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Notes

On the Fate of the Phenyl Ring in Polystyrene Photooxidation

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Introduction

There is a great disparity among published explanations for the marked decrease in the surface concentration of phenyl rings on the photooxidation of polystyrene (PS) with 254-nm UV. Several recent papers have addressed this question.[1-4] Our own work has signaled the difficulties in clearly identifying the products of PS photooxidation.[5]

Mailhot and Gardette[4] have argued, on p 4132, that low molecular weight aromatic products "may diffuse out of the polymer sample, resulting in a concentration gradient". They state that this diffusion is responsible for the loss of aromatic groups from the surface of photooxidized PS. In reality, either (1) any low-MW products could diffuse out of the polymer as volatiles or, (2) since photooxidation is a surface reaction, products may migrate into the polymer sample where they might remain. These two cases are explored here and both are shown to be improbable. A third possibility is discussed, (3) that of phenyl ring reactions, which lead ultimately to a decrease in the aromatic content of the PS film. As described below, we believe this interpretation provides the best explanation of the data reported on this subject.

Case 1: Volatilization. The paper by Mailhot and Gardette provides a starting point for discussing the possible volatilization of low molecular weight products of photooxidation. In that work, however, the photon flux employed is generally not linked to the number of moles of photooxidation products produced. It is therefore of value to consider the implications of an earlier quantitative work.[6] This will allow a comparison between the quantum yield of volatile aromatic photoproducts and the spectroscopically observed loss of aromatic moieties from a PS film during photooxidation.

Earlier work by Geuskens et al.[6] reports the quantum yield for formation of benzaldehyde ($\phi = 7.7 \times 10^{-5}$) and acetophenone ($4.1 \times 10^{-5}$) at 254-nm UV under 600 Torr of oxygen. These were the only two volatile aromatic compounds detected by Geuskens so that their combined quantum yields should account for most of the phenyl rings lost as low-MW products. Estimates of these values can be made for irradiation in 150 Torr of oxygen (~1 atm of air), since the quantum yield of oxygen reaction with PS increases linearly with oxygen partial pressure.[7] Thus, the following values should be used for comparison with the spectroscopic data obtained by us during PS photooxidation in air.[8]

$$\phi(\text{benzaldehyde}) = 1.9 \times 10^{-5}\ \text{mol/E}$$

$$\phi(\text{acetophenone}) = 1.0 \times 10^{-5}\ \text{mol/E}$$

We observed a 20% drop in the aromatic to aliphatic C–H stretch ratio, using a germanium ATR crystal, after 8×10^{-5} E/cm^2 of 254-nm UV irradiation in air[8] (Figure 1). At these infrared frequencies, this ATR crystal will sample about 0.7 μm into the PS film.[9] This 0.7-μm layer will have absorbed photo energy of approximately:

$$A = (ac)b = 0.223b$$

$$= (0.223)\,(0.7) \qquad \text{(ref 10)}$$

$$A = \log\,(I_0/I) = 0.156$$

$$I_0 = 8 \times 10^{-5}\ \text{E/cm}^2$$

$$I = \text{photon dosage absorbed below } 0.7\ \mu\text{m}$$

$$I_0 = 1.43I$$

$$0.698I_0 = I$$

$$(1 - I/I_0)(8 \times 10^{-5}) = 2.4 \times 10^{-5}\ \text{E/cm}^2 = \text{amount absorbed by the top } 0.7\ \mu\text{m}$$

Thus, the 0.7-μm layer should have produced a combined total of benzaldehyde plus acetophenone of

$$(2.4 \times 10^{-5}\ \text{E/cm}^2)(2.9 \times 10^{-5}\ \text{mol/E}) = 7 \times 10^{-10}\ \text{mol/cm}^2$$

The top 0.7 μm of a PS film contains 7×10^{-7} mol of PS repeat units. The production of aromatic volatile photooxidation products should therefore account for a

$$\frac{7 \times 10^{-10}}{7 \times 10^{-7}} = 1 \times 10^{-3} = 0.1\%\ \text{drop in the Ar–H/R–H ratio}$$

and not the reported 20% value. Thus, contrary to the claims of Mailhot and Gardette,[4] volatilization cannot be the origin of the loss of aromatic content we have reported[8] (Figure 1). Since volatilization cannot explain the observed decreases in the infrared Ar–H/R–H ratios, next, case 2, migration into the PS film, is considered.

Case 2: Migration. It is possible that low-MW aromatic products (e.g., acetophenone, benzaldehyde) might form during photooxidation and migrate into the PS film. This would create an apparent loss of aromatic content in the top surface of the PS film. The production of benzaldehyde and acetophenone requires a break in the PS main chain, since these low-MW compounds contain a nonaromatic carbon atom. It is, therefore, insightful to compare observed losses in the surface aromatic content with reported values for chain rupturing phenomena, i.e., chain scission.

