

## Photostabilizing Effect of Ni(II) Chelates in Polymers. I. Polystyrene

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### Synopsis

The photostabilizing effect of six Ni(II) chelates in films of polystyrene is compared with their efficiency in quenching triplet benzophenone and a correlation between the two established. In both polymer stabilizing and triplet quenching experiments, the diamagnetic chelates are more effective than the paramagnetic chelates, indicating that the structural arrangement of the ligand around the Ni atom is an important factor in both cases.

### INTRODUCTION

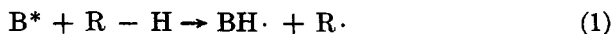
In the preceding paper,<sup>1</sup> Adamczyk and Wilkinson (AW) describe the commercial stabilizers used in light-sensitive polymers and summarize the possible mechanisms of their stabilizing action. Of these stabilizers, the Ni(II) chelates are of particular interest because of their considerable commercial potential.<sup>2-4</sup> Here, we report the first part of a study of their mechanism of stabilizing action in commercial polymers.

Some years ago, certain Ni(II) ketoxine chelates<sup>5</sup> were found to be efficient stabilizers for the light-sensitive polyolefins (e.g., polypropylene), and at that time it was suggested<sup>2</sup> from preliminary flash photolysis evidence that their stabilizing mechanism could be due to some type of triplet quenching process. Recently, AW<sup>6</sup>, in an elegant study using laser flash photolysis, showed that these chelates efficiently quench triplet molecules in solution. Though triplet quenching may occur in solution, it is by no means proven that these processes occur in a commercial polymer or, indeed, that the protective action of the stabilizer occurs by such a mechanism. Our first objective, reported here, was to compare the triplet quenching efficiencies of the same stabilizers used by AW with their stabilizing efficiency in a polymeric environment.

For their solution studies, AW<sup>1,6</sup> chose benzophenone as the triplet energy donor. For our initial study, therefore, polystyrene was an obvious choice as the light-sensitive polymer. Aromatic carbonyl groups are formed early in the photodegradation process.<sup>7</sup> Recently, also, we found that aromatic carbonyl compounds added to commercial polymers are very

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effective as light-induced prodegradants.<sup>8,9</sup> A detailed study of the benzophenone-sensitized degradation of polypropylene<sup>10</sup> indicated the main primary photochemical process to be one of hydrogen atom abstraction from the polymer backbone [ $B^*$  = benzophenone triplet;  $R-H$  = polymer]



The "free radical center"  $R\cdot$  is thus open to attack by oxygen, allowing the classic Bolland-Gee degradation mechanism to proceed.<sup>11</sup> If, however, the Ni(II) chelate (N) competes with (1) by quenching the photoactive triplet carbonyl groups in the polymer [analogous to  $B^*$ ]

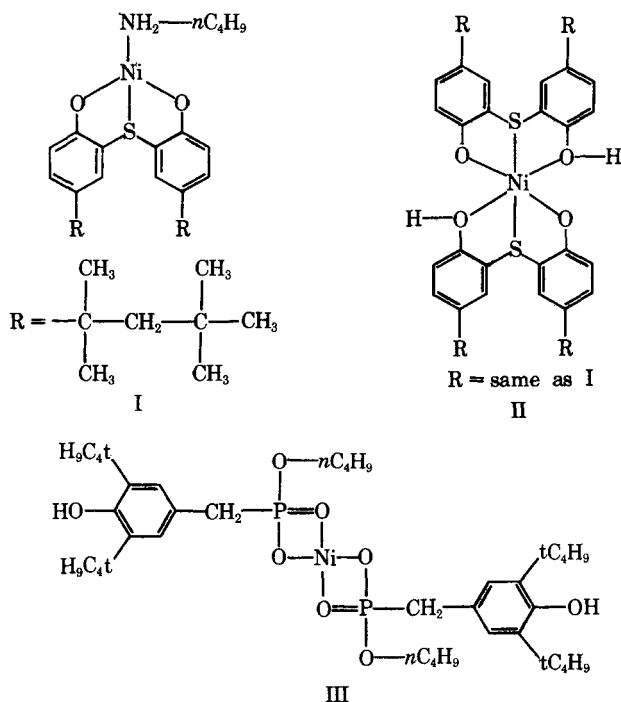


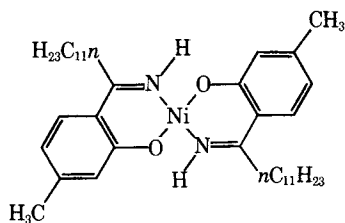
and the excited chelate  $N^*$  dissipates the energy in some harmless manner, then a protective mechanism of triplet quenching is clearly possible.

