

The Effects of Oxygen Diffusion on the Surface Photooxidation of Polystyrene

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Synopsis

This paper further illustrates the applicability of multiple internal reflectance infrared spectroscopy to the analysis of near-surface photooxidation. The results are compared with transmission infrared spectra to evaluate compositional gradients resulting from photooxidation and the influence of oxygen diffusion. The sample was a solvent-cast film of atactic, narrow distribution polystyrene, M_w of 100,000, that had been drawn to a ratio of 3.0 at 110°C by solid state coextrusion. Irradiation of these thin films, $\sim 25\mu\text{m}$ thickness, was performed on exposure to air at 35°C for periods of up to 6 h using a mercury source emitting at 254 nm. On photooxidation, a broad peak appears at 3200–3500 cm^{-1} , attributable to hydroperoxide formation. The most dramatic increase in the infrared spectra is found for a carbonyl band at 1730 cm^{-1} . It appears to result from an aromatic acid group since it is shifted to 1660 cm^{-1} on immersion of the oxidized polystyrene films in aqueous ammonium hydroxide. It is confirmed that the photooxidation of polystyrene occurs preferentially at the surface and that this reaction rate is greatly reduced in the drawn polystyrene film.

INTRODUCTION

Photooxidation and photodegradation of polystyrene (PS) have been widely investigated,¹ and subsequent work by many authors has attempted to determine the mechanism of PS photooxidation. However, published papers do not give a consistent theory, and frequently they are even contradictory. A major problem in studying polymer photooxidation is the low concentration of oxidation products in the early stages of reaction. In extensive photooxidation, volatile products make interpretation of the results difficult, due to complex secondary reactions. Carlsson and Wiles² studied the photooxidation of polypropylene by multiple internal reflection infrared spectroscopy (MIR-IR) and found a preferential surface initiation of photooxidation. They suggested that the presence of polymeric carbonyls or peroxides in the surface layer developed in film preparation, induced a preferential surface photooxidation. On the other hand, Wilson³ predicted that preferential surface oxidation might arise in certain gas-polymer reactions due to the low gas permeability in polymers. In this paper we will show the applicability of MIR-IR to the analysis of PS photooxidation, and the influence of oxygen diffusion is examined by comparing the MIR-IR spectra of photooxidation isotropic PS film with the transmission IR spectra of similar films and photooxidation drawn PS films. The mechanism of PS photooxidation is considered in the light of these new results.

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EXPERIMENTAL

Atactic polystyrene (PS) was purchased from Pressure Chemical Co., Pittsburgh, Pa.; its molecular weight and distribution were $M_w = 100,000$ and $M_w/M_n < 1.06$. Thin films of this PS were cast onto glass plate from 15% solution in distilled chloroform. A steady stream of nitrogen gas was passed over the films as they dried. The films were further dried *in vacuo* at 100°C for 4 days. Drawn PS films were obtained using the coextrusion technique developed in this laboratory.⁴ For the drawing matrix, a commercial polyethylene rod, $\frac{3}{8}$ in. in diameter, was split longitudinally into halves, resulting in smooth planar surface. The solvent cast PS film was placed between the two polyethylene halves and the cylindrical coassembly extruded through a conical die of 20° entrance hemiangle in an Instron Capillary Rheometer at 110°C in a nitrogen atmosphere. The extrusion draw ratio studied was 3.0 as deduced from the displacement on extrusion of ink marks drawn on the original PS film surface. The physical properties of this PS drawn by this method have been described.⁵ All the samples were stored in a vacuum container in the dark at room temperature.

A low-pressure mercury lamp (Minera Light UVS-54) was used which emits more than 90% of its light at 254 nm. No filter was deemed necessary. Every PS sample was placed in an oxidation cell at a distance of 5 cm from the mercury lamp in air. The atmospheric temperature was maintained at $\sim 35^\circ\text{C}$ during the irradiation.

All spectra were obtained with a Perkin-Elmer 283 infrared spectrophotometer. MIR-IR spectra were obtained using a Perkin-Elmer accessory with trapezoidal single pass reflecting crystals. MIR measurements were made with both KRS-5 and Ge crystals. The incident angles were 45° and 60° for KRS-5 and 30°, 45°, and 60° for Ge. The penetration depth of the IR beam into the sample was calculated using Harrick's equation.⁶

