# Cinnamylidene-Amine-Sensitized Photodegradation of Polyethylene

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## Synopsis

The activity of Schiff's bases of cinnamic aldehyde and aromatic amines in the controlled photodegradation of polyethylene (PE) was studied. N-cinnamylidene anilines containing different substituents in the amine ring (methyl group, halogen, or amine group) and N-cinnamylidene α-naphthyl amine were synthesized and introduced into the polyethylene films by compression molding or extrusion, and they were exposed to the filtered ultraviolet light produced by mercury lamp. The changes in molecular weight, tensile strength, and characteristic IR absorptions were followed during irradiation to control the processes undergoing in the polymer films. It was discovered that N-cinnamylidene anilines containing methyl or halogen substituents and N-cinnamylidene α-naphthyl amine accelerated the photodegradation of polyethylene. Their sensitizing activity increased when the mixtures of Schiff's bases and stannous laurate were introduced into the polymer. PE films containing these additives became brittle after 600 h exposure to the artificial UV light which was the equivalent of 1.5–2 years exposure to the natural sunlight in the medium geographic latitudes. The mechanism of the initial step of photodegradation is discussed.

## INTRODUCTION

In the early 1970s the necessity of broad application of photodegradable polymers was stated. It was expected that polymers degraded under the influence of the atmospheric agents would solve the problem of waste disposal.[1-3] Opponents to their broad application pointed out the ecological danger of environment pollution by the photodegradation products.[4,5] Photodegradable polymers, however, seem to be indispensible in the studies on degradation and stabilization processes in polymers.[6]

Incorporating the carbonyl group into the polymer in different ways is chemically advantageous because the mechanism of photodegradation sensitized by carbonyl is well defined and easy to control.[7-9] On the other hand, introducing the sensitizers into the polymer during processing is technologically more simple.

Schiff's bases containing the conjugated system of double olefin and imine bonds were suggested as photosensitizing additives for polyolefins.

Benzilidene anilines[10] of general structure and α-naphthyl amines[11,12]
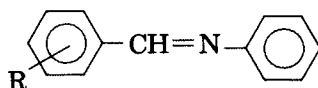


are chemically active when exposed to UV irradiation. α,β-Unsaturated imines were found to be the intermediates in the preparation of quinolines from unsaturated aromatic amines under the influence of UV light.[13] Some imines have been used as the antioxidants in rubber,[14] petrol,[15] and poly-

mers.[16-18] Gallagher[19] has found some interesting properties of *N*-cinnamylidene anilines during UV irradiation.

Metal salts used as sensitizers can cause synergistic effects when used in combination with other photoactive additives. Their activity is well explained on the basis of a redox mechanism.[20]

## EXPERIMENTAL

### Materials

Unstabilized polyethylene (PE) of low density in granular form was supplied by Zakłady Chemiczne "Oświęcim" as polyethylene II-020/FO. Schiff's bases were prepared by direct reaction of aldehyde and corresponding amine.[21] Metal laurates were synthesized by decomposition of an ethanolic solution of corresponding metal chloride with hot ethanolic solution of lauric acid.

### Compounding and Preparation of Films

All additives except chromium laurate were mixed with PE in powder form by trituration in a mortar. PE was previously powdered by precipitation from petrol solution by means of acetone. Chromium laurate was introduced into PE in solution. The corresponding amount of laurate was dissolved in ethyl acetate and mixed with polyethylene powder in a mortar. Ethyl acetate was then evaporated at room temperature under vacuum.

The mixtures were then homogenized when extruded in a melt flow indexer at 453 K under a load of 9.6 kg three times.

The films were compression-molded using stainless steel glazing plates.[22] The plates were maintained at 393 K under the pressure of $29.4 \times 10^3$ kN/$m^2$ for 15 s and then cooled to about 303 K by running cold water while maintaining full pressure.

The films for mechanical measurements were obtained by extruding the samples in granular form in Brabender–Plasti Corder type laboratory extruder.

### Irradiation of Films

The film samples were irradiated in a UV aging cabinet as described by Howard[23] and equipped with four mercury lamps type ASH 400. UV light was filtered by Pyrex glass to eliminate the waves shorter than 280 nm in order to simulate the irradiation conditions occuring in natural environment. Automatically controlled temperature in the cabinet was $295 \pm 2$ K with the light on. The distance between the samples and the light source was about 10 cm.

When filtered light was used, 1 h of irradiation in the cabinet corresponded to 1 h of exposure to summer sunlight.

