyed and blank-dyed PET yarns irradiated under carefully controlled oxidative conditions with artificial 3000-Å light. The extent of phototendering was assessed by measuring the yarn breaking strength, not as a function of irradiation time, but as a function of the total incident radiation. Other factors considered included the effect of titanium dioxide delusterant (TiO_2) and water vapor on the extent of phototendering.

The dye and polymer lowest excited states were identified with regard to their respective energies and transitions responsible for each state. The energy states and photophysical processes for the polymer and dyestuff alone were compared with those for the dyed polymer, and the results were used to explain the observed sensitizing properties of the dyestuff.

EXPERIMENTAL

Ultraviolet and visible absorption spectra were obtained using a Cary Model 14 or Model 118C spectrophotometer. Routine determinations of absorbance for concentration measurements by Beer's law were made using a Bausch and Lomb Spectronic 20 spectrophotometer. Yarn samples were knit on a Lawson Fiber Analysis Knitter (FAK) which features an automatic compensating yarn feed to ensure identical sample preparation. Atmospheric scouring and pressure dyeings were carried out in an Ahiba AG Model G6B dyeing machine. A Rayonet

Type RS Model RPR-208 preparative photochemical reactor was used to irradiate the samples. An MGR-100 merry-go-round assembly, in the center of the reactor, rotated the samples inside a circular bank of eight RUL-3000 Å low-pressure mercury, phosphor conversion lamps. Yarn tensile testing was performed on an Instron Model 1101 (TM-M) constant rate of extension testing machine. Luminescence measurements were obtained with a Perkin-Elmer Model MPF-3 fluorescence spectrophotometer equipped with corrected spectra, phosphorescence, and front surface accessories. A Tektronix Model 5103N storage oscilloscope was used to display luminescence decay curves and to measure the corresponding mean lifetimes. Low-temperature luminescence sample tube-spinning rates were measured using a Pioneer Photo-Tach Model 1030 tachometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Purification of "Latyl" Cerise B

One gram of commercial "Latyl" Cerise B [C. I. Disperse Red 59, 1-amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-anthraquinone, crude wet, du Pont] was extracted with 250 ml ethyl acetate in a Soxhlet extractor and recrystallized twice to give pyramidal metallic-brown crystals with mp 174.5–175.5°C.

ANAL. Calcd for $C_{17}H_{15}NO_5$: C, 65.16; H, 4.83; N, 4.47; O, 25.53. Found: C, 65.22; H, 4.88; N, 4.53; O, 25.37 (diff).

Aqueous Dyeing of Poly(ethylene Terephthalate) Yarn and Film

The yarn samples were mounted in the form of knit tubes while the film samples were rolled and fastened in the shape of a cylinder. The samples were scoured to remove any spin finish, knitting oil, or external contaminant that might be present. The samples were scoured for 20 min at 75–82°C with a 1% (by weight) aqueous solution of tetrasodium pyrophosphate (TSPP) in an Ahiba dyeing machine. The samples were then cooled to 69–75°C, removed from the machine, and rinsed with distilled water.

The dyeings were carried out in sealed pressure dyeing containers. The dyeing containers were filled (90%) with distilled water, heated to 60–75°C, and a measured weight of the commercial dye "Latyl" Cerise B was added. After 10 min, two to four samples were entered, the containers were sealed, and the temperature was raised slowly to 92–100°C and held for 15 min for exhaustion purposes. The bath temperature was then raised slowly to 121–124°C and held for 1 hr. The bath was then cooled to 69–75°C and the samples were removed, rinsed with distilled water, and dried at 70–80°C for 1 hr.

The same preparation and dyeing procedures, with the exception of the addition of the dye, were used to prepare the "blank-dyed" control samples.

Determination of Dye Concentration in Yarns and Films

One sample from each dyeing was analyzed to determine the concentration of dye present. The dye was stripped from the PET substrate using a method suggested by Monkman.⁹ The stripped yarn sample was dried at 70–80°C and weighed. The percent by weight dyeing was calculated from the above data and

was converted to molar concentration employing the corresponding density for the PET sample.

Irradiation Conditions

The dyed and blank-dyed knit samples were unraveled and mounted on separate wire frames (41×3 cm). Each frame held eight yarns attached by means of masking tape at each end. Each yarn was pretensioned prior to mounting with a 4.2-g weight (0.25 g/tex)¹⁰ to remove crimp and ensure uniform mounting tension.

The yarns, mounted on the wire frames, were placed into four identical Pyrex tubes (45×4.5 cm) equipped with a gas inlet at the bottom and an outlet at the top.

Compressed air was filtered ($13 \times 4 \text{ \AA}$ molecular sieves) and dried (Drierite towers) and delivered at 2.5 SCFH to each Pyrex tube at 40°C . [SCFH (air) = standard cubic feet of air per hour, where standard refers to the conditions of 70°F (21.1°C) and atmospheric pressure (760 mm Hg).]

For one experiment, it was desired to introduce water vapor into the air flow at a known concentration. This was accomplished by inserting a Milligan gas washer half-filled with distilled water into the air line between the rotameter and the sample irradiation tubes. The amount of water vapor picked up by the dry air as it passed through the gas washer was determined by measuring the weight gain of a known amount of Drierite in a small drying tube placed in the line on the exit side of the gas washer. Using the flow rate, adjusted to standard conditions, the time of flow, and the concentration of saturated aqueous vapor at the temperature of the exiting air flow, the percent relative humidity of the resultant air was determined.

For each dye concentration, a set of eight dyed and blank-dyed yarns were each irradiated simultaneously but in separate irradiation tubes. Irradiation times ranged from 5 to 60 hr.

Yarn Breaking Strength

The dyed and blank-dyed yarn breaking strengths were determined according to ASTM Standard D2256-69¹⁰ using a 25-cm gauge length and a 20-cm/min rate of extension which gave a time to break of 20 ± 3 sec for the unirradiated blank-dyed yarns. The samples were allowed to equilibrate at ambient conditions in the dark for at least 24 hr.

Actinometry

The light intensity of the irradiating lamps and its variation as the lamps aged was monitored using the potassium ferrioxalate chemical actinometer developed by Hatchard and Parker^{11,12} and modified by Baxendale and Bridge,¹³ Lee and Seliger,¹⁴ and Rurien.¹⁵ A Beer's law plot of the standard calibration data was linear, yielding a molar extinction coefficient ϵ of $1.22 \times 10^4 \text{ l./mole-cm}$ (literature value $1.11 \times 10^4 \text{ l./mole-cm}$).¹⁶ The measured lamp intensities were found to decrease from a maximum of 6.82×10^{15} to 2.18×10^{15} quanta/cm²/sec after 733.5 hr.

U.S.P. grade 95% ethanol was purified by fractional distillation and the purity checked by luminescence on excitation at 250 nm.¹⁷

Analysis of the yarn samples was found to show variable results in terms of reproducibility due mainly to the inherent inhomogeneity of the sample. The above problem was remedied by a technique similar to that described by Hollifield and Winefordner.¹⁸ The basic technique involves the rotation (1600–3300 rpm) of the sample tube within the Dewar during analysis so that any sample inhomogeneities are averaged, producing a steady emission.

Materials

The spectrophotometric-grade solvents ethyl acetate and N,N-dimethylformamide were purchased from Matheson, Coleman, and Bell; carbon tetrachloride, from J. T. Baker Chemical Co.; and dichloromethane, from Aldrich Chemical Co., Inc. U.S.P.-grade 95% ethanol, after further purification, was used for luminescence experiments. A ferrous ammonium sulfate vial for standard volumetric solution preparation was supplied by Anachemia Chemicals Ltd. Quartz phosphorescence sample tubes were custom fabricated by Wilmad Glass Company, Inc. "Latyl" Cerise B and "Latyl" Cerise B crude wet dye (C. I. Disperse Red 59) and Mylar Type A poly(ethylene terephthalate) film were gifts of E. I. du Pont de Nemours & Co. The poly(ethylene terephthalate) 150 denier, 32 monofilaments yarn was donated by the American Enka Corporation, while the 150 denier, 35 monofilaments sample was a gift from Dow Badische (Table I).

RESULTS AND DISCUSSION

Photophysical Processes in Poly(ethylene Terephthalate)

The absorption spectrum of a ~0.90-mil Mylar PET film (film I) versus air exhibited a slight attenuation of light at all wavelengths; the spectrum was

TABLE I
Yarn and Film Sample Properties

	Yarn Ia		Yarn II ^b		Film I ^c	
	Mfg. data	Exp. data	Mfg. data	Exp. data	Mfg. data	Exp. data
Denier/filaments	150/32		150/35		—	
Gauge	—		—		92	
Thickness mil	—		—		0.92	0.9 ^d
Twist, TPI	½ Z		¼ Z		—	0.90 ^e
Density, g/cc	—		1.361		1.395	
Draw ratio	3.47		—		—	
Refractive index, Abbe	—		—		1.64	
Birefringence	—		0.196		—	
Plasticizers	—		—		none	
% TiO ₂	none?	<9 ppm Ti <1.5 × 10 ⁻³ calcd.	0.30	0.144 Ti 0.240 calcd.	none?	

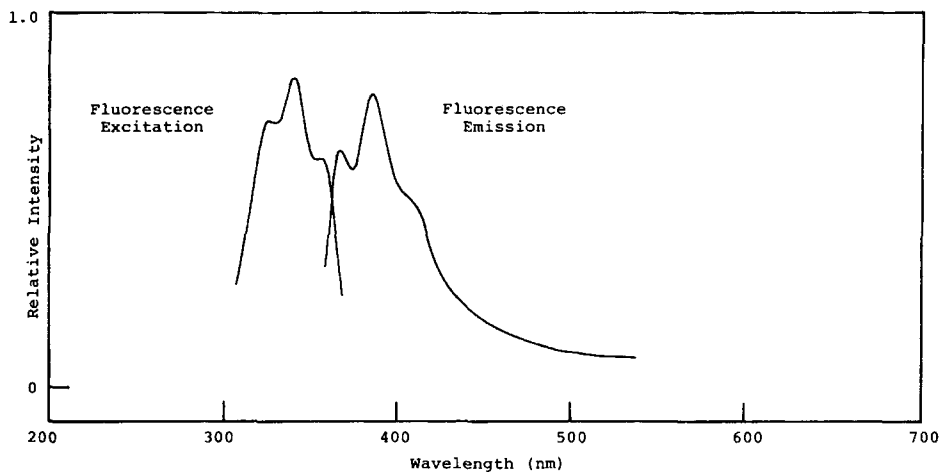
^a Enka "clear" PET yarn.

