

Photostabilizing Effect of Ni(II) Chelates in Polymers. II. Effect of Diamagnetic Chelates on Polypropylene Phosphorescence

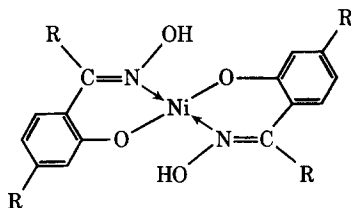
D. J. HARPER, J. F. McKELLAR,* and P. H. TURNER, *Imperial
Chemical Industries Limited, Organics Division, Hexagon House, Blackley,
Manchester M9 3DA, England*

Synopsis

Examination of the phosphorescence emission from polypropylene shows the lifetime of the emission to be unaffected by a hydroxybenzophenone light stabilizer but significantly shortened by a diamagnetic Ni(II) chelate stabilizer.

INTRODUCTION

Some years ago, diamagnetic Ni(II) chelates of the following structure



where R = alkyl group, were found to be effective light stabilizers for polyolefins, particularly polypropylene.¹ It was suggested² that they differed from conventional light stabilizers, such as the hydroxybenzophenones, in that their primary mechanism of protection was by effectively quenching photoexcited triplet carbonyl impurities in the polymer. A number of other Ni(II) chelates are also effective as polyolefin stabilizers,³ but since many of them are paramagnetic in character, a different mechanism of carbonyl quenching appears likely.⁴

There is now considerable theoretical and practical interest in these Ni(II) chelate light stabilizers, and much attention is being given to establishing the mechanisms by which they act.⁵⁻⁸ Recent laser flash photolysis studies^{9,10} have shown that the chelates quench triplet benzophenone; and in part 1 of this work¹¹ we reported a correlation for six of the chelate between their benzophenone triplet quenching efficiency and their effective-

* Present address: Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT Lancs., England.

ness as light stabilizers in polystyrene. It was also interesting that the diamagnetic chelates of the above structure were the more effective in both cases. Here, we briefly report a further feature of these chelates that we believe is relevant to their mechanism of polymer photostabilization.

EXPERIMENTAL RESULTS

Polypropylene phosphoresces in the wavelength region of 450-500 nm depending on the wavelength of the exciting light,² and plaques of the polymer were examined using an Aminco Bowman spectrophotofluorometer incorporating minor modifications to allow the convenient examination of polymer samples.¹² The phosphorescence spectra obtained were the same as reported earlier; but in these experiments, the mean lifetime of phosphorescence decay was also measured. Mean lifetime here is defined as the time taken for the emitted light to fall to $1/e$ (36.8%) of its original intensity.

The results of these lifetime measurements are shown in Figure 1 for polymer containing no light stabilizer (A), a hydroxybenzophenone stabilizer (B), and a diamagnetic chelate stabilizer (C). Although each sample of

