

Photophysical Processes in Poly(hexamethylene Adipamide)-Acid Dye Complexes: Energetics of Nylon 66 Phototendering

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Synopsis

The mechanism of dye-sensitized photo-oxidative degradation of nylon 66 was investigated. A known phototendering dye, C.I. Acid Blue 40 (1-amino-4-(*p*-aminoacetanilide)-2-anthraquinone sodium sulfonate), was used for this study. Excitation and emission spectra of the dyed and undyed nylons indicated that a ground-state complex between the dye and the polyamide was formed upon dyeing. The energy level of the complex's electronic states favor triplet-triplet energy transfer from the nylon to the complex. Quenching studies show that the energy transfer occurs efficiently with a rate constant of $45.8 \text{ l. mole}^{-1} \text{ sec}^{-1}$. An additional energy transfer occurs between the excited free dye and the complex by either a singlet-triplet or a triplet-triplet mechanism. Kinetic analysis of the nylon-complex energy transfer suggests that the triplet energy of nylon migrates 24 to 33 Å along the amide chromophores in an excitation fashion until an energy trapping complex is reached. Energy is then transferred by an exchange mechanism. Photo-oxidative studies verify that the dye-nylon complex sensitizes the polyamide photo-oxidative degradation at its own expense without dye photobleaching.

INTRODUCTION

The degradation of polyamides and many other synthetic polymers by radiant and/or thermal energy is a well-known phenomenon. Since the degradation of the polymeric substrate is accompanied by a deterioration in its mechanical performance, the protection of the substrate from potentially hazardous chemical environments is advantageous. This task can be best fulfilled if a thorough knowledge of the degradation mechanism is at hand. Yet, as with most interactions between radiation and matter, the mechanistic details are obscured by a host of interdependent influences.

Research efforts aimed at unraveling the mechanism of photodegradation events occurring in irradiated polyamides have progressed slowly. Photolytic and photo-oxidative degradation studies of polyamides, especially nylon 66, have prompted various mechanistic proposals of the photochemical paths available to the polymer following radiation absorption. The presence or absence of oxygen, impurities, occluded monomer, additives such as dyes, pigments, plasticizers and delustrants, and polymerization catalysts display varying roles in the photochemical and photophysical scheme of the polyamide. In addition to the effects of additives, the energy of incident radiation dictates the magnitude and the path through which chemical degradation proceeds.

Of particular interest to the plastics industry is the phenomenon of polymer phototendering by dyes and pigments. Various direct, acid, basic, sulfur, vat, and disperse dyes sensitize the photo-oxidative degradation of the host polymer.¹ The effect of the dye depends on the chemical nature of the polymer and appears to be dependent upon the light stability of the polymer substrate.¹ The extent of the dye-sensitized photo-oxidative degradation is also dependent upon the chemical nature of the dye. However, even within specific dye classes, the degree of phototendering may vary.²

Since the ability of a dye to photosensitize the degradation of polymers cannot be correlated with the structure or photochemical behavior of the dye,³⁻⁵ studies investigating the photophysical processes of various dyes have been undertaken. Dearman and Chan⁶ found that the emission spectra of substituted anthraquinones could be correlated with the ability of the dye to produce semiquinone radical ions. Dyes with a high quantum yield for production of the anthrahydroquinone phosphoresce and produce radicals which are detected by electron spin resonance spectroscopy. Anthraquinones with a low quantum yield of photoreduction fluoresce and give no detectable electron spin resonance spectrum. Dearman and Chan suggested that the triplet state of the dye was the reactive intermediate in the photoreduction of the anthraquinones in the alcohol solutions studied. Millich and Oster⁷ reported a similar relation between the phosphorescence of acridine dyes and their ease of photobleaching. Davies and co-workers² found that for two anthraquinone-based vat dyes which have comparable phototendering activities on cellulose, the primary photochemical and photophysical processes of the dyes differ. The vat dye that has a high quantum yield of phosphorescence is readily photoreduced to the anthrahydroquinone in alcoholic solution. In contrast, the vat dye that does not luminesce is readily reduced to the radical anion in alcoholic solution. Davies et al. offered such results as evidence that on a cellulose substrate the phototendering vat dyes are capable of undergoing quite different primary photochemical processes.

In addition to the unimolecular photophysical processes available to various tendering dyes, bimolecular photophysical events between the dye and the polymeric substrate may further complicate the chemistry of phototendering. Bimolecular photophysical processes which involve nonradiative electronic energy transfer from an excited donor (dye or polymer) to a ground-state acceptor (dye or polymer) serve to localize or delocalize energy absorbed by the dye-polymer system.

Several theoretical treatments of nonradiative energy transfer have been developed. These theories include energy transfer mechanisms based on diffusion-controlled collisions,⁸⁻¹⁰ multipole-multipole interactions,¹¹⁻¹³ exciton migration,^{14,15} and exchange interactions.^{13,16-18}

Although energy transfer between a polymer substrate and various additives has been investigated in recent years,¹⁹⁻²⁴ the role of energy transfer in dye-polymer systems has received little attention. Dearman et al.²³ investigated the effect of an acridine dye, proflavin, on the photophysical processes of nylon 66. Upon exciting the dyed nylon with 295 nm radiation, the nylon phosphorescence (400 nm) was quenched and the proflavin-delayed fluorescence and phosphorescence were sensitized.

Dearman et al. proposed that a triplet-singlet energy transfer from the nylon to the dye occurred by a dipole-dipole interaction. The importance of the dye's presence on the photodegradation of the nylon was not discussed, but the trans-

fer of energy from nylon to the dye indicates that a photoprotective action may be operable.

Isenberg et al.³⁵ observed dye-delayed fluorescence from DNA-acridine dye complexes upon irradiation of the system with wavelengths absorbed by the DNA. The dye-delayed emission was interpreted to be the result of a DNA triplet-dye singlet energy transfer. Bennett and Kellogg³⁶ suggested that the triplet-singlet transfer process in acridine orange-DNA complexes occurs through long-range multipole-multipole interactions.

In this research, an investigation of the primary photophysical processes involved in the phototendering of nylon 66 by an acid dye was undertaken. Attention was focused upon the electronic states of the polyamide and the dye that are involved in the photochemical degradation of the polymer substrate. Spectroscopic and accelerated photo-oxidative degradation studies were employed in an effort to define the photo-excited dye-substrate interaction responsible for tendering events. C.I. Acid Blue 40 (1-amino-4-(*p*-aminoacetanilide)-2-anthraquinone sodium sulfonate) was selected for this study. Although Acid Blue 40 displays moderate light fastness properties on nylon 66, the dye is known to sensitize the photochemical degradation of nylon. The luminescent behavior of simple N-alkylamides was investigated in an effort to define the electronic state of nylon 66 responsible for its characteristic emission.

EXPERIMENTAL

Materials and Analyses. Reagent-grade adipoyl chloride, 1-aminohexane, benzene, hexamethylenediamine, hexanoyl chloride, and pyridine were used as received (Aldrich Chem. Co.). USP ethyl alcohol (95%) used for luminescence studies was selected from various batches which exhibited the least luminescence. EPA (5:5:1 ether:isopentane:ethanol) solvent for low-temperature luminescence was purchased from Matheson, Coleman and Bell. Merck chromatograph-quality aluminum oxide was used for column chromatography. Mercapyl Blue 2GA (Acid Blue 40), bright nylon 66 (70 denier, 20 monofilaments) and dull nylon 66 (40 denier, 13 monofilaments) containing 2% titanium dioxide were gifts from E. I. du Pont de Nemours and Co.

Infrared analysis was obtained from a Perkin-Elmer Model 237B spectrophotometer. Excitation and emission spectra were recorded from a Hitachi Perkin-Elmer Model MPF-3 spectrofluorometer equipped with a phosphoroscope attachment. The phosphoroscope housed a variable-speed cam which could be operated up to 6500 rpm. A Tektronic Type 564 storage oscilloscope was used to measure luminescent lifetimes. Ultraviolet and visible transmission and reflectance spectra were obtained using a Cary 14 and a Beckman DBG spectrophotometers, respectively. A Bausch and Lomb Spectronic 20 was routinely used for optical density measurements. Nuclear magnetic resonance spectra were recorded using a Perkin-Elmer Model R 12B 60-MHz spectrometer. Ultraviolet degradations were performed using a Rayonet Model RPR-208 Type RS photochemical reactor equipped with eight Rayonet RUL-3000 Å sunshine phosphor lights. The eight lamps delivered 85 watts of 3000 Å radiation. Elemental analysis was obtained from Galbraith Laboratories, Knoxville, Tennessee.

Tensile strengths of the dyed and undyed nylon yarns, before and after irradiation, were measured on a constant rate of extension Instron Model TM-M tensile tester. A gauge length of 25.4 cm and an extension rate of 20 cm/min

were employed. The rate of extension was chosen such that the time to break for the control yarns was 20 ± 3 sec. All samples were conditioned in the dark for at least 24 hr at 70°F and 65% relative humidity.

Model Amides. N-Hexylhexanamide, 1,6-hexamethylenebis(hexanamide), and N,N'-bis(hexyl)adipamide were prepared using the Schotten-Bauman method. The amides were characterized as follows (unless indicated otherwise, all temperatures are °C):

N-Hexylhexanamide: mp 23–25°; bp 134–135°/0.090 mm (lit.³⁷ bp 108–111°/0.07 mm); IR (neat: 3300 (N—H stretching); 1550, 1250, 725 (N—H bending); 1640 (C=O); 1470 (CH₂ bending); 1380 (CH₃ bending); 2926, 2853 cm⁻¹ (CH₂ stretching); NMR (CDCl₃, ext TMS); 7.2 (N—H, 1H); 3.17 (CH₂—NH, 2H, quartet); 2.1 (CH₂—CO, 2H, triplet); 1.3 (CH₂, 14H, multiplet); 0.85 δ (CH₃, 6H, triplet).