### EXPERIMENTAL

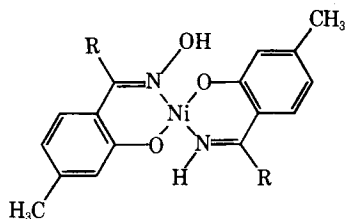
The polystyrene was obtained in powder form from stocks of standard commercial polymer made available by the Rubber and Plastics Research Association (RAPRA) of Great Britain, Shrewsbury, England.

The Ni(II) chelate stabilizers were obtained from commercial sources, except for IV, which was synthesized in these laboratories. The structures were:





IV



(a) R = CH<sub>3</sub>

(b) R = nC<sub>11</sub>H<sub>23</sub>

V

Chelates I–III are paramagnetic, while chelates IV and V are diamagnetic.

### Fabrication of Polymer Plaques

The polystyrene powder was dissolved in toluene together with the stabilizer at  $6.25 \times 10^{-3}$  moles per kg of polymer. Plaques were formed from the solutions by evaporation of the solvent at room temperature. Since all the chelates were readily soluble in toluene, it is reasonable to assume that they were well dispersed in the polymer plaque.

### Light Aging of Polymer Plaques

The plaques were exposed for measured intervals of time in a Xenotest 150 (manufactured by Quarzlampen GMBH, Hanau, Germany) at a temperature of 45°C and relative humidity of 60%.

The progress of photo-oxidation was monitored by determining the absorbance of the carbonyl oxidation products in the infrared region using a Perkin-Elmer 257 Grating IR Spectrophotometer. The infrared spectrum resulting from photo-oxidation was relatively complex, certainly more complex than that of the spectra observed in the benzophenone-sensitized degradation of polypropylene.<sup>11</sup> The absorbances of the three major carbonyl bands at 5.80, 5.87, and 5.92  $\mu\text{m}$  were averaged since they showed little significant variation in intensity relative to each other during the irradiation period. Although there was some variation in the thickness of the plaques, this also had little significant effect. This is clearly demonstrated later in the table summarizing the photodegradation data. For example, little difference was observed between chelates V (a) and V (b), although the maximum range in plaque thickness occurs with these two stabilizers.

The results of the irradiation experiments were treated graphically by plotting the averaged carbonyl absorbance against irradiation time. The degree of polymer degradation with the chelates present was then obtained from estimating the initial rate of carbonyl impurity generation as shown in Figure 2 (see later).

### Phosphorescence Measurements

These were made using a Baird-Atomic Fluorispec Model 109 with the phosphorescence attachment supplied by the manufacturer.

## RESULTS AND DISCUSSION

The polystyrene powder was examined for phosphorescence at 77°K, and a typical emission spectrum is shown in Figure 1. The spectrum is similar to that of many simple aromatic carbonyl compounds.<sup>12</sup> Although not detectable by IR prior to irradiation, it is evident that the UV absorbing groups were present as impurities in the polymer. Initiation of photo-degradation is thus readily possible by the primary photochemical process of hydrogen atom abstraction from the polymer backbone, i.e., analogous to reaction (1).

Typical curves of generation of carbonyl impurities resulting from irradiation of the polymer plaques are shown in Figure 2. The complete data are summarized in Table I. Also in the table we include the rate constants for the quenching of triplet benzophenone reported by AW.

The striking feature of the results in the table is that the chelates divide into two distinct groups with the following features: (a) The paramagnetic chelates are all relatively less effective as stabilizers for polystyrene and also are less effective as quenchers of triplet benzophenone. (b) The diamagnetic chelates are more effective in both processes.

