LUMINESCENCE AND DEGRADATION OF NYLON POLYMERS: PART I: PHOTO-OXIDATION PROCESSES INVOLVING PHOSPHORESCENT SPECIES

N. S. ALLEN, J. F. McKELLAR and D. WILSON

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Gt. Britain)
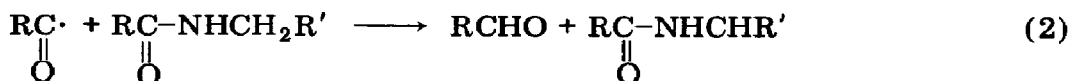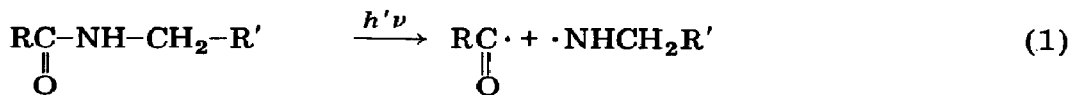
Summary

The thermal and photochemical oxidation of nylon polymers has been studied by luminescence spectroscopy. All the nylon polymers exhibit phosphorescence emission in the wavelength region 400 - 500 nm which is concluded to originate from impurity oxidation products formed during polymerization and processing. Mild oxidation of model amide compounds produces a phosphorescent species whose emission spectrum closely matches that of the polymer. The phosphorescence from the polymer and model amides exhibits several characteristic features that indicate their source to be α,β-unsaturated carbonyl groups. From a comparison of the phosphorescence excitation spectrum of the oxidized model amides with the absorption spectra of two possible general structural types of model α,β-unsaturated carbonyls, the phosphorescence is concluded to originate from dienone chromophoric units. These species appear to play an important rôle in the sunlight-induced oxidation of the polymer.
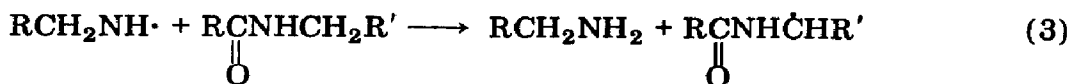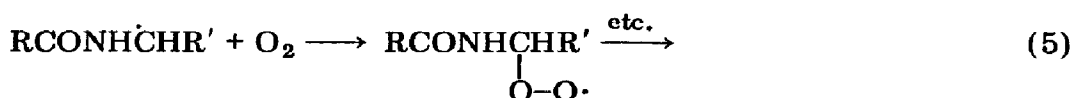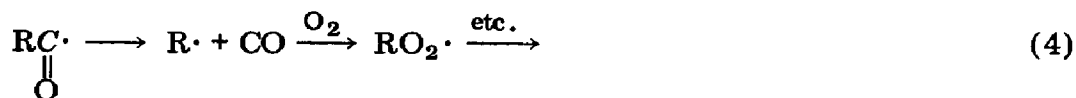

Introduction

In earlier studies on the photo-oxidation of nylon polymers the amide linkage has been considered to be the focal point of attack [1, 2]. Essentially two mechanisms are believed to operate in the light-induced degradation of nylon polymers depending on the wavelength of irradiation [1 - 3].

(1). With light of wavelengths <300 nm direct C–N bond scission occurs at the amide linkage to give free radical products which are capable of further reaction with the substrate, *e.g.*

$$\underset{\underset{O}{\|}}{RC}-NH-CH_2-R' \xrightarrow{h'\nu} \underset{\underset{O}{\|}}{RC}\cdot + \cdot NHCH_2R' \qquad (1)$$

$$\underset{\underset{O}{\|}}{RC}\cdot + \underset{\underset{O}{\|}}{RC}-NHCH_2R' \longrightarrow RCHO + \underset{\underset{O}{\|}}{RC}-NHCHR' \qquad (2)$$

$$RCH_2NH\cdot + RCNHCH_2R' \longrightarrow RCH_2NH_2 + RCNH\dot{C}HR' \qquad (3)$$
$$\quad\;\; \overset{\|}{O} \qquad\qquad\qquad\qquad\qquad\quad \overset{\|}{O}$$

