

Electron Spin Resonance Studies on Photodegradable Polymers

JOHN J. WINDLE and BERNARD FREEDMAN, *Western Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Berkeley, California 94710*

Synopsis

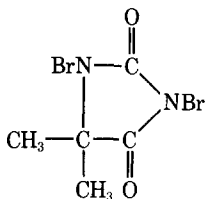
Films of polyethylene (PE), polypropylene (PP), and polystyrene (PS) containing 1% of selected halogen compounds and films without additives were UV irradiated (253.7 nm) at 77°K and their electron spin resonance (ESR) spectra compared. In each case, the spectra were characteristic of the polymer, and the presence of the additive mainly enhanced the radical yield. No signal was observed for the additives alone after irradiation, suggesting that when incorporated into the polymer, they serve as photosensitizers rather than as primary sources of free radicals in promoting photochemical degradation.

INTRODUCTION

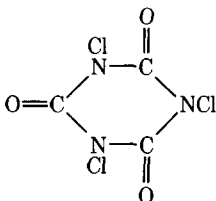
In previous studies,^{1,2,3} it was shown that the photodegradability of PE, PP, and PS exposed to an RS sunlamp and to natural sunlight was enhanced by incorporating various additives into the polymers. One of the additives, N-bromosuccinimide (NBS), is known to dissociate via free-radical formation when used as an allylic brominating agent.⁴ It was of interest to determine whether NBS and the other halogen-containing compounds employed as additives operated via free-radical mechanisms during the photodegradation of the polymers. To investigate this possibility, we used ESR to search for evidence of free radicals in the photodegraded films. None was found, suggesting that if free radicals were formed, they may have been too short-lived at room temperature to be detected. We therefore undertook to study the UV photolyses of PE, PP, and PS films at liquid nitrogen temperature, by ESR, in an effort to ascertain the role of the additives in the primary photochemical processes.

EXPERIMENTAL

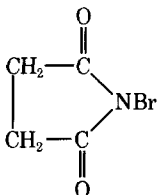
The procedures used to prepare films with and without additives have been described previously.^{1,2,3} For the ESR studies, three additives were selected on the basis of their effectiveness in promoting degradation of the polymers when exposed to either UV illumination or to sunlight.^{1,2,3} The additives and their structures are as follows:



1,3-dibromo-5,5-dimethylhydantoin (1,3 DBDH)



trichloroisocyanuric acid (TCI)



N-bromosuccinimide (NBS)

In methylene chloride solution, these compounds exhibited strong UV absorption below 300 nm.

ESR spectra were obtained using a Varian E-3 EPR spectrometer equipped with a multipurpose ESR cavity and a variable-temperature accessory.

Samples in the form of rectangular strips 19–25 mm long and 1–2 mm wide were cut from the polymer films. Three strips were placed in standard, 3-mm-I.D. quartz ESR tubes and their net weight determined. The tubes were then sealed in air or after evacuation.

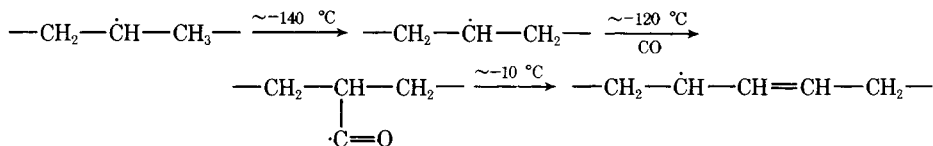
The samples were irradiated at liquid nitrogen temperature in a quartz Dewar illuminated from either side by two 15-W germicidal lamps (General Electric, G15T8). After 30 min of irradiation, the tubes were immediately transferred to the ESR cavity, without warming, and spectra were obtained at various temperatures between -170°C and room temperature. Any radicals formed by the radiation with lifetimes less than a few seconds at -170°C would not be detected in these experiments.

No attempt was made to determine absolute free-radical yields. Quantitative changes in relative radical concentration were determined by comparing signal amplitudes. Such comparisons are valid providing the line shape and hyperfine splittings remain unchanged. Changes in free-radical concentration were calculated and normalized relative to the unmodified polymers.

RESULTS AND DISCUSSION

The effects of UV irradiation on PE,^{5,6} PP,^{6,7} and PS⁶ have been studied by a number of investigators using ESR spectroscopy. Tsuji⁵ observed an eight-line spectrum for PE irradiated with UV light at -196°C in nitrogen which he at-

tributed to free radicals of the type $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_3$. Other investigators^{8,9} reported that UV irradiation of PE gave a sextet attributed to $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ radicals. In spite of considerable effort by these authors and others, the identification of the primary radical(s) produced by UV irradiation of PE at low temperature is still not satisfactorily resolved. Tsuji⁵ also reported that upon warming, the $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_3$ radicals undergo the following changes:



The latter species, allylic radicals, persisted up to room temperature. When PE was irradiated with UV light in the presence of air or oxygen, the same radicals were produced at -196°C as in a nitrogen atmosphere. However, upon warming to -130°C , an asymmetric spectrum attributed to peroxy radicals is formed. At 0°C , the peroxy signal gradually gave way to a fine-line spectrum due to allylic radicals.^{5,6}

We obtained ESR spectra for PE with and without additives which were generally in accord with those reported by others for the same conditions and temperatures. In our experiments, we did not attempt to resolve the discrepancies in the literature concerning the nature of the PE free radicals formed at -196°C by UV irradiation.

No free radicals associated with the additives alone or in the presence of the polymers were found. The major effect of the additives on PE when irradiated at -196°C was to increase the ESR signal intensity indicating a higher yield of free radicals compared to the unmodified samples.