^b Dow Badische PET yarn.

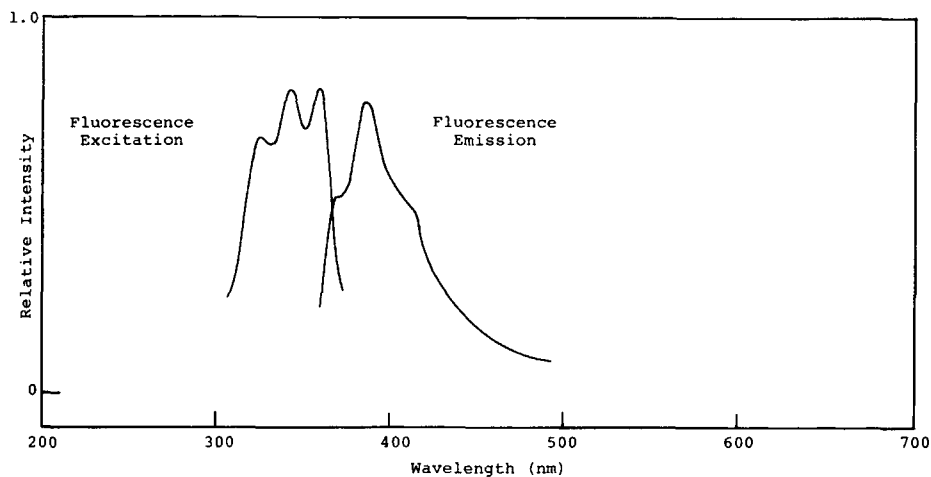
^c DuPont Mylar R Type A PET film.

^d Micrometer caliper.

^e Infrared interference fringe pattern.



(a)



(b)

Fig. 1. (a) Corrected fluorescence excitation and emission spectra of poly(ethylene terephthalate) yarn containing less than 9 ppm Ti (yarn I), at room temperature. Excitation scan: Em λ 388 nm, Ex slit 3 nm, Em slit 10 nm. Emission scan: Ex λ 342 nm, Ex slit 10 nm, Em slit 3 nm. (b) Corrected fluorescence excitation and emission spectra of poly(ethylene terephthalate) yarn containing 0.240% TiO_2 (yarn II), at room temperature. Excitation scan: Em λ 388, Ex slit 3 nm, Em slit 10 nm. Emission scan: Ex λ 342, nm, Ex slit 10 nm, Em slit 3 nm. (c) Corrected fluorescence excitation and emission spectra of poly(ethylene terephthalate) film containing no TiO_2 (film I), at room temperature. Excitation scan: EM λ 388 nm, Ex slit 3 nm, Em slit 10 nm. Emission scan: Ex λ 342 nm, Ex slit 10 nm, Em slit 3 nm.

dominated by the intense absorption of wavelengths less than ~ 312 nm. The onset of absorption near 310 nm agrees with the results of Marcotte et al.¹⁹ The presence of similar absorption bands have also been reported^{7,19} for various model terephthalate esters.

Employing the data of Marcotte et al.¹⁹ and assuming a film density of ~ 1.385 g/cm³ (partly crystalline nonoriented PET)²⁰ and also assuming that each PET repeat unit contains only one chromophore (or at the most two, in the case of carbonyl chromophores), the following approximate molar extinction coefficients

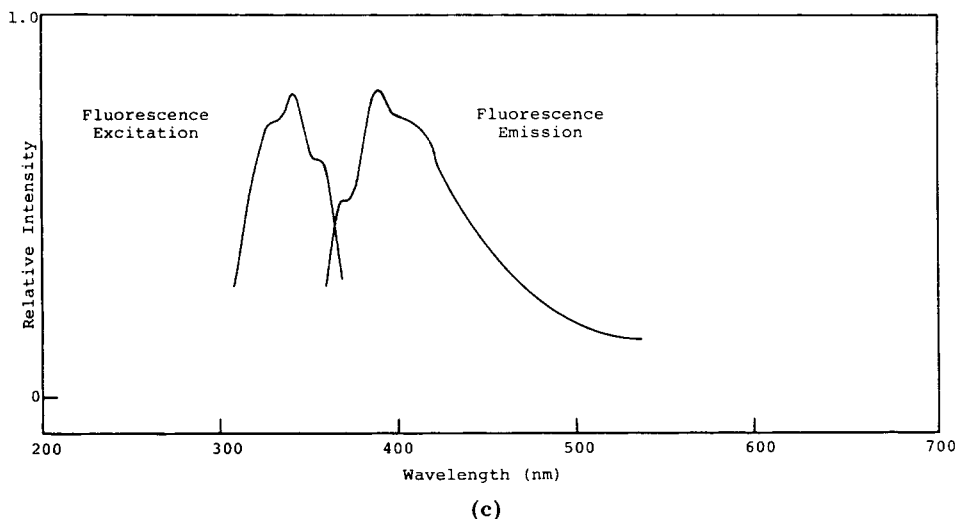


Fig. 1 (continued)

were calculated for the PET absorption bands: 240 nm ($\epsilon \sim 1.37 \times 10^4$ l./mole-cm), 270 nm ($\epsilon \sim 2.10 \times 10^3$ l./mole-cm), and 290–310 nm ($\epsilon \sim 1.27\text{--}0.64 \times 10^3$ l./mole-cm). These values are of the same general magnitude as those reported by Cheung⁷ for methanol solutions of model phthalate esters.

The corrected fluorescence excitation and emission scans for the various PET samples are presented in Figure 1(a), 1(b), and 1(c). The spectra are all quite similar with respect to position of the excitation and emission bands, with most of the differences arising from variations in peak intensities. Excitation bands were noted at ~ 326 , 342, and 358 nm, while emission bands were located at ~ 369 , 390, and 412 nm.

The fluorescence emission data for film I compare favorably with the uncorrected spectrum by Day and Wiles² for a Mylar PET film. In addition, the PET fluorescence properties are, in general, similar to those found for PET model phthalate esters by Cheung.⁷

The low-temperature (77°K) luminescence spectrum for yarn I, Figure 2(a), exhibited the expected increased band sharpness and small 0–0 band separation.

Figure 2(b) and 2(c) represent the uncorrected* phosphorescence excitation and emission spectra for the PET yarn I and yarn II samples at 77°K. Both samples are similar, each possessing a 310-nm excitation and a ~ 454 -nm emission with a mean lifetime τ of 1.0–1.4 sec. No room temperature phosphorescence was detected for any of the PET samples.

The low-intensity phosphorescence excitation plateau, ranging from 340 to 370 nm for the yarn II sample [see Fig. 2(c)] is attributed to the presence of TiO_2 in the polymer since it is absent in the TiO_2 -free sample [yarn I, see Fig. 1(c)] and because it becomes more evident in PET samples containing increasing amounts of TiO_2 . In addition, the excitation wavelengths, i.e., 340–370 nm, agree

* The phosphorescence accessory of the Perkin-Elmer Model MPF-3 fluorescence spectrophotometer is used for measuring low-temperature fluorescence and phosphorescence spectra. The corrected spectra accessory is inoperable under these conditions.

