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Source: Photochemistry and Photobiology, 81(4):777-782.
Published By: American Society for Photobiology
DOI: http://dx.doi.org/10.1562/2004-11-30-RA-387R.1
URL: http://www.bioone.org/doi/full/10.1562/2004-11-30-RA-387R.1

Photochemistry and Photobiology, 2005, 81: 777–782

Symposium-in-Print: VIII ELAFOT, La Plata, Argentina, 2004

Vacuum-ultraviolet Photochemically Initiated Modification of Polystyrene Surfaces: Chemical Changes¶,‡

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Received 30 November 2004; accepted 30 January 2005

ABSTRACT

Fourier-Transform infrared (FTIR) spectroscopy and surface energy analysis (contact angle measurements) have been performed as a means of identification and quantification of the functionalization of polystyrene surfaces upon vacuum ultraviolet- (VUV-) photochemically initiated oxidation. Photochemical oxidation was performed in the presence of water vapor and molecular oxygen using a pulsed Xe_2-excimer radiation source (λ_{exc}: 172 nm). Surface oxidation was studied as a function of two parameters: irradiation time and distance between sample and radiation source. During the first 1–2 min of irradiation, an increase of the concentrations of hydroxyl (OH) and carbonyl (C=O) groups on the surface was observed, both reaching limiting values. As expected, the rate of oxidation diminished exponentially with increasing distance between the radiation source and the surface of the polystyrene film. Changes in the surface energy due to the introduction of these polar (*i.e.* OH and C=O) groups were also determined. The densities of the functional groups decreased upon washing with acetonitrile, and analysis of the washing solution by means of gas chromatography-mass spectrometry (GC-MS) revealed the presence of a large number of products. The application of pulsed Xe_2-excimer radiation sources as a valuable alternative to conventional means (*i.e.* laser and plasma) for the photochemical oxidation and surface modification of polystyrene is discussed.

INTRODUCTION

Vacuum-ultraviolet (VUV) radiation produced by excimer lamps is inciting increasing interest as means to oxidize polymer surfaces (1–11). Compared with low-pressure Hg arcs, principal advantages of VUV excimer radiation sources are their working temperatures of less than 80°C, hence avoiding infrared (IR) emission and (sample) heating effects, and higher monochromatic radiant exitances. Excimer radiation sources may be preferred to laser and plasma techniques for the treatment of large surface areas as well as for the simplicity of the irradiation equipment used, taking into account that plasma systems require most often vacuum lines and controlled gas mixtures.

The pulsed Xe_2-excimer radiation source (λ_{exc}: 172 ± 12 nm) is of special interest due to its high luminescence efficiency (~ 40%). Irradiation of the polymer surface by high-energetic photons (7.2 eV) may lead to different electronically excited states than those reached by conventional UV-C radiation, *e.g.* low-pressure Hg arc (λ_{exc}: 254 nm), which in turn may exhibit different reactivities.

In one of our projects, we focus on the oxidation of surfaces of polystyrene (PS) films, aiming for a simple but controlled surface functionalization. Oxidation is initiated by the radiation of a Xe_2*-radiation source in the presence of molecular oxygen and water (vapor). We are aware of two independent investigations, where Xe_2*-radiation sources have been used to irradiate PS (10,11). Tanaka *et al.* (10) investigated the physicochemical changes of vinyl polymers (polyethylene, PS, and poly(vinyl alcohol)) induced by Xe_2-excimer radiation in the presence of dry air or nitrogen by determining contact angle measurements and using Fourier-transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS). By FTIR analysis of PS samples irradiated in dry air, only one new absorption band to be associated with the carbonyl function was observed. It is interesting to note that, in earlier publications, the formation of hydroxyl groups had been observed in addition to newly formed carbonyl functions, when PS surfaces were irradiated at 254 nm in the presence of oxygen (12–14). Hozumi *et al.* (11) studied the VUV-photochemical surface modification of PS using as Xe_2*-source, focusing on the impact of atmospheric pressure on surface energy (contact angle), thickness, and elemental composition (both determined by XPS) of the photo-oxidized layer.

