

Photooxidation of Polystyrene: Irradiation at 254 and 365 nm

E. P. OTOCKA, *Eastman Kodak Company, Rochester, New York*,
S. CURRAN, *Monsanto Co., Springfield, Massachusetts*, and ROGER S.
PORTER,* *Department of Polymer Science and Engineering, Materials
Research Laboratory, University of Massachusetts, Amherst,
Massachusetts 01003*

Abstract

Studies have been made of the near surface photooxidation of atactic polystyrene films prepared in the absence of air. The samples were photooxidized on exposure to air at two frequencies, 254 and 365 nm, using a calibrated mercury irradiation source with filters. Most studies were made at 40°C and as a function of irradiation time with the reactions characterized by changes in molecular weight and composition. The former was evaluated by gel permeation chromatography and the latter by transmission Fourier transform infrared spectroscopy and by multiple-internal-reflectance infrared spectra using different angles and different crystals to evaluate compositions as a function of film depth. Species identified in photooxidation include the generation of hydroperoxides and the appearance of carbonyl bands with the latter identified by the spectral shift associated with the exposure of the photooxidized polystyrene surface to ammonia. These results suggest that principal products of near-surface oxidation of polystyrene are carboxylic acids.

INTRODUCTION

Many investigations of the photooxidation of polystyrene (PS) have resulted in a variety of proposed reaction mechanisms.¹⁻³⁰ Methods employed to characterize the reaction intermediates include mass spectroscopy, gas chromatography, infrared spectroscopy, fluorescence spectroscopy, and, most recently, ESCA.³¹

The purpose of this work is to continue the clarification of the photodegradation process, with emphasis on the wavelength dependence on the course of degradation, using infrared spectroscopy as the primary characterization method. At 254 nm PS is a strong absorber, and thus virtually all photochemistry occurs within microns of the polymer surface. Peeling and Clark³⁰ have used ESCA to good advantage in a recent study of photooxidized PS surface. They showed that peroxy and carboxylic acids appear to be the major products of irradiation by the full mercury lamp spectrum. Their study also revealed that, at steady state, hydroperoxides were the next most populous species at the surface, followed by ketones/aldehydes. The majority of their oxidation products were considered to result from hydroperoxide decomposition. Their work also lends support to the Ranby and Rabek¹² suggestion of direct aromatic ring oxidation. Peeling and Clark observe a significant decline in the [(C—C) + (C—H)] to

* To whom correspondence should be addressed.

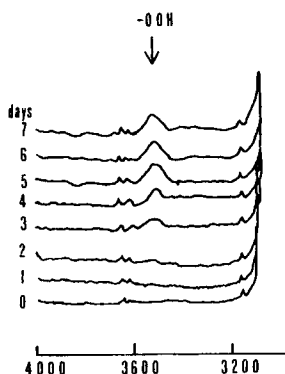


Fig. 1. Infrared FTIR absorbance peaks for hydroperoxide groups and carboxylic acid groups at various exposure times for 365 nm irradiation of PS film in air.

$C^-(O)_x$ ratio, and many workers observed that benzene is not found among the volatile species of photooxidation.³⁰

EXPERIMENTAL

Photolysis at 254 nm was achieved by low-pressure mercury lamp exposure for a simple water-jacketed thermostatted quartz cell through which air could be drawn. Actinometry established the intensity as $778 \mu\text{W}/\text{cm}^2$ for test conditions. Periodic recalibration indicated no change in lamp output. A filtered, medium-pressure mercury lamp was used for 365 nm photolysis using the same cell and film geometries as in the 254 nm exposure study. The cell was thermostatted at 40 or 85°C for the duration of the irradiation.