(2). With light of wavelengths >300 nm the presence of oxygen is necessary for degradation to occur. The processes here again involve the formation of radical products formed from direct C–N bond scission. Oxidative attack can then take place at the methylene group α to the nitrogen atom, as for reactions (1), (2) and (3) above. The free radical species undergo further propagative reactions with oxygen to form peroxy radicals *e.g.*

$$R\dot{C}\cdot \longrightarrow R\cdot + CO \xrightarrow{O_2} RO_2\cdot \xrightarrow{etc.} \qquad (4)$$
$$\overset{\|}{O}$$

$$RCONH\dot{C}HR' + O_2 \longrightarrow RCONHCHR' \xrightarrow{etc.} \qquad (5)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{O-O\cdot}{|}$$

One important criticism of these two reaction schemes is that the same initiation reaction involving direct C–N bond scission has been postulated to occur with light of wavelengths above and below 300 nm [2 - 4]. The question then arises as to why oxygen is necessary for degradation of the polymer to occur with light >300 nm since degradation could just as easily occur in its absence. This suggests that the sunlight-induced oxidation of nylon polymers with light >300 nm is more complex than hitherto realized.

It has been suggested that "chromophoric impurity centres" in the commercial polymer are involved in the photo-oxidation but their precise nature or function has not yet been established [3 - 5]. Further, since the amide carbonyl group does not absorb light at wavelengths >260 nm it appears to us that impurity chromophores must be responsible for the major portion of the light absorbed (*i.e.* that portion of the wavelength range of sunlight) that is responsible for photo-oxidation of the polymer under the exposure conditions of technological application. Indeed, recent work has shown that the commercial nylons exhibit phosphorescence from impurity chromophores that absorb light in the wavelength region 290 - 350 nm [6 - 10].

Contrary to these conclusions, Roberts and coworkers [11, 12] have recently suggested that the phosphorescence emission from nylon polymers is from the amide chromophore itself and that the absorption process for light above 290 nm involves a weak spin-forbidden singlet–triplet transition. Their evidence for this conclusion was based on their observation of a weak emission from several "pure" model amide compounds, but many other workers have shown that simple "pure" amide compounds just do not phosphoresce [6 - 10, 13, 14]. For example, studies by McGlynn and coworkers [13, 14] have shown that only structurally perturbed amide chromophores such as (I) can phosphoresce via the absorption process proposed by Roberts *et al.* [11, 12].

(I)
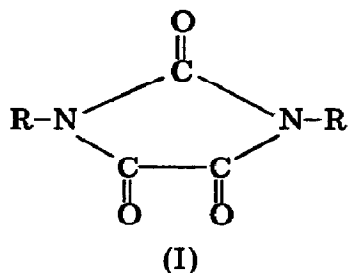
It is difficult to see how such structures can be present in the commercial polymer even allowing for the undoubted influence of strong intermolecular hydrogen bonding forces that exist between adjacent chains in either the crystalline or amorphous regions of the polymer [15].

Here we report on the phosphorescence properties of the commercial nylons *e.g.* the -6, -6, 6, -11 and -12 polymers. Also, since light stability is known to be markedly influenced by their thermal history [5] we have examined the effect of both thermal and photochemical oxidation on the polymer phosphorescence. Finally, the thermal oxidation of model amide compounds such as N,N'-di-n-butyladipamide and N,N'-dicaproylhexamethylene diamine has been studied to obtain information on the identity of the phosphorescent species in the polymer.

Experimental

Materials

Nylon polymer in chip and film form (125 μm) containing no commercial additives was obtained from I.C.I. Ltd as also was the sample of nylon-6,6 salt.

Zone-refined samples of N,N'-di-n-butyl adipamide (m.p. 167.5 °C) and N,N'-dicaproylhexamethylenediamine (m.p. 141.8 °C) were obtained from the Fine Chemicals Service of I.C.I. Ltd, and used without further purification.

The α,β-unsaturated carbonyl compounds pent-3-ene-2-one and 2,6-dimethyl-hept-2,5-diene-4-one were purified by distillation under vacuum.

Polymerization

The nylon-6,6 polymer was prepared in a laboratory autoclave, by the method recommended by White and Jones [16]. Samples of molten polymer were extruded at each stage of the polymerization process, rapidly quenched with water and cut to a fine chip form.

Thermal oxidation

Nylon-6,6 film was oxidized in an oven for 1 h at 180 °C.

Samples of the model amide compounds were heated in an oil bath at 180 °C in 5 mm O.D. quartz tubes under vacuum and in air for 30 minutes.