In addition to these published data, the objective of our project is to elucidate the mechanisms leading to the observed surface modifications. For that purpose, products of the VUV-photoinitiated oxidation of PS films were identified, and a more detailed photophysical characterization of the irradiated samples was un-

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¶Posted on the website on 2 February 2005

‡Presented as a poster at the VIII ELAFOT, La Plata, Argentina, 8–12 November 2004

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Abbreviations: ATR, attenuated total reflectance; DTGS, deuterated triglycine sulfate; FTIR, Fourier-transform infrared spectroscopy; GC/MS, gas chromatography/mass spectrometry; PS, polystyrene; SNV, standard normal variate; VUV, vacuum ultraviolet; XPS, x-ray photoelectron spectroscopy.

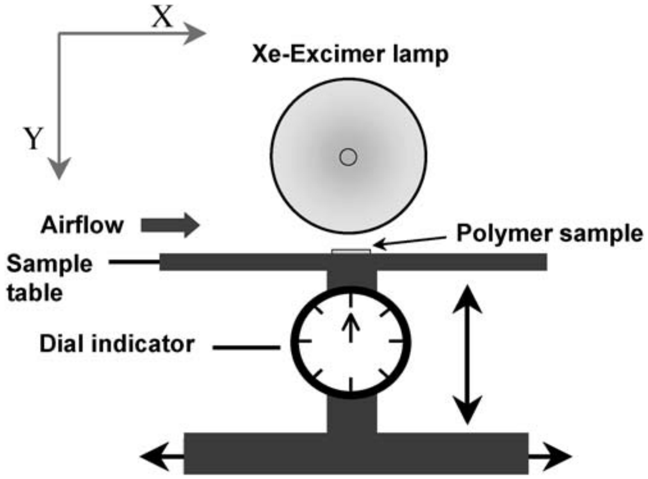

Figure 1. Schematic diagram of experimental set-up.

dertaken together with FTIR and contact angle measurements in function of irradiation time. The results of these mechanistic investigations were prerequisite to understanding and optimizing the nanoscale structuring of PS surfaces, already reported (11).

MATERIALS AND METHODS

Polystyrene films of 0.125-mm thickness were purchased (Goodfellow GmbH, Bad Nauheim, Germany). The films were placed on a horizontally moving table, ensuring a balanced irradiation of the total surface (x axis, Fig. 1). A XERADEX™ pulsed tubular Xe_2*-radiation source (Radium Lampenwerk, Wipperfuerth, Germany; electrical power: 20 W; diameter: 4 cm; length: 12 cm, λ_{exc}: 172 ± 12 nm, radiant power: 8 W, exitance: 50 mW/cm^2) was used as radiation source. The equipment is placed in a glove box, ensuring control of the gas phase implied in the functionalization processes. Irradiation was performed at different distances (y axis, Fig. 1) between the surfaces of the radiation source and the film and for different times of irradiation. The distance is measured by a high-precision dial indicator. Homogeneous irradiation of sample surface was always achieved because the length of the lamp and maximum displacement of the table (±15 cm) are much larger than the typical sample dimensions (1×1.5 cm^2).

Potential local heating of the sample could be avoided by directing a constant air flow parallel to the irradiated surface. The surface temperature during irradiation was monitored by means of a thermosensor and remained generally between 25 and 30°C. However, during irradiation experiments at small distances ($\leq$2 mm), the surface temperature reached 50°C.

Functionalization of the PS surface was identified and quantified by FTIR spectroscopy (Equinox 55, Bruker Optik GmbH, Ettlingen, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector using a SPECAC (Woodstock, GA, USA) Golden Gate attenuated total reflectance (ATR) module with a diamond crystal of 1×1 mm^2(??)). For each sample (*i.e.* each irradiation experiment with defined gas phase, time, and distance of irradiation) a total of seven spectra were collected, every spectrum taken at a different area of the total sample surface. IR Spectra were smoothed (to reduce noise) and a standard normal variate (SNV) method was used to correct for baseline differences originating from scattering effects (15).