### Measurement Techniques

IR absorption spectra were recorded using a UR-20 Spectrophotometer (East Germany) and were used for estimating the increase in carbonyl

absorbance peak at 1720 cm$^{-1}$ during irradiation. The results were expressed by carbonyl index $I_{CO}$ defined as

$$I_{CO} = A_{1720}/d$$

where $A_{1720}$ = absorbance of carbonyl group and $d$ = thickness of the film (mm). UV absorption spectra were recorded using a Specord Spectrophotometer Model UV-vis (East Germany).

ESR spectra were recorded by means of microwave Varian Spectrometer Model E-5. The samples were kept in vacuum for 1 h before registering the spectra to remove oxygen. The measurements conditions: frequency 9.233 GHz, magnetic induction 3275 G, and amplification 8 × 10$^5$. A Varian "strong pitch" standard containing 3 × 10$^{15}$ spins/cm was used for spin concentration calculations.

Molecular weights of PE were determined in the viscosity method, using $p$-xylene solutions and calculated from the Mark–Houwink equation by means of the following constants: $\alpha$ = 0,63, $K$ = 0.00135/100 cm$^3$.

Tensile strength measurements were made using an Instron Tensile Tester Model TTDM with crosshead speed 5 cm/min at room temperature.

## RESULTS AND DISCUSSION

The photochemical activity of some Schiff's bases of cinnamic aldehyde and aniline derivatives in PE degradation was studied.

Tests were carried out in two steps. In the first step in which nonfiltered UV light was used for irradiation the most active cinnamylidene amines were chosen. The $N$-cinnamylidene anilines containing chlorine or bromine atom in the aromatic ring and the $\alpha$-naphthyl amine showed the best sensitizing properties (Table II). They absorbed the UV light the most intensively (Table I). $N$-cinnamylidene nitroanilines weakly absorbing the UV light were less active than $N$-cinnamylidene aniline. On the other hand, symmetrically built $N,N'$-cinnamylidene $p$-phenylenediamine stabilized polyethylene, although its molar extinction was as high as molar extinction of $N$-cinnamylidene $\alpha$-naphthyl amine. Thus the ability to sensitize the

TABLE I
Molar Extinction Coefficients of the Schiff's Bases in the Region 250–350 nm

| Schiff's base | Absorption maximum (nm) | $\epsilon \times 10^{-4}$ (dm$^3$ m$^{-1}$ cm$^{-1}$) |
|---|---|---|
| $N$-cinnamylidene $o$-bromoaniline | 300 | 3.54 |
| $N$-cinnamylidene $p$-bromoaniline | 300 | 3.41 |
| $N$-cinnamylidene $p$-toluidine | 290–300 | 2.34 |
| $N$-cinnamylidene $p$-chloroaniline | 290–300 | 3.30 |
| $N$-cinnamylidene $p$-nitroaniline | 300 | 2.09 |
| $N$-cinnamylidene $o$-bromo-$p$-nitroaniline | 300 | 1.49 |
| $N,N'$-bis-cinnamylidene $p$-phenylene diamine | 370 | 2.77 |
| $N$-cinnamylidene $\alpha$-naphthyl amine | 300 | 2.71 |
| $N$-cinnamylidene aniline | 290–300 | 2.28 |
| $N$-benzylidene aniline | 250–300 | No maximum 0.48 |
| $N$-benzylidene $\alpha$-naphthylamine | 250–300 | No maximum 0.50 |

TABLE II
Results of testing the Sensitizing Activity of Schiff's Bases[a]

