

# Vacuum-ultraviolet photochemically initiated modification of polystyrene surfaces: morphological changes and mechanistic investigations†‡

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Vacuum-ultraviolet (VUV) irradiation ( $\lambda_{\text{exc}}$ : 172 ± 12 nm) of polystyrene films in the presence of oxygen produced not only oxidatively functionalized surfaces, but generated also morphological changes. Whereas OH- and C=O-functionalized surfaces might be used for *e.g.* secondary functionalization, enhanced aggregation or printing, processes leading to morphological changes open new possibilities of microstructurization. Series of experiments made under different experimental conditions brought evidence of two different reaction pathways: introduction of OH- and C=O-groups at the polystyrene pathways is mainly due to the reaction of reactive oxygen species (hydroxyl radicals, atomic oxygen, ozone) produced in the gas phase between the VUV-radiation source and the substrate. However, oxidative fragmentation leading to morphological changes, oxidation products of low molecular weight and eventually to mineralization of the organic substrate is initiated by electronic excitation of the polymer leading to C–C-bond homolysis and to a complex oxidation manifold after trapping of the C-centred radicals by molecular oxygen. The pathways of oxidative functionalization or fragmentation could be differentiated by FTIR-ATR analysis of irradiated polystyrene surfaces before and after washing with acetonitrile and microscopic fluorescence analysis of the surfaces secondarily functionalized with the *N,N,N*-tridodecyl-triaza-triangulenium (TATA) cation. Ozonization of the polystyrene leads to oxidative functionalization of the polymer surface but cannot initiate the fragmentation of the polymer backbone. Oxidative fragmentation is initiated by electronic excitation of the polymer (contact-mode AFM analysis), and evidence of the generation of intermediate C-centred radicals is given *e.g.* by experiments in the absence of oxygen leading to cross-linking (solubility effects, optical microscopy, friction-mode AFM) and disproportionation (fluorescence).

## Introduction

In a previous paper, we reported the results of the VUV-photochemically initiated oxidation of surfaces of polystyrene (PS) films and particles.<sup>1</sup> Quantitative FTIR-ATR-analyses of the irradiated surfaces revealed the formation of carbonyl and hydroxyl functional groups at the polymer surface that led to changes in surface energy, as evidenced by contact angle measurements. Irradiation time dependent analyses revealed that such functionalization could not exceed a given surface concentration, and this observation was interpreted by evoking oxidative damages, such as chain scission, formation of fragments of low molecular weight and oxidation products that either absorb the incident radiation or scavenge hydroxyl radicals, atomic oxygen and/or ozone formed in the gas phase between the VUV-radiation source

and the substrate. Such debris could actually be analyzed (GC-MS) from acetonitrile washing solutions, and VUV-irradiated and subsequently acetonitrile-washed surfaces of polystyrene films exhibited a considerable lower surface density of carbonyl and hydroxyl functional groups.

Beside oxidative functionalization that might be used for *e.g.* secondary functionalization, enhanced aggregation or printing, oxidative fragmentation might be exploited to introduce morphological changes on films and, hence, new possibilities of microstructurization. Parallel to our investigations, Hozumi *et al.* have shown that morphological changes on polystyrene surfaces could indeed be introduced by VUV radiation.<sup>2</sup>

The photochemical stability of polystyrene under solar and UV-C radiation was a topic of interest in the 1970s, but morphological changes were neither studied nor observed.<sup>3–7</sup> Irradiation of the organic polymer surface by highly energetic photons (172 nm, 7.2 eV) will involve higher electronically excited states than those reached by conventional UV-C radiation and may either decay to lower excited states or react, against Kasha's rule, by *e.g.* C–C-bond homolysis.