A narrow molecular weight distribution PS from Pressure Chemical Co. was used throughout the course of this investigation. Films were prepared by dissolving PS in distilled-in-glass THF (Burdick and Jackson) to a concentration of 5–10%. Solutions were purged with N_2 , cast onto clean glass at 20°C, and slowly dried for 48 h under an N_2 blanket. Vacuum oven drying at 65–80°C for 96 h followed. During this period the oven was flushed with N_2 several times. Complete solvent removal (<0.1%) was confirmed by thermogravimetric analysis. Films were stored in the dark under N_2 until needed. Film thickness was $\sim 50 \mu$ in all cases.

Transmission Fourier transform IR spectra were obtained on a Nicolet 7199 System, using 200 scan summations. This method was applied to the 365 nm irradiated samples only. Multiple internal reflectance (MIR) spectra were taken on a Perkin-Elmer 283 Spectrometer with a Perkin-Elmer MIR attachment for the 254 nm irradiated samples. Both KRS-5 (45°, 60°) and Germanium (30°, 45°, 60°) crystals were employed. Penetration depths were calculated from Harricks equation.³¹

In this initial work, satisfactory FTIR subtraction of the reference spectrum of unoxidized PS from spectra taken during various stages of oxidation was not readily achieved. We have resorted to the less satisfactory ratio method where absorptions in the carbonyl region were ratioed to the methylene bending absorption at 1450 cm^{-1} . For MIR spectra, a drawback was encountered in our

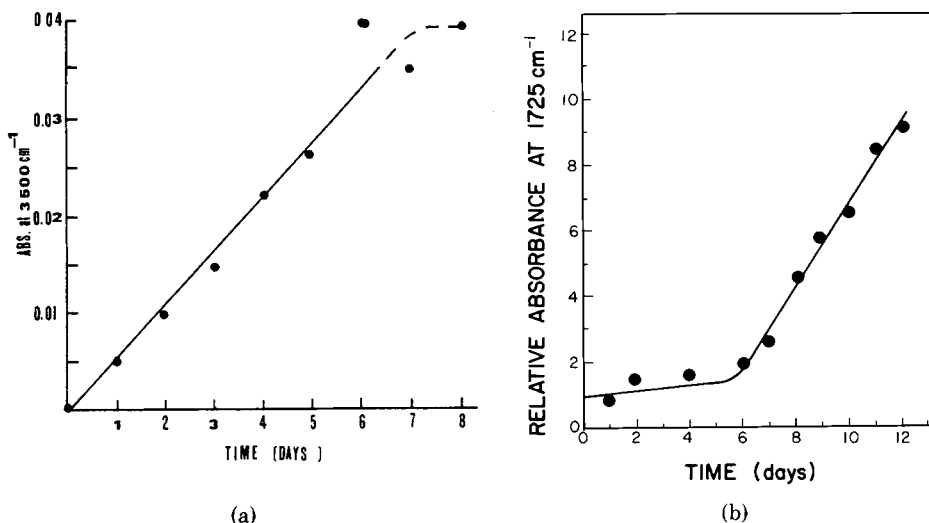


Fig. 2. Change in IR absorbance at (a) 3500 cm^{-1} and (b) 1700 cm^{-1} as a function of 365 nm irradiation time of PS film in air.

inability to monitor the region of hydroperoxide absorption. Again, because of the difficulty in mounting specimens reproducibly, the same relative absorption method for the carbonyl region was used.

Gel permeation chromatography was carried out on a Wafers Associates Model 201 GPC unit with five μ -Styragel columns of 10^6 , 10^5 , 10^4 , 10^3 , and 500 \AA indicated pore sizes. THF was the GPC solvent. PS samples were eluted before and after irradiation to assess changes in molecular weight distribution.

RESULTS AND DISCUSSION

For PS films exposed in air to 365 nm irradiation, FTIR clearly shows absorptions arising from hydroperoxides (3550 cm^{-1}) and carbonyl species ($1680\text{--}1740\text{ cm}^{-1}$), as seen in Figure 1. The time-dependent change of the former species is shown in Figure 2. It is evident that the formation of hydroperoxide initiates the reaction, with carbonyl species only appearing once hydroperoxide concentration reaches a steady state.