Photo-oxidation

The nylon-6,6 film was irradiated in a Xenotest-150 weatherometer (Original Hanau, Quartzlampen, GmbH). The exposure conditions were for natural sunlight simulation (45% relative humidity; 40 °C).

Luminescence measurements

Corrected phosphorescence spectra were obtained using a double grating (1200/mm) Hitachi Perkin-Elmer MPF-4 spectrofluorimeter equipped with two R446-F photomultiplier tubes. Phosphorescence lifetime measurements (<0.1 s) were obtained by coupling the sample intensity signal from the fluorimeter to a Tetronix DM-64 storage oscilloscope and adjusting the speed of the chopper until a stationary wave form of the phosphorescence decay was obtained. Phosphorescence lifetimes >0.1 s were obtained by chopping the excitation light with an electrically controlled shutter built into the instrument and storing the decay on the oscilloscope screen.

Results

Phosphorescence spectra of all the nylon polymers except that of nylon-6,6 chip (Table 1) consisted of broad bands with emission maxima between 400 - 500 nm. The emission wavelength maxima varied on changing the excitation wavelength. Differences in phosphorescence lifetimes were also observed. In general, the lifetimes were longer for those bands of shorter wavelength. The emission lifetimes were also longer from the more densely crystalline nylon-6,6 and nylon-6 compared to those of the less densely crys-talline nylon-11 and nylon-12 [15]. A final feature of the phosphorescence spectrum of nylon-6,6 was that when the polymer was in chip form it showed two distinct emission bands, when an excitation wavelength between 300 and 320 nm was used. Table 1 shows that following spinning of the chip into filament form only one broad emission band is observed.

Polymerization of nylon-6,6 salt

Weak phosphorescence emission was initially observed from samples of the nylon-6,6 salt that is used for polymer preparation. In the polymeriza-tion process, the polymer is prepared in stages [16] and after each stage samples were extracted for examination. These showed that the intensity of the phosphorescence emission markedly increased and exhibited structure similar to that already described for the nylon-6,6 polymer, after stages 3 and 4 (Fig. 1). There was also a gradual increase in the phosphorescence emission lifetime after each successive polymerization stage. However, when nylon-6,6 salt was heated for 1 h at 180 °C under vacuum conditions (0.1 Torr) there was no evident generation of phosphorescence.

Thermal oxidation of nylon-6,6 polymer

On thermally oxidizing nylon-6,6 chip at 180 °C in air the polymer acquired new longer wavelength phosphorescence emission bands and lost its

TABLE 1

Phosphorescence properties of nylon polymers.

Polymer	Excitation, λ (nm)	Emission, λ (nm)	Mean lifetime, τ (s)
Nylon-6,6 chip	295 max 310 315	410 max 415; 460 420; 460; 480	2.10 1.6; 0.6 0.7; 0.25; 0.20
Nylon-6,6 fibre	295 max 300 315	450 460 470	1.20 0.70 0.30
Nylon-6 chip	282 max 300 310	390(s); 420; 455(s) 460 470	1.7; 1.6; 1.1 0.80 0.58
Nylon-11 chip	269(s); 273 300 310	423; 450(s) 460 465	1.0; 0.88 0.60 0.60
Nylon-12 chip	268; 286(s) 300 310	363(s); 410 465 475	1.0 0.60 0.60

τ = Time for phosphorescence to decay to $1/e$ of its initial intensity. (s) = shoulder.
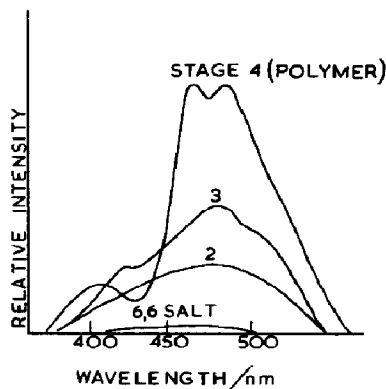

Fig. 1. Changes in phosphorescence after successive stages of the polymerization of nylon-6,6. Excitation λ = 315 nm.