In the present work, we have used the VUV-photochemical technique to induce morphological changes in order to get more detailed information on the mechanism of the VUV-photolysis of polystyrene surfaces, and irradiations were either carried out in the presence of molecular oxygen (normal atmosphere)

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with or without addition of water vapor or in a pure nitrogen atmosphere. FTIR-ATR, contact-mode and friction-mode AFM, contact angle measurements, optical and fluorescence microscopy as well as fluorescence spectroscopy were used as means of analysis to investigate the polymer surfaces.

## Materials and methods

### Sample preparation

Polystyrene (PS) foil of 0.125 mm thickness (Goodfellow GmbH, Bad Nauheim, Germany) and powder (MW: 44000, Aldrich Chem. Co.) were used as received. Due to its rough surface, commercially available foil could not be used for AFM investigations, and PS films of 50 to 100 nm thickness were prepared by spin coating technique using  $5 \times 10$  mm Si (100) wafers (Wacker, Germany) with a native oxide layer as support. In a first step, a jet of solid  $\text{CO}_2$  particles was used to clean the  $\text{SiO}_2$  surfaces, and subsequently, the wafers were immersed into a solution of 20%  $\text{H}_2\text{O}_2$  (30%) and 80%  $\text{H}_2\text{SO}_4$  to oxidize any remaining organic impurities. Finally, the supports were rinsed with de-ionized water and dried in a nitrogen stream. For the spin coating process, a solution of PS (0.001 g) in THF (0.3 ml, Roth, ROTISOLV<sup>®</sup>, HPLC, non-stabilized) was dropped onto the  $\text{SiO}_2$  surface rotating at 3000 rev  $\text{min}^{-1}$ . The rotor on which the supports were fixed for film preparation was mounted in a Teflon cavity with a glass cover. Since holes might be formed in the PS films due to high relative humidity conditions, the cavity was flooded with dry nitrogen before and during the spin coating process to obtain a relative humidity of less than 20%. The spin coating process was stopped after 30 s.

### VUV-irradiation

The equipment used for the VUV-irradiation of PS films and powder was already described.<sup>1</sup> A pulsed tubular  $\text{Xe}_2^*$ -excimer radiation source (XERADEX<sup>™</sup>, Radium Lampenwerk, Wipperfuerth, Germany; electrical power: 20 W; diameter: 4 cm; length: 12 cm,  $\lambda_{\text{exc}}$ :  $172 \pm 12$  nm, radiant power: 8 W, exitance: 50  $\text{mW cm}^{-2}$ ) was used as radiation source. The design of the reactor permits a precise control of the distance between the radiation source and the PS surface to be irradiated as well as of the time of irradiation. Homogeneous irradiation of the PS surface was ensured by keeping the size of the sample ( $1 \times 1.5$   $\text{cm}^2$ ) smaller than the length of the lamp (*vedi supra*) and the maximum distance of displacement of the table ( $\pm 15$  cm). Horizontal displacement of the table in either direction took 19 s. Potential local heating of the sample was avoided by directing a gas flow (air or nitrogen) of constant velocity parallel to the surface under irradiation.

For some experiments, a TEM copper net (Agar Scientific) was placed on the surface of the polymer as a mask. To ensure an intimate contact between the net and the polymer surface, a cover made of synthetic quartz (SUPRASIL<sup>®</sup>, Heraeus), transparent for VUV-radiation, was placed on the sample during the irradiation.

### Ozonization

Ozonolysis was brought about by the exposure of the polymer films in a tubular reactor to ozone, generated from an ozoniser (SANDER, Germany). Ozone concentrations were continuously

analyzed by in line UV-spectrometry (HP 8452A diode array spectrophotometer).

### Analytic techniques

FTIR-ATR analyses were made as described in ref. 1.

Morphological studies were carried out with optical microscopy (DMRE light microscope, Leica, Germany) and multi mode atomic force microscopy (AFM, DI, USA) connected to a NanoScope IIIa controller (DI, USA). Bar-shaped Si cantilevers (NT-MDT, Russia) with typical force constants between 0.6 and 1.8  $\text{N m}^{-1}$  were used.

