

Mechanism of Photostabilization of Polypropylene by Nickel Oxime Chelates

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Synopsis

Recent work has shown that certain nickel oxime chelates act as effective light stabilizers for polypropylene. The mechanism of their protective action was examined by spectrophosphorimetry and flash photolysis. Examination of the phosphorescence from the commercial polymer shows that it is due to aldehydic carbonyl groups. From flash photolysis observations of the triplet quenching action of a range of nickel chelates it is suggested that stabilization by the oxime chelates is achieved by a mechanism of efficient energy transfer from the photoreactive carbonyl group to the chelate, where the energy is harmlessly dissipated. The efficiency of this quenching action is primarily dependent on the spatial configuration of the ligand around the central metal atom in the chelate.

INTRODUCTION

For the stabilization to ultraviolet light of polyolefins several different types of stabilizer are used. The most common are the "ultraviolet screen" (carbon blacks, copper phthalocyanine pigments, etc.) and the "ultraviolet absorber" (2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, etc.); the mechanism of their protective action is now fairly well understood.¹ In recent years, however, several examples have been given in the literature of a new type of ultraviolet stabilizer, the so-called "reactive" stabilizer, which is believed to operate by a mechanism of excitation energy transfer from the polymer to the stabilizer.²⁻⁵ In general, these stabilizers are fairly complex chelates of the transition metals, usually nickel, and their exact mode of protective action is not at all clear.

Recent work in these laboratories⁶ has shown that the nickel (Ni^{II}) chelates prepared from 2-hydroxyphenylketoximes, when used in conjunction with an antioxidant system, are particularly effective as light stabilizers for polypropylene. This is demonstrated in Figure 1 for both outdoor and artificial exposure conditions, in which the performance of an example of this class of chelate is compared with that of an effective member of the ultraviolet absorber type.

In the work reported here we have attempted to gain some insight into the stabilizing mechanism of these nickel oxime chelates by using the techniques of spectrophosphorimetry and flash photolysis. The work may be considered in two parts. First, spectrophosphorimetry is used to establish

the presence, and to examine the nature, of the photoreactive carbonyl groups known to be present in the commercial polymer.⁷ Second, the technique of flash photolysis is used to examine the effect of these chelates on a photoexcited species (triplet anthracene). This technique is particularly useful for observing intermolecular energy-transfer processes directly,⁸ and a preliminary account of our observations with a range of nickel chelates has already been given.⁹

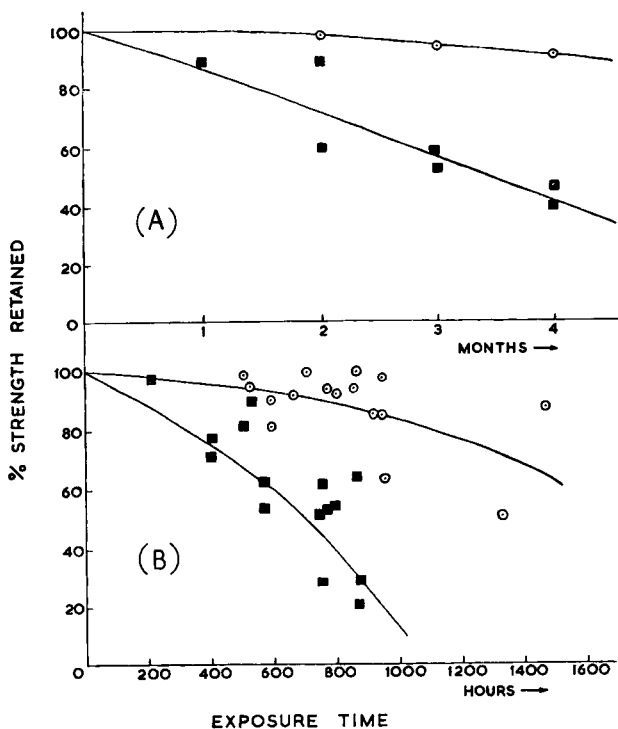


Fig. 1. Polypropylene yarn exposure test for (○) nickel bis(*syn*-methyl 2-hydroxy-4-methyl phenyl ketoxime) and (■) 2-hydroxy-4-*n*-octyloxy-benzophenone. Exposure A carried out in Florida; exposure B carried out in Weather-O-Meter. Both stabilizer systems contained 0.5% ultraviolet stabilizer, 0.1% Topanol CA, 0.5% Negenox DLTP, and 0.4% calcium stearate.

Finally, we have compared the triplet quenching efficiency of three of these oxime chelates with their effectiveness as stabilizers in both polypropylene yarn and film.