Absorption bands appearing in the IR spectra that can be associated to new functional groups on the PS surface were integrated. The integrated intensities were corrected for the variation of the sample-crystal contact usually encountered in ATR measurements. For this purpose, integrated values of the absorption band of interest were normalized by means of the integrated value of a reference absorption band of the same spectral region, assumed not to be altered during the irradiation process (Fig. 2). Absorption bands located between 2800 and 2950 cm^{-1} (C-H stretching vibration) and 1451 and 1500 cm^{-1} (=C-H and ring C=C stretching vibration) were taken as references for OH and for C=O, respectively (see Fig. 2).

Data presented in this report represent the mean values calculated from a set of seven normalized values obtained from seven IR spectra taken from one irradiated sample, the error being estimated from the standard deviation of the seven values. These mean values are proportional to the concentrations of the functional groups associated to the respective absorption bands and are presented after subtracting the values of a nonirradiated sample.

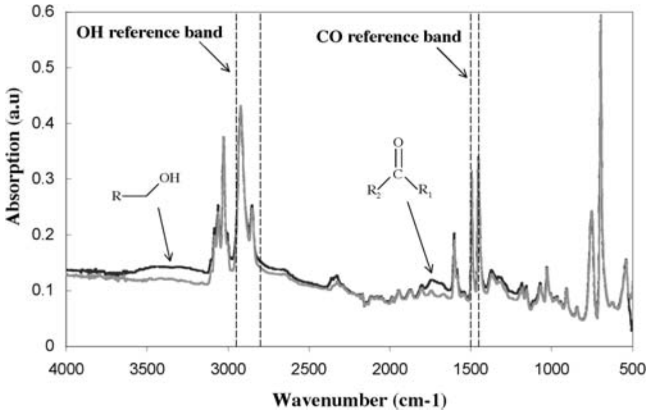

Figure 2. Typical (IR) spectra of nonirradiated and irradiated polystyrene films. Reference absorption bands used for the normalization procedure are indicated.

It is worth noting that the penetration depth of VUV-radiation (optical path length) into the polymer films is significantly smaller than that of the probing IR radiation. Based on the Lambert-Beer Law and assuming the density of molecules in solid PS to be 6×10^{21} molecules cm^{-3} and the absorption cross-section per molecule at 172 nm to be 35×10^{-18} cm^2 molecule^{-1} (16), an optical path length of 110 nm may be evaluated. In contrast, the IR probing is taking place with penetration depths of the order of a few micrometers.

Potential fragmentation of irradiated polymer material was assessed by washing the irradiated surfaces with acetonitrile (Rotisolv®, HPLC grade $\geq$ 99.9%, Carl Roth GmbH + Co, Karlsruhe, Germany) subsequent to the first spectroscopic analysis. Acetonitrile does not contain hydroxyl or carbonyl groups and would therefore not interfere in repeated FTIR analyses, if some solvent would remain in the polymer matrix. For the contact angle measurements, irradiated samples were washed with methanol (LiChrosolv®, high-performance liquid chromatography grade, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany). PS is insoluble in both solvents.

Sample surfaces were washed by immersing the polymer films for a period of 5 min into a well-stirred volume of solvent. Subsequently, the films were allowed to dry under normal atmosphere for several hours before repeating the analytic procedures.

Acetonitrile solutions were analyzed after the washing process by GC/MS. A HP Series II GC-MS equipped with a HP-5MS column (30 m × 0.25 mm × 0.25 μm) was used (Agilent Technologies Deutschland, GmbH), (carrier gas: He; flow rate: 1.2 mL/min; temperature program: 50°C [2 min], increase to 110°C at a rate of 10°C/min; increase to 280°C at a rate of 50°C/min).

The static contact angle of PS with a polar solvent (water, droplets of 5×10^{-7} L) was measured with a goniometer (OCA 20, Data Physics Instruments GmbH, Filderstadt, Germany). All contact angles were determined by averaging measured values at five different points on each sample surface. The error was calculated from the standard deviation of these five measurements.

RESULTS AND DISCUSSION

VUV-irradiation of PS films under normal atmosphere lead to the appearance of two new IR-absorption bands, one located between 1600 and 1800 cm^{-1}, the other located between 3000 and 3500 cm^{-1}. We associate the absorption between 1600 and 1800 cm^{-1} to the presence of carbonyl groups and the one between 3000 and 3500 cm^{-1} to the presence of hydroxyl groups. Examples of IR spectra taken from nonirradiated and irradiated samples are shown in Fig. 2.