original shorter wavelength band (410 nm) (see Fig. 4 later). The excitation λ_{max} of the polymer also shifted to longer wavelengths (*i.e.* >300 nm) into the near ultra-violet region of natural sunlight. Further, nylon-6,6 fibre, having undergone some degree of thermal oxidation during spinning exhibits similar longer wavelength phosphorescence emission bands to those of thermally oxidized chip. In the absence of oxygen, the same thermal treatment had no effect on the phosphorescence.
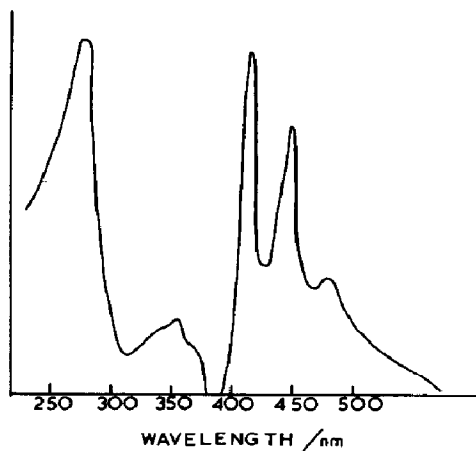
Fig. 2. Phosphorescence excitation and emission spectrum of the thermally oxidized model amides in EPA glass at 77 K.
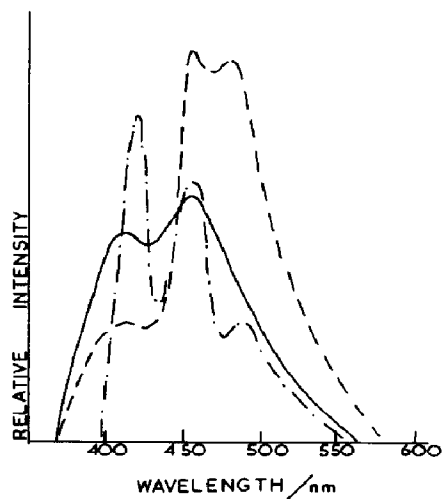Fig. 3. Comparison of the phosphorescence emission from nylon-6,6 chip (excitation λ = 310 nm) (——) (S × 300), (excitation λ = 315 nm) (----) (S × 450) with that from the thermally oxidized model amides (excitation λ_{max} = 273 nm and 350 nm) (—·—).
S x = sample signal sensitivity.

Thermal oxidation of model amides

Neither amides showed significant emission before heating or even after heating under vacuum. The amides were subjected to heating periods of about 30 min at temperatures just above their melting points ($\sim$180 °C). After the same heating period in the presence of air, however, phosphorescence emission was observed and will be described and compared with the corresponding emission from nylon-6,6 polymer.

The phosphorescence emission from the model compounds was highly structured and the wavelength maxima did not vary on changing the excitation wavelength. Figure 2 shows the phosphorescence excitation and emission spectra obtained from the thermally oxidized model amide compounds dissolved in EPA glass at 77 K. It is seen that the excitation spectrum has a distinct maximum at 273 nm with rather weak and diffuse structure above 300 nm. The emission spectrum is highly structured with wavelength maxima at 417, 448.5 and 485 nm and a vibrational-splitting of 1685 cm^{-1} (see Table 3 later). The lifetime of the emission was 5 ms.

Figure 3 compares the phosphorescence emission from the oxidized model amide compounds with that from the nylon-6,6 polymer. Although the polymer emission λ_{max} values vary with change in the excitation wavelength the two spectra are remarkably similar and both have a mean vibrational splitting of about 1700 cm^{-1} (see Table 3 later). However, the mean lifetimes of the phosphorescence emission from the oxidized model amides and polymer differ and the reason for this will be discussed later.
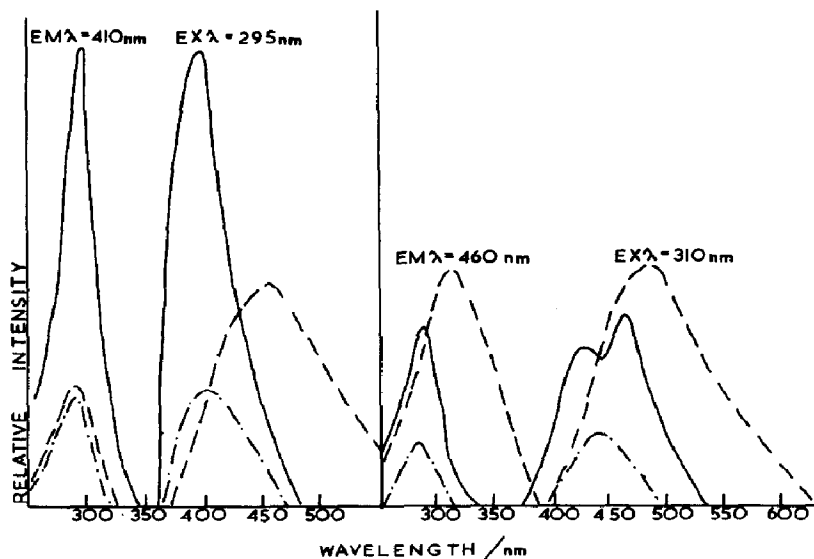
Fig. 4. Phosphorescence spectrum of nylon-6,6 film before (——) and after thermal oxidation at 180 °C for 1 h (----) and photo-oxidation in a Xenotest —150 weatherometer for 450 h (·—·—·).