Infrared spectra were recorded from the front and back sides of a 20-μm-thick film of photooxidized PS using a KRS-5, 45° ATR crystal. The front surface (Figure 2)

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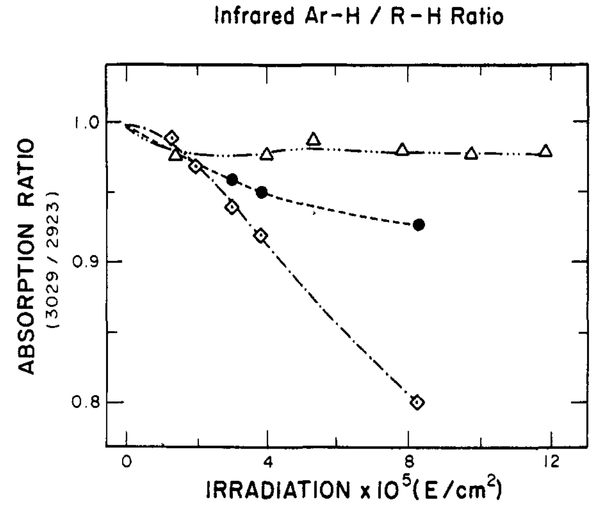

Figure 1. FTIR analysis for change in aromatic–aliphatic ratios—on polystyrene UV irradiation in air at 254 nm: (△) transmission spectrum; (○) 3 depth of penetration for KRS-5 45° (top 2.8 μm); (⊡) top 0.7 μm of film, 3 depth of penetration for Ge 45°.

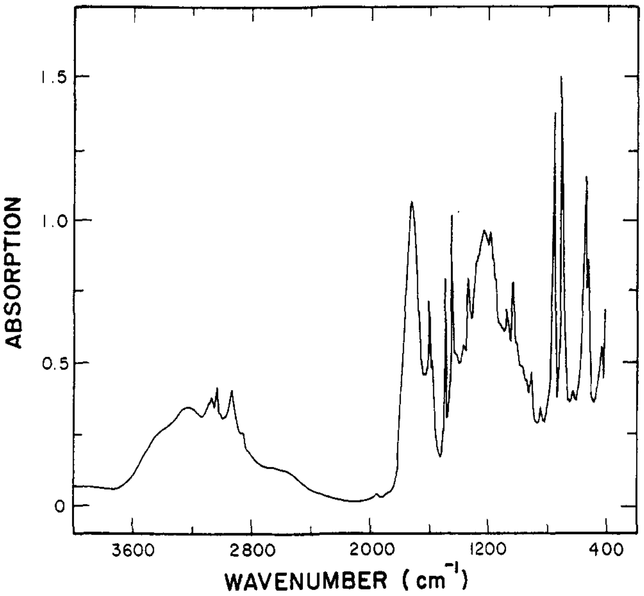

Figure 2. ATR-FTIR analysis of aromatic–aliphatic ratios at polystyrene surfaces after 1×10^{-4} E/cm^2 of UV exposure in air. Front surface: top spectrum.

shows a 13% decrease in the Ar–H/R–H ratio after 1×10^{-4} E/cm^2 of UV dosage, while the back shows a 1% decrease (Figure 3) (experimental uncertainty is ±2%). At the C–H stretch infrared wavelengths used, the sampling depth is about 3 μm into either surface of the 20-μm-thick film.

The formation of low-MW aromatic compounds in the top 3 μm of the film could allow them to be distributed throughout the entire 20-μm-thick film. If it is assumed that the low-MW products are distributed evenly throughout the film, it can be shown that a total of a 15.3% drop is required in each of the top 3 μm's of film, and an 2.3% increase in Ar–H content results in each of the other 20 μm's of the film. Thus 2.3–15.3 = −13% in aromatic content in the top surface, as plotted in Figure 2.

Using the data of Geuskens et al.,[11] it is possible to describe the number of chain breaks that should occur in the top 3 μm of the PS film. Their work reports the quantum yield of chain scission to be 5×10^{-4} and cross-linking to be 1×10^{-4} at 600 Torr of O_2. Assuming that the quantum yield increases linearly with oxygen partial pressure, then $\phi = 1.25 \times 10^{-4}$ in air (150 Torr of O_2).