EXPERIMENTAL

Spectrophosphorimetric Measurements

For the measurements an Aminco-Bowman Spectrophotofluorometer (No. 4-8202) with phosphorescence attachment was used. The experimen-

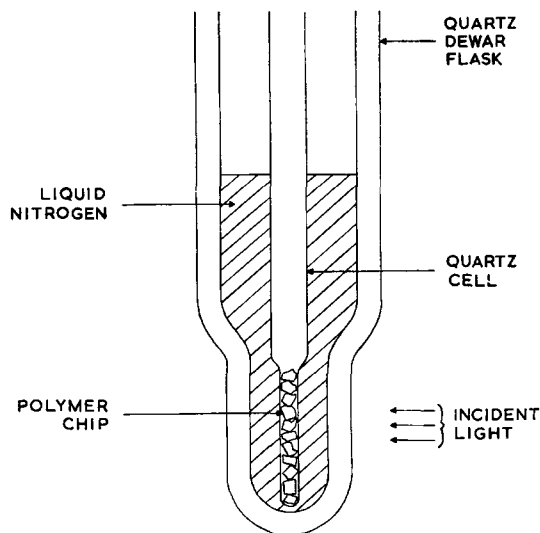


Fig. 2. Experimental arrangement for detection of phosphorescence from polypropylene chip.

tal arrangement for obtaining phosphorescence from the polymer is shown in Figure 2. Preliminary experiments were carried out with polypropylene powder, chip, and film, and it was found that with chip of about 1 mm. diameter the strongest and most reproducible spectra were obtained. Attempts were made to obtain total luminescence (i.e., fluorescence and phosphorescence) spectra from the chip by dispensing with the rotating can, but these experiments were unsuccessful, owing to scattering effects.

To record the type of spectra obtained from the polymer samples, the following procedure was employed. Each sample was excited with approximately monochromatic light at fixed wavelengths throughout the wavelength region that produced light emission from the samples. The phosphorescence spectrum produced by each of these excitation wavelengths was recorded. The emission monochromator was then set at the wavelength peak (λ_{\max}) of the phosphorescence spectrum and the corresponding excitation spectrum recorded. In order to simplify the presentation of the results given in tabular form later, only the location of the peaks (λ_{\max}) and distinctive shoulders (S) in the spectra are given. This method allows us to see any shift in λ_{\max} that may occur with excitation wavelength, a feature which is of significance in the interpretation of the results.¹⁰

Flash Photolysis Measurements

The apparatus and experimental procedure used for the flash photolysis measurements has been described previously.¹¹ Photoflash energies of 450 joules per flash and 25–50 joules per flash were used for the experiments with the fluid solvents (benzene, ethanol, and methanol) and the viscous solvent (liquid paraffin), respectively.

Materials

The polymer used for the spectrophosphorimetric measurements was unstabilized (MFI = 2) polypropylene powder supplied by Imperial Chemical Industries Ltd. (Plastics Division). Samples of tape were obtained by extruding the molten polymer through a Shaw P1 Screw Extruder operating at a temperature range of 180–200°C. along the barrel. Samples of film were obtained by pressing out the powder at a temperature of about 200°C. with a pressure of 3000 lb./in.² for 30 sec.

The anthracene used in the flash photolysis measurements was purified by zone refining, the molten zone receiving twenty passes. All impurities except carbazole were reduced to a concentration below 10 ppm. The carbazole concentration was in the region 0.01–0.1%. The liquid paraffin (BP grade) was purified by passing it through two columns of activated alumina. The percentage transmission for a 10-mm. path length at 250 $m\mu$ was 80%.

The nickel chelates were prepared by refluxing an ethanolic solution of the appropriate ligand (2 moles) and nickel chloride (1 mole) for 1 hr. After cooling to 25°C. and neutralizing of the solution, the solid chelate was filtered off, washed copiously with water, and dried at 60°C. When required, the chelates were purified by recrystallization from dimethylformamide.

The other chemicals used were of the highest purity available (usually Analar grade) and were not purified further.

RESULTS

Examination of Polypropylene by Spectrophosphorimetry

Typical λ_{\max} values for the uncorrected phosphorescence and excitation spectra obtained from a sample of extruded polymer chip are given in Table I. An estimate of the relative intensities of the phosphorescence spectra at the various excitation wavelengths is also given. We found that the powder and film samples gave the same phosphorescence and excitation spectra as the chip, with minor variations in the λ_{\max} values, but the overall intensity of the spectra was considerably less than that of the chip.