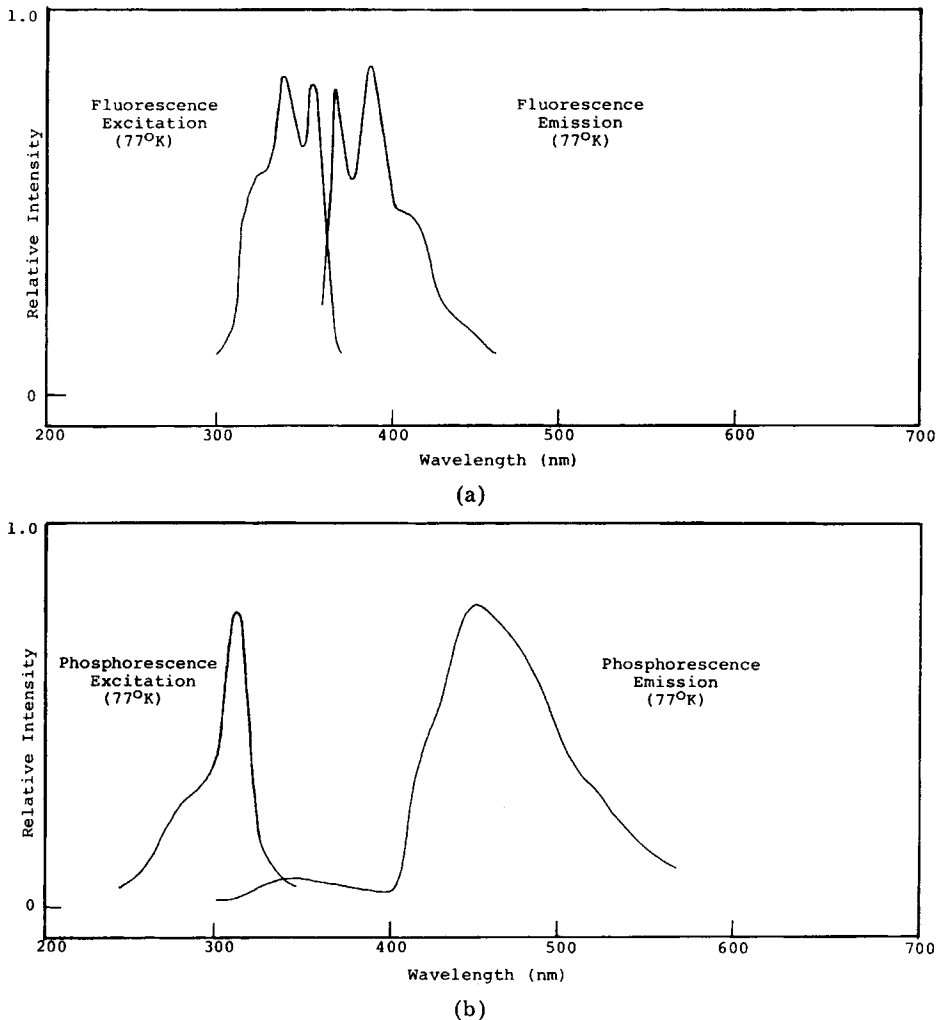


Fig. 2. (a) Uncorrected fluorescence excitation and emission spectra for poly(ethylene terephthalate) yarn containing less than 9 ppm Ti (yarn I), at 77°K. Excitation scan: Em λ 390 nm, Ex slit 2 nm, Em slit 10 nm. Emission scan: Ex λ 345 nm, Ex slit 10 nm, Em slit 2 nm. (b) Uncorrected phosphorescence excitation and emission spectra for poly(ethylene terephthalate) yarn containing less than 9 ppm Ti (yarn I), at 77°K. Excitation scan: Em λ 450 nm, Ex slit 10 nm, Em slit 10 nm. Excitation scan: Em λ 310 nm, Ex slit 10 min. Spinning sample, lifetime (τ) 1.4 sec. (c) Uncorrected phosphorescence excitation and emission spectra for poly(ethylene terephthalate) yarn containing 0.240% TiO₂ (yarn II), at 77°K. Excitation scan: Em λ 454 nm, Ex slit 2 nm, Em slit 16 nm. Emission scan: Em λ 312 nm, Ex slit 8 nm, Em slit 5 nm. Lifetime (τ) 1.0 sec.

well with the 365-nm excitation reported by Taylor et al.²¹ for TiO₂ delusterant in nylon 6,6.

The PET fluorescence and emission bands do not appear to be due to the vibrational structure characteristic of a single chromophore since the bands do not occur at equal wave-number intervals. In addition, the relative excitation and emission-band intensities were found to be wavelength dependent, giving further evidence that more than one chromophore is involved. A detailed analysis of the interrelationships of the excitation and emission bands revealed

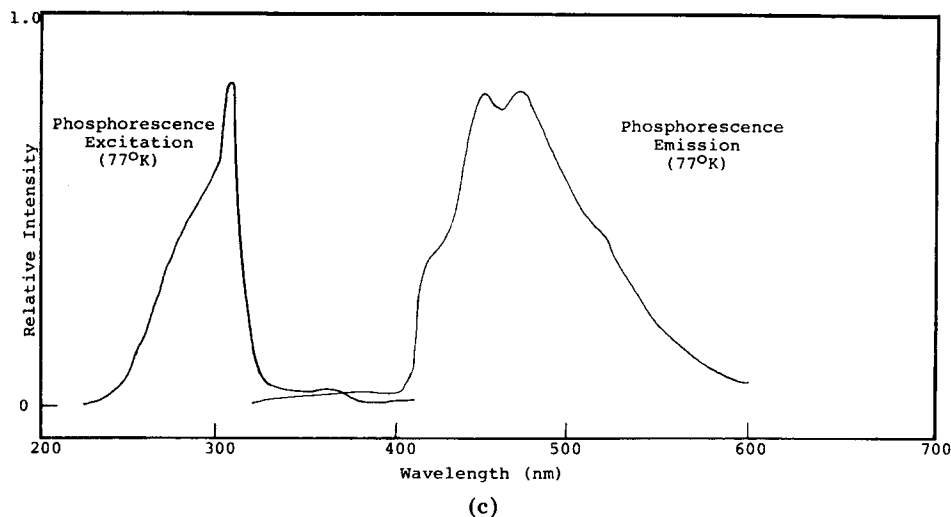


Fig. 2 (continued)

that there were at least two independent contributions. The fact that the fluorescence and phosphorescence excitation bands do not coincide also implies that PET phosphorescence is due to a different chromophore.

The possibility that the PET fluorescence or phosphorescence is derived from trace impurities within each polymer sample is unlikely. This conclusion is based on the similarity of the luminescence properties of diverse PET polymer samples, ranging from yarn to film and produced by different manufacturers, and on agreement of the spectral data with the luminescence properties of model terephthalate esters.

Pacifici and Straley²² have reported that the mono- and dihydroxyterephthalate moieties in surface-oxidized PET possess fluorescent properties with emission maxima at 459 (mono) and 435, 510 (w) (di) with excitation at 340 and 309 nm. Our data lead us to conclude that these are not the chromophores which are responsible for the luminescent properties of the film and fiber samples reported here.

If it is assumed that the crystalline and amorphous regions of PET possess different luminescence properties, the complex nature of the luminescence spectra may be assigned to differences in the degree of crystallinity of the samples. It could also arise from different isolated luminescent chromophores situated along the polymer chain or from the characteristic luminescence from various molecular weight species in the distribution, ranging from oligomer to polymer, present in each sample.

The approximate extinction coefficients calculated for PET, coupled with the absorption data for model phthalate esters, suggest that the PET absorption bands at 240, 270, and 290–310 nm are due to π, π^* transitions. Considering these band assignments, the PET phosphorescence excitation band at 310 nm would also be a π, π^* state, while the fluorescence excitations, 326–358 nm, would have to be attributed to an n, π^* state located under the long wavelength shoulder of the 290–310 nm absorption. The phosphorescence emission band at 454 nm is most likely a $^3(\pi, \pi^*)$ state because of the long phosphorescence lifetime²³ and the large S_1-T_1 energy splitting ($\sim 8000 \text{ cm}^{-1}$).²⁴

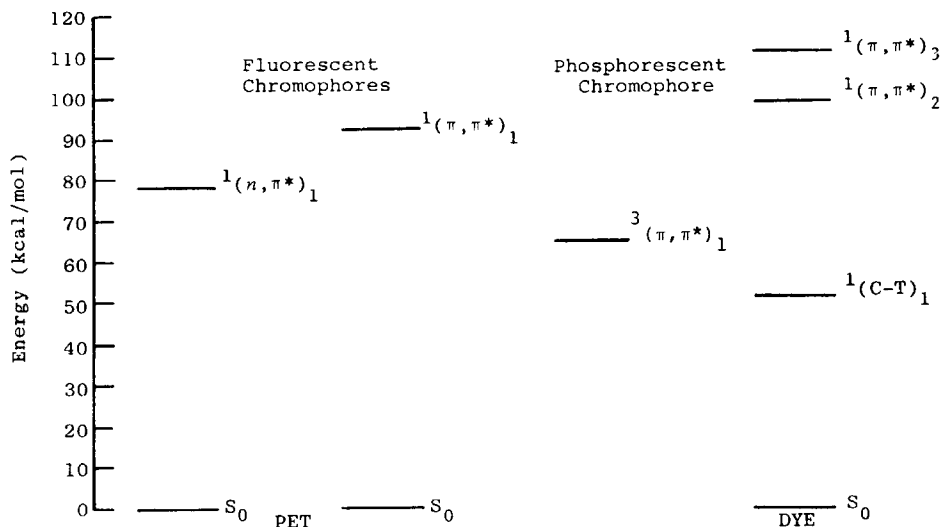


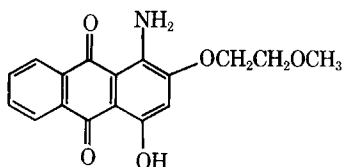
Fig. 3. The major electronic energy levels and band assignments for poly(ethylene terephthalate) (PET) and 1-amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-anthraquinone (C. I. Disperse Red 59).

The O-O bands for PET fluorescence and phosphorescence yield the following electronic state energies: $S_1 \cong 78.1$ kcal/mole (n, π^*); $S_1' \cong 92.3$ kcal/mole (π, π^*) (fluorescent chromophores); $T_1' \cong 69.8$ kcal/mole (phosphorescent chromophore). The lowest electronic energy levels and their band assignments are diagrammed in Figure 3.

In terms of the phototendering of PET alone, analysis of its absorption spectrum reveals that the onset of absorption at ~ 310 nm, which lies within the high-energy range of terrestrial sunlight, coincides with the critical wavelength for PET photodegradation.⁵ The same wavelength, 310 nm, also produces phosphorescence from the polymer, which implies that the triplet state may be involved in the photodegradation of PET.

Photophysical Processed in C. I. Disperse Red 59

C. I. Disperse Red 59, 1-amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-anthraquinone,



was initially developed²⁵ as an anthraquinone dye for cellulose acetate. It is reported to act as a phototendering sensitizer when used to dye PET. The ultraviolet-visible absorption spectrum of the purified dyestuff, $5.60 \times 10^{-5} M$ in dichloromethane, reveals three main absorption regions, i.e., ~ 256 , ~ 287 , and 450–550 nm.

The corrected fluorescence excitation and uncorrected emission spectra of

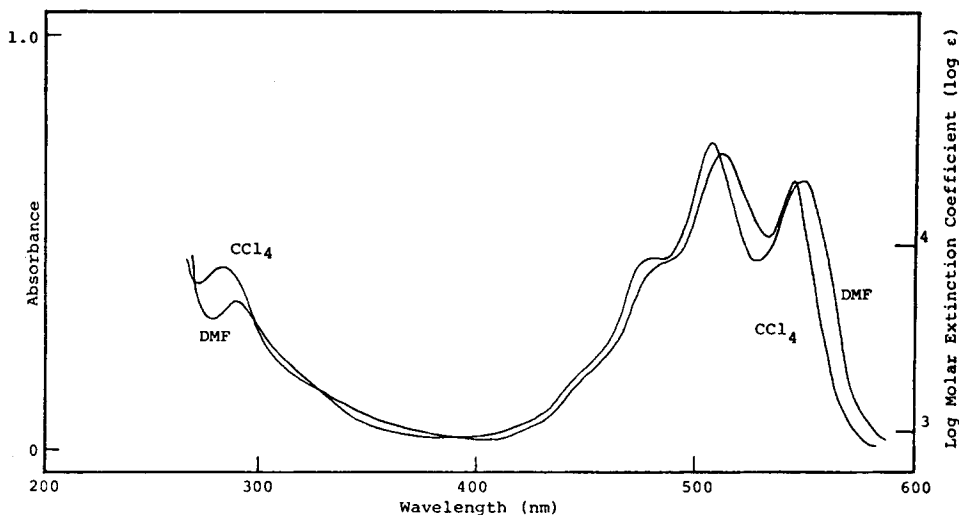


Fig. 4. Absorption spectra of $5.00 \times 10^{-5}M$ solutions of C. I. Disperse Red 59 in carbon tetrachloride (CCl_4) and *N,N*-dimethylformamide (DMF), respectively, measured in 1-cm cells with corresponding pure solvents as reference.

a dichloromethane solution of the dyestuff are shown in Figure 5. The band maxima for the excitation spectrum were nearly identical to those obtained by absorption measurements, while the emission spectrum exhibited a structured band with a maximum of 568 nm.