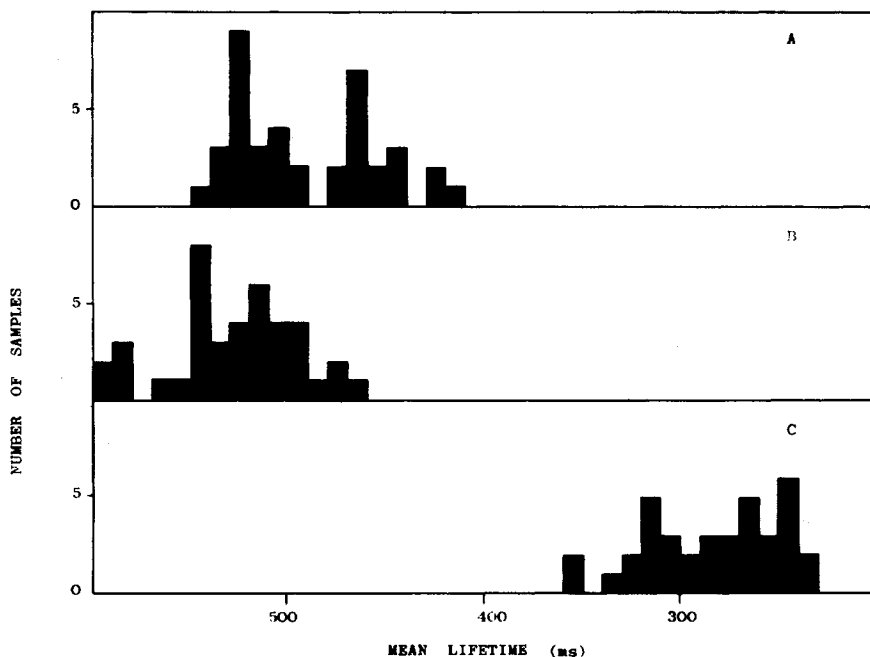


Fig. 1. Phosphorescence emission from polypropylene plaques at 77°K. Excitation wavelength, 300 nm; emission wavelength, 465 nm. The plaques were 0.05 cm thick and contained the normal additives for fabrication.² Samples A contained no light stabilizer, samples B contained 0.5% (by weight) 2-hydroxy-4-*n*-octyloxybenzophenone, and samples C contained 0.5% (by weight) nickel bis(*syn*-methyl-2-hydroxy-4-methyl phenyl ketoxime).

polymer examined had a slightly different mean lifetime, by examining a large number of samples it was possible to obtain a statistically meaningful result. In the figure, the data are presented in the form of histograms comparing the number of samples examined with the mean lifetime of each sample determined. It is seen that in all cases the polymer samples containing the chelate exhibited significantly shorter lifetimes than those of the other two.

In addition to this lifetime difference, a further feature of the results is the remarkably long lifetimes of the phosphorescence emission of the polymer. Certain other commercial polymers show lifetimes of a similar order of magnitude, and this will be reported on later.¹³ The long-lived phosphorescence from polypropylene was reported by Shaw,¹⁴ who assigned it to the emission of triplet carbonyl impurities in the polymer. Although the complexity of phosphorescence emission from polyolefins has since been demonstrated,¹⁵ there appears to be no reason to doubt Shaw's original assignment.

Like many other commercial polymer light stabilizers, it is now becoming apparent from recent work that it is possible that a diamagnetic chelate of the above structure may protect the polymer to photodegradation by several, quite different mechanisms.^{6,8} However, the fact that the chelate significantly reduces the lifetime of potentially photoactive impurities in the polymer matrix¹⁶ is clear evidence that at least one of them is by a mechanism of quenching of electronically excited states.

References

1. P. J. Briggs and R. J. Hurlock, (to Imperial Chemical Industries Ltd.) U.K. Pat. 1,220,087 (1968).
2. P. J. Briggs and J. F. McKellar, *J. Appl. Polym. Sci.*, **12**, 1825 (1968).
3. J. E. Bonkowski, *Text. Res. J.*, **39**, 243 (1969).
4. J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, **90**, 1001 (1968).
5. O. Cicchetti, *Advan. Polym. Sci.*, **7**, 70 (1970).
6. D. J. Carlsson, T. Suprunchuk, and D. M. Wiles, *J. Appl. Polym. Sci.*, **16**, 615 (1972).
7. D. J. Carlsson, D. E. Sproule, and D. M. Wiles, *Macromolecules*, **5**, 659 (1972).
8. B. Felder and R. Schumaker, *Angew. Makromol. Chem.*, **31**, 35 (1973).
9. A. Adamczyk and F. Wilkinson, *J. C. S. Faraday II*, **68**, 2031 (1972).
10. A. Adamczyk and F. Wilkinson, *J. Appl. Polym. Sci.*, **18**, 1225 (1974).
11. D. J. Harper and J. F. McKellar, *J. Appl. Polym. Sci.*, **18**, 1233 (1974).
12. J. F. McKellar and P. H. Turner, *Fluorescence News*, **7**, 4 (1973) (Publication of the American Instrument Co., Silver Spring, Maryland 20910).
13. N. S. Allen, J. F. McKellar, and G. O. Phillips, to be published.
14. G. Shaw, Ph. D. Thesis, University of Sheffield, England, 1967.
15. I. Boustead and A. Charlesby, *Eur. Polym. J.*, **3**, 459 (1967); *Proc. Roy. Soc. (London)*, **A315**, 271 (1970).
16. D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 587 (1969).

Received November 9, 1973

Revised January 22, 1974