RESULTS AND DISCUSSION

The IR spectra show distinctive changes on photooxidation. A broad peak at 3200–3500 cm^{-1} appears, attributable to hydroperoxide formation.⁷ In the initial stage of photooxidation, an acetophenone peak at 1685 cm^{-1} ⁸ is separable from the 1730 cm^{-1} band; however, after long exposure time, this comparatively weak band overlaps the strong 1730 cm^{-1} band. The most dramatic change in peak intensity is found in the 1730 cm^{-1} band. Although this band assignment has not been firmly established, as discussed later, it was felt that this peak is appropriate for monitoring the photooxidation of PS. A factor which may affect the peak height in MIR-IR is the possible variation in contact between the sample and the face of the reflection element. To reduce this problem, the peak heights were ratioed to that of the band at 1450 cm^{-1} , a bending mode of $-\text{CH}_2-$ in PS,⁹ which is found not to change in intensity after the 6-h test for photooxidation. The relative intensities were then normalized to the same ratio of band obtained prior to irradiation. This value has been considered the normalized intensity (NI). The NI for the 1730 cm^{-1} band for the PS samples exposed for different irradiation times is plotted against penetration depth in Figure 1. It is clear that, at every irradiation time, the extent of oxidation decreases with increasing penetration depth. This means that photooxidation occurs preferentially at the film surface. In the present study, all the samples were prepared under the

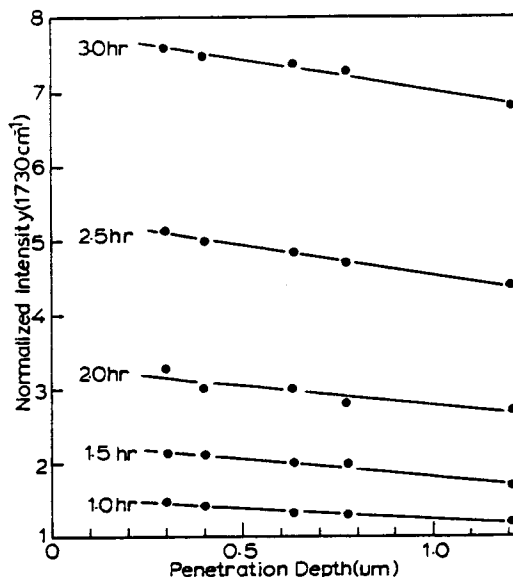


Fig. 1. Variation in normalized intensity for the 1730 cm^{-1} band with penetration depth in PS film at different irradiation times.

nitrogen atmosphere and were stored *in vacuo*. Therefore, the introduction of impurities in the film surface during the sample preparation was unlikely. The drawing of polymers has been shown to substantially reduce the permeability to gases.^{10,11} To evaluate the importance of oxygen gas permeability on the preferential surface photooxidation, the IR spectra of photooxidized isotropic PS film were compared with those of drawn PS. Due to the restriction of sample geometry of drawn PS, the MIR-IR spectra were of limited signal to noise ratio. Therefore, we used the conventional transmission IR method to compare drawn and undrawn PS. This also provides information on all the changes that occurred across the film thickness. The normalization procedure used for the peak intensity of transmission IR spectra is identical with that for the MIR-IR spectra. The NI of the 1730 cm^{-1} band for the drawn and undrawn PS film is plotted against irradiation time in Figure 1. For comparison, film surface data obtained by MIR-IR are also included. It is evident that photooxidation occurs preferentially at the film surface and that little reaction occurs in the bulk of the samples even on prolonged irradiation. Furthermore, the photooxidation rate is greatly reduced in the drawn PS film. The sample thickness for the drawn PS was $\sim 25\ \mu\text{m}$, similar to that of the isotropic PS sample. Therefore, the difference is absorbed UV energy between drawn and undrawn samples is negligible. After 1.5 h irradiation, Figure 2 indicates that there is a significant photooxidation on the film surface. On the other hand, the changes that occur in the bulk of the isotropic PS are small up to 3 h of irradiation. In the drawn sample, photooxidation is markedly less even after 6 h of irradiation. This suggests that the photooxidation involves an induction step in the film interior. All the samples were stored in vacuum. The first contact they have with oxygen is when they are placed in the oxidation cell under air for 15 min prior to irradiation. This time allows diffusion of oxygen to PS surface. With time, oxygen can diffuse ever deeper; however, the diffusion rate is apparently greatly reduced by chain orientation of PS.

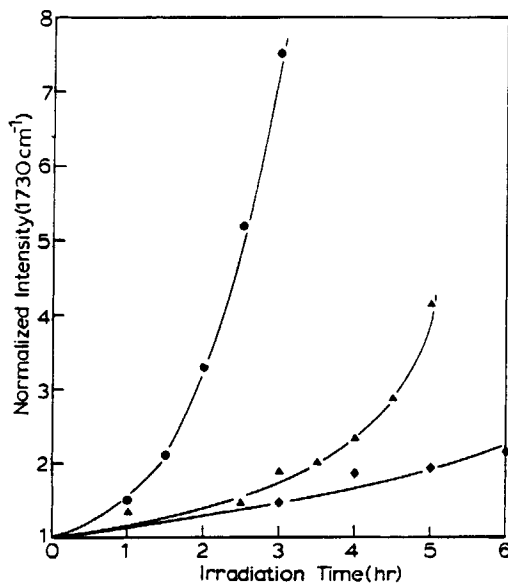


Fig. 2. Effect of irradiation time on the normalized intensity at 1730 cm^{-1} : (●) surface ($0.3\ \mu\text{m}$); (▲) bulk isotropic; (◆) bulk drawn PS.