Figure 6 illustrates the effect of lowering the temperature to 77°K on the band structure of the uncorrected fluorescence excitation and emission spectra of a rigid solution of the dye in 95% ethanol. Both spectra exhibit what appears to be strong vibrational structure with a separation of 1350 cm^{-1} for the emission spectra.

In agreement with the work reported previously by Cheung,⁷ no phosphorescence attributable to the dyestuff was obtained from dye solutions in 95% ethanol at room temperature or glassed at 77°K. In addition, saturation of the above solution with nitrogen gas prior to phosphorescence measurement produced no dye phosphorescence. An attempt to obtain phosphorescence using benzophenone as a sensitizer was also unsuccessful.

Although the dyestuff used for this study is somewhat complex, containing three auxochromic substituents, it is still possible to draw general conclusions concerning the origin of its absorption and luminescence bands and, as a result, its expected phototendering activity.

Analysis of the absorption spectra (Fig. 4) of the dye used in this study, 1-amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-anthraquinone, in terms of band intensity and solvent shift data, and comparison with the absorption data and band assignments for similar, 1,4-disubstituted 9,10-anthraquinones²⁶⁻³⁴ led to the following band assignments: The two longest wavelength absorption bands, ~ 546 and ~ 510 nm, are assigned as charge transfer (*C-T*) bands involving the intramolecular hydrogen bonding of the amino and hydroxy substituents with the anthraquinone carbonyls, while the remaining bands in the visible region, ~ 483 and 451 nm, are either *C-T* or π, π^* in nature. The two bands in the ultraviolet region, ~ 287 and ~ 256 nm, are relatively unaffected by the attached

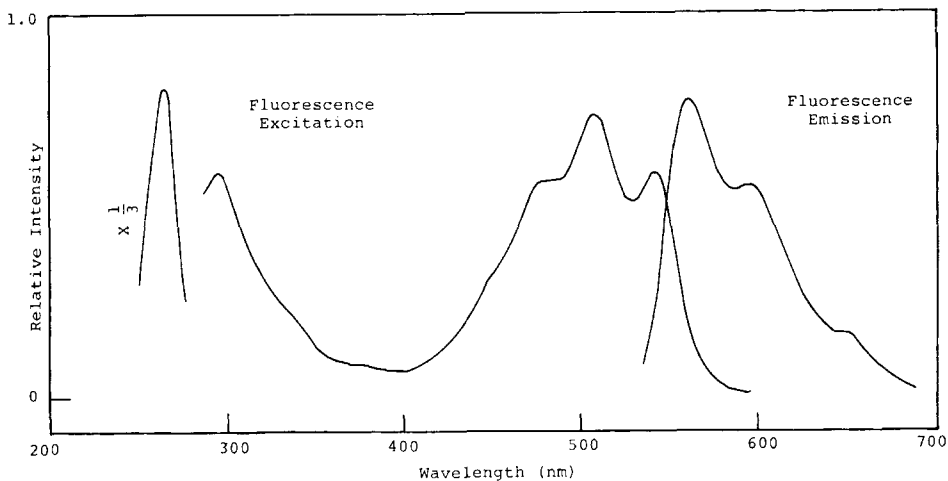


Fig. 5. Corrected fluorescence excitation and uncorrected emission spectra of $5 \times 10^{-6}M$ C. I. Disperse Red 59 in dichloromethane at room temperature. Excitation scan: Em λ 580 nm, Ex slit 10 nm, Em slit 5 nm. Emission scan: Em λ 510 nm, Ex slit 10 nm, Em slit 5 nm.

auxochromes and are therefore assigned as π, π^* bands, as in the unsubstituted 9,10-anthraquinone.

Anthraquinones possessing a lowest n, π^* excited state are highly reactive toward hydrogen abstraction, thus allowing them to initiate photo-oxidation reactions. This is due to the change in the carbonyl polarity that occurs when a nonbonding electron, situated on the carbonyl oxygen, is promoted to an antibonding π^* orbital having a significant spatial contribution at the carbonyl carbon atom, thus resulting in a partial positive charge residing on the carbonyl oxygen.

The converse situation arises for the case where the lowest excited state is $C-T$

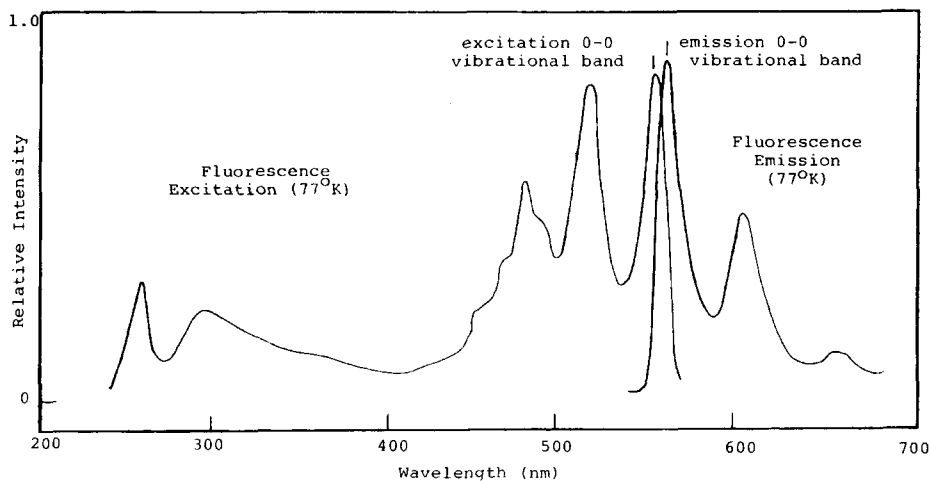


Fig. 6. Uncorrected fluorescence excitation and emission spectra of C. I. Disperse Red 59 in 95% ethanol at 77°K. Excitation scan: Em λ 608 nm, Ex slit 4 nm, Em slit 10 nm. Emission scan: Ex λ 520 nm, Ex slit 10 nm, Em slit 4 nm.

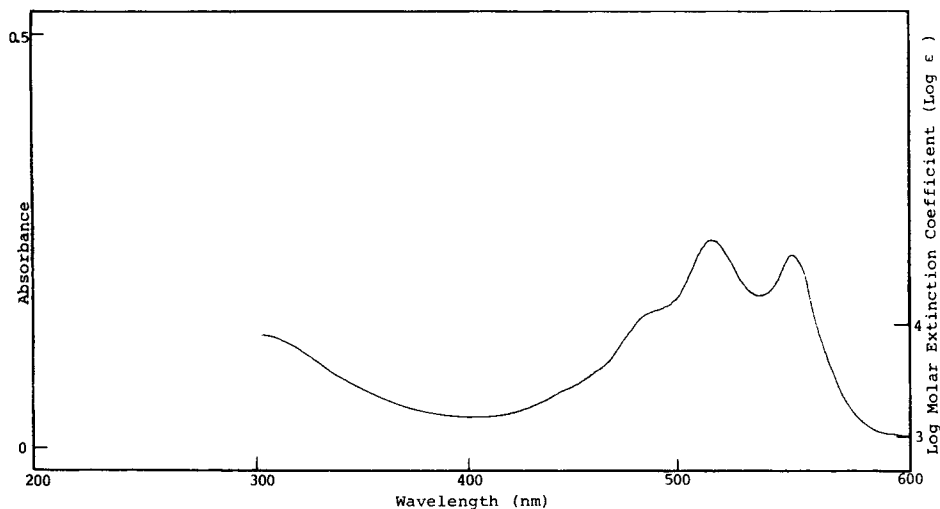


Fig. 7. Absorption spectrum of $6.70 \times 10^{-3}M$ C. I. Disperse Red 59 in ~ 0.90 mil Mylar [poly(ethylene terephthalate)] film (film I), with blank-dyed film I as reference.

in nature, such as occurs when the carbonyl is intramolecularly hydrogen bonded to another substituent. Under these conditions, the electron movement in the carbonyl is opposite to the electron shift in an n, π^* transition and, therefore, the $C-T$ state has little hydrogen abstraction tendency. Since the lowest excited state of C. I. Disperse Red 59 is also $C-T$ in nature, the dye would be expected to exhibit a negligible tendency to function as a photo-initiator of PET phototendering by hydrogen abstraction.

The lack of detectable phosphorescence from the dyestuff C. I. Disperse Red 59 and its structural similarity to other known "poor sensitizers"⁸ give further evidence that it should not act as a sensitizer to PET phototendering. Applying the usual criteria to the spectra for C. I. Disperse Red 59 yields the following main excited electronic energy levels: $S_1 \cong 51.1$ kcal/mole; S_2 (287 nm band) $\cong 98.6$ kcal/mole; S_3 (256 nm band) $\cong 111$ kcal/mole. The dye energy levels and band assignments are shown diagrammatically in Figure 3.

Photophysical Processes in Poly(ethylene Terephthalate) Dyed with C. I. Disperse Red 59

The absorption spectrum of the dye within the polymer matrix (film I) is displayed in Figure 7. An identical blank-dyed PET film was employed as the reference material. In the wavelength region for which PET is transparent, the dye absorption spectrum is nearly identical to its solution spectrum (see Fig. 4), although the bands are slightly red shifted, ~ 300 cm^{-1} , in the polymer. The apparent lack of absorption of the dyed film below ~ 303 nm is due to the strong attenuation of both the sample and reference beams by the PET for wavelengths less than ~ 310 nm. The similarity of the absorption spectra for the dye in solution and in the polymer matrix and the absence of any new absorption bands preclude the formation of an absorbing species due to a dye-polymer complex and, therefore, the operation of the dye as a photo-optical sensitizer.