ANAL. Calcd for C₁₈H₃₆NO: C, 72.88; H, 12.66; N, 7.03; O, 8.03. Found: C, 72.30; H, 12.53; N, 6.93; O (diff), 8.24.

1,6-Hexamethylenebis(hexanamide): mp 142–144° (lit.³⁸ mp 142–143°); IR (KBr pellet): 3300 (N—H stretching); 1534, 1250, 695 (N—H bending); 1630 (C=O); 1470, 730 (CH₂ bending); 1375 (CH₃ bending); 2926, 2853 cm⁻¹ (CH₂ stretching); NMR (CDCl₃, ext TMS); 5.7 (N—H, 2H); 3.3 (CH₂—NH, 4H, quartet); 2.25 (CH₂—CO, 4H, triplet); 1.4–1.7 (—CH₂—, 20H, multiplet); 0.96 δ (CH₃, 6H, triplet).

ANAL. Calcd for C₁₈H₃₆N₂O₂: C, 69.16; H, 11.63; N, 8.97; O, 10.24. Found: C, 69.05; H 11.53; N 8.92; O (diff), 10.51.

N,N'-Bis(hexyl)adipamide: mp 161–162°; IR (KBr pellet): 3300 (N—H stretching); 1534, 1275, 685 (N—H bending); 1635 (C=O); 1470, 728 (CH₂ bending); 1375 (CH₃ bending); 2926, 2853 cm⁻¹ (CH₂ stretching); NMR (CDCl₃, ext TMS): 6.3 (N—H, 2H); 3.3 (—CH₂—NH, 4H, quartet); 2.3 (CH₂—CO, 4H, triplet); 1.7–1.4 (—CH₂—, 20H, multiplet); 0.95 δ (CH₃, 6H, triplet).

ANAL. Calcd for C₁₈H₃₆N₂O₂: C, 69.16; H, 11.63; N, 8.97; O, 10.24. Found: 69.38; H, 11.58; N, 8.58; O (diff), 10.19.

Dye Purification. Salt and impurities were removed from the commercial sample of the dye by continuous Soxhlet extraction with 100% ethanol. Organic impurities were removed by column chromatography (Al₂O₃, Merck).

ANAL. Calcd for C₂₂H₁₆N₃O₆SN₃: C, 55.81; H, 3.41; N, 8.88; S, 6.89. Found C, 55.62; H, 3.51; N, 8.75; S, 6.73.

Aqueous Dyeing of Nylon 66 Yarns. The dyebaths were prepared by dissolving 0.05 to 0.20 g commercial Acid Blue 40 [du Pont Merpacyl Blue 2GA; CI CI 62125; 1-amino-4-(*p*-aminoacetanilide)-2-anthraquinone sodium sulfonate] in 300 ml distilled water. Two nylon samples were dyed in each bath at the boil for 30 min. The dyebaths were cooled to room temperature, and the dyeings were allowed to proceed for an additional hour. The dyed samples were removed from the dyebaths and washed with water to remove all adhering dye liquor. A control sample was prepared in a similar fashion with the exception that no dye was added to the dyebath.

One sample from each dyeing was used to determine the percent dye uptake. The dye was stripped from the various dyed samples following the method of Monkman.³⁹ The weight per cent add-on for each dyeing was determined from

the concentration of dye in the stripping baths and the weight of the stripped nylons. The add-on values were converted to molar concentrations assuming a nylon density of 1.14 g/ml.

Irradiation Conditions. The dyed and undyed knitted nylon tubes were unraveled in 16-in. lengths and mounted on plywood strips 16 × 1.5 in. Eight yarn samples for each dye concentration were used. In order to ensure uniform tension on the mounted yarns, a 2.2-g tension was applied when mounting the samples. The yarn samples were conditioned in the dark in a stream of dry air for 6 hr. Compressed air was passed through two drying tubes filled with CaCl₂ before reaching the yarn samples. An air flow rate of 10–11 standard cubic feet per hour (SCFH) was used.

After conditioning the samples in a stream of dry air, the nylon yarns were placed in Pyrex tubes (20 × 1.75 in.) equipped with a gas inlet and outlet. The Pyrex tubes were mounted on a rotating Rayonet "merry-go-round" which was housed within the Rayonet photochemical reactor. The distance between the "sunshine phosphor" lights and the face of the samples measured 3 in. Because the rotating "merry-go-round" was motor driven at the top of the reactor, the Pyrex tubes were mounted with the gas inlets and outlets facing the bottom of the reactor. A stream of dry air (10–11 SCFH) was passed into the Pyrex vessels via a rotating bushing. The nylon yarn samples were irradiated from 5 to 135 hr at 42–47° and a photon intensity (with a Pyrex filter) of 4×10^{17} quanta ml⁻¹ min⁻¹ at the lamps' surfaces (reported by the manufacturer).

Low-Temperature Phosphorescence Studies. Approximately 1-mg samples or 1-ml portions of saturated ethanol solutions of Acid Blue 40, N-hexylhexanamide, N,N'-bis(hexyl)adipamide, and 1,6-hexamethylenebis(hexanamide) were added to quartz sample tubes (1 × 15 mm). The sample tube was very cautiously lowered into a quartz Dewar containing liquid nitrogen and the phosphorescence spectra was recorded. Dyed and undyed single-yarn samples were handled in a similar fashion. Bulking the yarns prior to their placement into the sample tubes was found to enhance emission intensity and give better reproducibility.

Actinometry. Radiation intensity was measured using the potassium ferrioxalate chemical actinometer developed by Hatchard and Parker⁴⁰ and modified by Baxendale and Bridge⁴¹ and Kurien.⁴² The intensity of the 3000-Å lights, 3 in. from the lamp surface, was computed to be $I_0 = 6 \times 10^{14}$ quanta sec⁻¹ ml⁻¹.

RESULTS AND DISCUSSION

Photophysical Processes in Bright Nylon 66. The excitation and emission spectra of nylon 66 at 77°K are shown in Figure 1. An excitation maximum at 290 nm and a broad structureless emission with a maximum centered at 400 nm are observed. These excitation and emission wavelengths correspond to the values reported by Dearman et al.³³ and Taylor et al.³⁴ for nylon 66 films and yarns. The nylon luminescence decays exponentially with a mean lifetime of 1.9 sec at liquid nitrogen temperature, 77°K. No luminescence of the nylon yarns was observed at room temperature. The long lifetime of the luminescing state, the large wavelength difference between excitation and emission wavelengths, and the observation of emission at low temperature only suggest that the emitting state is a triplet. Dearman and co-workers³³ proposed that the long-lived emitting state was a ³(II-II*) triplet state, since the long lifetime and the large energy

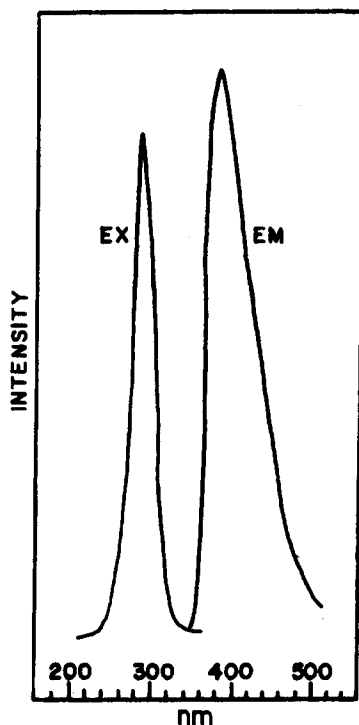


Fig. 1. Excitation and emission spectra of bright nylon 66 at 77°K.

splitting between singlet and triplet manifolds are characteristic of aromatic hydrocarbons.⁴³ However, since the lowest-lying excited states of alkyl amides are ($n-\Pi^*$) states, the question arises as to whether or not the nylon phosphorescence is due to nylon or an impurity. Dearman et al.³³ suggested that the nylon phosphorescence may be due to an impurity since they did not observe luminescence of room-temperature or low-temperature solutions of *N,N*-diethylacetamide, *N,N*-di-*tert*-butylpropionamide, *N*-ethylacetamide, or *N*-propylpropionamide.

Luminescence studies of *N*-hexylhexanamide, *N,N'*-bis(hexyl)adipamide, and 1,6-hexamethylenebis(hexanamide), representing the nylon 66 repeat unit, were undertaken as an effort to identify the nylon phosphorescing state. The crystalline bisamides were repeatedly crystallized from 95% ethanol (selected from various samples based on low luminescence), and *N*-hexylhexanamide was distilled twice to ensure purity. The excitation and emission spectra of the model amides are shown in Figures 2 and 3. These spectra are assigned on a *tentative* basis since the ethanol used for recrystallization of the bisamides contained luminescent impurities. The recorded spectra were obtained using neat samples. *N*-Hexylhexanamide at 77°K emits 440 nm radiation with a mean lifetime of 0.6 sec upon excitation with 300-nm radiation. Both the excitation and emission are observed to be fairly broad maxima (see Fig. 2). *N,N'*-Bis(hexyl)adipamide was observed to emit blue light with a maximum emission of 415 nm upon excitation with 265-nm radiation. The mean lifetime of luminescence at 77°K is 0.2 sec. 1,6-Hexamethylenebis(hexanamide) was also observed to emit blue light upon excitation at 77°K with 285 nm radiation. The luminescence is a broad range of wavelengths with a maximum occurring at 460 nm and a mea-

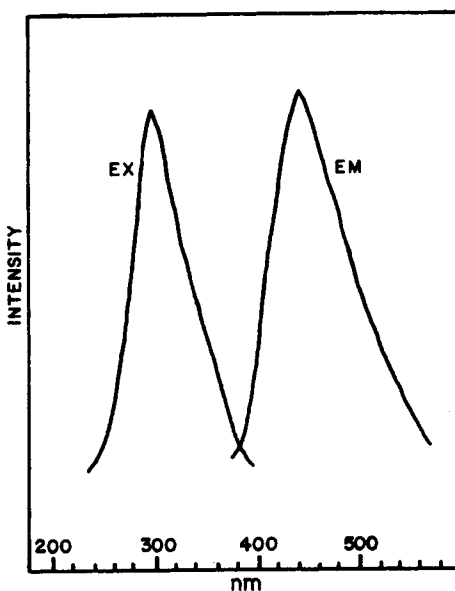


Fig. 2. Excitation and emission spectra of N-hexylhexanamide at 77°K.