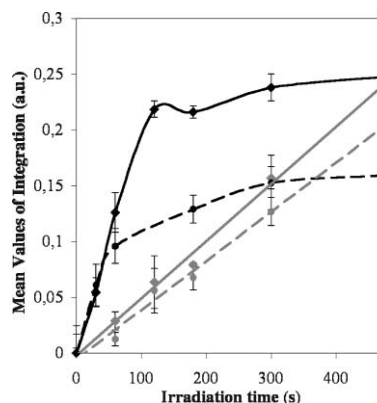
Fluorescence analyses were made by fiber optics coupled fluorescence spectroscopy (Model FL900CDT, Edinburgh Analytical Instruments) and fluorescence microscopy. For the latter, a DMRE light microscope with fluorescence module (Leica, Germany), in combination with a CCD camera (DC480, Leica, Germany) was used.

Contact angle measurements were made as described in ref. 1. Oxidative fragmentation of irradiated polymer material was assessed by washing irradiated surfaces with acetonitrile (Sigma Aldrich, HPLC grade) in which polystyrene is not soluble. Cyclohexane (Sigma Aldrich, HPLC grade) was used in some experiments to dissolve original polystyrene after irradiation. In both cases, sample surfaces were washed by immersing the polymer films for a period of 5 min into a well stirred volume of the solvent. Subsequently, the films were dried in a stream of nitrogen.

## Results and discussion

### Oxidative surface functionalization and structuring

VUV-photochemically initiated oxidation of polystyrene (PS) produces a hydroxyl and carbonyl group functionalized surface.<sup>1</sup> The corresponding surface concentrations increase with irradiation time but reach rapidly a plateau value (Fig. 1). Assuming that there is proportionality between IR-absorption and surface concentration, the corresponding rates of functionalization may be explained by both, the incident photon flux (depending on the

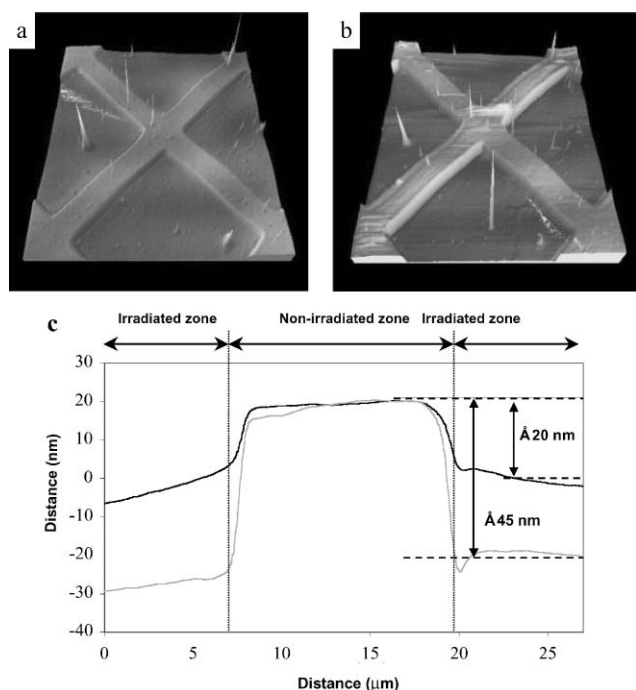


**Fig. 1** Relative integrated IR-absorption values of C=O-groups generated at the surface of PS-films by VUV-irradiation (distance of irradiation: 4 mm) in normal atmosphere (black line) and by ozone ( $2.3 \times 10^{-4}$  M, gray line) vs. irradiation and reaction times, respectively. The dotted lines represent the evolution of the relative integrated IR-absorption values of C=O-groups after washing the irradiated samples with acetonitrile.

distance between radiation source and sample) and the concentration of oxidant species (hydroxyl radicals, atomic oxygen, ozone) primarily generated in the gas phase.