The fact that considerable chain scission has occurred after the 14-day irradiation at 365 nm was confirmed by GPC. Table I shows the before and after comparison of PS molecular weights. The average number of scissions per chain, N , can be calculated as a function of time t from

$$N_t = \frac{\bar{M}_n^0 - \bar{M}_n t}{\bar{M}_n t}$$

TABLE I
Molecular Weights of Polystyrene Changes on Irradiation in Air at 365 nm

	Initial	After 14 days
\bar{M}_n	110,000	83,500
\bar{M}_w	126,000	100,000
\bar{M}_w/\bar{M}_n	1.06	1.20

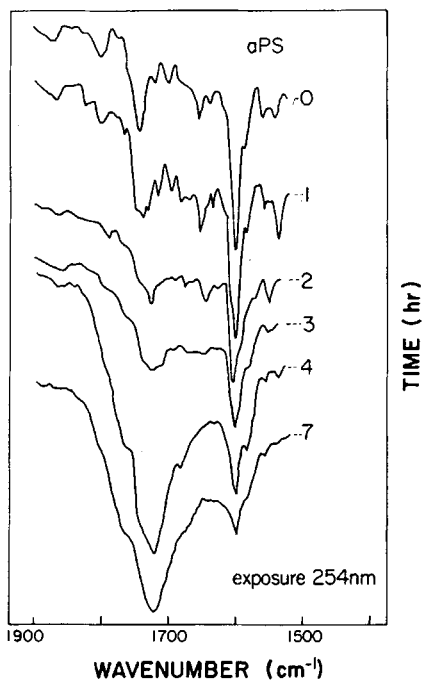


Fig. 3. The MIR carbonyl region of polystyrene as a function of irradiation time at 254 nm in air.

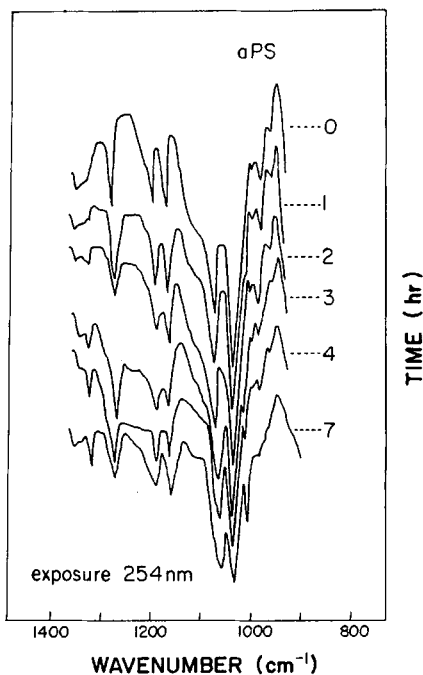


Fig. 4. Growth of the 1340 cm⁻¹ peak and the terminal vinyl peak, 995 cm⁻¹ as seen by MIR as a function of 254 irradiation time for PS film in air.

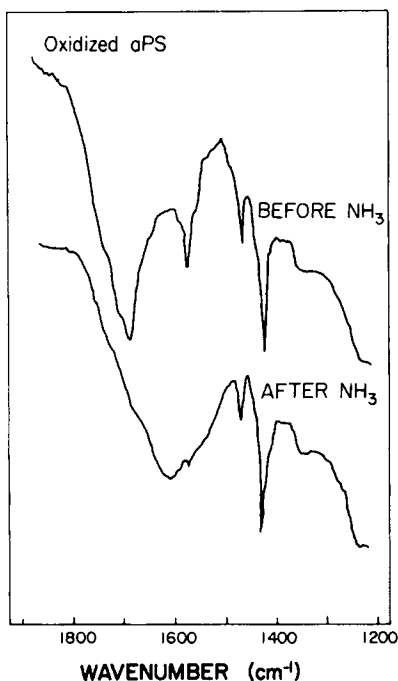


Fig. 5. Shift in the carboxylic acid peak in the MIR spectrum upon ammonia treatment.

which yields a value of $N = 0.43$ for 14 days exposure at 365 nm. The broadening of the MWD is consistent with a random scission process. The long exposure at this wavelength was chosen to provide uniform and extensive reaction for reliable GPC measurement.