Figures 8 and 9 are examples of the dye-polymer fluorescence, indicating that

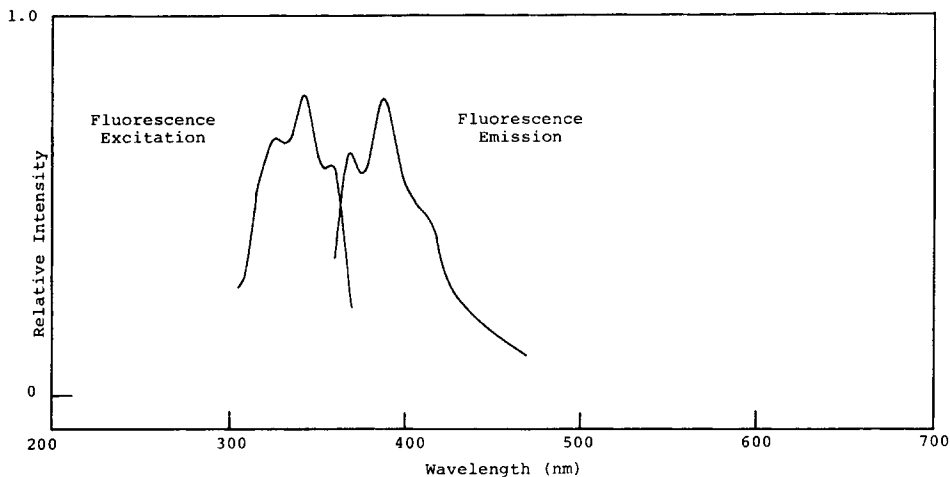


Fig. 8. Corrected fluorescence excitation and emission spectra for 0.0287% (by weight) C. I. Disperse Red 59-dyed poly(ethylene terephthalate) yarn containing less than 9 ppm TiO_2 (yarn I), at room temperature. Excitation scan: Em λ 388 nm, Ex slit 3 nm, Em slit 10 nm. Emission scan: Ex λ 342 nm, Ex slit 10 nm, Em slit 3 nm.

the PET and the dyestuff retain their original fluorescence properties even when combined. The dye-corrected fluorescence excitation scan reaffirms the bathochromic shift noted previously for its absorption spectra in PET. The dye fluorescence emission was also "red" shifted in the polymer $\sim 450 \text{ cm}^{-1}$ to ~ 538 and $\sim 610 \text{ nm}$.

The phosphorescence excitation and emission spectra of a 0.421% (by weight) C. I. Disperse Red 59 dyed yarn (yarn I) at 77°K is depicted in Figure 10. The phosphorescence emission is characterized by a band at $\sim 454 \text{ nm}$, corresponding to the normal phosphorescence of blank-dyed PET, and a second emission band

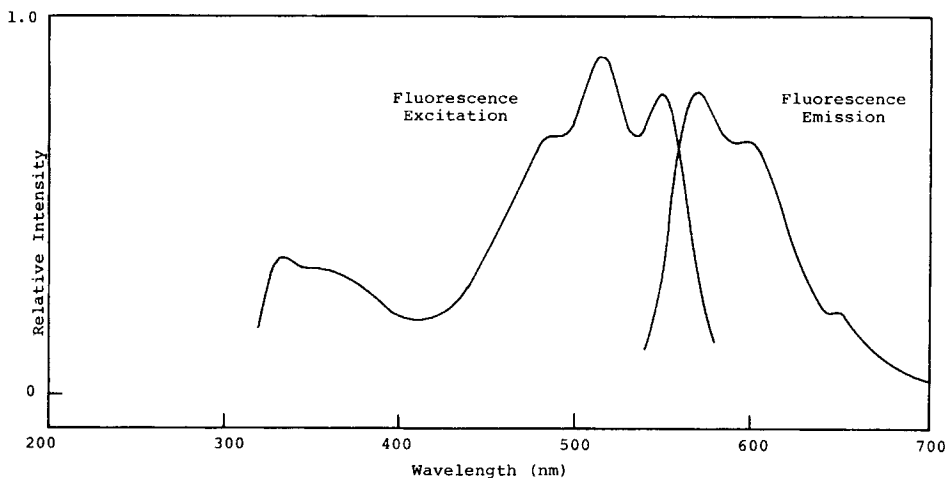


Fig. 9. Corrected fluorescence excitation and uncorrected fluorescence emission spectra for 0.0287% (by weight) C. I. Disperse Red 59-dyed poly(ethylene terephthalate) yarn containing less than 9 ppm Ti (yarn I), at room temperature. Excitation scan: Em λ 610 nm, Ex slit 3 nm, Em slit 10 nm, filter 350 nm. Emission scan: Ex λ 520 nm, Ex slit 10 nm, Em slit 3 nm.

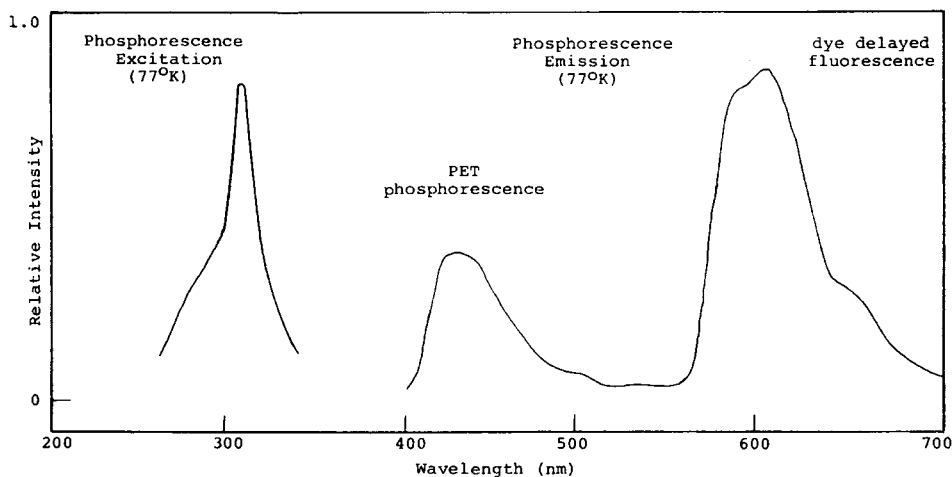


Fig. 10. Uncorrected phosphorescence excitation and emission spectra for 0.421% (by weight) C. I. Disperse Red 59-dyed poly(ethylene terephthalate) yarn containing less than 9 ppm Ti (yarn I), at 77°K. Excitation scan: Em λ 585 nm, Ex slit 10 nm, Em slit 10 nm. Emission scan: Ex λ 310 nm, Ex slit 10 nm, Em slit 10 nm; lifetime (τ) 0.3 sec (430 nm), 0.2 sec (610 nm).

appearing at the same wavelength (\sim 585 and 610 nm) and with the same band shape as the fluorescence emission of the dyestuff. Increasing the dye concentration quenched the 454-nm PET phosphorescence band and increased the emission due to the dye relative to the PET emission band, as shown in Figure 11. The mean lifetime of the PET phosphorescence was also found to decrease with the dye concentration, while the lifetime for the dye emission paralleled that of the PET phosphorescence.

The phosphorescence spectra indicated that energy transfer, not from the dye to the PET as would be expected for a sensitizer of polymer photodegradation, but from the polymer to the dye had occurred. Analysis of the phosphorescence

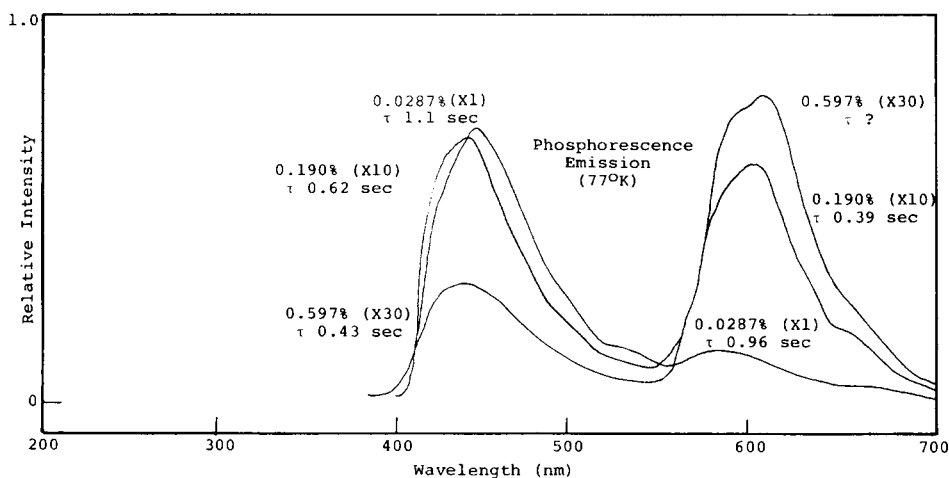
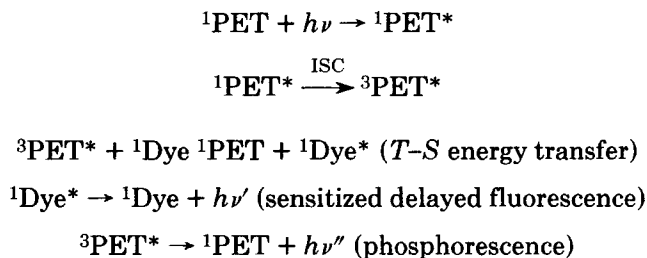


Fig. 11. Uncorrected phosphorescence emission spectra for 0.0287%, 0.190%, and 0.597% (by weight) C. I. Disperse Red 59-dyed poly(ethylene terephthalate) yarn containing less than 9 ppm Ti (yarn I), at 77°K. Emission scan: Ex λ 310 nm, Ex slit 10 nm, Em slit 10 nm; spinning samples.

spectra and lifetimes coupled with the data for the dye fluorescence revealed that energy transfer was occurring from the triplet state of the polymer, $^3\text{PET}^*$, causing the dye to be raised to its first excited singlet state, $^1\text{Dye}^*$, resulting in the emission of PET-sensitized dye delayed fluorescence as diagrammed below:



Triplet-singlet (T - S) energy transfer from PET to the dyestuff is spin forbidden for electron exchange interaction and exciton migration radiationless transfer mechanisms.³⁸ The decrease in the mean lifetime of the donor species (PET) with increasing acceptor (dye) concentration and the invariance of the donor emission spectrum with increasing acceptor concentration indicate that the transfer involves a long-range dipole-dipole interaction.