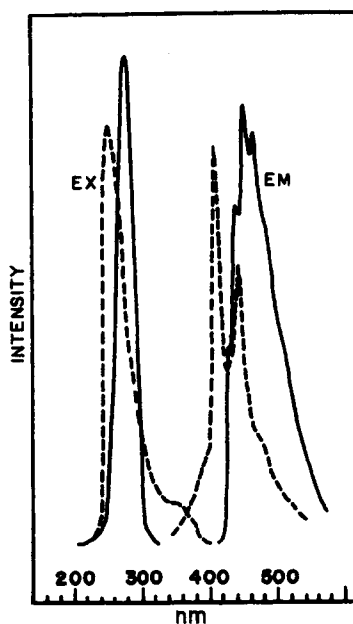
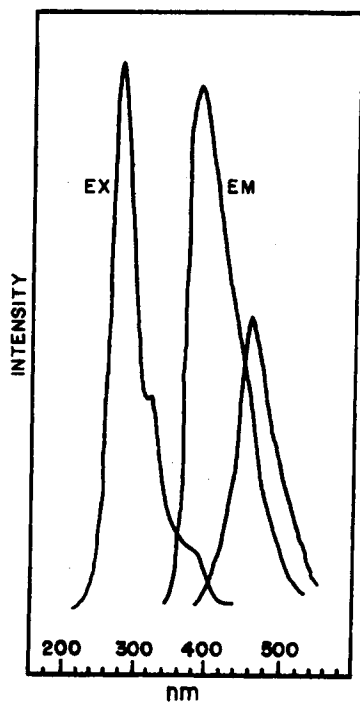


Fig. 3. Excitation and emission spectra of N,N'-bis(hexyl)adipamide (---) and 1,6-hexamethylenebis(hexanamide) (—) at 77°K.

sured lifetime of 0.2 sec. The amide luminescence is interpreted to be phosphorescence based on the observed lifetimes, on the large difference between excitation and emission wavelengths, and on the absence of emission at room temperature.

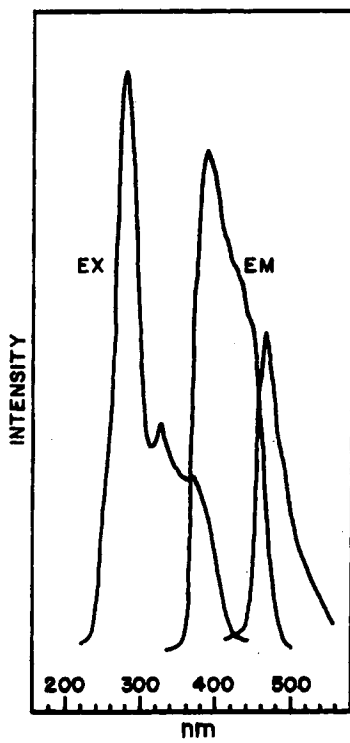
The electronic transition occurring upon excitation is believed to be a ${}^1(n-\pi^*)$ singlet transition since the excitation energies of the three amides correspond

to the ($n-\Pi^*$) absorption observed in alkyl ketones and amides.^{44,45} Poly-(methyl vinyl ketone)^{22,46} excitation (300 nm) and phosphorescence (440 nm) support this view.



nm

(a)



nm

(b)

Fig. 4 (continued)

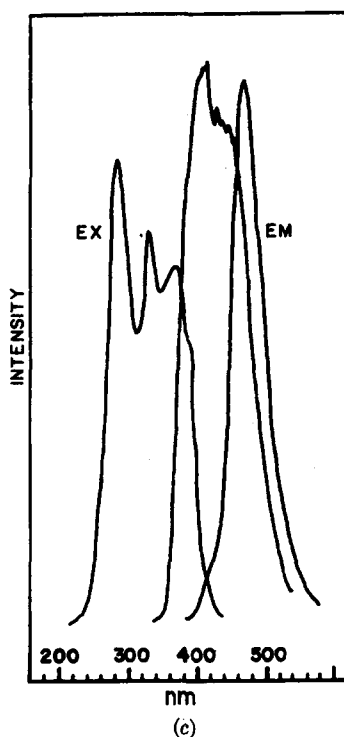
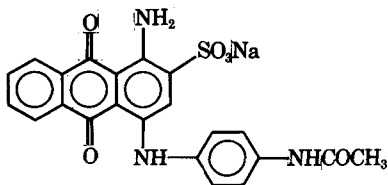


Fig. 4. Excitation and emission spectra of (a) dyed ($0.53 \times 10^{-2}M$) bright nylon 66 at $77^\circ K$; (b) dyed ($1.10 \times 10^{-2}M$) bright nylon 66 at $77^\circ K$; and (c) dyed ($1.75 \times 10^{-2}M$) bright nylon 66 at $77^\circ K$. EX: 290 nm, EM: 400 nm, EX: 330 and 380 nm, EM: 470 nm.

McGlynn and co-workers⁴⁵ suggested that for amidic molecules, the lowest triplet state may be a $^3(\Pi-\Pi^*)$ which is nonemissive, a mixed $^3(\Pi^*-\Pi^*)/{}^3(n-\Pi^*)$ state which is weakly emissive, or a $^3(n-\Pi^*)$ state which is strongly emissive. In view of McGlynn's investigation, it is possible that a mixed $^3(\Pi-\Pi^*)/{}^3(n-\Pi^*)$ lowest excited triplet state applies to the model amides and the nylon, even though appreciable π character is absent in alkylamides. Irrespective of the nature of the emissive state, the observation that the model amides weakly phosphoresce suggests strongly that the nylon 66 emission occurs from the polymeric amide chromophores and not an impurity.

Photophysical Processes in Nylon 66 Dyed with Acid Blue 40. Bright nylon yarns were dyed with C.I. Acid Blue 40 from aqueous dyebaths. Dye weight per cent add-ons ranged from 0.25% to 0.92%, which corresponds to 5.3×10^{-3} to $1.95 \times 10^{-2}M$ in nylon based on a polymer density of 1.14 g/ml. These relatively low values were employed in order to facilitate the measurement of their luminescence spectra. C.I. Acid Blue 40 is an anthraquinone dye of known structure:



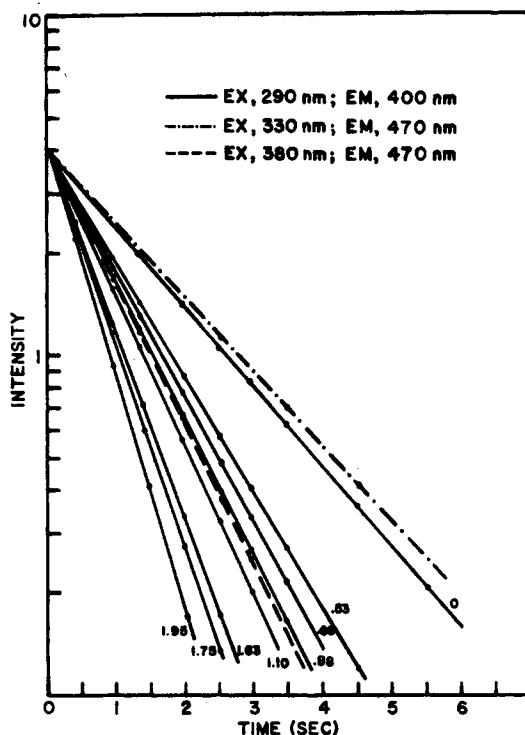


Fig. 5. Exponential decay of undyed and dyed nylon 66 phosphorescence at 77°K. The concentration of dye $\times 10^{-2}M$ is given for each decay curve. The 470 nm emission is constant for all dye concentrations upon excitation at 330 and 380 nm.

Excitation and emission spectra of the dyed bright nylons were recorded at 77°K, and representative spectra are shown in Figure 4. The excitation spectra of the dyed nylon samples exhibit maxima at 290, 330, and 380 nm. The relative intensities of the 330 and 380 nm maxima increase with increasing dye concentration. The emission spectra of the dyed samples display maxima at 400 and 470 nm. Both emissions decay exponentially, irrespective of the dye concentration (see Fig. 5). Excitation of the dyed nylons with 290-nm radiation is followed by emission of 400-nm radiation. This excitation and emission corresponds to the spectrum of the undyed nylon (see Fig. 1). Upon excitation of the samples with either 330 or 380 nm radiation, emission occurs with a maximum at 470 nm. These excitation maxima are attributed to the dye since neither are observed for the undyed bright nylon. Inspection of the luminescent properties of the dye revealed that commercial and purified samples of the dye did not luminesce at room temperature or 77°K when examined in varying glassing solvents or crystalline form. This unexpected observation indicated that the photophysical processes available to the dyed nylon were a result of some undefined interaction between the polyamide and the dye.