The VUV-radiation absorbed by molecular oxygen (normal atmosphere) generates atomic oxygen and subsequently ozone, both capable of oxidizing the polystyrene surface. However, oxidation with ozone showed a totally different reaction profile (Fig. 1). For ozone concentrations calculated to be at least 10 times higher than those present in the space between the VUV-radiation source and the substrate, the rates of functionalization was found to be much smaller than in the case of the photochemical experiments. Furthermore, the corresponding IR-absorption-values of OH- and C=O-groups did not reach plateau values under the chosen experimental conditions.

VUV-irradiation of PS films through TEM nets led to images composed of photolyzed and non-photolyzed parts of sample surfaces, and in addition to the chemical changes, morphological changes due to VUV-irradiation could be described in detail by microscopic techniques. In normal atmosphere, these experiments produced images of the mask imprinted onto the PS surface (Fig. 2), the AFM image analyses revealing a microstructure consisting of small cavities of 20 nm depth separated by PS barriers of 5  $\mu\text{m}$  width (Fig. 2c). Such morphological changes can only be explained by an oxidative fragmentation of PS.



**Fig. 2** AFM images of PS-films irradiated (172 nm) through a TEM net before (a) and after washing with acetonitrile (b), and corresponding contour analysis (c). Time of irradiation: 10 min, distance 4 mm.

In fact, washing of the irradiated sample surfaces with acetonitrile yielded, on one hand, a solution of oxidation products of low molecular weight<sup>1</sup> and, on the other hand, an increased apparent depth of the cavities to approximately 45 nm (Fig. 2a and 2b), indicating that debris of a VUV-photochemically initiated oxidative fragmentation was eliminated from the surface.

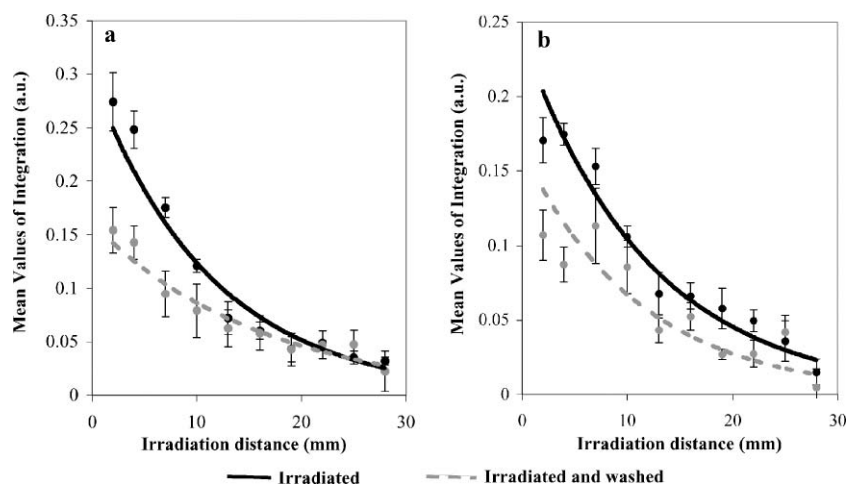
The surprisingly high definition of the microstructures suggests that the main reaction path does not involve diffusion of reactive species. Consequently, neither free hydroxyl radicals nor atomic oxygen or ozone could be at the origin of the fragmentation mechanism.

The high resolution may, however, be explained by an electronic excitation of the polymer and the subsequent generation of C-centered radicals that react with molecular oxygen, hence leading to C–C-bond homolysis (polymer backbone fragmentation) and subsequent peroxy radical generation initiating a manifold of thermal reactions, *e.g.* hydrogen abstractions, hydroxyl radical generation, all enhancing the oxidation of the polymer and of the fragmentation products. This interpretation is supported by the results of the GC-MS analyses of acetonitrile washing solutions<sup>1</sup> showing that the vast majority of the detected and identified compounds were oxidation products of aliphatic chain fragments. Hydroxyl radicals, atomic oxygen and ozone are known to oxidize aromatic functions as well,<sup>2,6,8–10</sup> but corresponding products (*e.g.* phenolic compounds) were only detectable in minute quantities.