The majority of experimental cases where T - S transfer has been shown to occur involve the incorporation of the donor and acceptor in either a glassed solvent or a polymer matrix. However, in these cases, the dispersing medium generally does not participate in the energy transfer process. The work by Dearman and Lang³⁶ concerning the energy transfer occurring in proflavine-dyed nylon 6,6 films is apparently the only previously reported case of T - S energy transfer in which the donor species was a man-made polymer.

In order to provide further evidence that the delayed fluorescence of C. I. Disperse Red 59 is due to long-range T - S energy transfer from PET and to further characterize this transfer process, kinetic experiments were carried out in order to determine the experimental critical transfer distance R_0 . A series of PET yarn I samples were dyed with C. I. Disperse Red 59 to give dye concentrations of 0.256 (0.0058), 0.686 (0.0156), 1.26 (0.0287), 2.82 (0.064), 5.32 (0.121), 8.36 (0.0190), and $8.71 \times 10^{-3}M$ (90.198% by weight), respectively. The uncorrected PET phosphorescence emission spectra and mean lifetimes were obtained for the above samples and a blank-dyed yarn sample. The ratio of the donor lifetime in the absence of acceptor to the lifetime in the presence of the acceptor, τ_D/τ_D^0 , and the corresponding donor emission quantum yield ratio, ϕ_D/ϕ_D^0 (determined by measuring the areas under the appropriate donor emission curves), were calculated. The resulting data were plotted versus the acceptor concentration according to the method employed by Ermolaev and Svshnikova³⁷ and are reproduced in Figure 12. The donor lifetime data gave a critical acceptor concentration, $[A]_{1/2}$, of 6.45×10^{-3} mole/l. which yields an experimental critical transfer distance of 39.5 Å. The magnitude of the critical transfer distance definitely indicates the existence of long-range energy transfer. In addition, the ratio of the initial slope of ϕ_D/ϕ_D^0 to that of τ_D/τ_D^0 is approximately equal to 2, as predicted for resonance excitation energy transfer by Galanin.³⁸

The critical transfer distance R_0 calculated above is merely a measure of the

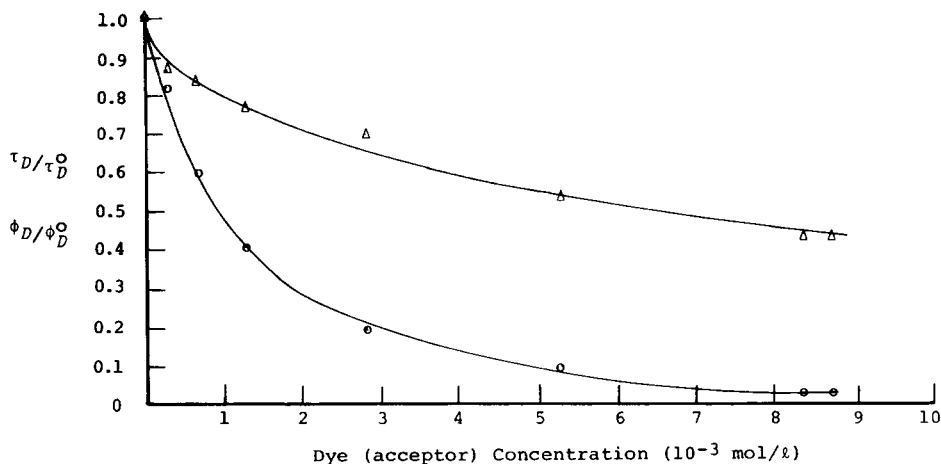


Fig. 12. Ratio of PET (donor) phosphorescence lifetime (τ_D) and quantum yield (ϕ_D) relative to values in the absence of acceptor, τ_D/τ_D^0 and ϕ_D/ϕ_D^0 , respectively, as a function of C. I. Disperse Red 59 (acceptor) concentration: (Δ) τ_D/τ_D^0 ; (O) ϕ_D/ϕ_D^0 .

distance dependence of an energy transfer mechanism for a given donor-acceptor pair and should be a constant under these conditions. For most donor-acceptor pairs, there are at least two types of radiationless electronic energy transfer mechanisms which may apply, with the dominant one depending upon the donor-acceptor separation, viscosity, and/or temperature. For the C. I. Disperse Red 59-dyed poly(ethylene terephthalate), the only other possible energy transfer would be S-S energy transfer. However, the PET fluorescence does not appreciably overlap the dye absorption spectrum, and therefore its contribution should be small [see Fig. 1(a)-1(c)]. Under these conditions, T-S energy transfer should occur not only over donor-acceptor separations of 20-60 Å but also for much smaller separations. The transfer of electronic energy from the PET to C. I. Disperse Red 59 proves that the reverse process cannot occur and therefore does not produce dye-sensitized phototendering of PET by electronic energy transfer.

In summary, referring to the electronic excited states characteristic of the dye C. I. Disperse Red 59 and the polymer poly(ethylene terephthalate) (see Fig. 3), it is apparent that direct (photophysical) energy transfer from the dye to the polymer is unlikely due to the unfavorable energy dispositions, i.e., $E_{\text{PET}^*} \gg E_{\text{Dye}^*}$, and to the observed energy transfer in the opposite direction. An analysis of the expected photoactivity of the dyestuff, in terms of hydrogen abstraction or the generation of a third photoreactive species, indicates that it ought to be unreactive and function as a photoprotective agent by dissipating absorbed radiant energy photophysically through its intramolecularly hydrogen-bonded states.

Photo-oxidation of Dyed and Blank-Dyed Poly(ethylene Terephthalate)

Our initial photodegradation experiments were designed to investigate the effect of dye concentration on the phototendering of poly(ethylene terephthalate) (PET). Many factors other than the incorporation of dye molecules into a

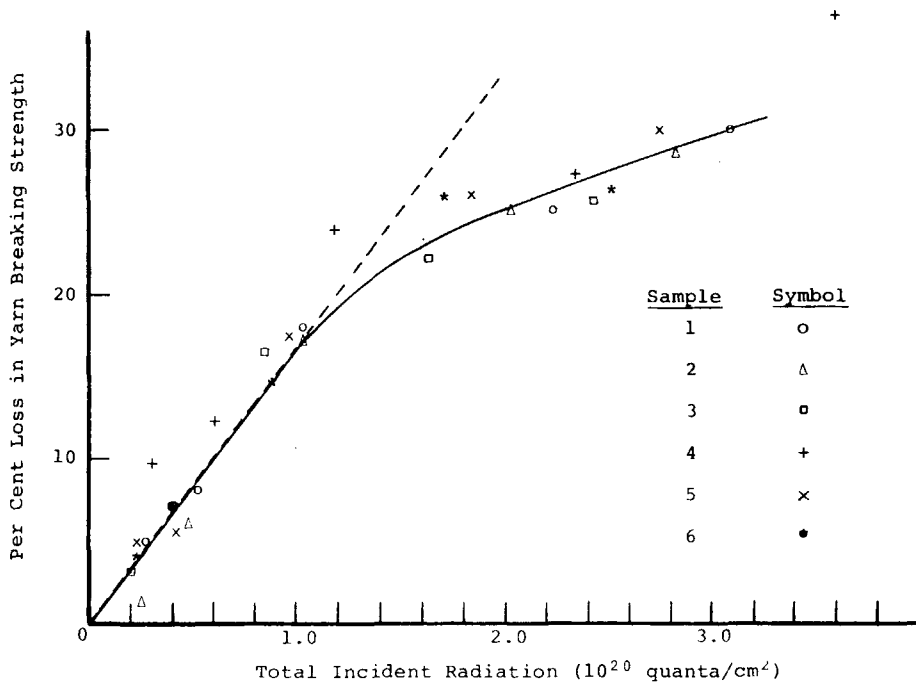


Fig. 13. Percent loss in yarn breaking strength as a function of total incident radiation for blank-dyed PET yarns (yarn I) irradiated in dry air.

polymer matrix may also have a sensitizing effect on the photodegradation of a polymer, e.g., the presence of titanium dioxide (TiO_2) delusterant, carriers for dyeing, atmospheric and/or internal moisture, etc. Therefore, the first experiments were carried out under conditions in which as many as possible sensitizing agents, other than the dye itself, were eliminated.

The PET yarn samples (yarn I) employed were essentially free of TiO_2 (anatase), containing less than 9 ppm Ti. The scoured yarn samples were dyed at 121–124°C under pressure without the aid of a carrier and were flushed with dry air.

A series of six dyed yarn samples (yarn I, samples 1–6) containing 0.064%, 0.121%, 0.198%, 0.344%, 0.597%, and 0.811% (by weight) C. I. Disperse Red 59 were irradiated, along with the corresponding blank-dyed samples, from 5 to 60 hr in the photochemical chamber.

With increasing exposure to radiation the dyed and blank-dyed samples, in general, became weaker and more brittle and exhibited lower percent elongations at break. No visible photofading of the dyed yarns was apparent (not quantized).

The variation in the radiation intensity within the photolysis chamber due to lamp aging was monitored periodically by actinometry. The variation of the incident-light intensity during the course of the experiments was taken into account by measuring the resultant extent of photo-oxidation, expressed as the percent loss in yarn breaking strength, as a function of the total incident quanta rather than as a function of irradiation time. This, in effect, approximates conditions of irradiation at constant light intensity.

