Direct Evidence for the Generation of Phenyl Radicals and Cross-Linking during the Photolysis of Polystyrene Film

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ABSTRACT: Strips of polystyrene held under ultra high vacuum have been exposed to 240–600-nm ultraviolet radiation, and the resultant photodegradation products were identified by mass spectrometry. These *in situ* experiments provide the first ever conclusive evidence for phenyl radical formation during the photolysis of polystyrene film.

Introduction

Polystyrene consists of an alkyl chain polymeric backbone, to which phenyl rings are attached. For over 40 years, there has been a continuing debate over the precise mechanistic description of ultraviolet (UV)-induced photodegradation of this material. Photolysis of polystyrene in the solid state has been postulated to depend upon the mobility of free radicals within the polymer matrix and their bimolecular recombination.[1] Polystyrene absorbs strongly in the spectral range below 280 nm, and this is attributed to a $S_0 \rightarrow {}^1S$ transition of the phenyl ring.[2,3] Other parts of the polymer backbone (i.e., $-CH-$, $-CH_2$) do not absorb light in the 200–280-nm wavelength region. Reaction under ultraviolet irradiation is considered to occur via direct absorption of photons by the polystyrene macromolecule to create excited states with a total energy content in excess of that required for homolytic scission of some of the bonds along the polymer chain. This may lead to the formation of phenyl radicals and atomic hydrogen and rupture of the main hydrocarbon backbone, which in turn could give rise to scission and cross-linking processes.[1,4] Concurrently, the photoexcited polymer may lose energy via re-emission, vibrational relaxation, or by decay to lower lying electronically excited states. However, the relative importance of these various reaction pathways is not clearly established.

In this paper we describe a systematic approach which is aimed at elucidating the precise nature of the photochemistry taking place at the polystyrene surface during UV exposure. This comprises directing a quadrupole mass spectrometer at the UV-irradiated polymer substrate under an ultra-high-vacuum environment and thereby capturing all of the photoejected species (Figure 1). Previous mass spectrometry studies have been restricted to the sampling of the gaseous photolysis products via a separate quartz cell; such investigations have disclosed that there is evolution of molecular hydrogen, water, carbon monoxide, carbon dioxide, and benzene,[5-7] however, these experiments were incapable of detecting short-lived intermediate species, e.g., phenyl radicals.

Experimental Section

Photolysis experiments were carried out in a purpose-built ultra-high-vacuum (UHV) chamber (base pressure 2×10^{-10} Torr). This was equipped with a VG SX200 quadrupole mass spectrometer which had been multiplexed to a PC computer (this allowed up to 50 different mass profiles to be tracked simultaneously). An Oriel 200-W low-pressure Hg–Xe arc lamp (emitting a strong line spectrum in the 240–600-nm region) was run at 100 W to irradiate the sample through a sapphire port (cut-off wavelength 141–161 nm). A high-purity polystyrene film (BP) was washed with isopropyl alcohol and dried in a vacuum oven at 35 °C prior to transfering into the UHV chamber via a fast insertion lock. The line-of-sight mass spectrometer to substrate distance was fixed at 3 cm; a closer proximity resulted in a slight amount of thermal degradation at the polymer surface arising from heat emitted by the ionizer filament.

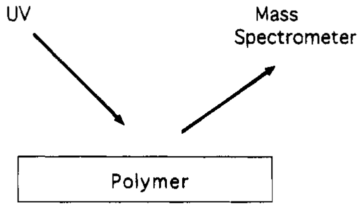

Figure 1. Schematic for *in situ* photolysis experiments.

Typically, 500 data points were collected for each mass over the duration of a photolysis experiment. Prior to each run, the UHV chamber walls were outgassed by exposure to UV, with the polymer film held well back from the line-of-sight to the sapphire port. Subsequently, the UV shutter was closed and the polymer was pushed into position (with the line-of-sight to the UV source and the mass spectrometer); after 165 s, the shutter was opened for 83 s and finally closed for the remaining 786 s. This sequence of shutter manipulations produced the typical mass profiles described in the next section.