Under similar experimental conditions (type of VUV-radiation source, normal atmosphere, ranges of distance and irradiation time), the appearance of an absorption band related to hydroxyl groups

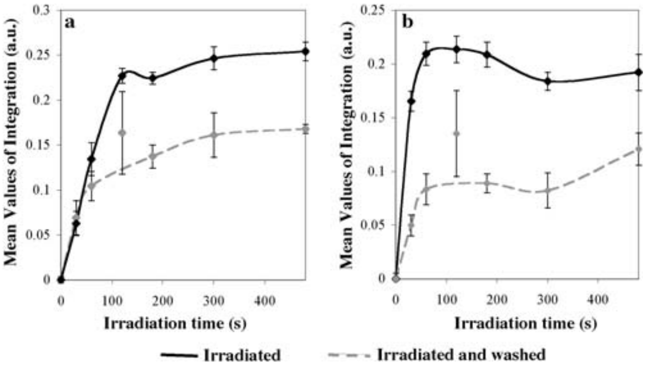

Figure 3. Evolution of the mean value of integration of CO (a) and OH (b) absorption bands as a function of irradiation time, before and after washing with acetonitrile. Distance of irradiation: 4 mm.

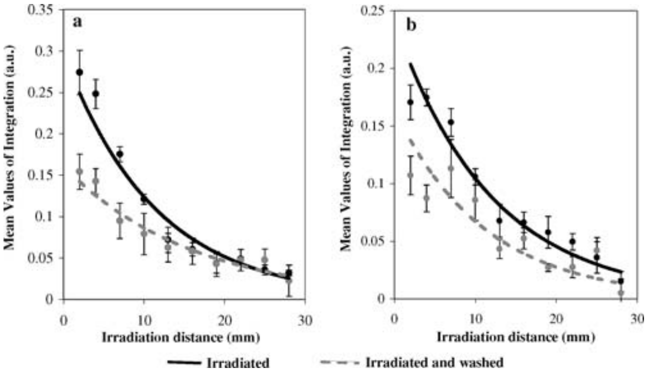

Figure 4. Evolution of the mean value of integration of CO (a) and OH (b) absorption bands as a function of irradiation distance, before and after washing with acetonitrile. Time of irradiation: 2 min.

was not reported (10), and it might be that, under their analytical conditions, the authors could not detect this rather broad peak showing a much lower signal-to-noise ratio than the well-structured absorption band of the carbonyl function.

Progressing conversion of the functionalization was determined from the normalized integration of the new IR-absorption bands, and mean values were calculated from a set of seven normalized values obtained from seven IR spectra taken from one irradiated sample. These mean values are proportional to the concentrations of the functional groups associated to the respective absorption bands and are presented after subtracting the values of a non-irradiated sample.

Figure 3 shows these mean values and, hence, the increase of the concentrations of carbonyl and hydroxyl functions at the surface of a PS film as a function of irradiation time, at a fixed distance of irradiation of 4 mm. Concentrations of both groups increase during the first 2 min of irradiation, reaching limiting values after this time. In the early stage of irradiation, the polymer is oxidized and functional groups are introduced to the surface. Oxidation apparently stops at a given degree of functionalization. This limiting value might also be obtained by pathways of oxidation (*e.g.* fragmentation of the polymer backbone) producing low-molecular products that evaporate from the polymer surface or that are mineralized by a succession of oxidation reactions. Rates of formation, evaporation, and/or mineralization of hydroxyl and carbonyl functionalized products might be in a kind of equilibrium and present apparent limited rate of conversion.

In contrast, no limiting values of the rate of functionalization were found at even longer times of irradiation, when similar investigations were carried out with UV-C irradiation (Hg low pressure arc [λ_{exc}: 254 nm]). The concentration, instead, was found to increase linearly over the entire irradiation time (12,17,18). Such a difference in behavior suggests that the photochemically initiated oxidation may involve different mechanisms depending on the wavelength of excitation.