| Additive | Concentration (wt %) | Irradiation time (h) | $I_\infty$ | Molecular weight | |
|---|---|---|---|---|---|
| | | | | Before irradn. | After irradn. |
| N-cinnamylidene p-toluidine | 0.1 | 80 | 0.63 | 25,000 | 16,000 |
| | 0.5 | 80 | 0.63 | 25,200 | 15,900 |
| | 1.0 | 80 | 0.71 | 24,900 | 15,100 |
| N-cinnamylidene o-bromoaniline | 0.02 | 40 | 0.51 | 28,000 | 15,400 |
| | 0.05 | 40 | 0.69 | 28,200 | 15,000 |
| | 0.1 | 40 | 0.97 | 27,300 | 12,100 |
| | 0.5 | 40 | 1.47 | 27,700 | 11,800 |
| | 1.0 | 40 | 1.23 | 26,800 | 11,500 |
| N-cinnamylidene p-bromoaniline | 0.1 | 40 | 0.76 | 28,800 | 15,200 |
| | 0.5 | 40 | 0.70 | 26,100 | 14,700 |
| | 1.0 | 40 | 0.85 | 25,700 | 14,000 |
| N-cinnamylidene p-chloroaniline | 0.1 | 40 | 0.57 | 25,900 | 16,200 |
| | 0.5 | 40 | 0.82 | 26,400 | 14,800 |
| | 1.0 | 40 | 0.69 | 25,700 | 15,000 |
| N-cinnamylidene p-nitroaniline | 0.1 | 40 | 0.16 | 26,300 | 23,000 |
| | 0.5 | 40 | 0.52 | 26,000 | 21,300 |
| | 1.0 | 40 | 0.14 | 27,100 | 25,200 |
| N-cinnamylidene o-bromo-p-nitro aniline | 0.05 | 40 | 0.69 | 26,400 | 16,900 |
| | 0.1 | 40 | 0.76 | 25,800 | 15,300 |
| | 0.5 | 40 | 0.70 | 27,000 | 16,000 |
| N,N'-bis-cinnamylidene p-phenylene diamine | 0.5 | 80 | 0.10 | 30,000 | 29,400 |
| | 1.0 | 80 | 0.05 | 27,200 | 28,000 |
| | 2.0 | 80 | 0.10 | 28,300 | 27,600 |
| N-cinnamylidene α-naphthylamine | 0.02 | 40 | 0.51 | 29,500 | 22,300 |
| | 0.05 | 40 | 0.69 | 29,300 | 16,600 |
| | 0.1 | 40 | 0.75 | 30,600 | 13,300 |
| | 0.5 | 40 | 0.76 | 29,800 | 15,400 |
| | 1.0 | 40 | 0.34 | 29,800 | 23,400 |
| N-cinnamylidene aniline | 0.1 | 80 | 0.63 | 24,200 | 15,700 |
| | 0.5 | 80 | 0.69 | 25,500 | 14,800 |
| | 1.0 | 80 | 0.71 | 25,200 | 15,100 |
| N-benzylidene aniline | 0.1 | 80 | 0.39 | 28,900 | 20,500 |
| | 0.5 | 80 | 0.33 | 29,300 | 20,500 |
| | 1.0 | 80 | 0.33 | 29,000 | 21,000 |
| N-benzylidene α-naphthylamine | 0.1 | 80 | 0.21 | 30,100 | 28,900 |
| | 0.5 | 80 | 0.25 | 30,000 | 29,300 |
| | 1.0 | 80 | 0.22 | 29,800 | 29,000 |
| Polyethylene without additive | — | 80 | 0.55 | 28,800 | 21,000 |

[a] Films irradiated with nonfiltered UV light.

polymer photodegradation is closely correlated with the molecule structure. The spectral properties, however, can only partly qualify the substance as photodegradation sensitizer.

Comparing the activities of N-cinnamylidene amines with the weak sen-

sitizing properties of $N$-benzylidene amines, I showed that the conjugated system of double olefin and imine bonds was responsible for the sensitizing activity of $N$-cinnamylidene amines.

In the second step the polyethylene films containing the most active $N$-cinnamylidene amines, i.e., $N$-cinnamylidene $o$-bromoaniline and $N$-cinnamylidene $\alpha$-naphthyl amine, were irradiated with the filtered UV light during 600 h. The irradiation resulted in an average decrease of PE molecular weight about 2–2.5 times and of tensile strength about 15% in comparison with nonirradiated films (Fig. 1). The greatest changes of the film properties occurred during the first 100 h of irradiation.