Photo-oxidation

On sunlight simulated (Xenotest-150; 40 °C; 45% relative humidity) photo-oxidation of the nylon-6,6 film further interesting changes in the phosphorescence occurred. First, Fig. 4 shows that on irradiation there was an overall decrease in the intensity of the phosphorescence emission together with a shift of the emission λ_{max} to shorter wavelengths. Second, Table 2 shows that on photolysis of previously thermally oxidized nylon-6,6 film, where the longer wavelength bands are strongly evident (see above), a decrease in the relative intensities of the longer wavelength emission bands is observed together with a shift in their λ_{max} to shorter wavelengths. The emission intensity of the unirradiated film at 455 nm was used as the reference.

Discussion

The striking similarity between the phosphorescence from the thermally oxidized "nylon-6,6 model" amides and that of the commercial nylon-6,6 polymer clearly indicates the chemical nature of the emitting species must be of a type common to both. Also, since the excitation spectrum extends above 300 nm then, for the reasons given above, it is likely that the phosphorescent species may participate in the photo-oxidation of the polymer. Further, since thermal oxidation produces a marked shift to longer wavelengths in the excitation spectrum of the phosphorescence, evidently this will also favour an increase in the photosensitivity of the commercial polymer to sun-

TABLE 2

Effect of irradiation on the phosphorescent oxidation products of
thermally oxidized nylon-6,6 film (125 μm).

Irradiation time (h)	Excitation, λ (nm)	Emission, λ (nm)	Ratio excitation band intensities (ref emission = 455)
0	280	455	1.0
25	280	435	0.85
68	280	430	0.80
100	280	430	0.75
0	300	465	0.95
25	300	460	0.60
68	300	455	0.53
100	300	450	0.50
0	320	480	0.88
25	320	475	0.38
68	320	470	0.32
100	320	470	0.31

TABLE 3

Wavenumbers of peaks in the phosphorescence emission spectra
of nylon-6,6 chip, thermally oxidized model amides and a typical
dienone.

	λ (nm)	$\nu \times 10^2$ (cm^{-1})	$\Delta\nu \times 10^2$ (cm^{-1})
Nylon-6,6 chip	410 - 420	244 - 238	
	450 - 460	222 - 217	17.00
	475 - 480	210 - 208	
Model amides*	417	239.8	
	448.5	222.9	16.85 ± 10
	485	206.2	
Dienone[†]	415.2	240.9	
	446.4	224	16.70 ± 50
	480.9	207.9	

*In EPA glass at 77 K.
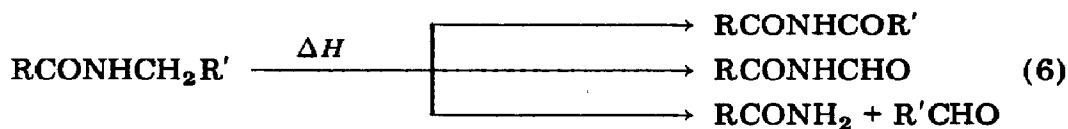[†]4,4'-diphenylcyclohexadienone in EPA glass [23] at 77 K.

light — an effect we have also noted with the commercial polyolefins, parti-
cularly polypropylene [8, 17]. Finally, the photochemical reactions that
these impurities undergo are of interest in stabilizing the polymer to the
oxidative processes induced by sunlight; this topic will be examined in sub-
sequent parts of this work. A preliminary note on the mechanism of the
stabilizing effect of halide ions has been published [18].