Reference to Figure 13 shows the excellent correlation between the PET

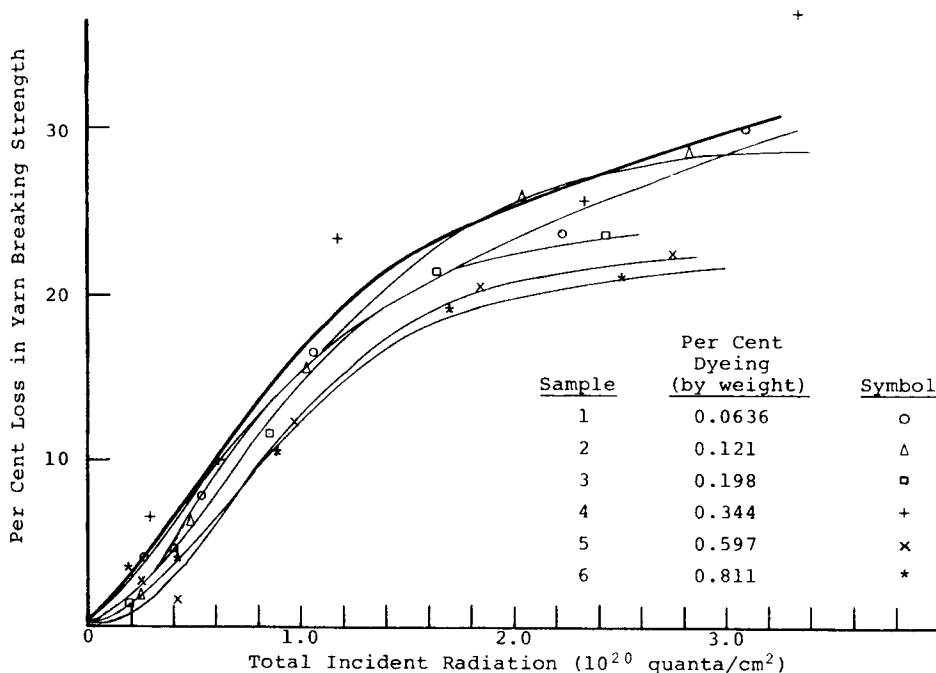


Fig. 14. Percent loss in yarn breaking strength as a function of total incident radiation for dyed PET yarns (yarn I) irradiated in dry air: (—) dyed yarns; (—) average curve for blank-dyed yarn (yarn I).

photodegradation data obtained for the various blank-dyed samples when plotted on a total incident radiation scale. The first sample irradiated in the series, sample 4, deviates somewhat from the "general" curve presumably because it was exposed during the initial period when the lamp intensities were rapidly changing. Therefore, the data obtained for this sample will be neglected for all comparative purposes.

The photo-oxidation rate curves for the dyed PET yarns are given in Figure 14. Comparison of the data for the dyed yarns with the "general" photo-oxidation curve for the blank-dyed PET yarn reveals that although the degradation curves are similar in shape, none of the dye concentrations produced a sensitized phototendering of the polymer. In fact, the dye was found to act increasingly as a photoprotective agent as its concentration in the polymer increased.

The lack of any evidence for dye-sensitized phototendering of PET under the conditions of the first experiment was surprising since C. I. Disperse Red 59 is reported by the supplier to be a possible sensitizer of poly(ethylene terephthalate) phototendering. Inasmuch as the initial experiments were designed to analyze the interactions of the polymer and dyestuff alone, it seemed quite possible that some other species or agent was required in order for the dye to sensitize PET photodegradation.

Commercial PET fibers normally contain TiO_2 (anatase) dispersed throughout the polymer as a delusterant in the range of 0.05% to 2.0%.³⁹ To determine if there was a synergistic photosensitizing effect between TiO_2 and the dyestuff, a commercial PET yarn sample (yarn II) containing 0.24% TiO_2 was dyed to give a concentration of 0.181% (by weight) C. I. Disperse Red 59. The dyed and

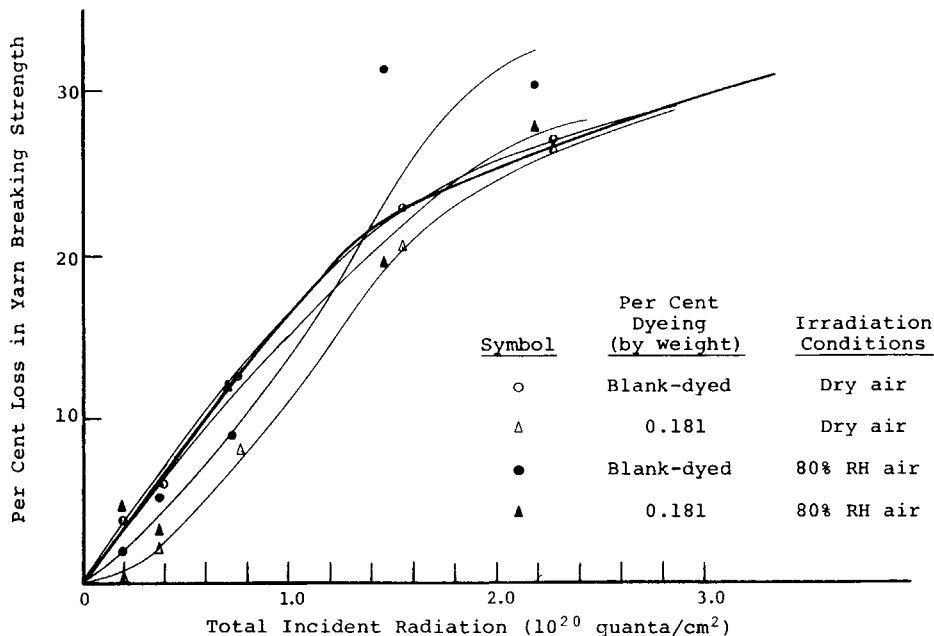


Fig. 15. Percent loss in yarn breaking strength as a function of total incident radiation for dyed and blank-dyed PET yarn (yarn II) irradiated in dry and 80% relative humidity air: (—) yarn II; (—) average curve for blank-dyed yarn I, irradiated in dry air.

blank-dyed samples were irradiated under the same conditions employed for the previous samples. The resulting rate of photo-oxidation curves are depicted in Figure 15. Analysis of the dyed versus the blank-dyed data again indicates that no sensitized phototendering occurred. In addition, comparing the photodegradation curve for the blank-dyed yarn II with the average curve for the blank-dyed yarn I samples, the TiO_2 did not seem to have a sensitizing effect on the rate of PET phototendering.

In the TiO_2 -sensitized phototendering of polymers, water vapor may play an important, if not necessary, role.⁴⁰ Therefore, another set of samples, identical to those used in the above experiment, were irradiated as before except that the system was flushed with air containing water vapor (80% R.H.). The photodegradation curves for these samples are also depicted in Figure 15. Although the data for these samples exhibit more scatter than for the previous samples, it is still obvious that dye-sensitized phototendering has not occurred. Relating the photodegradation curve for the blank-dyed yarn II irradiated at 80% R.H. to the curve for the same yarn irradiated in dry air indicates, however, that TiO_2 -sensitized phototendering of PET does occur when irradiation takes place in the presence of water vapor.

Kinetics of PET Photodegradation

In addition to indicating the reproducibility of the tensile test data when plotted on a total incident radiation abscissa, Figure 13 shows an initial (pseudo-) zero-order rate of PET phototendering (see Appendix).

Using a method of least-squares analysis of the initial data in Figure 13, a value

of $k_{hv} = 1.69 \times 10^{-19}\%$ breaking strength loss/quantum absorbed/cm² = $1.02 \times 10^5\%$ breaking strength loss/einstein absorbed/cm², where einstein = 6.02×10^{23} quanta, was obtained. This rate constant calculated above may represent a true zero-order rate constant reflecting the primary photolytic reaction occurring in PET photo-oxidation, or it may be a pseudozero-order rate constant characterizing the overall rate of PET photo-oxidation.

The change in the slope of the PET photodegradation curve, at a total incident radiation level of about 10^{20} quanta/cm², may be caused by several possible factors. Since the photodegradation of PET with irradiation wavelengths less than 310 nm occurs primarily at the polymer surface,² extended exposure results in the formation of a thin layer or "skin" of photo-oxidized polymer. This surface layer is capable of functioning as a radiation-absorbing barrier, thus protecting the underlying undegraded polymer. The inflection in the rate curve could also be due, in part, to a photodegradation mechanism in which scission of the weakest polymer links predominates initially, followed by the breaking of stronger chain links at a reduced rate after the weak links have all been broken.

CONCLUSIONS

The fluorescence and phosphorescence properties of poly(ethylene terephthalate) (PET) have been determined, and the corresponding electronic transitions have been tentatively assigned and quantified. The identification of the lowest excited electronic states, from which most photochemical and photo-physical processes occur, provides an insight into PET photodegradation reactions and the possible interactions with other excited electronic species.

Analysis of the absorption and luminescence characteristics of C. I. Disperse Red 59 [1-amino-2-(2-methoxyethoxy)-4-hydroxy-9,10-anthraquinone], compared with those reported for similar compounds, indicated that the dyestuff, which fluoresces but does not phosphoresce, possesses a lowest singlet *C-T* excited state. Comparing the expected photosensitizing properties of the dyestuff to 9,10-anthraquinone, which possesses a lowest $^1(n,\pi^*)$ excited state and undergoes intersystem crossing to the triplet state in high yield ($\phi_{ISC} = 0.90$),³⁵ one finds a complete reversal of sensitizing behavior. The ability to initiate photoreactions by hydrogen abstraction or by energy transfer from the triplet state is great for 9,10-anthraquinone, but almost nonexistent for the dye.

At room temperature, the luminescence characteristics of the C. I. Disperse Red 59-dyed PET were nearly identical to those of the individual components. At 77°K, triplet-singlet energy transfer from PET to the dyestuff resulted in a sensitized delayed dye fluorescence. A kinetic analysis of the transfer process yielded a critical acceptor (dye) concentration $[A]_{1/2}$ of 6.45×10^{-3} mole/l., which gave a critical transfer distance R_0 of 39.5 Å. The large transfer distance, linked with the spectral and lifetime characteristics of the donor (PET) and acceptor (dye) emissions, identified the energy transfer mechanism as being due to a long-range dipole-dipole (Coulombic) interaction.