In order to increase the sensitizing activity of the cinnamylidene amines, they were mixed with the transition metal laurates when added to PE. The mixtures containing 0.5% $N$-cinnamylidene $o$-bromo aniline or 0.1% $N$-cinnamylidene $\alpha$-naphthyl amine and manganous or ferrous or stannous laurate in amounts from 0.5 to 2% were applied. The irradiation of PE films containing the above systems with the filtered light indicated that only stannous laurate cooperated with the Schiff's base in accelerating PE photodegradation. After 200 h irradiation of the films containing $N$-cinnamylidene amine and stannuous laurate the molecular weight of polyethylene decreased about 4–5 times and tensile strength dropped down by 30% (Fig. 2). These films irradiated for 600 h with the filtered UV light became brittle. The decrease in the tensile strength of the films occurred almost regularly during the whole period of irradiation (Fig. 3).
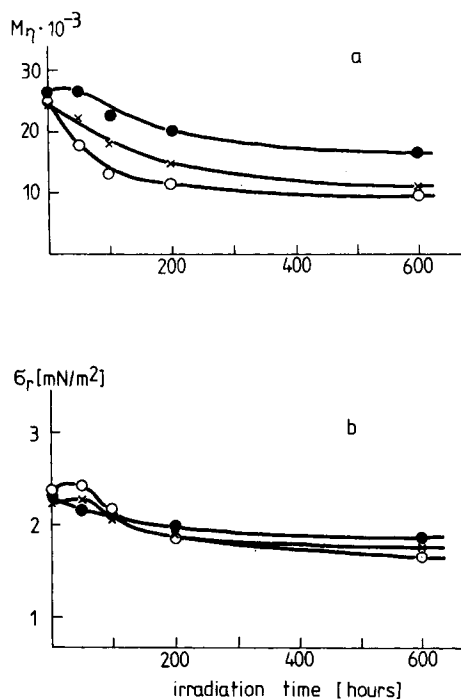


Fig. 1. Changes in the molecular weight $M_\eta$ (a) and the tensile strength $\sigma_r$ (b) of the PE films irradiated with the filtered UV light, containing: ($\bigcirc$) 0.5% of $N$-cinnamylidene $o$-bromoaniline (NCBA); ($\times$) 0.1% of $N$-cinnamylidene $\alpha$-naphthylamine (NCNA); ($\bullet$) 0.5% of $N$-cinnamylidene aniline (NCA).

Studying the mechanism of the photodegradation reaction in the initial stage, I examined the free radical generation in the powdered $N$-cinnamylidene amines during their irradiation in the ESR spectrometer cell. The ESR spectra showed the presence of free spins in nonirradiated amines possibly caused by imperfect removal of oxygen from the samples. Their concentration, however, did not change during the irradiation (Fig. 4). The concentration of free spins in the most active $N$-cinnamylidene $o$-bromoaniline increased from $2.06 \times 10^{10}$ to $2.21 \times 10^{10}$ spins/cm in comparison with the spin concentration increase in irradiated $\alpha$-azobisisobutyronitrile from 0 to $5.95 \times 10^{12}$ spins/cm. $N,N'$-biscinnamylidene $p$-phenylene diamine which did not accelerate the PE photodegradation showed a similar increase in the spin concentration as $N$-cinnamylidene $o$-bromoaniline. Therefore, the initiation of the photodegradation reaction by free radical generation in the amine molecule was not an explanation.

Direct hydrogen abstraction from polyethylene by excited states of the Schiff's bases would inevitably lead to further decomposition of the sensitizer molecule. Present experiments (IR spectrophotometry) gave no evidence for such reaction.

It is now generally agreed that hydroperoxides play a key role in free radical initiation.[24-27] Their classical formation, however, in the reaction $P \cdot + O_2 \rightarrow POO \cdot$ followed by $PO_2 \cdot + RH \rightarrow POOH + P \cdot$ could not be ac-
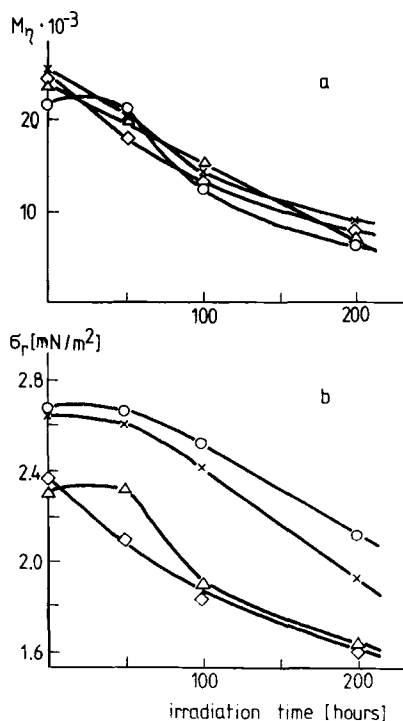