Formation of low-molecular oxidation products may be shown by washing the irradiated surfaces and analyzing the washed surface as well as the resulting solution. In fact, an important decrease of the degree of functionalization was found upon washing of the irradiated surfaces with acetonitrile. The effect of sample washing is that of a reduction in concentration of both functional groups involved, as shown in Fig. 3. The carbonyl function exhibiting a much better defined (*i.e.* narrow) IR-absorption band, the respective functionalization may be followed in more detail than that related to the hydroxyl group. The mean values of integration in function of irradiation time determined for samples before and after washing with acetonitrile permit differentiating three stages of carbonyl functionalization:

1. In the early stage of the photo-oxidation (0–30 s, Fig. 3), the concentration of carbonyl groups increases linearly. The mean values of integration being the same before and after washing, these carbonyl groups are most probably attached to the polymer chain and are therefore not eliminated from the surface by the washing process.
2. The polymer backbone is oxidatively broken and products of low molecular weight are produced and deposited on the surface at irradiation times >30 s (Fig. 3). The increasing difference between the curves established for unwashed and washed samples may be due to an increasing mass of debris during longer times of irradiation (<120 s, Fig. 3), which can be dissolved in an appropriate solvent. Inversely, the slower increase of the rate of functionalization obtained for the washed samples may be attributed to an increasing importance of the layer of oxidation products, which prevents further oxidative degradation of the underlying (native) polymer.
3. Finally, at longer times of irradiation (>120 s, Fig. 3), oxidation products are formed that evaporate or migrate from the surface permitting photochemically generated new products from the surface of the native polymer. The thickness of the layer of these products of low molecular weight is thought to remain constant, as the difference between the curves established for unwashed and washed samples remains constant with increasing irradiation time.

The observation of limited mean values of integration for carbonyl and hydroxyl groups bound to the polymer (curves of washed samples, Fig. 3) may be explained by a mechanism where early functionalization of PS is followed by oxidative fragmentation of the backbone.

The effect of the distance of irradiation on the rate of formation of functional groups on the surface of the polymer was studied by irradiating a series of samples during a fixed time of 2 min at distances between 2 and 28 mm. The corresponding results are shown in Fig. 4. As expected, highest rates of functionalization were found at close distances and may be explained by the fact that, under these conditions, absorption of the radiant exitance by molecular oxygen and water vapor in the gas phase is minimal. At the same time, there

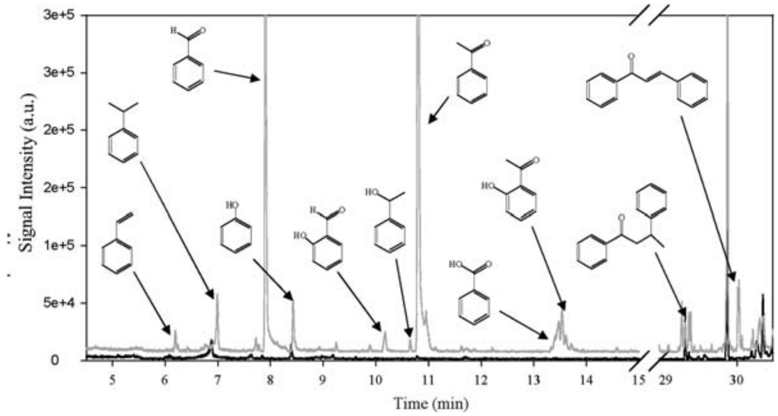

Figure 5. Gas chromatograms of acetonitrile used to wash native polystyrene powder (black line) and irradiated polystyrene powder (grey line). Identification by mass spectrometry.

is a high probability of impact of photochemically generated atomic oxygen and hydroxyl radicals at the polymer surface. This interpretation is supported by the observed exponential dependence of the experimentally determined rates of functionalization from the distance of irradiation.

At short distances, the difference between mean values of integration is highest, implying that polymer backbone fragmentation is very efficient. As the distance of irradiation increases, this difference diminishes until conditions are reached (15 mm) where no apparent fragmentation is taking place and all functional groups formed are bound to the polymer backbone. The results suggest that the importance of the layer of polymer debris depends on the incident VUV radiation and on the surface temperature.