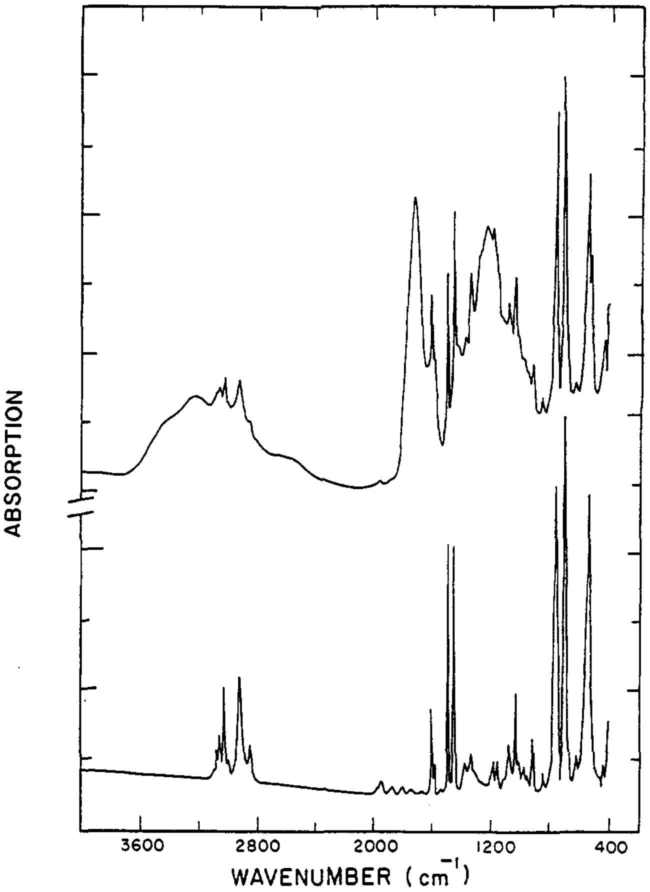

Figure 3. Front surface: top spectrum. Back surface: bottom spectrum. Same conditions as in Figure 2.

The top 3 μm of PS film absorbs 79% of the incident UV at 254 nm. Thus, the present results at 1×10^{-4} E/cm^2 total dosage have absorbed a total of 7.9×10^{-5} E/cm^2 in the top 3 μm. Thus,

$$(7.9 \times 10^{-5}\ \text{E/cm}^2)(1.25 \times 10^{-4}\ \text{scissions/E}) = 9.9 \times 10^{-9}\ \text{mol of scissions/cm}^2$$

A PS film of 1 cm^2 × 3 μm contains 1.26×10^{18} repeat units, or 2.1×10^{-6} mol of repeat units. This suggests

$$\frac{9.9 \times 10^{-9}\ \text{mol of scissions}}{2.1 \times 10^{-6}\ \text{repeat units}} = 4.7 \times 10^{-3}\ \frac{\text{scissions}}{\text{repeat unit}}$$

which is less than 1 scission per 100 repeat units.

Returning to our infrared data, we observed a 13% drop in the Ar–H/R–H ratio in the top 3 μm of PS film. In the preceding paragraphs, we concluded this resulted in a 15.3% breakage rate of aromatic groups in the PS chains. Comparing the number of aromatic groups broken from the chains to the above calculated number of scissions gives

$$0.153/0.0047 = 32\ \text{low-MW aromatic products per scission}$$

This result suggests an unreasonably long kinetic chain length for PS photooxidation reactions. The kinetic chain length of hydroperoxide decomposition was thought to have a value of about 5,[12] which might reasonably be expected to be a chain-reaction process. Since even hydroperoxide decomposition has a shorter kinetic chain length than our estimated value of 32, it is unlikely that migration into the film could explain the loss of aromatic groups observed with FTIR-ATR in Figure 2.

Note that this value is somewhat higher than that reported for the vacuum thermolysis of PS at 300 °C,[13] so that, in the presence of oxygen at 25 °C (i.e., below T_g), it seems much too high. Once formed, PS free radicals would quickly add molecular oxygen from air to form peroxy radicals which would prevent extensive unzipping of the chain at ambient temperature.[14]

Case 3: **Ring Reactions.** Finally, it has been shown that hydroxyl radicals (which would form from peroxides or hydroperoxides decomposition) are known to react with the phenyl rings of benzene and toluene.[15,16]

$$\phi \text{ or } \phi\text{-CH}_3 + \text{H}_2\text{O}_2 \xrightarrow[\text{cat.}]{} \phi\text{-OH or HO-}\phi\text{-CH}_3 \rightarrow \text{colored products}$$

$$\phi + \text{OH} \xrightarrow{\text{N}_2} \phi\text{-OH}$$

$$\phi + \xrightarrow{\text{O}_2} \phi\text{-OOH}$$

It is therefore reasonable to believe that the phenyl ring does react to some degree during PS photooxidation. Indeed, benzene has been shown to undergo photooxidative ring opening[17] to form compounds having the structure proposed by Rabek and Ranby.[18] Further, the reaction of PS with hydroxyl radicals in CH_2Cl_2 solution produced products with spectra consistent with these ring-opening reactions.[19] Since the loss of aromatic groups via volatilization or migration appears to be quite minor, the best explanation is that of the clearly-plausible ring-opening reaction.

In light of the high quantum yield of CO_2 during PS photooxidation, it would be informative to compare PS containing ^{13}C-labeled phenyl rings with PS containing ^{13}C-labeled backbones. This should provide direct, quantitative information on the importance of phenyl ring reactions during PS photooxidation, since the labeled $^{13}CO_2$ could be readily detected.

Conclusions

The above discussion has shown that the loss of aromatic structures from PS during photooxidation with 254-nm UV cannot be explained by either volatilization or diffusion of low molecular weight photoproducts from the film surface. In view of the reactivity of phenyl rings in such a photooxidative environment, together with reported PS molecular weight changes that occur, it is clear that reactions occur on both the pendant phenyl ring and the PS backbone.

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