From these features it is concluded that the observed preferential surface photooxidation of PS film likely results from the oxygen-polymer reaction controlled by the slow oxygen permeation to the PS interior.

Surface analysis of oxidized PS can provide some insights to the mechanism of PS photooxidation. As shown in Figures 1 and 2, the concentration of products at the film surface is higher than that in the bulk. The NI at 3350 , 1730 ,

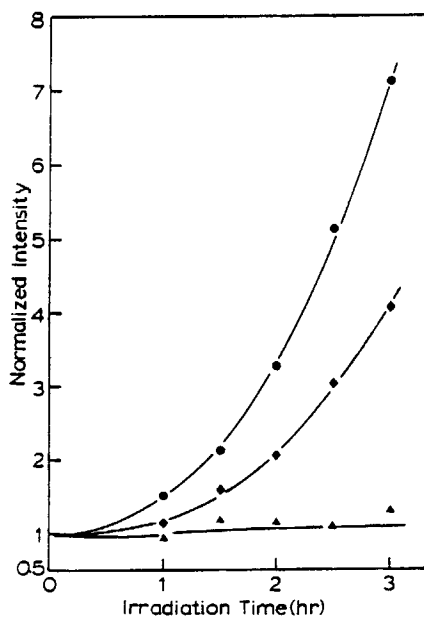


Fig. 3. Effect of irradiation time on the normalized intensity obtained from MIR-IR spectra at (●) 1730 cm^{-1} , (◆) 3350 cm^{-1} , and (▲) 1602 cm^{-1} .

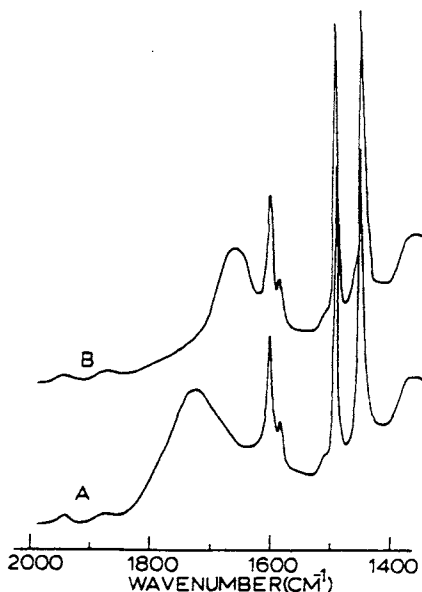


Fig. 4. MIR-IR spectra irradiated PS (3 h), before (A) and after (B) treatment with NH_4OH for 4 h.

and 1602 cm^{-1} bands in the film surface region are plotted against irradiation time in Figure 3. The NI of the 3350 cm^{-1} band, due to the formation of hydroperoxide,⁷ increases with increasing irradiation time in accord with prior study.¹² The NI of the 1730 cm^{-1} band also increases with irradiation time. There has been disagreement in the abundant literature over the assignment of this peak. Rabek and Ranby¹³ attributed it to a phenyl ring opening reaction to produce dialdehydes. On the other hand, Geuskens et al.⁷ attributed it to formation of aliphatic ketones. If carbonyl groups are formed by photooxidation of PS, acid formation may result from the Norrish type reaction. The assignment of the 1730 cm^{-1} band was evaluated by the following test. A photooxidation PS film was immersed in concentrated aqueous ammonium hydroxide. After washing with water and drying, MIR-IR spectra were recorded with the results shown in Figure 4. The 1730 cm^{-1} band which appeared in the untreated sample shifts to 1660 cm^{-1} in accord with prior study.¹⁴ This indicates the formation of an ammonium salt which could only be possible if the original oxidized film contained an acid. PS exhibits a strong absorption at 1602 cm^{-1} due to C=C stretch in the phenyl ring.⁹ As seen in Figure 3, the NI of this band does not change even after 3-h irradiation. This indicates that phenyl ring loss, including any phenyl ring opening,¹³ is negligible during this photooxidation of PS. From these results and with the assumption of a Norrish-type reaction, an aromatic such as benzoic acid rather than aliphatic acid is suggested. However, more information is necessary for firm evaluation.

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