The mean lifetime (see Table I) of the 470 nm emission is 0.20 sec when the dyed nylon is excited with 330 nm radiation and 0.10 sec when excited at 380 nm. These mean lifetimes are constant over the dye concentration range studied. The difference in the 470 nm emission lifetimes at the two excitation wavelengths indicates that two different species are responsible for the phosphorescence. The ultraviolet-visible spectrum of the dye ($10^{-5}M$ in ethanol) reveals that the

TABLE I
Mean Lifetimes and Reciprocal Intensity of Nylon 66 Phosphorescence for Undyed and Dyed Nylon Yarns

| (D) $\times 10^{-2}M/\%$ add-on | Mean lifetimes, sec | | | $1/I_{400}$ |
|---------------------------------|--------------------------|--------------------------|--------------------------|-------------|
| | EX: 290 nm EM: 400 nm | EX: 330 nm EM: 470 nm | EX: 380 nm EM: 470 nm | |
| 0 | 1.9 | — | — | 1.0 |
| 0.53/0.25 | 1.3 | 0.20 | 0.10 | 0.33 |
| 0.68/0.32 | 1.2 | 0.20 | 0.10 | 0.30 |
| 0.88/0.42 | 1.1 | 0.20 | 0.10 | 0.32 |
| 1.10/0.52 | 1.0 | 0.20 | 0.10 | 0.41 |
| 1.63/0.77 | 0.80 | 0.20 | 0.10 | 0.48 |
| 1.75/0.83 | 0.75 | 0.20 | 0.10 | 0.45 |
| 1.95/0.92 | 0.65 | 0.20 | 0.10 | 0.53 |

dye's electronic transitions occur at 625, 385, 285, and 234 nm. Thus, it is possible that the 380 nm electronic excitation observed in the dyed nylon may arise from direct excitation of the dye. Since the dye is transparent at 330 nm, the dyed nylon excitation at that wavelength is not an outcome of direct excitation of the dye on the fiber. The 470 nm emission is believed not to be a triplet state of the dye since, even if the dye phosphoresced, its emission wavelength would be greater than 625 nm assuming that emission occurs from the lowest energy triplet state. (Azulene,⁴⁷ substituted azulenes,⁴⁸ pyrene,⁴⁹ and 3,4-benzopyrene⁵⁰ are the few exceptions which have been observed to fluoresce from the second excited singlet state.) Thus, the 470 nm phosphorescence must be a triplet state associated with the unknown 330-nm singlet state.

Since dyes are postulated to exist in restricted spatial conformations within a polymer network, the concept of a dye-polymer complex formed by hydrogen bonding, Van der Waal attractions, or electrostatic interactions has been proposed by various researchers.⁵¹ The proposal of a complex formation between the nylon and Acid Blue 40 proves to be an attractive explanation for the 330- and 470-nm electronic states of the dyed fiber. However, experimentally this was difficult to prove unequivocally. Mixtures of each model compound with varying concentrations (10^{-3} to $10^{-2}M$) of dye equivalent to the molar concentration of dye in nylon were prepared. In all cases, the excitation and emission spectra of the mixtures correspond to the excitation and emission spectra of the pure model compounds. The excitation and emission spectra of the various dyed nylons dissolved in a 2:1 90% HCO₂H:ETOH (v/v) glassing solvent at various concentrations (0.1, 1.0, and 4.0 g/l.) were identical to the undyed bright nylon excitation and phosphorescence spectra. A dye solution ($10^{-4}M$ in ethanol) and nylon yarn composite system was prepared by immersing the yarn in the ethanol dye solution contained in a quartz sampling tube. The excitation and emission spectra recorded at 77°K were also identical to the spectra of the undyed nylon. These results indicate that there exists an intimate relation between the dye and the polymer in solid solution. The liquid solution models of dye and fiber failed to exhibit the 330-, 380-, and 470-nm electronic states, verifying that a complex between ground-state dye molecule(s) and the ground-state polyamide substrate exists.

An alternative explanation of the observed excited states of the dyed nylon is dye aggregation affects. Dimer, trimer, etc., dye aggregates which may lumi-

nesce may form within the polymer substrate during or after dyeing. However, this seems unlikely since the dyed-nylon visible reflectance spectra display maximum absorptions at 625 and 390 nm analogous to the visible transmission spectrum. Also, no luminescence from solid dye or concentrated ($10^{-2}M$) ethanol solutions was observed, as mentioned previously.

Evidence suggesting the formation of a dye-nylon complex simplifies the photophysical characteristics of the dyed nylon excitation and emission spectra. Excitation of the dyed polyamide to its first excited singlet state at 290 nm is followed by efficient intersystem crossing to the nylon phosphorescing triplet state at 400 nm. Excitation of the dyed nylon with 330 nm radiation promotes a dye-nylon complex to its first excited singlet state. The dye-nylon complex singlet state is depopulated by intersystem crossing to the 470 nm phosphorescing triplet state. Excitation of the dyed polyamide with 380 nm radiation activates a dye molecule to its second excited singlet state. This singlet state is depopulated by transferring its energy to the dye-nylon complex triplet state via the S_2 or T_2 state of the dye since emission at 470 nm is observed upon excitation at 380 nm. Measurements of the mean lifetime of the nylon phosphorescence with increasing dye concentration indicated that an additional energy transfer occurred from the nylon triplet state to the dye-nylon complex triplet state. Table I and Figure 5 display the measured decrease of the nylon phosphorescence lifetime and intensity, respectively, with increasing dye concentration which strongly suggests that the nylon emitting state is quenched by the dye-nylon complex through a triplet-triplet transfer mechanism.

The total photophysical processes available in the dyed nylon 66 are displayed in the modified Jablonskii energy diagram constructed in Figure 6. Radiative and nonradiative processes are depicted by straight and wavy lines, respectively. Energy absorption is notated by intensity values I_a , and energy emission is indicated by reciprocal lifetime, $1/\tau$, values such that $1/\tau = k_p \text{ sec}^{-1}$, the rate of phosphorescence.

Based on the excitation and emission data, two energy transfer processes are known to occur in this dyed polyamide system. Energy transfer between the nylon and the dye-nylon complex proceeds through a triplet-triplet transfer mechanism. Energy transfer between the free dye (noncomplexed) and the dye-nylon complex proceeds through either a singlet-triplet or a triplet-triplet mechanism. The luminescence data for the dyed nylons indicate that a singlet-triplet transfer may predominate since excitation of the dyed nylon with 380 nm radiation (which corresponds to the S_2 state of the dye) results in emission from the complex. Excitation of the dye to its second excited singlet state may be followed by intersystem crossing to the second excited triplet state of the dye and energy transfer to the triplet state of the complex could occur. However, the energy of the T_2 state of the dye is unknown. It may be a higher energy state than the T_1 state (470 nm) of the complex, in which case triplet energy transfer would occur or it may be a lower energy state than the T_1 state of the complex and triplet transfer would be hindered.

The exact nature of the dye-nylon complex is unknown. Since acid dyes from ammonium salts with the polyamide's free amine and groups upon dyeing,^{52,53} it is conceivable that the complex is the dye-nylon salt. Mixtures of Acid Blue 40 and hexamethylenediamine or 1-aminoethanol in ethanol exhibited excitation and emission spectra (EX: 335 nm, EM: 470 nm; and EX: 320 nm, EM: 450 nm, respectively) similar to the excitation and emission spectra of the dyed

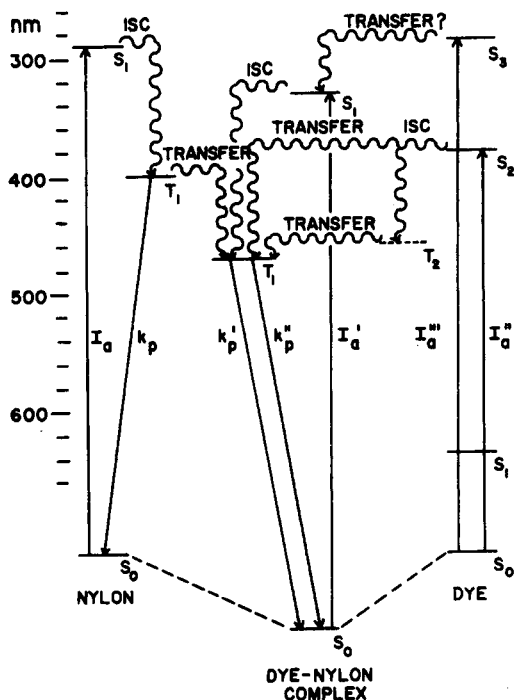


Fig. 6. Energy level diagram showing the energy transfer processes between nylon 66 and the dye-nylon complex and the free dye and the dye-nylon complex. Wavy lines are nonradiative events and solid lines are radiative processes. The unknown energy of the free dye's T_2 state is depicted by the broken line energy state.,

nylons. However, the absorption spectra of the ammonium salts of the dye did not differ from the spectrum of the sodium salt of the dye. This indicates that the luminescence from the dye ammonium salt should occur at wavelengths greater than 625 nm. Thus, the observed luminescence from the dye-amine mixtures is most probably fortuitous emission from an impurity. Mixtures of hexamethylenediamine or 1-aminohexane with sulfuric or formic acid in ethanol did not luminesce at room temperature or 77°K, indicating that the ammonium salt is not responsible for the characteristic dye-nylon complex emission.

In view of these results, the nature of the dye-nylon complex and the free dye are uncertain. The free dye is probably the dye-nylon ammonium salt, and the dye-nylon complex is attributed to either a dispersed type dye in the nylon or a dye-nylon ammonium salt complexed with an adjacent polyamide molecule. Since Acid Blue 40 dyes basic dyeable nylon, the dispersed dye is favored as the energy-trapping complex.