Recently Charlesby and Partridge⁷ examined the nature of the luminescence emitted from thin films of polyolefins, using an apparatus somewhat different from that used here. They found that both polyethylene and polypropylene emit phosphorescence bands in the region 450–500 $m\mu$. They were also able to observe a fluorescence band from polyethylene at 375 $m\mu$ and two fluorescence bands from polypropylene at 320 and 375 $m\mu$. By comparing the spectra obtained from polyethylene with those obtained from model aldehydic and ketonic carbonyl compounds they concluded that the species responsible for the phosphorescence bands from polyethylene are carbonyl groups, mainly aldehydic groups located at the ends of the molecular chains.

TABLE I
Phosphorescence and Excitation Spectra from Polypropylene^a

Excitation wavelength, m μ	Excitation spectrum, m μ	Phosphorescence spectrum, m μ	Relative intensity
225	290, 325(S)	465	Weak
250	" "	465	Mod. strong
275	" "	465	Strong
300	" "	465	Strong
325	" "	470	Mod. strong
350	" "	470, 490(S)	Weak
375	" "	485, 520(S)	Weak
400	" "	510	V. Weak

^a The λ_{\max} values are estimated to ± 5 m μ . (S) denotes shoulder.

Our results are in good agreement with those of Charlesby and Partridge; indeed, our observations of the wavelength location of the excitation spectra add further weight to the conclusion that the phosphorescence is due to carbonyl groups. Carbonyl groups, in general, absorb light in the wavelength region 280–350 m μ .

In Table II are given the phosphorescence spectra of some simple aldehydes and ketones taken under the same experimental conditions as those listed in Table I. The wavelength location of these spectra indicate that the phosphorescent carbonyl groups in polypropylene are mainly aldehydic in type. Again, in further agreement with Charlesby and Partridge, the observation in Table I of a definite shift in λ_{\max} at the higher excitation wavelengths indicate that there must be more than one type of alkyl chain attached to these aldehydic groups.

TABLE II
Phosphorescence Spectra of Various Aldehydes and Ketones

Compound	Phosphorescence, λ_{\max}
Acetaldehyde	495
Propionaldehyde	480
<i>n</i> -Caproaldehyde	465
Laurylaldehyde	465
Acetone	450
Diethylketone	450
Cyclopentanone	440

Examination of Nickel Chelates by Flash Photolysis

The effect of nickel chelates on the lifetime and intensity of triplet anthracene was determined for chelates prepared from the following ligands: (1) *syn*-methyl 2-hydroxy-4-methylphenyl ketoxime, (2) dimethylglyoxime, (3) diphenylglyoxime, (4) *syn*-methyl 2-hydroxy-4-methylphenyl *N*-*n*-butyl ketimine, (5) 2-hydroxyphenyl *N*- β -hydroxyethyl aldimine, (6) *N,N'*-1,2-

di(2-hydroxyphenyl aldimino)ethylene, (7) *N,N'*-1,2-di(2'-aminophenyl aldimino)ethylene, (8) *N,N'*-1,2-di-(2'-hydroxyphenyl aldimino) benzene, (9) *syn*-methyl 2-hydroxy-4-methyl phenyl *N*-phenyl ketimine, (10) pentan-2,4-dione, (11) 1-phenylbutan-1,3-dione, (12) 1,3-diphenyl-propan-1,3-dione, (13) salicylaldehyde, (14) 8-hydroxyquinoline, (15) 2-hydroxy-4-methyl acetophenone, (16) bis(2-hydroxy-5-*t*-octylphenyl) sulfide, (17) bis(2-hydroxy-5-*t*-octylphenyl)sulfone.

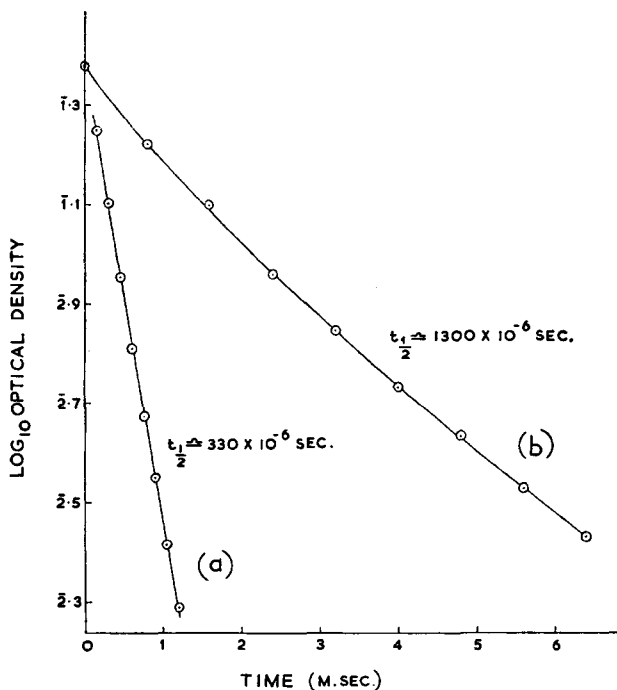
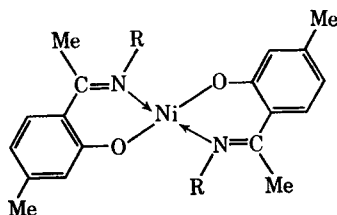