The ESR spectrum reported for PP irradiated in air at liquid nitrogen temperature consists of a four-line spectrum composed of broad and narrow components superimposed.^{8,9,11} The narrow quartet (1:3:3:1) disappeared after several hours and is attributed to methyl radicals.⁸ The broad quartet has been variously assigned to $\dot{\text{C}}\text{H}_2-\text{CH}(\text{CH}_3)\text{CH}_2-$ radicals,⁸ to $-\text{CH}(\text{CH}_3)-\dot{\text{C}}\text{H}-$ (CH_3) $\text{CH}-$ radicals,⁹ and also to $-\text{CH}_2-\text{CH}(\dot{\text{C}}\text{H}_2)\text{CH}_2-$ radicals.^{11,12} We obtained quite similar spectra for PP samples irradiated in air and under vacuum, with and without additives, and found that in most instances a larger signal is formed in the presence of additives. Again, we made no attempt to identify the radical species nor to resolve the differences in interpretation suggested above for the broad-component spectrum of PP.

Very few results on the ESR spectrum of UV-irradiated PS have been published. Browning et al. observed a broad singlet (no g value or line width reported) which was tentatively assigned to phenyl radicals.⁹ Other investigators reported that at -196°C , a symmetrical singlet with a width of about 20 gauss is produced attributed to $-\text{CH}_2-\dot{\text{C}}(\phi)\text{CH}_2-$ radicals.¹³ Upon warming to room temperature in air, the spectrum changed to an asymmetric line characteristic of peroxy radicals.¹³

Our results for PS, UV-irradiated under vacuum at liquid nitrogen temperature, appear to differ from those described above. With or without additives, we find a slightly a symmetric signal about 14 gauss wide with a small shoulder on the low-field side of the spectrum. Upon warming to room temperature, the

TABLE I
ESR Comparison of UV-Irradiated Polymers Under Vacuum at -170°C

Polymer	Normalized signal amplitude	Signal ratio
PE	29	1
PE 1% NBS	45	1.5
PE 1% TCI	58	2.0
PE 1% 1, 3 DBDH	64	2.2
PS	37	1
PS 1% NBS	79	2.1
PS 1% NBS	85	2.3
PS 1% 1, 3 DBDH	107	2.9
PS 1% TCI	132	3.6
PP	52	1
PP 1% TCI	176	3.4
PP 1% NBS	45	0.9
PP 5% NBS	104	2.0
PP 1% 1, 3 DBDH	47	0.9

signal decreased in amplitude but did not change in shape. The presence of additives served only to enhance the signal intensity.

The results of our studies are summarized in Table I. The normalized signal amplitude is shown for the various additives used. An uncertainty of about 10% is estimated as indicated by the spread in the results for two different PS 1% NBS samples shown in Table I. The ratio of the normalized amplitudes of the signals of the treated polymers to that of the untreated is shown in the third column. In each case, a larger signal resulted when additives were present with the exceptions of PP 1%, 1,3 DBDH and PP 1% NBS, which showed no change. However, NBS added to PP at the 5% level caused a twofold increase in the ESR signal.

For each polymer, the same spectrum was obtained in air as under vacuum at -170°C , indicating that oxygen had no influence on the primary photochemical processes. On warming, the polymers were observed to undergo the same radical transformation in air or under vacuum, at the same temperatures, as reported by others. No effects from the additives on the ESR signal behavior upon warming were discernable.

Conclusions

From our observations, it appears that the additives are acting as photosensitizers and that the primary photochemical process is a transfer of energy from the excited singlet state of the additive chromophore to the polymer, resulting in the formation of free radicals. The reactive nature of the free radicals, as indicated by their transformations and decay upon warming, may explain the increased photodegradation which the modified polymers have been observed to undergo when illuminated with a sunlamp at room temperature.

References

1. B. Freedman and M. J. Diamond, *J. Appl. Polym. Sci.*, **20**, 463 (1976).
2. B. Freedman, *J. Appl. Polym. Sci.*, **20**, 911 (1976).

3. B. Freedman, *J. Appl. Polym. Sci.*, **20**, 921 (1976).
4. C. Djerassi, *Chem. Rev.*, **43**, 291 (1948).
5. K. Tsuji, *Amer. Chem. Soc. Prepr., Div. Org. Coat. Plast. Chem.*, **35**, 167 (1975).
6. K. Tsuji, *Advan. Polym. Sci.*, **12**, 131 (1973).
7. B. Ranby, J. F. Rabek, and Z. Joffe, *Degradability of Polym. and Plast. Conf. Pap.*, IEE, London, Nov. 27-28, 1973.
8. B. Ranby and H. Yoshida, *J. Polym. Sci. C*, **12**, 263 (1966).
9. H. L. Browning, H. D. Ackermann, and H. W. Patton, *J. Polym. Sci. A-1*, **4**, 1433 (1966).
10. K. Tsuji and T. Takashita, *J. Polym. Sci. B*, **10**, 185 (1972).
11. K. Tsuji and T. Seiki, *Polym. J.*, **1**, 133 (1970).
12. M. Iwasaki, T. Ichikawa, and K. Toriyama, *J. Polym. Sci. B*, **5**, 423 (1967).
13. P. I. Selivanov, E. I. Kirillova, and E. I. Waksimov, *Vysokomol. Soedin.*, **8**, 1418 (1966); *C. A.* **65**, 17073h (1966).

Received June 2, 1976

Revised July 14, 1976

Reference to a company or product name does not imply approval or recommendation of that product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.