Plateau values of relative integrated IR-absorptions of both hydroxyl and carbonyl functions depended surprisingly on the distance between radiation source and polymer film surface and therefore on the incident photon flux.<sup>1</sup> In fact, it was expected that the apparent rate of oxidative functionalization would depend on irradiation distance, and that the corresponding absorption values would converge to one plateau value with time of irradiation. However, the VUV-photochemical process might not only lead to surface functionalization, but also to parallel or subsequent backbone fragmentation. Different concentrations of products of oxidative fragmentation deposited on the irradiated surface might then lead to quasi steady-state situations determined primarily by parameters such as VUV-transmittance of the debris layer, rate of photochemical oxidation of the low molecular weight oxidation products and the efficiency of trapping of reactive oxygen species by this layer.

In contrast to VUV-irradiation, the reaction of ozone with the PS surface is producing only small amounts of debris that can be dissolved by acetonitrile (Fig. 1). Assuming that oxidative functionalization is primarily due to the reaction of reactive oxygen species with the PS surface, whereas oxidative fragmentation would be a parallel process initiated by the electronic excitation of the polymer, the surface concentration of these low molecular weight oxidation products and, hence, a fraction of the relative integrated IR-absorption values would depend on the irradiation distance (Fig. 3). IR-absorption-values depend on irradiation time, as foreseen,<sup>1</sup> but, in fact, the differences between the corresponding OH- and C=O-surface concentrations of irradiated and irradiated and washed films were also found to diminish with increasing distance.

In line with the mechanistic hypothesis, the importance of the IR-absorption of the oxidized debris diminishing with irradiation distance may be explained with the distance dependent rate of VUV-photochemical backbone fragmentation, followed by a dominant thermal oxidation manifold to produce oxidized fragmentation products that are subsequently mineralized. With increasing distance, the formation of oxidized fragmentation products (C=O-groups) was found to decrease below detection limits, and only oxidative functionalization could be found (Fig. 3a). For hydroxylated compounds (Fig. 3b), the distance of irradiation,

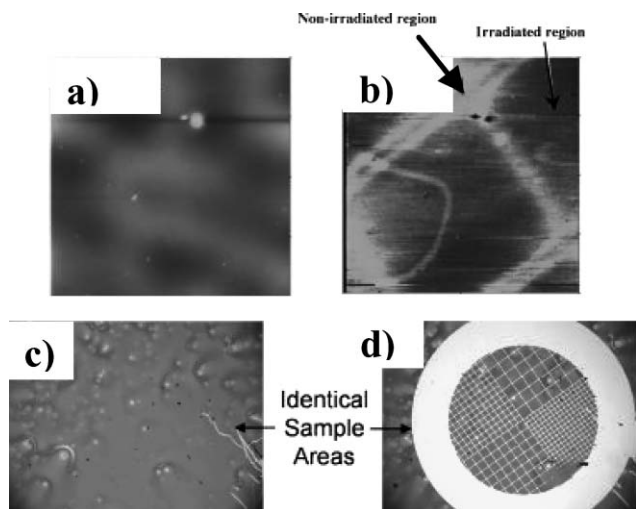


**Fig. 3** Relative integrated IR-absorption values of C=O-groups (a) and OH-groups (b) generated by VUV-irradiation (172 nm, 2 min) at the surface of PS-films under normal atmosphere and measured before and after acetonitrile washing vs. the distance of irradiation between the radiation source and the film surface.