Nylon 66 yarns containing 2% titanium dioxide were dyed with Acid Blue 40, and the excitation and emission spectra of the undyed and dyed dull nylons were recorded at 77°K. The excitation spectrum of the dull nylon displays a maxima at 290 and 365 nm (see Fig. 7), which agrees with the spectra published by Taylor et al.³⁴ The 290 nm excitation is the nylon electronic transition, and the weak 365 nm excitation is attributed to the titanium dioxide. Maximum emission occurs at 400 nm upon excitation of the dull nylon with 290 nm energy and at 480 nm upon exciting the dull nylon with 365 nm radiation. Since the intensities of the titanium dioxide excitation and emission are an order of magnitude

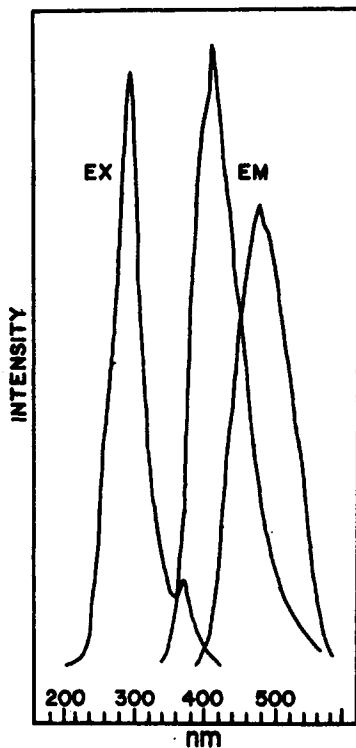


Fig. 7. Excitation and emission spectra of dull nylon 66 at 77°K. EX: 290 nm, EM: 410 nm; EX: 365 nm, EM: 480 nm.

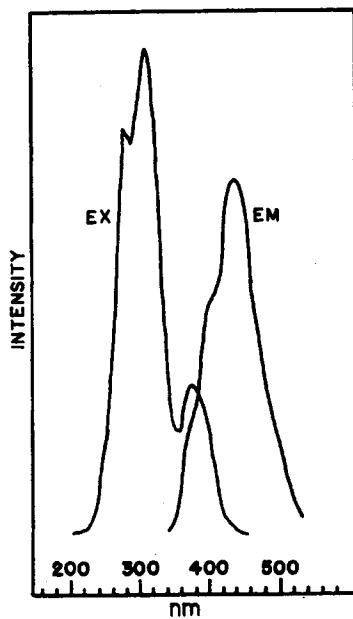
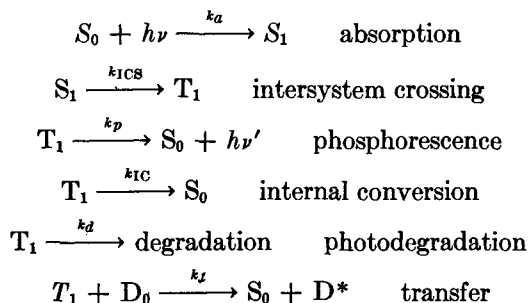


Fig. 8. Excitation and emission spectra of dyed ($0.53 \times 10^{-2}M$) dull nylon 66 at 77°K. EX: 290 nm, EM: 400 nm; EX: 330 and 380 nm, EM: 470 nm.

less than the nylon excitation and emission intensities and the energetics of the nylon and delustrant do not favor energy transfer,³⁴ the titanium dioxide does not alter the photophysical pathways of the nylon.

The excitation and emission spectra of the dyed dull nylon, shown in Figure 8, indicate that the presence of the delustrant does not alter the electronic transitions or the energy transfer mechanisms of the nylon-dye system. A transfer of triplet energy from the dye-nylon complex to the emitting state (480 nm) of the titanium dioxide is possible, but experimental evidence substantiating such a transfer was obscured due to the low intensity of the delustrant transitions and the loss of resolution by the light-scattering titanium.

Kinetic Analysis of the Energy Transfer Processes Occurring in Dyed Nylon 66. At 77°K, nylon 66 emits 400 nm radiation upon excitations at 290 nm. This emission is quenched upon dyeing the nylon with C.I. Acid Blue 40. The magnitude of the phosphorescence quenching, measured by the decrease in emission intensity and lifetime, increases with increasing dye concentration. The kinetics of such a quenching process have been well defined for solution and rigid media studies at low concentrations of donor and acceptor. Assuming that absorption, emission, and intersystem crossing processes are unimolecular and that quenching or transfer events are bimolecular, the following photophysical pathways must be included in the kinetic scheme:



where S and T refer to the singlet and triplet states of the nylon, D is the acceptor or dye-nylon complex, k is the rate constant, and "degradation" is the photochemical decomposition of the nylon. The rate expressions for these events are as follows:

$$dS_1/dt = k_a(S_0) = I_a \quad \text{absorption} \quad (1)$$

$$-dS_1/dt = k_{\text{ISC}}(S_1) \quad \text{intersystem crossing} \quad (2)$$

$$-dT_1/dt = k_p(T_1) = I_p \quad \text{phosphorescence} \quad (3)$$

$$-dT_1/dt = k_i(T_1) \quad \text{internal conversion and photo-degradation} \quad (4)$$

$$-dT_1/dt = k_t(T_1)(D) \quad \text{transfer} \quad (5)$$

where I_a and I_p respectively refer to the intensity of absorption and phosphorescence, and the rates of internal conversion and photodegradation are given in a collective rate constant, k_i , to aid in simplification of the kinetic treatment of the transfer process.

Assuming that a steady-state concentration of nylon singlet and triplet states is rapidly attained under steady illumination (excitation) conditions, the following Stern-Volmer equation may be derived:

$$1/I_p = 1/I_a (1 + k_i/k_p + k_t(D)/k_p). \quad (6)$$

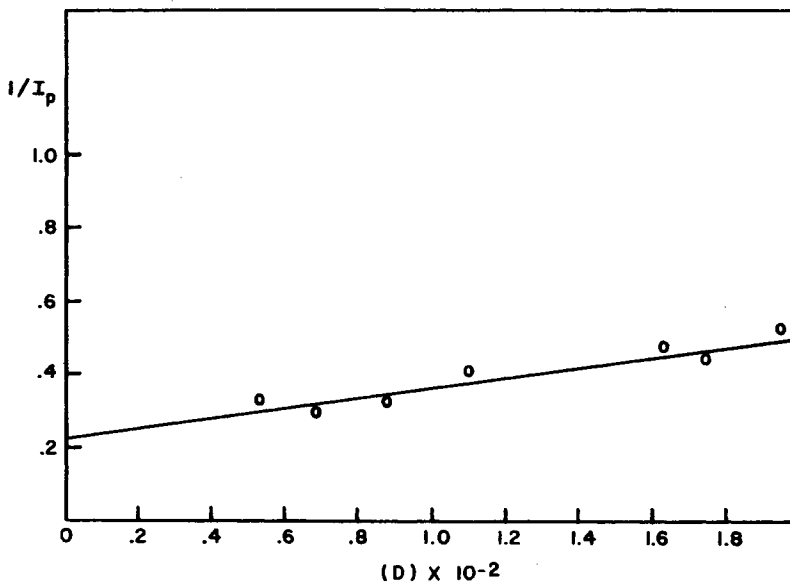


Fig. 9. Reciprocal of the intensity of nylon 66 phosphorescence as a function of dye concentration.

Since the emission intensity is dependent upon quencher concentration, only relative values of intensity and not absolute quantum values are needed.

Using the intensity data reported in Table I, a Stern-Volmer plot was constructed, as shown in Figure 9. The nylon phosphorescence intensity values are an average of at least eight individual measurements for a given dye concentration. The reproducibility of the intensity data was hampered since excitation and emission intensities were recorded from the surface of the nylon fibers. However, a linear trend is evident, and a least-squares analysis yields a slope of $k_t/k_p = 14.9$ l./mole. The magnitude of the transfer to phosphorescence ratio indicates that the dye-nylon complex efficiently quenches the triplet state of the polyamide.

The transfer rate constant may be evaluated from the dyed-nylon phosphorescence lifetimes since the mean lifetime of the nylon emitting state is dependent upon the sum of the processes which depopulate the polyamide triplet states. From eqs. (3) through (5) given previously, the mean lifetime of the nylon triplet state can be expressed as

$$\tau = [k_i + k_p + k_t(D)]^{-1}. \quad (7)$$

Figure 10 displays the linear relationship between $1/\tau$ and the dye concentration for the dyed bright nylon. A departure from linearity is evident at the higher dye concentrations. A least-squares analysis, neglecting the data for the greatest dye concentration ($1.95 \times 10^{-2}M$), yields a slope of $k_t = 45.8$ l. mole⁻¹ sec⁻¹ and an intercept of $k_i + k_p = 0.51$ sec⁻¹. The nonlinear increase of $1/\tau$ at the high dye concentration results from the dye absorbing the 290 nm incident radiation.

Theoretical Treatment of the Dyed Nylon 66 Triplet-Triplet Transfer. Several theoretical formulations pertaining to nonradiative energy transfer from a donor to an acceptor species have been proposed. Theoretical treatments of triplet-triplet transfer have been offered by Perrin,⁵⁴ Ermolaev,⁵⁵ Dexter¹³ and

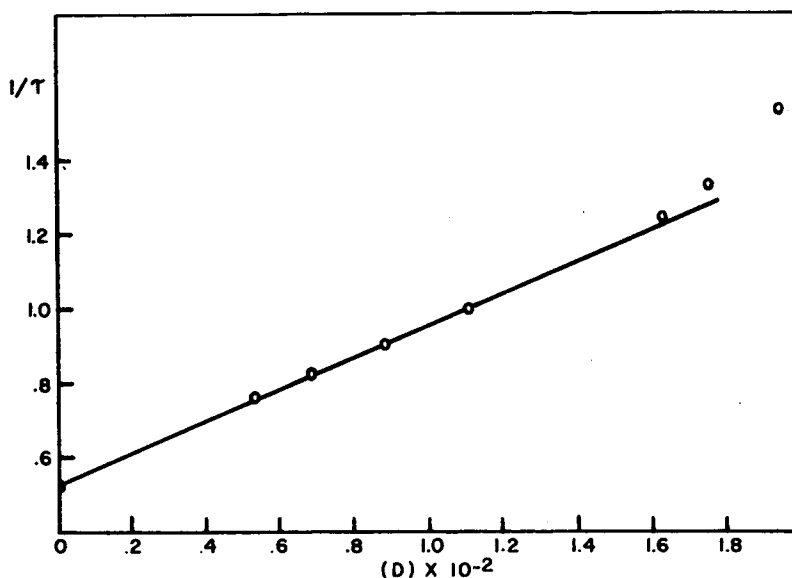


Fig. 10. Reciprocal lifetime of nylon 66 phosphorescence as a function of dye concentration.