Experiments were repeated with the polymer out of the line-of-sight of the mass spectrometer ionization source and ultraviolet irradiation. Masses 2 (H_2), 18 (H_2O), 28 (CO), and 44 (CO_2) were seen to increase (originating from the walls of the chamber); however, this increase was negligible in comparison with signals measured during the photolysis experiments.

Results and Discussion

A whole variety of photoejected species were identified during UV exposure of the polystyrene film. The stoichiometrical compositions are listed in order of decreasing intensity (uncorrected for mass spectrometer sensitivity) as follows: 2 (H_2), 18 (H_2O), 41 (C_3H_5), 28 (C_2H_4), 43 (C_3H_7), 55 (C_4H_7), 39 (C_3H_3), 44 (C_3H_8), 67 (C_5H_7), 57 (C_4H_9), 69 (C_5H_9), 53 (C_4H_5), 81 (C_6H_9), 1 (H), 77 (phenyl radical), 51 (C_4H_3), 50 (C_4H_2), 53 (C_4H_5), 79 (C_6H_7), 54 (C_4H_6), 65 (C_5H_5), 71 (C_5H_{11}), 95 (C_7H_{11}), 45 (C_2H_5O), 70 (C_5H_{10}), 78 (benzene), 52 (C_4H_4), 91 ($C_7H_7^+$, the tropylium ion), 63 (C_5H_3), 105 (C_8H_9), 97 (C_7H_{13}),

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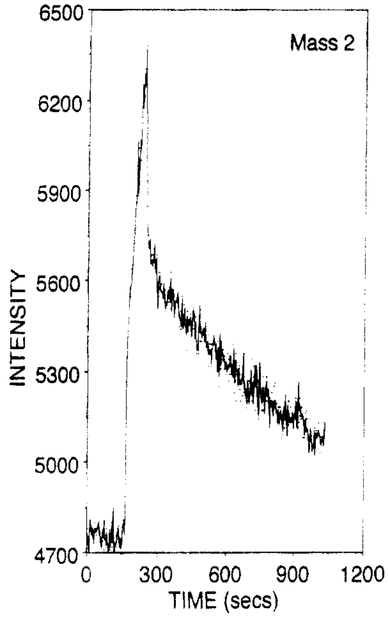


Figure 2. Mass 2 intensity profile before, during, and after UV irradiation of the polystyrene film.

109 (C_8H_{13}), 107 (C_8H_{11}), 103 ($CH_2{=}C^+Ph$), 76 (C_6H_4), 115 (C_9H_7, a bicyclic aromatic species). It should be noted that the sensitivity of the quadrupole mass spectrometer used in these experiments drops off with increasing mass number. All of these masses undergo a sharp rise in signal intensity during UV irradiation and subsequently fall off in magnitude upon removal of the photon source. The rate of decay of each individual mass back toward the base line is found to vary, and examination of these profiles has proven to offer an invaluable insight into the mechanistic aspects of the degradative photochemistry of interest.

Atomic and Molecular Hydrogen. By running a background spectrum of the analysis chamber, molecular hydrogen (mass 2) was found to be the main residual gas, with an associated peak at mass 1 arising from the fragmentation of molecular hydrogen within the ionizer of the quadrupole mass spectrometer.

UV irradiation of the polystyrene film results in a rapid rise in both mass 1 (atomic hydrogen) and mass 2 (molecular hydrogen) signals (Figure 2). Their relative concentrations did not appear to change over the duration of the experiment, thereby signifying that hydrogen radicals are unable to desorb in sufficient numbers away from the polymer surface. Instead they may participate in the generation of molecular hydrogen either by $H^\bullet + H^\bullet$ recombination or via hydrogen abstraction from neighboring polymer molecules. Photoexcitation of the phenyl groups in polystyrene initiates fission of C—H bonds via intramolecular energy transfer:[8] the relative increase in C—H dissociation energy is phenyl > secondary > tertiary; the latter is weakest due to resonance stabilization of the resultant free radical center.