The analysis of the washing solution revealed a large variety of oxidation products removed from the irradiated polymer surface. Figure 5 shows the chromatograms of acetonitrile solutions originating from the washing process of native polystyrene (black line) and of irradiated polystyrene (grey line) films. Formation of styrene is a typical result of the photolysis of polystyrene, the unzip reaction (19) of an end-standing radical leading to the formation of the monomer (Fig. 6a). However, the main products of the backbone fragmentation are acetophenone and benzaldehyde. Among the many pathways leading to their production, oxidation of styrene is shown in Fig. 6b. Phenol derivatives indicate the presence of hydroxyl radicals and their electrophilic addition to the aromatic system (Fig. 6c). Atomic oxygen and/or hydroxyl radicals may also abstract hydrogen from the aliphatic backbone of the polymer (Fig. 6d), and the C-centered radicals will subsequently react with molecular oxygen, yielding peroxyl radicals, known as key intermediates of oxidative degradation (20).

Yellowing of polystyrene upon UV irradiation may be found in numerous reports and was explained either by the formation of conjugated π-bond sequences in the polymer backbone (21–23) or by the formation of conjugated dicarbonyl functions (22). Among the conjugated π-bond sequences, benzalacetophenone was proposed as a possible chromophore of this yellowing effect (24). In fact, our analyses confirm the production of benzalacetophenone (Fig. 5).

Although phenol derivatives were identified, products of subsequent oxidative degradation, such as quinoid compounds or products of ring-opening reaction sequences, could not be detected. In contrast with the proposal of Hozumi *et al.* (11) that active oxygen species would mainly react with the aromatic systems, the

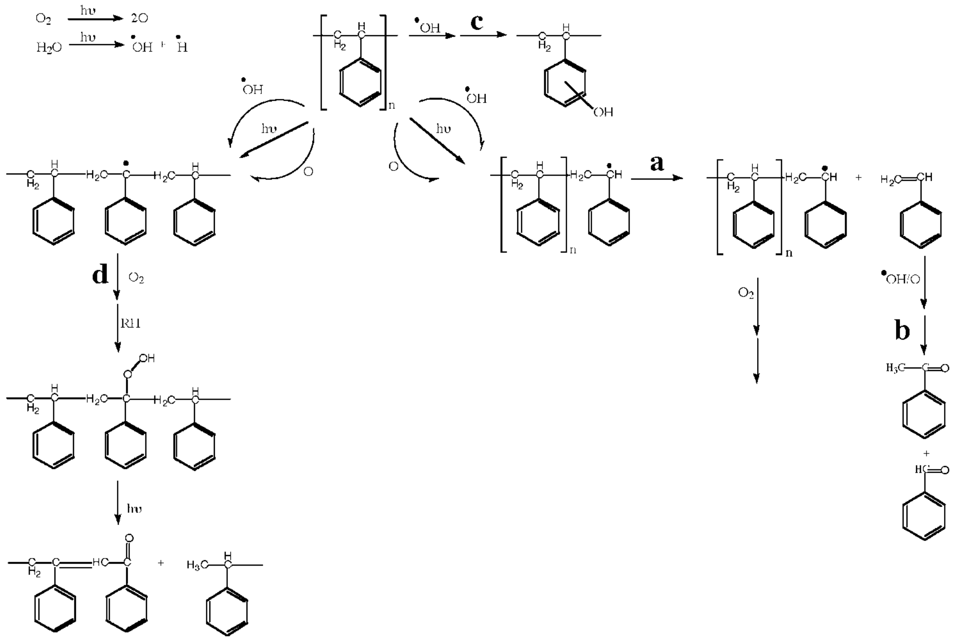

Figure 6. Main pathways of reaction of the VUV photochemically initiated oxidation of polystyrene.

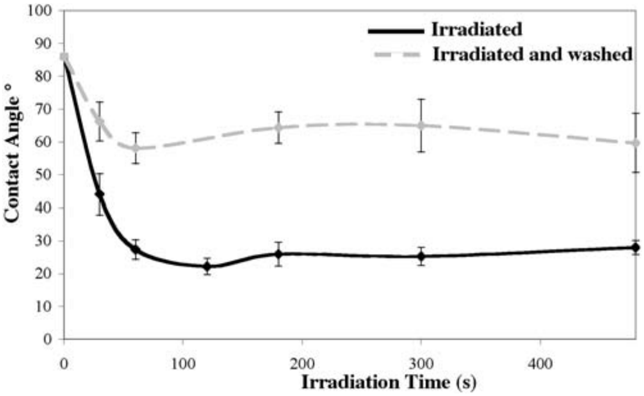

Figure 7. Evolution of the contact angle of polystyrene films as a function of irradiation time, before and after washing with methanol. Distance of irradiation: 4 mm.

results of this investigation seem to indicate that oxidation reactions are mainly involving the aliphatic backbone of the polymer.