The photo-oxidation studies of dyed and blank-dyed poly(ethylene terephthalate) yarns revealed that the dyestuff did not sensitize the photodegradation of TiO₂-containing or TiO₂-free PET over a wide range of dye concentrations and irradiation conditions designed to approximate natural exposure. Furthermore, at high concentrations, the dye exhibited a photoprotective effect.

The only evidence obtained for sensitized PET phototendering was for a blank-dyed titanium dioxide-containing yarn irradiated in 80% relative humidity air, thus emphasizing the importance of moisture in the TiO_2 -sensitized process. Kinetic analysis of the phototendering data for blank-dyed PET indicated an initial (pseudo-) zero-order reaction with a rate constant of $1.69 \times 10^{-19}\%$ breaking strength loss/quantum absorbed/ cm^2 .

The photo-oxidation activity of C. I. Disperse Red 59 found experimentally is consistent with the results obtained from the study of the photophysical processes occurring in the dye and polymer. Analysis of the dyed polymer absorption and luminescence spectra indicates that a dyed-polymer complex is not formed and, therefore, the dye cannot function as a photo-optical sensitizer. Due to the inverted relationship of the dye-polymer lowest excited energy levels,

$$\begin{aligned} & {}^3(\pi, \pi^*)_1 \quad {}^1(C-T)_1 \\ & > \\ & (E_{\text{PET}^*} \quad E_{\text{Dye}^*}) \end{aligned}$$

the dye should be incapable of efficient direct (photophysical) energy transfer to the polymer. Further evidence for this was found when it was determined that energy transfer actually took place in the opposite direction, from the polymer to the dye, by a dipole-dipole long-range resonance excitation energy transfer mechanism.

Based on the electronic energy levels characteristic of PET, dyes in general should be incapable of sensitizing photoreactions in PET by a direct (photophysical) energy transfer process. In order for a dye to appear colored, it must absorb visible radiation, therefore limiting the energy of its lowest electronic excited state to a maximum of approximately 70 kcal/mole. Therefore, a few dyes would possess lowest excited states with sufficient electronic energy to allow efficient transfer of PET. Of course, this does not eliminate the possibility of photosensitization by other mechanisms.

Appendix

Kinetics of Chain Scission Photodegradation of Polymers

For a polymeric system in which photodegradation occurs randomly and all bonds are identical, the zero order reaction rate is given by⁴¹

$$-\frac{dn}{dt} = \phi I_a \quad (1)$$

where n is the number of intact chain links, I_a is the intensity of light absorbed by the polymer (quanta/sec), ϕ is the quantum yield of photodegradation (chain scissions/quantum absorbed), and t is the time (sec).

If it is assumed that the breaking strength b of a textile yarn is proportional to the number of unbroken chain bonds present in a polymer,⁴² and if the other stipulations applying to eq. (1) are approximated, then the zero-order reaction rate for PET phototendering can be written as

$$\begin{aligned} -\frac{db}{dt} &= k \phi I_a \\ &= k' I_a \end{aligned} \quad (2)$$

where k is a proportionality constant and $k' = k\phi$. Integration of eq. (2) yields

$$b_0 - b_t = k'I_a t \quad (3)$$

where b_t represents the yarn breaking strength at time t and b_0 is the initial yarn breaking strength.

According to the Beer-Lambert law,

$$I = I_0 e^{-alc} \quad (4)$$

where I_0 is the monochromatic light intensity (quanta/sec) incident at the surface of an absorbing sample of concentration c (moles/l.), I is the light intensity transmitted through a thickness l (cm) of the sample, and a (l./mole-cm) is the molar extinction coefficient which depends upon the wavelength of the light and the nature of the absorbing species.

The light intensity absorbed by a sample, I_a , is defined by

$$I_a = I - I_0 \quad (5)$$

Combining eqs. (4) and (5) and substituting for I_a in eq. (3) gives

$$b_0 - b_t = k'I_0(1 - e^{-alc})t \quad (6)$$

For the case of strong absorption, which should apply to PET yarn irradiated at 300 nm,

$$1 - e^{-alc} \cong 1$$

and, therefore,

$$b_0 - b_t \cong k'I_0 t \quad (7)$$

Converting the left side of eq. (7) to the percent loss in yarn breaking strength, $[(b_0 - b_t)/b_0] \times 100$, and the incident light intensity to units of quanta/cm² yields

$$\begin{aligned} \left(\frac{b_0 - b_t}{b_0}\right) \times 100 &= \frac{100k'A}{b_0} \left(\frac{I_0}{A} t\right) \\ &= k_{hv} \left(\frac{I_0}{A} t\right) \end{aligned}$$

where A is the area of the sample (cm²), I_0/A is the incident-light intensity (quanta/cm²), and $k_{hv} = 100k'A/b_0$ is the phototendering rate constant.

Since $(I_0 t)/A$ represents the total radiation intensity (quanta/cm²) incident on the sample at time t , a plot of the loss in the yarn breaking strength versus the total incident radiation intensity should be linear, with a slope equal to the phototendering rate constant k_{hv} .

One of the authors, R.G.M., gratefully acknowledges the support of the J. E. Serrine Textile Foundation during a portion of this work. This manuscript was taken from a dissertation submitted by R. G. Merrill to Clemson University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Textile and Polymer Science, May 1976.

References

1. M. Day and D. M. Wiles, *J. Polym. Sci., Polym. Lett. Ed.*, **9**, 665 (1971).
2. M. Day and D. M. Wiles, *J. Appl. Polym. Sci.*, **16**, 175 (1972).
3. M. Day and D. M. Wiles, *J. Appl. Polym. Sci.*, **16**, 203 (1972).
4. M. Day and D. M. Wiles, *Can. J. Chem.*, **49**, 2916 (1971).
5. M. Day and D. M. Wiles, *J. Appl. Polym. Sci.*, **16**, 191 (1972).
6. P. Blais, M. Day, and D. M. Wiles, *J. Appl. Polym. Sci.*, **17**, 1895 (1973).
7. P. R. Cheung, M.S. thesis, Clemson University, Clemson, S.C., Dec. 1974.
8. H. Dearman and A. Chan, *J. Chem. Phys.*, **44**, 416 (1966).
9. J. R. Monkman, *J. Soc. Dyers Colour.*, **87**, 16 (1971).
10. American Society for Testing Materials, D2256-69, ASTM Standards, 1971, Supplement Part 24, p. 364.
11. C. A. Parker, *Proc. R. Soc. London, Ser. A*, **220**, 104 (1953).
12. C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
13. J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

14. J. Lee and H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964).
15. K. C. Kurien, *J. Chem. Soc. B* **10**, 2081 (1971).
16. J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966.
17. C. A. Parker, *Proc. Soc. Anal. Chem.*, **3**, 158 (1966).
18. H. C. Hollifield and J. D. Winefordner, *Anal. Chem.*, **40**, 1959 (1968).
19. F. B. Marcotte, D. Campbell, J. A. Cleaveland, and D. T. Turner, *J. Polym. Sci., Polym. Chem. Ed. A-1*, **5**, 481 (1967).
20. A. B. Thompson and D. W. Woods, *Nature*, **176**, 78 (1955).
21. H. Taylor, W. Tincher, and W. Hamner, *J. Appl. Polym. Sci.*, **14**, 141 (1970).
22. J. G. Pacifici and J. M. Straley, *J. Polym. Sci. B*, **7**, 7 (1969).
23. A. Somersall and J. Guillet, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C13**(2), 135 (1975).
24. R. P. Wayne, *Photochemistry*, American Elsevier, New York, 1970.
25. R. C. Johnson (to du Pont), U.S. Pat. 2,768,052 (Oct. 23, 1956).
26. W. Flaig, J. C. Salfeld and E. Baume, *Justus Liebig's Ann. Chem.*, **618**, 117 (1958).
27. R. Peters and H. Sumner, *J. Chem. Soc.*, **Part 2**, 2101 (1953).
28. H. Meir, in *The Chemistry of Synthetic Dyes*, Vol. 4, K. Venkataraman, Ed., Academic Press, New York, 1971, Chap. 7.
29. G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).
30. G. Porter, in *Reactivity of the Photoexcited Organic Molecule*, Wiley-Interscience, New York, 1967, pp. 70-110.
31. S. Nagakura and A. Kuboyama, *J. Amer. Chem. Soc.*, **76**, 1003 (1954).
32. J. W. Sidman, *J. Amer. Chem. Soc.*, **78**, 4567 (1956).
33. R. Morton, *Biochemistry of Quinones*, Academic Press, New York, 1965.
34. L. Lang, Ed., *Absorption Spectra in the Ultraviolet and Visible Region*, Vols. VI and VIII, Academic Press, New York, 1965.
35. A. Lamola and N. J. Turro, in *Technique of Organic Chemistry*, Vol. XIV, P. A. Leermakers and A. Weissberger, Eds., Interscience, New York, 1969.
36. H. Dearman, F. Lang, and W. Neely, *J. Polym. Sci., Polym. Phys. Ed. A-2*, **7**, 497 (1969).
37. V. L. Ermolaev and E. B. Sveshnikova, *Sov. Phys.-Dokl. (Engl. Transl.)*, **8**, 373 (1963); *Dokl Akad. Nauk SSSR*, **149**, 1295 (1963).
38. M. D. Galanin, *Sov. Phys.-JETP (Engl. Transl.)*, **1**, 317 (1955); *Zh. Eksp. Teor. Fiz.*, **28**, 485 (1955).
39. M. J. Wall and G. C. Frank, *Text. Res. J.*, **41**, 32 (1971).
40. G. S. Egerton and K. M. Shah, *Text. Res. J.*, **38**, 130 (1968).
41. B. Ranby and J. Rabek, *Photodegradation, Photooxidation, and Photostabilization of Polymers*, Wiley, New York, 1975.
42. T. Alfrey, Jr., in *High Polymers*, Vol. VI, Interscience, New York, 1948.

Received June 22, 1976

Revised September 14, 1976