Inokuti and Hirayama.¹⁸ These authors suggested that the energy transfer is dependent upon the distance between the donor and the acceptor. They proposed that the rate as well as the mechanism of transfer were dependent upon the acceptor concentration. (The Stern-Volmer⁵⁶ kinetic analysis, discussed in the previous section, assumes that the transfer is independent of the donor-acceptor distance.) Perrin⁵⁴ and Ermolaev⁵⁵ observed that generally the intensity of donor luminescence decreases exponentially with increasing quencher concentration. Perrin and Ermolaev independently derived eq. (8) relating the donor luminescence intensity with the acceptor concentration:

$$\log 1/I = (V N' C/2.303) + \log 1/I_0 \quad (8)$$

where I_0 and I are the intensity of donor luminescence in the absence and in the presence of acceptor, respectively; V is the volume of the quenching sphere; C is the concentration of acceptor in moles/l.; and $N' = 6.02 \times 10^{20}$, which converts the acceptor concentration from moles/l. to molecules/cm³. Perrin's treatment differs from the Stern-Volmer analysis in that a linear relationship is predicted between $\log 1/I$ and the dye (acceptor) concentration as compared to the reciprocal emission equation of Stern and Volmer. Using the same intensity data, a Perrin plot was constructed which is displayed in Figure 11. A least-squares analysis yields a slope of $V N'/2.303 = 16.2 \text{ cm}^3$.

The slope of the Perrin plot yields a value for the volume V of the quenching sphere. The radius, R_0 , of the quenching sphere is the maximum allowed distance over which quenching may occur. A quenching sphere of $6.17 \times 10^{-20} \text{ cm}^3$ and a critical transfer radius of $R_0 = 24.6 \text{ \AA}$ are computed from the data. These values, although they are approximate, agree with the R_0 values of 36 \AA and 26 \AA reported by David and co-workers for the poly(vinylbenzophenone)-naphthalene¹⁹ and poly(phenyl vinyl ketone)-naphthalene²⁰ systems, respectively. Converting the quenching sphere volume to a critical concentration value, C_0 , in moles/l., using the relation $C_0 = (3 \times 10^3) \times (4 \pi N R_0^3)^{-1}$ yields $C_0 = 2.6 \times 10^{-2} M$, which is greater than the most concentrated dyed yarn studied. This

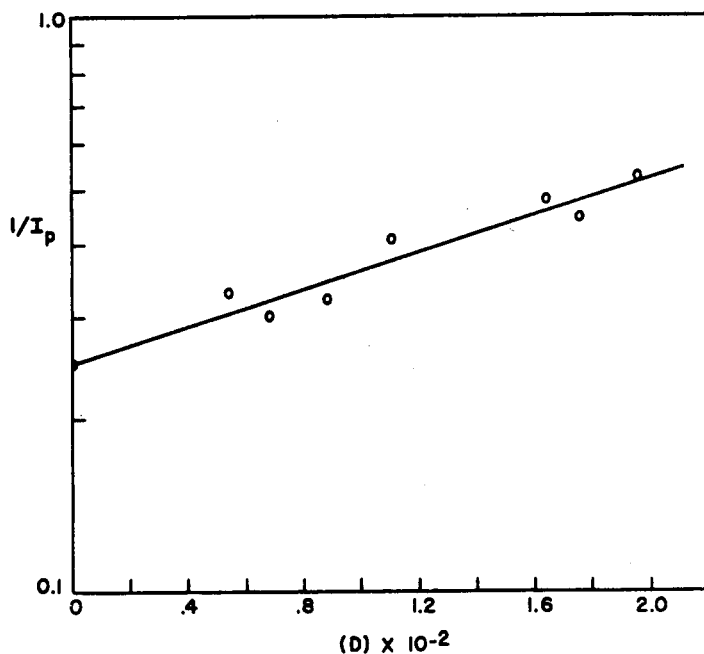


Fig. 11. Log of the reciprocal phosphorescence intensity of nylon 66 as a function of dye concentration.

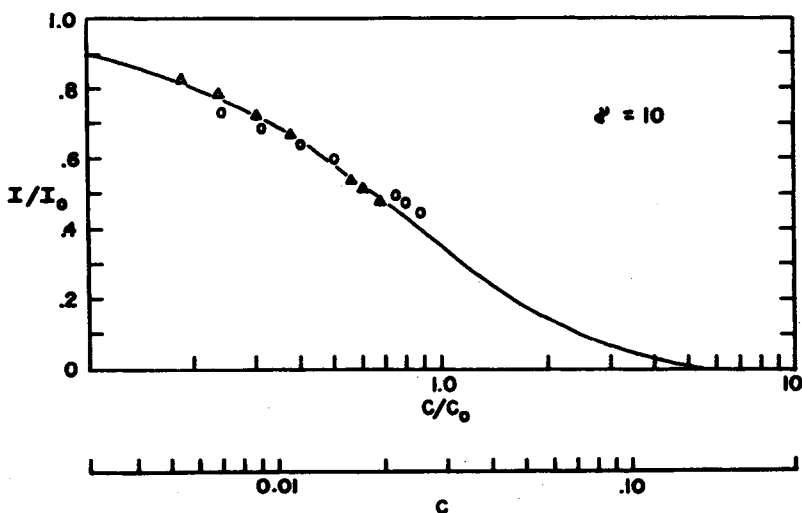


Fig. 12. Relative phosphorescence yield of nylon 66 as a function of the critical concentration: solid line, theoretical decay function; (O) data from Stern-Volmer treatment; (Δ) data from Perrin treatment.

discrepancy indicates the approximate nature of the Perrin model as applied to the dyed nylon transfer data.

Inokuti and Hirayama¹⁸ modified Dexter's¹³ expression for triplet-triplet energy transfer, and they outlined a graphic method for the evaluation of C_0 and R_0 using intensity or lifetime data. Theoretical decay curves of donor luminescence or lifetime as a function of the ratio of the acceptor concentration to the

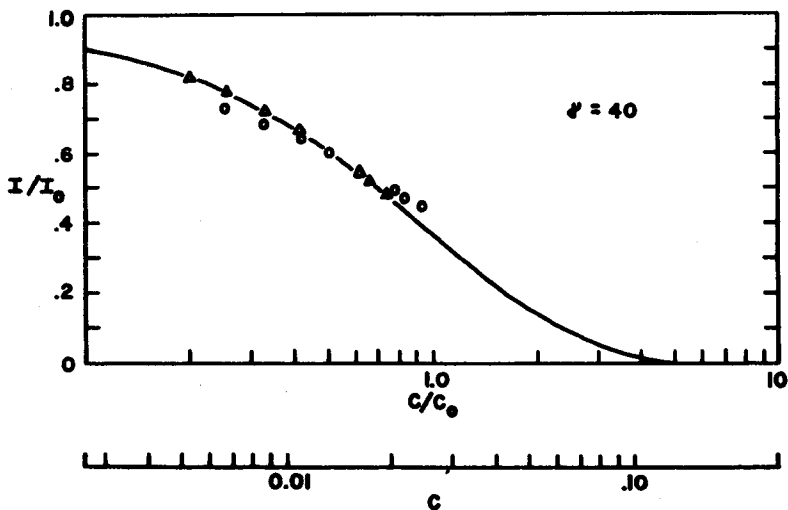


Fig. 13. The relative phosphorescence yield of nylon 66 as a function of the critical concentration: solid line, theoretical decay function; (O) data from Stern-Volmer treatment; (Δ) data from Perrin treatment.

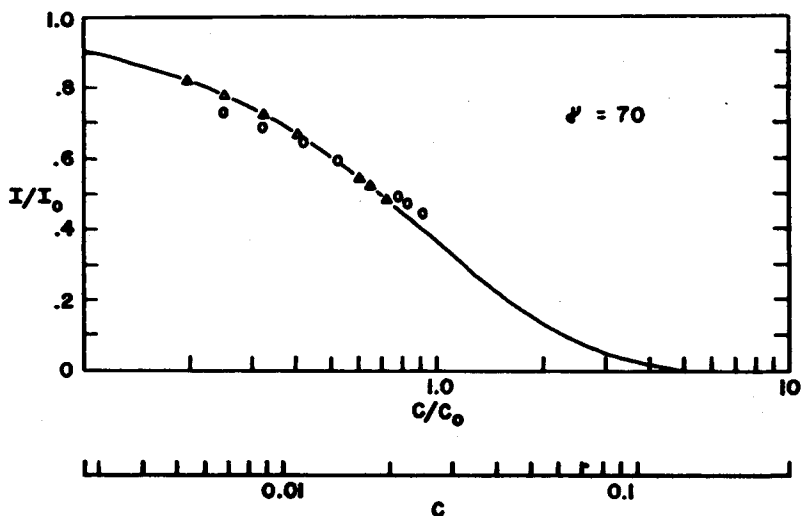


Fig. 14. Relative phosphorescence yield of nylon 66 as a function of the critical concentration: solid line, theoretical decay function; (O) data from Stern-Volmer treatment; (Δ) data from Perrin treatment.

critical concentration were constructed for various values of γ , where $\gamma = 2R_0/L$ in which L is a constant termed the "effective average Bohr radius."