Molecular Benzene and Phenyl Radicals. Benzene (mass 78) and phenyl radicals (mass 77) were measured in abundance during these photolysis studies. The desorption behavior of both products is similar to the trends reported for hydrogen evolution (Figure 3). Fragmentation of benzene molecules within the ion source of the quadrupole mass spectrometer can yield some minor peaks at masses 52, 51, and 77 (each with approximately 20% of the mass 78 intensity). However, the increase in signal strength of mass 77 upon exposure to ultraviolet radiation is comparable to that observed for mass 78 and cannot therefore be attributed solely to benzene fragmentation within the ion source, but it must also possess a contribution from desorbing phenyl radicals. The possibility of mass 77 being a daughter ion of a short polymer chain can also be ruled out, since mass 77 was present in much greater abundance than any potential parent oligostyrene species (for instance, mass 91 is widely reported to be much more intense than either mass 77 or mass 78 during electron impact ionization of low molecular weight polystyrene[9,10]). Furthermore, the mass 77 and 78 mass profiles are different in shape relative to the mass 91 photodesorption profile.

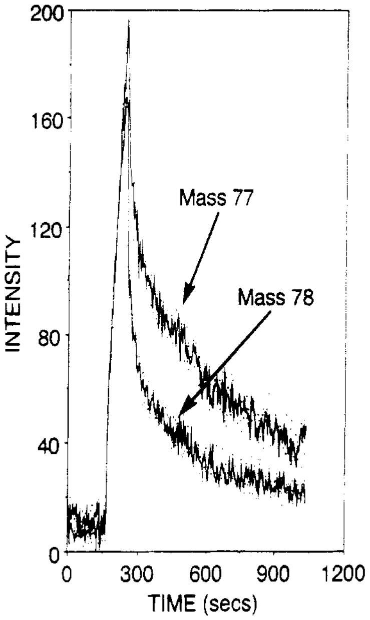


Figure 3. Mass 77 and mass 78 intensity profiles before, during, and after UV irradiation of the polystyrene film.

Evolution of benzene during polystyrene photolysis is consistent with previously postulated theories.[5,6] Photoexcitation of the phenyl ring in the polymer induces $C_6H_5{-}C{<}$ bond rupture via intramolecular energy transfer from the absorbing aromatic centers, thereby creating a phenyl radical.[1,2] Such phenyl radicals have limited mobility within the bulk polymer, before they form benzene by either hydrogen abstraction from adjacent polymer chains or combination with a stray hydrogen radical. Alternatively, such phenyl species may partly react with macroradicals in their vicinity.[4,8] Until now there has been no direct evidence for the aforementioned description.

Comparison of the post-irradiation peak profiles for phenyl radicals (mass 77) with molecular benzene (mass 78) reveals that the benzene signal intensity drops much more rapidly than that observed for the phenyl species. Therefore, both recombination of phenyl radicals with atomic hydrogen and hydrogen abstraction by the phenyl radicals from neighboring polymer chains are strongly coupled to the presence of UV; i.e., a reduction in H atom concentration upon termination of UV exposure will cause a concomitant attenuation in benzene evolution, while excess phenyl radicals will be left to pursue alternative reaction pathways (e.g., desorption, recombination with free radical centers, etc.).