Fig. 2. Changes in the molecular weight $M_\eta$ (a) and the tensile strength $\sigma_r$ (b) of the PE films irradiated with the filtered UV light, containing: (○) 0.5% of NCBA and 1.0% of stannuous laurate; (×) 0.5% of NCBA and 2.0% of stannuous laurate; (△) 0.1% of NCNA and 1.0% of stannuous laurate; (◇) 0.1% of NCNA and 2.0% of stannuous laurate.
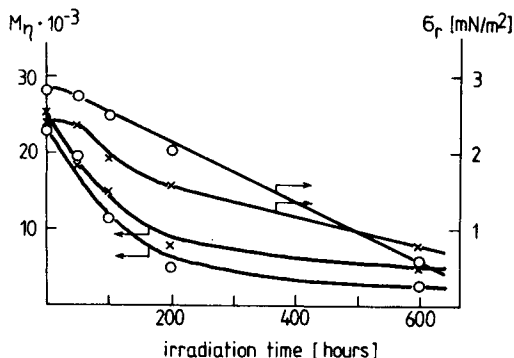
Fig. 3. Changes in the molecular weight $M_\eta$ and the tensile strength $\sigma_r$ of the PE films irradiated with the filtered UV light, containing: (◯) 0.5% of NCBA and 2.0% of stannuous laurate; (×) 0.1% of NCNA and 2.0% of stannuous laurate.

celerated by Schiff's bases, which did not initiate the formation of free radicals in the polymer matrix. Instead the energy of the excited states of the cinnamylidene amines could increase the concentration of singlet oxygen and probability of its direct reaction with unsaturations present in polyethylene. This theory, quite popular some years ago,[28-30] was strongly questioned on the basis of kinetics considerations.[24,31] A number of recent observations appear to suggest that oxygen–polymer charge transfer complexes break down on photolysis to form hydroperoxides.[32,33] The formation
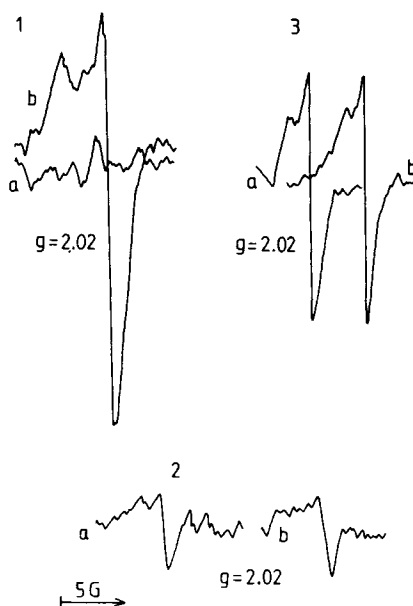


Fig. 4. ESR spectra of the Schiff's bases before (a) and after (b) irradiation with nonfiltered UV light for 30 min: (1) control AIBN; (2) N-cinnamylidene o-bromoaniline; (3) N,N'-bis-cinnamylidene p-phenylene diamine.

TABLE III
Changes in the Physical Properties (Molecular weight $M_\eta$ and Tensile Strength $\sigma$) of the Sensitizers Containing Polyethylene Films after 200 h Irradiation with the Filtered UV Light

| Sensitizor | Film properties before irradiation | | Film properties after irradiation in | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | Vacuum | | Air | | Oxygen | |
| | $M_\eta$ | $\sigma_0$ | $M_\eta$ | $\sigma_x$ | $M_\eta$ | $\sigma_x$ | $M_\eta$ | $\sigma_x$ |
| 1 | 25,300 | 2.35 | 24,100 | 2.35 | 12,100 | 1.95 | 12,500 | 1.88 |
| 2 | 23,000 | 2.81 | 22,800 | 2.70 | 5200 | 2.03 | 3900 | 1.80 |
| 3 | 24,600 | 2.25 | 23,000 | 2.19 | 14,600 | 1.92 | 13,800 | 1.90 |
| 4 | 23,200 | 2.31 | 21,800 | 2.36 | 9200 | 1.58 | 7600 | 1.48 |
| PE without additive | 28,800 | 2.61 | 27,100 | 2.60 | 20,800 | 2.56 | 20,200 | 2.20 |

[a] Sensitizing systems were: (1) 0.5% of $N$-cinnamylidene $o$-bromoaniline (NCBA); (2) 0.5% of NCBA and 2% of stannuous laurate; (3) 0.1% of $N$-cinnamylidene $\alpha$-naphthylamine (NCNA); (4) 0.1% of NCNA and 2% of stannuous laurate.

of CT complexes in the systems containing $N$-cinnamylidene amines was not examined, but it can be suggested that any amount of energy absorbed by the sensitizer and transferred to the oxygen–polymer system will accelerate the reaction of CT complexes photolysis and photodegradation of the polymer chain.