Fig. 3. First-order plots of triplet anthracene decay in deoxygenated liquid paraffin: (a) chelate present, photoflash energy 50 joules; (b) chelate absent, photoflash energy 25 joules.

Strong quenching of triplet anthracene was observed with chelates (1) and (2), a weaker effect with (3)–(7), and none with (8)–(17). An example of this quenching effect is shown in Figure 3 with chelate (1). This figure shows two first-order plots of the decay of triplet anthracene in liquid paraffin solvent, with and without the chelate present. It is seen that the presence of the chelate has a marked effect in reducing the half-life of decay of the triplet anthracene ($t_{1/2}$) and also that it changes the kinetics of decay from complex to first-order (second-order and zero-order plots for decay (b) of the Figure also do not give a straight line).

Of particular interest here, however, are the results obtained with the chelates (1), (4), and (9). These all have the structure



In chelate (1) $R = OH$, in (4) $R = n-C_4H_9$, and in (9) $R = C_6H_5$. The chelates differ only in R , the group substituted on the ligand nitrogen atom. We find a strong correlation between the triplet quenching efficiency of these chelates and their effectiveness as ultraviolet stabilizers in polypropylene. The results are summarized in Table III. It is seen from the table that two independent test methods have been used for determining the stabilizing efficiency of the chelates: retention of yarn toughness and formation of carbonyl groups in films as determined by infrared spectrometry. For comparison, the corresponding results obtained from the stabilizer of the "ultraviolet absorber" type shown in Figure 1 are included in Table III.

TABLE III
Triplet Quenching Effect and Ultraviolet Stabilizing Activity
of Chelates (1), (4), and (9)

Stabilizer	Quenching effect on triplet anthracene	Toughness of yarn ^a retained after exposure in Weather-O-Meter, %		Time for polypropylene plastic films ^c to absorb 0.06% O ₂ as carbonyl on exposure to Xeno- test, hr.
		500 hr. ^b	600 hr. ^b	
Chelate (1)	Strong	52	53	2,000
Chelate (4)	Moderate	47	23	825
Chelate (9)	None	17	8	470
2-Hydroxy-4- <i>n</i> -octyl- oxybenzophenone	None	—	20	650
None (same antioxidants)	—	—	3	—

^a Profax 4/160 (a thermally degraded polypropylene supplied by Hercules Co.). Spinning temp. 225°C., draw ratio 4:1; 0.5% UV stabilizer, 0.1% Topanol CA, 0.5% Negenox DLTP, 0.4% calcium stearate. Toughness of yarn = tenacity (g./den.) \times extension at break (%) $\times 2 \times 10^{-2}$.

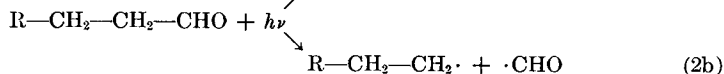
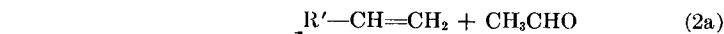
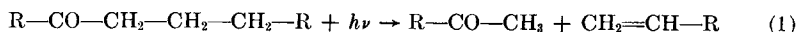
^b Separate exposures.

^c Polypropylene (MFI = 3) 0.02-in. thick films. Compression-molded at 190°C. for 2 min.; 0.5% UV stabilizer, 0.25% Negenox DLTP.