Hydrocarbon Fragments. Mass 91 ($C_7H_7^+$, the tropylium ion) is characteristic of aromatic hydrocarbons and polystyrene,[9,10] and therefore its presence is indicative of cleavage occurring along the main aliphatic backbone

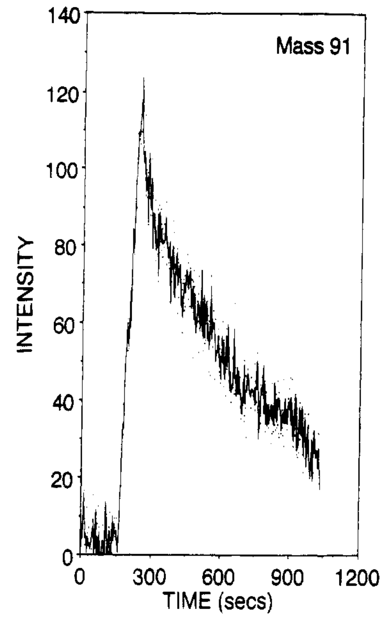
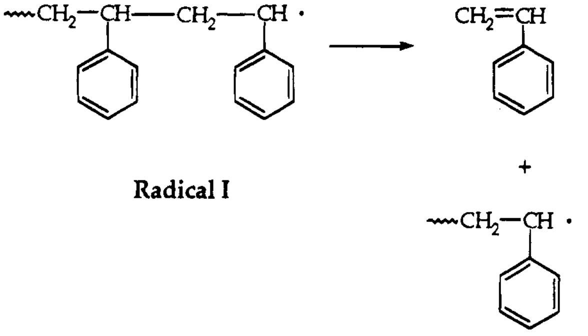


Figure 4. Mass 91 intensity profile before, during, and after UV irradiation of polystyrene film.

Scheme 1. "Unzipping" of a Polystyrene Radical To Produce Styrene



of polystyrene during photolysis (Figure 4). Breakup of the polymer chain in this manner may produce oligomers of polystyrene which can fragment in the ion source of the quadrupole to form the tropylium cation. Experiments performed with the mass spectrometer filament switched off failed to give any mass 91 signal, thereby proving that no charged species are evolved from the surface during photolysis. A gradual decay in the signal intensity was noted for this mass following the extinction of UV irradiation. This can be attributed to the extensive molecular and steric interactions experienced by these broken-up polymer chains at the substrate surface, which will tend to hinder their departure. Furthermore, it is important to note that this fragment has a different peak profile to masses 77 and 78, and therefore the latter cannot be exclusively daughter species of oligostyrene species.

A wide range of other hydrocarbon fragments was also emitted from the polystyrene surface during photolysis. These can be associated with extensive breakup of the polymer chain as well. Masses 41, 43, 55, 57, 69, and 97 have been previously identified in the SIMS spectra of hydrocarbon polymers[11] (e.g., polyethylene and polypropylene) and are attributed to fragment types C_nH_{2n+1} and C_nH_{2n-1}. Masses 39 (C_3H_3), 51 (C_4H_3), 63 (C_5H_3), 103 ($CH_2{=}CPh$), and 115 (C_9H_7, a bicyclic aromatic species) are reported to be fragments in the SIMS spectrum of polystyrene[9,11,12] (as well as the previously mentioned masses 77 and 91). Other significant hydrocarbon fragments were 67 (C_5H_7), 53 (C_4H_5), and 81 (C_6H_9). Mass 28 could be assigned to either carbon monoxide (CO) or ethylene (C_2H_4); however, mass 27 was detected in the correct proportion to conclusively prove that ethene molecules must be evolved during backbone scission. The mass fragments 104 and 105 evolved during photolysis must be C_8H_8 and C_8H_9, respectively.[13] During photolysis, styrene C_8H_8 (mass 104, this was checked by using pure styrene) could be formed by the "unzipping" reaction[4] given in Scheme 1. Radical I is produced during the photolysis of polystyrene via intramolecular energy transfer from excited phenyl groups to break the C−C main-chain bond.[4] $C_8H_9^+$ (mass 105) has been detected during SIMS analysis of polystyrene[9,11,12] and is also present in the standard mass spectrometric analysis of polystyrene;[10] therefore, these species probably originate from short-chain polymer oligomers. C_3H_8 (mass 44) was also identified from fragmentation pattern analysis.