Figures 12-14 display the theoretical curves (solid lines) for I/I_0 versus C/C_0 for $\gamma = 10, 40,$ and 70 , respectively. As expected, the Stern-Volmer emission intensity decay does not coincide with the exchange mechanism decay function. However, the nylon decay intensities for the Perrin model fit the exchange mechanism for all values of γ . Comparison of the Perrin model and the exchange interaction model for the nylon 66 quenching is given in Table II. The similarity of the R_0 and C_0 values indicate that if the triplet-triplet transfer from nylon to the dye-nylon complex occurs via a Perrin type decay of the donor lumines-

TABLE II
Comparison of Theoretical Quenching Models for the Triplet-Triplet
Transfer Between Nylon 66 and Acid Blue 40

| Model | C_0, M | $T_0, \text{\AA}$ |
|----------------------|-----------------------|-------------------|
| Perrin Treatment | | |
| Exchange interaction | | |
| treatment | 2.60×10^{-2} | 24.6 |
| $\gamma = 10$ | 2.90×10^{-2} | 24.0 |
| $\gamma = 40$ | 2.65×10^{-2} | 24.7 |
| $\gamma = 70$ | 2.70×10^{-2} | 24.5 |

TABLE III
Nonradiative Transfer Efficiencies for Dyed Bright Nylon 66

| $(D) \times 10^{-2}$, mole/l. | $f = k(D)/$ $[k_i + k_p + k_t(D)]$ | $f' = (I_0 - I)/I_0$ | |
|-----------------------------------|---------------------------------------|----------------------|--------|
| | | Stern-Volmer | Perrin |
| 0.53 | 0.322 | 0.266 | 0.180 |
| 0.68 | 0.378 | 0.313 | 0.220 |
| 0.88 | 0.440 | 0.353 | 0.275 |
| 1.10 | 0.495 | 0.405 | 0.333 |
| 1.63 | 0.593 | 0.511 | 0.447 |
| 1.75 | 0.610 | 0.522 | 0.474 |
| 1.95 | 0.635 | 0.551 | 0.520 |

cence, the transfer occurs by an exchange mechanism over a relatively large distance (24 Å).

Critical concentrations and critical transfer radius values may also be evaluated from the transfer efficiency f . The quantum efficiency of nonradiative energy transfer of nylon triplet energy to the dye-nylon complex may be defined as the ratio of the rate of transfer to the sum of the rates of all photo-processes:

$$f = k_t(D)/[k_i + k_p + k_t(D)]. \quad (9)$$

When the rate of nylon quenching is equal to the sum of the rates of all processes, the efficiency f is 0.50. The dye concentration corresponding to $f = 0.50$ may be defined as a critical concentration, C_0' . The transfer efficiencies for the various dye concentrations are listed in Table III. Interpolation of the data yields $f = 0.50$ at a dye concentration of $C_0' = 1.10 \times 10^{-2}M$. This corresponds to $R_0 = 33.1 \text{\AA}$. Since f is based on the Stern-Volmer kinetic scheme which is a distance independent transfer function, the C_0' and R_0 values are significant only in comparison with the critical values obtained by the Perrin and exchange interaction models.

Nonradiative transfer efficiencies may also be evaluated from donor emission intensity data. The transfer efficiency f' is defined as

$$f' = (I_0 - I)/I_0. \quad (10)$$

The transfer efficiencies of the dyed nylons based on the intensity data of the least-squares analysis of the Stern-Volmer and Perrin models are given in Table III. Interpolation of the data to $f' = 0.50$ yields $C_0' = 1.55 \times 10^{-2}M$, $R_0 = 29.6 \text{\AA}$ and $C_0' = 1.86 \times 10^{-2}M$, $R_0 = 27.8 \text{\AA}$ for the Stern-Volmer and the Perrin treatments, respectively.

These treatments of the kinetic and intensity data offer approximate values for the critical transfer radius ranging from 24 to 33 Å. This distance corresponds to an energy transfer occurring over a distance equal to three (24 Å) or four (33 Å) amide groups of the nylon based on the polyamide crystal repeat distance⁵⁷ of 17.2 Å. These large R_0 values suggest that the nylon triplet energy migrates from one amide function to the next in an exciton fashion until a dye molecule is encountered which acts as an energy trap. Based on the dyed-nylon photophysical study, the dye molecule of the dye-nylon complex is responsible for the trapping process.

A quantitative evaluation of the energy migration can be obtained from the theory of Voltz and co-workers.⁵⁸ These authors expressed the transfer rate constant for singlet-singlet transfer in terms of diffusion D and migration L coefficient and obtained

$$k_t = 2 \Pi N(D + L)R_0 10^{-3} \text{ l. mole}^{-1} \text{ sec}^{-1} \quad (11)$$

where N is Avogadro's number and R_0 is the critical transfer distance for which the probability of transfer is $p = 0.50$ if $R \leq R_0$ and $p = 0$ if $R > R_0$. For triplet-triplet transfer in nylon at 77°K, $D = 0$ and R_0 is defined by Perrin's model where $p = 1$ if $R \leq R_0$ and $p = 0$ if $R > R_0$, so that

$$k_t = 4 \Pi N L R_0 10^{-3} \text{ l. mole}^{-1} \text{ sec}^{-1}. \quad (12)$$

Solving eq. (12) for L using $k_t = 45.8 \text{ l. mole}^{-1} \text{ sec}^{-1}$ and $R_0 = 24.6 \text{ Å}$ yields a migration coefficient of $L = 2.68 \times 10^{-13} \text{ cm}^2/\text{sec}$. Elementary diffusion theory relates the frequency of transfer w to the migration coefficient by

$$w = 6L/\bar{r}^2 \quad (13)$$

where \bar{r} is the root-mean-square displacement in time $1/w$. For $\bar{r} = 8 \text{ Å}$ (mean distance between amide groups in nylon 66), the transfer frequency is $w = 2.5 \times 10^2 \text{ sec}^{-1}$. This frequency is extremely small compared to 10^{12} sec^{-1} reported for singlet energy migration in benzophenone crystal (59) and $7 \times 10^4 \text{ sec}^{-1}$ for triplet-triplet transfer between poly(vinylbenzophenone) and naphthalene.¹⁹ However, considering that the mean lifetime of the nylon 66 triplet state is approximately 2 sec, 500 transfers among the amide functions can occur before deactivation or quenching of the excited state occurs. This value is in accord with the number of transfers which occur in poly(vinylbenzophenone) during the lifetime of its excited triplet state.

Photo-oxidative Degradation of Undyed and Dyed Bright Nylon 66. Undyed and dyed nylon yarns were irradiated in dry air with 300 nm radiation. The yarns were exposed 3 in. from the lamps at an intensity of $6 \times 10^{14} \text{ quanta cm}^{-3} \text{ sec}^{-1}$. The extent of degradation during various time intervals of exposure was measured by the percent loss in breaking strength. Table IV presents these data for the undyed nylon and dyed nylons, containing 0.53×10^{-2} , 1.10×10^{-2} , and $1.75 \times 10^{-2}M$ Acid Blue 40, that were exposed to the radiation from 5 to 60 hr. Relatively little degradation of the undyed nylon occurs until 60 hr of exposure. The dyed nylons behaved similarly to the control yarns up to 30 hr of irradiation. After 60 hr of exposure, the nylon yarns containing 0.52% ($1.10 \times 10^{-2}M$) and 0.83% ($1.75 \times 10^{-2}M$) dye degraded much less than the undyed nylon, indicating that the dye is photoprotecting the polyamide. However, the nylon containing 0.25% ($0.53 \times 10^{-2}M$) dye is observed to degrade more rapidly than the control nylon after 40 hr of irradiation, suggesting that a phototendering process occurs at low dye concentration. In addition to the photo-

TABLE IV
Per Cent Strength Loss of Undyed and Dyed Nylon 66 After Irradiation

| (D) $\times 10^{-2}M/\%$ add-on | Strength loss, % | | | | |
|------------------------------------|------------------|-------|-------|--------|-------|
| | 5 hr | 20 hr | 30 hr | 40 hr* | 60 hr |
| 0 | 0 | 7 | 9 | 12 | 59 |
| 0.53/0.25 | 6 | 9 | 9 | 46 | 65 |
| 1.10/0.52 | 0 | 3 | 9 | 11 | 11 |
| 1.75/0.83 | 0 | 5 | 5 | 15 | 15 |

* Irradiation time.

tendering at low dye concentration, a photobleaching of the dye was observed after 60 hr of exposure. This phenomenon was not observed with the nylon samples containing 0.52% and 0.83% dye.

The dependence of the polyamide degradation upon the dye concentration may be readily explained in terms of the dyed-nylon photophysical energetics. The dye polyamide displays excitation maxima at 290, 330, and 380 nm. Since the accelerated degradation studies were performed using 300 nm radiation (see experimental section), no excitation of the nylon (290 nm) to an excited electronic state could occur. However, 300 nm radiation is absorbed by the dye-nylon complex (330 nm). At high dye concentrations, most of the incident energy is absorbed by the free dye exciting the dye to its second excited singlet state. The excited dye may dissipate this energy by transfer to the dye-nylon complex, as discussed previously, or by radiationless decay to the ground state. The latter process was shown to be highly efficient since no luminescence of the dye was observed. This efficient energy delocalization serves as a mechanism to protect the polyamide substrate from energy localization and hence degradation. At low concentrations of dye most of the incident radiation is absorbed by the dye-nylon complex. Following absorption, intersystem crossing to the triplet manifold of the complex occurs. The triplet energy (470 nm) may be delocalized by phosphorescence or tunneling (radiationless internal conversion to the ground-state singlet). The long lifetime (0.20 sec) of the triplet state indicates that internal conversion to the ground state of the complex is not efficient and that the energy is localized for a sufficient time to warrant a chemical reaction leading to the polyamide degradation. For the nylon containing 0.25% dye, the complex absorbs 71% of the incident radiation and phototendering occurs, whereas 60% of the incident radiation is absorbed by the free dye for the 0.83% dyed nylon and photoprotection occurs. The degradation that is observed at the higher dye concentrations is due to the transfer of energy from the free dye to the dye-nylon complex and the absorption of incident radiation by the complex.