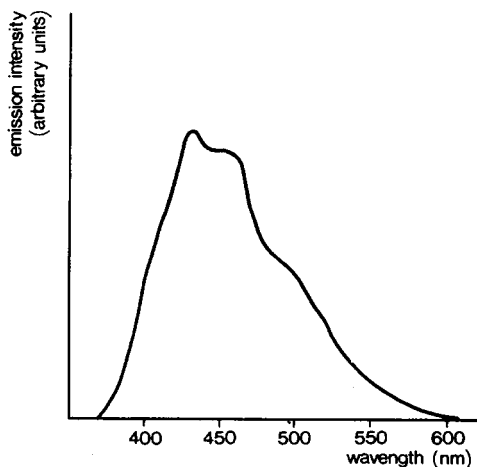


Fig. 1. Phosphorescence emission spectrum from polystyrene powder at 77°K.

TABLE I  
Summary of Polymer Stabilization and Benzophenone Triplet Quenching Data

Chelate	Plaque thickness, mm	Initial carbonyl formation rate $k, \text{sec}^{-1} \times 10^{-5}$	$k_q^{1,6}$ $10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$
None	0.224	50.9	—
I	0.175	8.3	0.53
II	0.229	11.1	1.10
III	0.239	9.4	0.41
IV	0.236	6.3	5.6
V(a)	0.175	3.3	5.9
V(b)	0.267	3.1	4.9

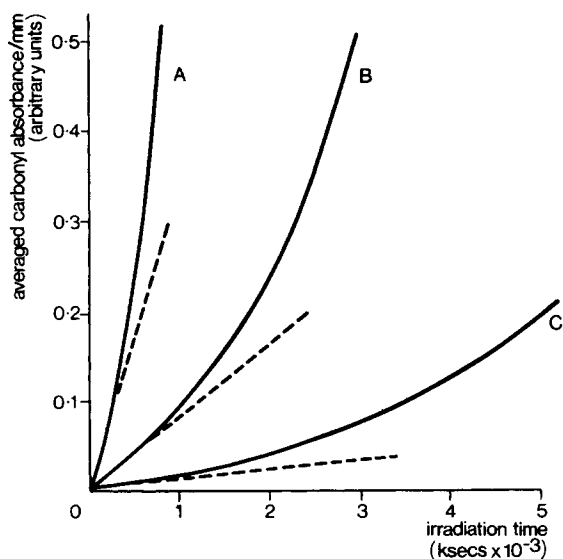


Fig. 2. Curves of generation of carbonyl impurities formed on irradiation of polymer plaques. Curve A, polymer only; curve B, polymer and chelate II; curve C, polymer and chelate V(b).

It is clear from these results that the structural arrangement of the ligand around the central Ni atom is a factor of significant importance in determining the stabilizing efficiency of the Ni(II) chelates in a polymeric environment. This confirms the earlier conclusion of Briggs and McKellar.<sup>2</sup> Also, since the two features of polymer stabilization and triplet quenching are clearly related, it would appear that a mechanism of energy transfer is involved.

However, direct quenching of the photoactive triplet carbonyl impurities in the polymer may not be the only mechanism of stabilization.<sup>13,14</sup> AW,<sup>1</sup> in the preceding paper, draw attention to the very interesting observation that Ni(II) chelates quench singlet oxygen molecules. Thus, we can envisage

a further stabilizing mechanism; one in which singlet oxygen molecules formed by deactivation of the triplet carbonyl impurities



are themselves deactivated by the chelate N



before they attack the polymer backbone.

In our work on the sensitized photodegradation of polypropylene,<sup>10</sup> we concluded that the dominant primary process-initiating photodegradation was hydrogen atom abstraction by reaction (1). In our view, a similar situation is also more probable with polystyrene. However, we are in complete agreement with AW that further work is required if we are to differentiate between the two possible mechanisms and thus to fully understand the stabilizing action of the Ni(II) chelates. This aspect is receiving attention in the laboratory of one of us (J. F. McK).

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