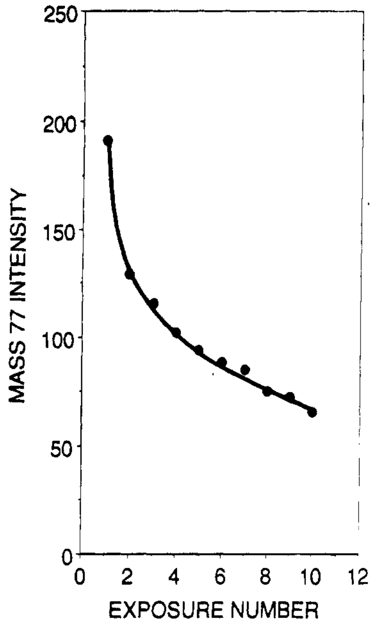


Figure 5. Mass 77 peak intensity as a function of the number of UV exposures.

Other Masses. Oxygenated products, such as water (mass 18) and C_2H_5O (mass 45) were detected during photolysis experiments despite stringent efforts to obtain a clean substrate. These molecules have also been detected in other studies.[5−7] There are a number of potential explanations for the origin of these species, which include the photolysis of impurities in the film or the desorption of trapped gases from within the polymer. However, to put this into context, it should be noted that the sensitivity of the quadrupole mass spectrometer used in these experiments dropped off significantly with increasing mass number. Therefore, water may not necessarily be present in large quantities. Furthermore, some water should be expected, since polystyrene is known to be permeable toward moisture transport.[14]

Further Exposures. Recurrent exposure of the polystyrene substrate to UV irradiation resulted in a gradual decrease in mass intensities (Figure 5). This behavior can be attributed to cross-linking taking place at the polymer surface following C−H bond cleavage, together with chain scission. This produces a polymer network containing a lower concentration of chromophoric phenyl centers, which will in turn hinder the substrate's susceptibility toward photodegradation.

Conclusions

Absorption of ultraviolet radiation by the phenyl centers in polystyrene results in phenyl radical desorption from the surface. Concurrently, intramolecular energy transfer between the phenyl chromophores and the polymer chain can create atomic hydrogen, which may either recombine or abstract from a neighboring polymer branch to produce molecular H_2. The phenyl radicals may also participate in combination with atomic hydrogen or hydrogen abstraction from adjacent polymer chains to form benzene. Any remaining hydrocarbon backbone radicals probably undergo cross-linking or combination with atomic hydrogen to create a less chromophoric surface. To summarize, the following reactions are believed to occur during the UV irradiation of polystyrene (PS):

$$\mathrm{PS} \xrightarrow{\mathrm{UV}} \mathrm{Ph}^{\bullet} \tag{I}$$

$$\mathrm{PS} \xrightarrow{\mathrm{UV}} \mathrm{H}^{\bullet} \text{ (via intramolecular energy transfer)} \tag{II}$$

Then

$$\mathrm{Ph}^{\bullet} + \mathrm{PS} \rightarrow \text{benzene} + \mathrm{PS}^{\bullet} \text{ (}\mathrm{H}^{\bullet}\text{ abstraction)} \tag{III}$$

$$\mathrm{Ph}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow \text{benzene} \tag{IV}$$

$$\mathrm{H}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow \mathrm{H}_2 \tag{V}$$

$$\mathrm{H}^{\bullet} + \mathrm{PS} \rightarrow \mathrm{H}_2 + \mathrm{PS}^{\bullet} \tag{VI}$$

$$\mathrm{PS}^{\bullet} + \mathrm{PS}^{\bullet} \rightarrow \text{cross-linking} \tag{VII}$$

Reaction II is an indirect process and cannot be expected to be as efficient as step I. This explains the relatively high yield of phenyl species observed in these experiments. Furthermore, on this basis, any reaction involving $H^{\bullet}$ should decay rapidly upon termination of UV irradiation, i.e., IV–VI—this is in fact what is observed. Subsurface or sterically restricted moieties (e.g., H_2, phenyl radicals, short polymer chains, etc.) continue to desorb over much longer periods of time.

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