Since Table 3 shows that the phosphorescence emission maxima of the
thermally oxidized model amides do not vary with a change in excitation

wavelength then we can assume that only one type of emitting species is involved. Further, the phosphorescence emissions from both polymer and oxidized model compounds exhibit several characteristic features that indicate their source to be carbonyl in nature. These are: (1) during conversion of the salt to the polymer the presence of oxygen is necessary to generate the phosphorescent species in the polymer; (2) on thermal treatment, oxygen is required to produce the emission from the model amide; (3) the magnitude of the vibrational splittings of their spectra are of the same magnitude as that for an aliphatic carbonyl group [19]; (4) many other commercial polymers exhibit phosphorescence in the same region (400 - 500 nm) and this has been attributed to carbonyl impurity centres [7, 8, 17].

Also of relevance is the work of Sagar [20, 21], who subjected simple N-alkyl and N,N'-dialkylamides to mild thermal oxidation conditions very similar to those employed here. It was found that this resulted in the formation of several carbonyl oxidation products by three distinct processes:

$$RCONHCH_2R' \xrightarrow{\Delta H} \begin{cases} \longrightarrow RCONHCOR' \\ \longrightarrow RCONHCHO \qquad (6) \\ \longrightarrow RCONH_2 + R'CHO \end{cases}$$

The phosphorescence from a number of these carbonyl oxidation products was examined, but although several gave broad structureless emissions around 450 nm none gave the structured spectrum shown in Fig. 2. However, if these ketonic/aldehydic groups are conjugated with ethylenic unsaturation then structured emission spectra similar to that shown in Fig. 2 are observed [22 - 24]. Further, in the early work [20, 21] on the degradation of model amides, traces of unsaturated carbonyl compounds were identified by g.l.c. The source of these groups could be from aldol type condensation reactions involving the primary carbonyl oxidation products shown in reaction scheme (6). A more precise identification of the type of unsaturated carbonyl species is obtained, as shown in the following section, by comparing the phosphorescence excitation spectrum of the oxidized model amide with the absorption spectra of model α,β-unsaturated carbonyl compounds.

Of the many types of α,β-unsaturated carbonyl compounds available only one of two possible general structural types could be responsible for the phosphorescence emission from the thermally oxidized model amide $i.e.$ enones or dienones (including enals and dienals). These structures may be distinguished more clearly from a comparison of their absorption spectra. Figure 5 compares the phosphorescence excitation spectrum of the thermally oxidized model amides with the absorption spectra of a typical enone (pent-3-ene-2-one) and dienone (2,6-dimethyl-hept-2,5-diene-4-one) [25]. It is seen that the absorption spectrum of the latter matches much more closely that of the model amide excitation spectrum than does a typical enone. The phosphorescence emission properties of α,β-unsaturated carbonyl compounds of the enone and dienone (or-al) type all exhibit structured phosphorescence emission spectra in the wavelength region 400 - 500 nm [22 - 24]. Table 3
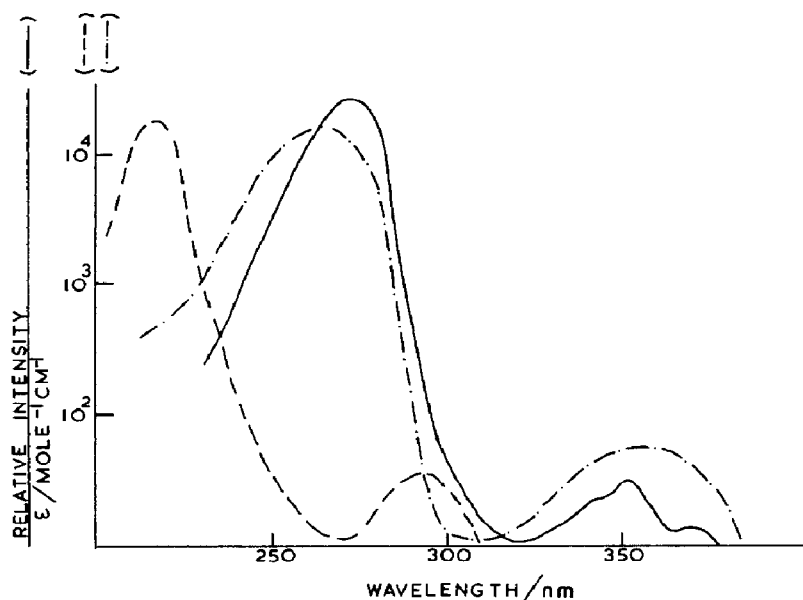
Fig. 5. Comparison of the phosphorescence excitation spectrum of thermally oxidized model amides in EPA glass at 77 K (——) with the absorption spectra of a typical enone, pent-3-ene-2-one (- - - -) and dienone, 2,6-dimethyl-hept-2,5-diene-4-one (— · — · —) in n-hexane.