The spectral changes in the carbonyl region of PS irradiated at 254 nm occur much more rapidly than with 365 nm exposure. Figure 3 shows the MIR spectra

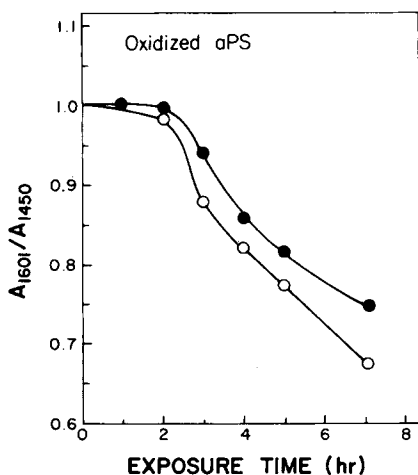


Fig. 6. Change in MIR absorbance at 1601 cm^{-1} , attributed to the phenyl ring of PS, as a function of 254 nm irradiation time in air. Depth (nm): (●) 1.22; (○) 0.39.

of the first 7 h of 254 nm irradiation. Additional peak growth was observed at 995 cm^{-1} (terminal vinyl) and 1340 cm^{-1} (unassigned), as seen in Figure 4. A companion study³² has confirmed the features presented here and has also shown that the relative absorption at 1725 cm^{-1} shows no apparent lag with regard to 3550 cm^{-1} (hydroperoxide) absorption. This is in substantial contrast to the previous description of 365 nm response of PS and suggests photodecomposition of hydroperoxides is occurring under 254 nm irradiation.

The identity of the carbonyl species absorption in the $1700\text{--}1800\text{ cm}^{-1}$ region was determined unambiguously by a simple chemical test. The irradiated films were exposed to NH_3 vapors over a concentrated aqueous solution for 4 h. The IR spectrum was then reexamined with the results shown in Figure 5. The absorption shifted near quantitatively from ~ 1730 to 1650 cm^{-1} . This behavior is only explainable if the absorbing species are carboxylic or peroxy acids. This finding is also in good agreement with the assignment of Peeling and Clark³⁰ that acids are the major product of photooxidation near the surface. However, at the depths probed by the MIR technique, the apparent ketone/aldehyde concentrations are much smaller than observed by ESCA.

Loss of skeletal ring vibrations (1601 cm^{-1}) has not been seen in the early stages of irradiation at 254 nm in this study or in the companion work of Ito and Porter.³² However, there is some indication of reduced 1601 intensity by MIR in the latter stages of the reaction shown in Figure 6. We intend to reinvestigate this question when satisfactory subtraction techniques are developed for the FT-MIR apparatus.

CONCLUSIONS

The observations of this work indicate that the photodegradation of polystyrene at 365 and 254 nm are similar. In both cases, carboxylic acids appear to be the major degradation products. The most notable differences appear to be in the hydroperoxide decomposition. For the shortwave exposure, final products are observed early in the degradation sequence, while their appearance is delayed at longer wavelengths, suggesting that hydroperoxides are not photochemically decomposed at 365 nm.

This study does not offer supportive evidence for direct ring oxidation at 254 nm, because no substantial ketone or aldehyde absorptions were observed. This aspect of the degradation mechanism will be the subject of further study.

An important aspect of clarifying the degradation mechanism will be a quantitative comparison of acid formation and chain scission. With the techniques now available, such a comparison should be possible and will be addressed in future work on this problem.

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