The results of present experiments do not allow us to specify the initiation mechanism of the Schiff's bases sensitized photodegradation of polyethylene. The key role of oxygen in the system seems to be undisputable. The polymer irradiated in vacuum did not degrade even in the presence of the most active sensitizing systems (Table III). Instead, increased concentration of oxygen in the environment resulted in accelerated photodegradation of PE.

Finally it could be concluded that $N$-cinnamylidene amines acted like typical sensitizers playing the role of light energy transformer to the oxygen–polymer system whatever the further reaction of hydroperoxides formation.

The synergistic effect discovered in the polyethylene films when the system $N$-cinnamylidene amine–stannuous laurate was used was probably due to the ability of stannuous salt to catalyze the hydroperoxide decomposition, but it was not studied in detail.

The practical applicability of the described systems seems to be limited. They did not secure the induction period, and deterioration of the mechanical properties of PE films started immediately after exposure. This makes the films useless for packaging materials requiring a relatively long period of stable mechanical properties before they start degrading. For such purposes the system needs modification.

# References

1. G. Scott, *Chem. Britain,* **9**, 267 (1973).
2. J. E. Guillet, *Plast. Eng.,* **30**, 48 (1974).

3. G. Scott, *Resource, Recovery Conserv.*, 1, 381 (1976); *Polymers and Ecological Problems*, New York, 1976, pp. 1–25, 27–44.

4. L. Taylor, *Chem. Tech.*, 9, 542 (1979).

5. E. M. Evans, *Degradability of Plastics*, London, 1973.

6. D. Gilead and G. Scott, *Developments in Polymer Stabilization*, London and New York, 1982, Vol. 5, pp. 71–106.

7. J. E. Pitts and J. K. S. Wan, *Photochemistry of Carbonyl Compounds*, New York, 1966.

8. P. I. Ploard and J. E. Guillet, *Macromolecules*, 5, 405 (1972).

9. K. Tsuyi, *Adv. Polym. Sci.*, 12, 131 (1973).

10. K. H. Grellman and E. Tauer, *J. Am. Chem. Soc.*, 95, 3104 (1964).

11. J. Shannon and H. Silbermann, *Tetrahedron Lett.*, 659 (1964).

12. P. J. Collin, *Tetrahedron Lett.*, 2063 (1965).

13. V. Ogata and K. Tagaki, *Tetrahedron*, 27, 1573 (1971).

14. Bridgestone Tire Co., Fr. Pat. 1529624 (1968).

15. H. G. Smith and T. S. Cantrell, U. S. Pat. 2560489 (1968).

16. F. Broich, Ger. Pat. 1028330 (1969).

17. H. Clough, Bri Pat. 787859 (1957).

18. H. A. Cyba, U. S. Pat. 3361712 (1968).

19. P. H. Gallagher, *Bl.*, 29, 968 (1921).

20. U. T. Kagyia, K. Takemoto, and M. Hagiwara, IUPAC Macromol. Symp., Long-Term Properties of Polymers and Polymeric Materials, Stockholm, 1976.

21. L. N. Ferguson and G. E. K. Brauch, *J. Am. Chem. Soc.*, 66, 1476 (1944); G. Peine, *Ber.*, 17, 2109 (1884).

22. M. V. Amin and G. Scott, *Eur. Polym. J.*, 10, 1019 (1974).

23. J. B. Howard and H. M. Gilroy, *Polym. Eng. Sci.*, 9, 286 (1969).

24. D. J. Carlsson, A. Garton, and D. M. Wiles, in *Developments in Polymer Stabilization*, London, 1979, Vol. 1, pp. 219–257.

25. D. J. Carlsson, A. Garton, and D. M. Wiles, in *Developments in Polymer Photochemistry*, London, 1980, Vol. 1, p. 93.

26. D. J. Carlsson, A. Garton, and D. M. Wiles, *Macromol. Chem.*, 181, 1841 (1980).

27. G. Scott, in *Developments in Polymer Degradation*, London, 1977, Vol. 1, p. 205.

28. M. L. Kaplan, *Chem. Tech.*, 1, 621 (1971).

29. M. L. Kaplan and P. G. Kelleher, *J. Polym. Sci.*, B9, 565 (1971).

30. J. F. Rabek, *Wiadomości Chemiczne*, 25, 293 (1971).

31. D. J. Carlsson, T. Suprunchuk, and D. M. Wiles, *J. Polym. Sci., Polym. Lett. Ed.*, 14, 495 (1976).