Supportive evidence that the phototendering mechanism proceeds through the complex is obtained from an analysis of the photophysical events in the irradiated undyed and dyed nylon yarns. Table V lists the excitation and emission wavelengths and the mean lifetimes of the undyed and dyed nylon yarns at 77°K after 30, 60, 100, and 128 hr of exposures to the 300-nm radiation source described for the degradation experiments. The intensity of the 300-nm lamps was 20 quanta $\text{cm}^{-2} \text{sec}^{-1}$ less than the intensity recorded during the accelerated light weathering. (At this reduced intensity, no photobleaching of the dye was

TABLE V
Excitation and Emission Maxima and Mean Lifetimes* of Undyed and Dyed Nylon 66 After Various Exposure Times to 300 nm Radiation

| (D) × 10 ⁻³ M | 30 hr | | | 60 hr | | | 100 hr | | | 128 hr | | |
|--------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | EX, nm | EM, nm | τ, sec | EX, nm | EM, nm | τ, sec | EX, nm | EM, nm | τ, sec | EX, nm | EM, nm | τ, sec |
| 0 | 280 | 410 | 0.80 | 275 | 415 | 0.20 | 275 | 420 | 0.20 | 275 | 420 | 0.20 |
| 0.53 | 280 | 420 | 0.60 | 280 | 420 | 0.60 | 300 | 440 | 0.30 | 300 | 440 | — |
| 0.68 | 280 | 420 | 0.50 | 280 | 420 | 0.45 | 280 | 420 | 0.60 | 280 | 420 | 0.60 |
| 0.88 | 280 | 420 | 0.45 | 280 | 420 | 0.40 | 280 | 420 | 0.45 | 280 | 420 | 0.60 |
| 1.10 | 285 | 420 | 0.40 | 285 | 420 | 0.30 | 280 | 420 | 0.40 | 280 | 420 | 0.50 |
| | 330 | 460 | — | 330 | 460 | — | 280 | 420 | 0.35 | 280 | 420 | 0.40 |
| 1.63 | 285 | 420 | 0.35 | 285 | 420 | 0.20 | 285 | 420 | 0.30 | 280 | 420 | 0.35 |
| | 330 | 460 | — | 330 | 460 | — | 330 | 460 | — | 330 | 460 | — |
| 1.75 | 285 | 420 | 0.30 | 285 | 420 | 0.30 | 285 | 420 | 0.20 | 280 | 420 | 0.30 |
| | 330 | 460 | — | 330 | 460 | — | 330 | 460 | — | 330 | 460 | — |
| 1.95 | 285 | 420 | 0.25 | 285 | 420 | 0.30 | 285 | 420 | 0.30 | 280 | 420 | 0.30 |
| | 330 | 460 | — | 330 | 460 | — | 330 | 460 | — | 330 | 460 | — |

* The dash (—) indicates that the lifetime was not measurable.

observed even after 128 hr of exposure.) After 30 hr of exposure, the undyed nylon exhibits excitation at 280 nm and emission at 410 nm, with a mean lifetime of 0.80 sec. After 60, 100, and 128 hr of exposures, the undyed nylon excitation and emission maxima remain constant at 275 and 420 nm, respectively, with a mean lifetime of 0.20 sec. The shift in the undyed nylon excitation appears to correlate with the degree of nylon chain cleavage until some limiting value of chain length is reached. At this point, any further decrease in the degree of polymerization (D.P.) does not affect the electronic states of the amide chromophores. This assumes that the amide functions behave as conjugated chromophores until some minimum D.P. is attained which does not favor conjugation and the amide groups act as isolated chromophores. The bathochromic shift in the singlet-triplet energy splittings with a decrease in D.P. support this argument.

After 30 to 128 hr of irradiation, the excitation and emission spectra of the nylons containing 0.25%, 0.32%, and 0.42% dye resemble the spectra of the undyed degraded nylons. The lack of excitation maxima at 330 and 380 nm indicates that the dye-nylon complex deteriorates upon exposure to the ultraviolet radiation. Since the excitation and emission maxima of these exposed samples correspond to the spectra of the degraded undyed nylons, it appears that the nylon degradation proceeds through the complex at the complex's expense.

The excitation and emission spectra of the 0.77 ($1.63 \times 10^{-2}M$) to 0.92% ($1.95 \times 10^{-2}M$) dyed nylons display excitations at 285–280 and 330 nm and emissions at 420 and 460 nm after 30 to 128 hr of exposures. These excitations and emissions correspond to the degraded nylon and the dye-nylon complex maxima. No excitation maximum at 380 nm was observed although it is expected if the dye-nylon complex is present. However, excitation of the exposed samples (0.77–0.92%) with 380 nm energy resulted in a very weak (5% of that for 330 nm excitation) emission of 460 nm radiation. The concentration of the complex may be reduced to the extent that energy transfer from an excited dye molecule would have to occur over too great a distance, $R \gg R_0$, and the transfer probability would be greatly reduced.

The tensile and photophysical data suggest that the dye-nylon complex is responsible for the nylon phototendering. The complex, acting as an energy trap, quenches the excited states of the polyamide and the free dye by transfer processes. This quenching localizes the absorbed energy in the triplet state of the complex which is sufficiently long-lived to initiate photochemical degradation processes. The initiation of nylon photo-oxidative degradation was reported⁶⁰ to occur by hydrogen abstraction from the carbon alpha to the amide nitrogen. The energy of the dye-nylon complex singlet (330 nm) and triplet (470 nm) is sufficient for such a hydrogen abstraction. Thus, even though the acid dye accelerates the nylon degradation, the initiation and propagation paths may very well be the same since the phototendering degradation of the dyed nylon proceeds without the photodecomposition of the dye.

Energy of 300 to 5000 nm reaches the earth's surface from the sun. This is insufficient to excite nylon 66 to its first excited singlet state (290 nm). Singleton and co-workers⁶¹ observed that nylon 66 degraded much slower when exposed to visible light as compared to ultraviolet exposure. Visible light energy promotes nylon 66 to an upper vibrational level within the ground electronic state, and energy delocalization by vibrational decay is highly efficient. Ultra-

violet energy promotes nylon 66 to an excited electronic state in which energy delocalization is less efficient, thereby increasing the probability of chemical decomposition of the polymer substrate.

The photophysical study of nylon 66 dyed with Acid Blue 40 revealed that the energetics of the system involved electronic transitions at 290, 330, and 380 nm. As discussed previously, exposure of the undyed nylon to sunlight leads to slow degradation occurring via upper vibrational levels of the ground state. However, upon exposure of the dyed nylon to sunlight, electronic transitions (330 and 380 nm) occur increasing the probability of photo-oxidative degradation. Thus, incorporation of Acid Blue 40 into the polymeric substrate of the nylon introduces lower-energy electronic states which are accessible to the nylon upon excitation by sunlight.

CONCLUSIONS

The luminescent behavior of the model amides, *N*-hexylhexanamide, *N,N'*-bis(hexyl)adipamide, and 1,6-hexamethylenebis(hexanamide), suggests that the characteristic phosphorescence of nylon 66 occurs from the amide chromophore. This luminescent triplet state is probably of mixed $^3(n - \Pi^*)/{}^3(\Pi - \Pi^*)$ character since a destruction of the amide chromophore conjugation by photo-oxidative degradation results in a decrease in luminescent intensity and an increase in the singlet-triplet energy splitting.

Excitation and emission spectra of the undyed and Acid Blue 40 (62125)-dyed nylon 66 yarns indicate that a dye-nylon complex between the ground states of the dye and the polyamide is formed during dyeing. Quenching studies indicate that a triplet-triplet energy transfer between the excited nylon and the complex occurs efficiently with a transfer rate constant of $45.8 \text{ l. mole}^{-1} \text{ sec}^{-1}$. An additional energy transfer occurs between the excited free dye and the complex by either a singlet-triplet or a triplet-triplet mechanism. Kinetic analysis of the triplet-triplet nylon complex transfer indicates that the nylon triplet energy migrates 24 to 33 Å along the amide chromophores in an exciton fashion until a dye-nylon complex is encountered. At this point, energy transfer occurs by an exchange interaction mechanism. The presence of titanium dioxide appears to have no influence on the photophysical processes of the dyed nylon.

The exact chemical nature of the dye-nylon complex and the free dye is unknown. Luminescence and photo-oxidative studies suggest that the dye-nylon ammonium salt is the "free dye" and the energy-trapping complex is formed between the polyamide and a dispersed-type Acid Blue 40 dye molecule.

The photo-oxidative studies verify that the dye-nylon complex acts as an energy trap which sensitizes the nylon 66 photochemical degradation. The complex initiates the nylon degradation at the expense of the complex. Since no photobleaching of the acid dye is observed in the early stages of degradation, the deterioration of the complex probably occurs due to the photochemical destruction of the polyamide at the complex site.

The incorporation of Acid Blue 40 into the nylon 66 effectively alters the electronic states available to the dye-nylon system upon exposure to sunlight. The electronic states of the undyed polymer are not accessible to the nylon exposed to sunlight. The free dye and the dye-nylon complex possess lower-energy electronic states which serve to localize the radiant energy from the sun.

Such energy localization effectively initiates photo-oxidative processes in the nylon substrate.

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