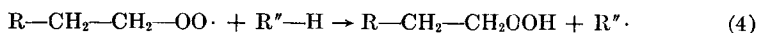
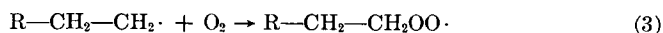
DISCUSSION

It is generally believed that the carbonyl groups present in commercial polyolefin polymers initiate photodegradation of the polymer.^{12,13} Nei-

man¹⁴ has proposed the following primary processes for the two types of carbonyl group:



The plausibility of these postulated processes is supported by conventional and flash-photochemical studies of the simpler aldehydes and ketones.¹⁵⁻¹⁷ Oxidative degradation of the polymer can then proceed by the well-known Bolland-Gee mechanism,



and further degradation can be initiated by photodecomposition of the hydroperoxides formed by reaction (4):



Our spectrophosphorimetric observations of polypropylene show that, of the *phosphorescent* carbonyl groups present in the polymer, the majority are of the aldehydic type. At first sight this suggests that primary processes (2a) and (2b) must be the predominant ones. However, Charlesby and Partridge⁷ have pointed out that the luminescence from a ketonic carbonyl group very rapidly diminishes with increasing dialkyl chain length, so that an isolated ketonic carbonyl on an "infinite" polymethylene chain may be virtually nonluminescent. Since it is possible, therefore, that these nonluminescent ketonic groups may be present in polypropylene, then the possibility of some contribution from process (1) cannot be ruled out.

Our flash photolysis observations of the quenching of triplet anthracene are of particular interest, since they suggest a mechanism by which the nickel oxime chelates act in a "reactive" stabilizing capacity. Recent work¹⁸⁻²⁰ on the photochemistry of the simple aliphatic aldehydes and ketones shows that for light above 300 m μ dissociation, as exemplified in processes (1) and (2) occurs mainly from the triplet state. Since these chelates effectively quench triplet anthracene, it appears very likely that they will effectively quench triplet carbonyl groups in the polymer. If the photochemical energy transferred from the triplet carbonyl groups is harmlessly dissipated by the chelate, then its presence in the polymer will give rise to an overall reduction in the number of carbonyl groups initiating photodegradation by processes (1) and (2). The strong correlation in Table III between triplet quenching efficiency and stabilizing activity certainly supports this view. The synergistic effect of the antioxidant system used with the chelate is probably due to its interrupting the reaction sequences (3) and (4),¹⁴ initiated by the carbonyl groups, which escape the quenching mechanism.

As we have pointed out earlier,⁹ we do not yet know the exact nature of this energy-transfer process. The evidence from chelates (1), (4), and (9) indicates that the magnitude of the quenching effect is primarily dependent on the spatial configuration of the ligands around the central metal atom in the chelate. To obtain further information on its nature, we are engaged in a detailed kinetic study of the effect of metal oxime chelates on photo-excited molecules. These results will be reported elsewhere.

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References

1. W. L. Hawkins and F. H. Winslow, in *Crystalline Olefin Polymers*, R. A. V. Raff and K. W. Doak, Eds., Interscience, New York, 1964, Ch. 8.
2. J. A. Melchore, *Ind. Eng. Chem. Prod. Res. Dev.*, **1**, 232 (1962).
3. R. G. Schmitt and R. C. Hirt, *J. Appl. Polymer Sci.*, **7**, 1565 (1963).
4. H. H. Hormann, *Ind. Eng. Chem. Prod. Res. Dev.*, **5**, 92 (1966).
5. A. P. Pivovarov, Y. A. Ershov, and A. F. Lukovnikov, *Soviet Plastics*, **10**, 11 (1967).
6. Imperial Chemical Industries Ltd., Brit. Pat. Appl. 44655/65.
7. A. Charlesby and R. H. Partridge, *Proc. Roy. Soc. (London)*, **A283**, 312 (1965).
8. G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961).
9. P. J. Briggs and J. F. McKellar, *Chem. Ind. (London)*, **1967**, 622.
10. C. A. Parker and W. T. Rees, *Analyst*, **87**, 83 (1962).
11. J. F. McKellar, *Proc. Roy. Soc. (London)*, **A287**, 363 (1965); J. H. Allen and J. F. McKellar, *Lab. Pract.*, **16**, 991 (1967).
12. A. Pross and P. Black, *J. Chem. Soc. Ind. (London)*, **69**, 113 (1950).
13. A. R. Burgess, *Natl. Bur. Std. (U.S.) Circ. No.* **525**, 149 (1953).
14. M. B. Neiman, *Ageing and Stabilization of Polyolefins*, Consultants Bureau, New York, 1965, Ch. 4.
15. J. Guillet and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A233**, 153 (1955).
16. G. Herzberg and D. Ramsay, *Proc. Roy. Soc. (London)*, **A233**, 34 (1955).
17. J. F. McKellar and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A254**, 147 (1960).
18. C. S. Parmenter and W. A. Noyes, *J. Am. Chem. Soc.*, **85**, 416 (1963).
19. J. Heiklen and W. A. Noyes, *J. Am. Chem. Soc.*, **81**, 3858 (1959).
20. D. S. Weir, *J. Am. Chem. Soc.*, **83**, 2629 (1961).

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