compares the phosphorescence emission characteristics of a typical cyclic dienone (4,4-diphenylcyclohexadienone) [23] with those of the model amide emission and polymer. It is seen that the wavelength maxima and vibrational splittings of all emissions are very similar.

One important point to note is that the lowest triplet $\eta\pi^*$ and $\pi\pi^*$ excited states of α,β-unsaturated carbonyls are almost degenerate [22 - 24]. Further, the relative positions of these energy levels are markedly influenced by both structural and environmental factors [22 - 24]. In very rigid environments, e.g. on silica gel or in a polymer matrix, long-lived emissions (up to 5 s) have been observed from α,β-unsaturated carbonyl compounds due to an increase in the energy of the triplet $\eta\pi^*$ excited state relative to that of the $\pi\pi^*$ state [22, 24]. In a strongly hydrogen bonded matrix such as nylon-6,6 [15], this effect would be even more marked since the $\pi\pi^*$ and $\eta\pi^*$ energy levels would undergo corresponding bathochromic and hypsochromic shifts respectively and relatively long lived emission from these dienone chromophores situated in the molecular backbone of the polymer would be expected. This is precisely what is observed with all the nylon polymers. Table 1 shows that for a range of nylon polymers an increase in their emission lifetimes is observed with an increase in the density of their crystallinity [15] in the order nylon-6,6 > nylon-6 > nylon-11 and nylon-12.

The results clearly show that the effects of thermal and photochemical oxidation on the phosphorescence from nylon-6,6 polymer are markedly different. In the former process emission bands at longer wavelengths were generated, whereas they were not generated as a result of photo-oxidation. Indeed, in the photo-oxidation experiments there was a distinct shift in the

phosphorescence emission to shorter wavelengths. This suggests that if the longer wavelength phosphorescing products were formed during photo-oxidation then they would be consumed as intermediates during the overall reaction. Their generation during thermal oxidation would, of course, render the polymer potentially more photoactive by virtue of increasing its capacity for absorbing sunlight in the ultra-violet region 300 - 350 nm. In fact, a consumption of these longer wavelength species was observed during photolysis (Table 2).

It has been reported that photo-oxidation of polyamides and model amide systems favours aliphatic amine and carboxylic acid product formation [3, 4, 8, 26] whereas thermal oxidation favours ketonic/aldehydic carbonyl product formation [8, 20, 21]. The fact that aliphatic amines and carboxylic acids do not phosphoresce in the wavelength region 400 - 500 nm [19] clearly explains the absence of longer wavelength phosphorescing products during photo-oxidation. Indeed, Marek and Lerch [26] found that diketones and dialdehydes were reactive intermediates in the photo-oxidation of nylon-6,6 polymer. Succinic acid was identified as one of the main final products.

Interestingly, our observations on nylon-6,6 are similar to those of Beavan and Phillips [24] who studied the thermal and photochemical oxidation of polybutadiene. They found that on thermal oxidation of the polymer unsaturated carbonyls were formed and that on subsequent photo-oxidation these unsaturated carbonyls were converted to saturated carbonyl products.

To summarize, therefore, the bathochromic shift that occurs in the phosphorescence spectrum of nylon-6,6 is due to the build up of phosphorescent ketonic/aldehydic carbonyl oxidation products. On photo-oxidation the corresponding hypsochromic shift of the phosphorescence emission and overall decrease in its intensity is due to a consumption of the α,β-unsaturated carbonyl (dienone) impurities to give saturated carbonyl products. These, in turn, are photolyzed further to give non-phosphorescent dicarboxylic acids.

Acknowledgements

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