The contact angle (water) diminished with increasing time of irradiation from 90° to 25° (Fig. 7, constant distance of irradiation: 4 mm). Carbonyl and hydroxyl functionalization of the polymer surface increases the polarity of the surface and, consequently, leads to a decrease of the contact angle with increasing irradiation time. These results are in excellent agreement with the mean value of integration of the absorption band surfaces determined by FTIR. The total change (decrease) in contact angle was practically completed within the first 2 min of irradiation (Fig. 7), matching the time of irradiation needed to reach the limiting values of carbonyl and hydroxyl group functionalization (Fig. 4). Furthermore, no changes in surface energy could be detected after the limiting values of polar group concentrations were reached.

After washing the irradiated surfaces with methanol, the surface energies increased but did not return to their original value of the nonirradiated samples. Again, this result is in excellent agreement with the FTIR measurements. Oxidation products of low molecular weight are removed by the washing process, leading to a decrease in (surface) polarity and therefore an increase in contact angle. The fraction of polar groups covalently bound to the polymer backbone is accounting for the difference in contact angle observed between nonirradiated and washed, irradiated samples.

Finally, Fig. 8 depicts the contact angle as a function of distance of irradiation for experiments using an irradiation time of 2 min. The smallest value of contact angle was found for samples irradiated at shortest distance. Supporting the results of the FTIR analyses, the contact angle decreases as the surface concentration of carbonyl and hydroxyl groups is increased. At short distances of irradiation (<5 mm), where polymer fragmentation is most efficient, a large difference of surface energy values was found between unwashed and washed samples (Fig. 8). At irradiation distances ≥18 mm, no difference (larger than experimental error) in contact angle could be observed between washed and unwashed samples, suggesting that, in this range of irradiation distance, fragmentation does not take place under the given experimental conditions.

DISCUSSION

VUV photochemically initiated oxidation using a pulsed Xe_2*-radiation source is a very efficient and fast process for treatment (functionalization) of PS surfaces. Carbonyl and hydroxyl groups generated on the surface of PS films decrease the surface energy of the polymer. The combination of FTIR analysis and contact angle measurements ensures a quantitative determination of the rate of functionalization. Experimental conditions were found that lead to substantial oxidative fragmentation of the polymer backbone and to the accumulation of polar polymer debris of low molecular weight at the surface of the polymer films. Nevertheless, the experimental parameters could be adjusted to optimize the formation of polar groups covalently bound to the polymer and, hence, to minimize backbone fragmentation.

The experimental set-up described allows homogeneous irradiation of larger samples, and the use of pulsed Xe_2*-radiation sources represent a valuable alternative to laser- or plasma-induced processes for the oxidation and surface modification of polymers.

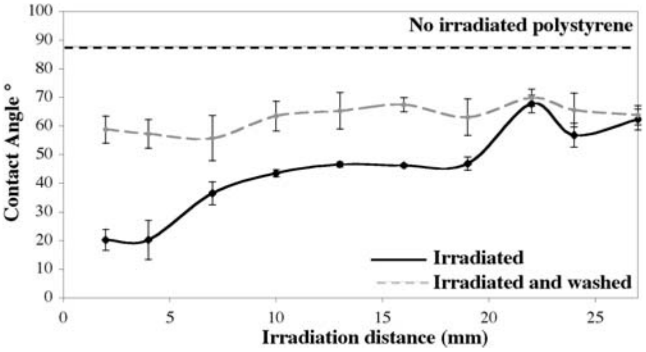

Figure 8. Evolution of the contact angle of polystyrene films as a function of irradiation distance, before and after washing with methanol. Time of irradiation: 2 min.

Acknowledgement—The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft (D.F.G.).

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