where the two functions converge, is outside the experimental domain, indicating that, to a minor extent, reactive oxygen species might also initiate fragmentation processes. Well defined microstructures (Fig. 2b) already suggested that reactive oxygen species produced in the gas phase could not play an important role in the fragmentation processes observed at the surface of the PS-films. However, the rates of such diffusion controlled processes also diminish with increasing distance, due to the rather short lifetimes of hydroxyl radicals and atomic oxygen and to the diminishing concentration of such reactive oxygen species close to the organic surface. Therefore, the distance dependent IR-absorption values reported in Fig. 4 result from a combination of two processes, VUV-photolysis of the surface producing backbone fragmentation and low-molecular weight oxidation products as intermediates of mineralization, and oxidation of the organic surface by reactive

oxygen species produced by VUV-radiation in the gas phase between radiation source and sample. The first is dominating at shorter, the latter at larger distances of irradiation.

The different plateau values of relative integrated IR-absorption reported in Fig. 1 may then be explained by different rates of VUV-photochemical backbone homolysis due to different transmitted photon fluxes and assuming similar rates for the subsequent thermal oxidation processes. This interpretation implies, however, (i) that VUV-radiation is transmitted through the thin (approximately 20 nm) layer of fragments to photolyze the polymer, (ii) that molecular oxygen may easily diffuse through this layer and react with the C-centered radicals to peroxy intermediates, hence triggering the thermal oxidation manifold, and that (iii) VUV-radiation and/or reactive oxygen species in the gas phase are further oxidizing (mineralizing) the intermediate oxidation products.



**Fig. 4** PS-film irradiated through a TEM net in the absence of molecular oxygen. Contact (a) and friction (b) mode AFM analyses. Optical microscopic image before (c) and after washing (d) with cyclohexane. Irradiation time: 10 min, distance: 4 mm.

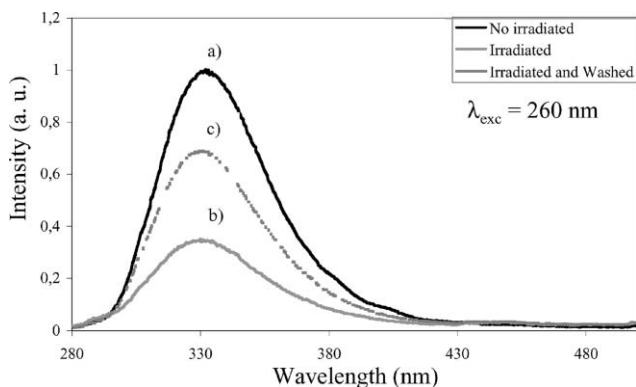
### Cross-linking

In accord with the proposed mechanism of oxidative fragmentation, no microstructures as shown in Fig. 1 could be detected for samples irradiated under nitrogen (Fig. 4a). When the friction energy between the irradiated polystyrene surface and the tip of the cantilever was measured, the mask could, however, be clearly recognized (Fig. 4b) giving evidence that chemical changes had taken place.

The expected cross-linking was confirmed by producing negative images of the TEM net due to the difference of solubility of irradiated and non-irradiated PS. When the “latent image” of the TEM mask (Fig. 4c) was washed with cyclohexane, a solvent in which native polystyrene is soluble, only the non-irradiated parts were dissolved (Fig. 4d). These very efficient cross-linking experiments confirm earlier mechanistic proposals<sup>11–13</sup> and show clearly that VUV-photolysis of the PS-surface generating C-centered radicals on the aliphatic chain of the polymer is an important initial step of the oxidative degradation process in the presence of molecular oxygen.

## Fluorescence

The fluorescence of PS ranging from 290 to 390 nm ( $\lambda_{\text{exc}} < 270$  nm, Fig. 5a) is attributed to an excimer emission resulting from the interaction of two adjacent benzene rings in the polymer chain.<sup>14</sup> After irradiation of the polymer under normal atmosphere, the intensity of the excimer fluorescence decreased to about 30% of its original value (Fig. 5b), confirming earlier results.<sup>15–17</sup> Based on the results of the VUV-photochemical investigation, this decrease might be attributed to three main effects:



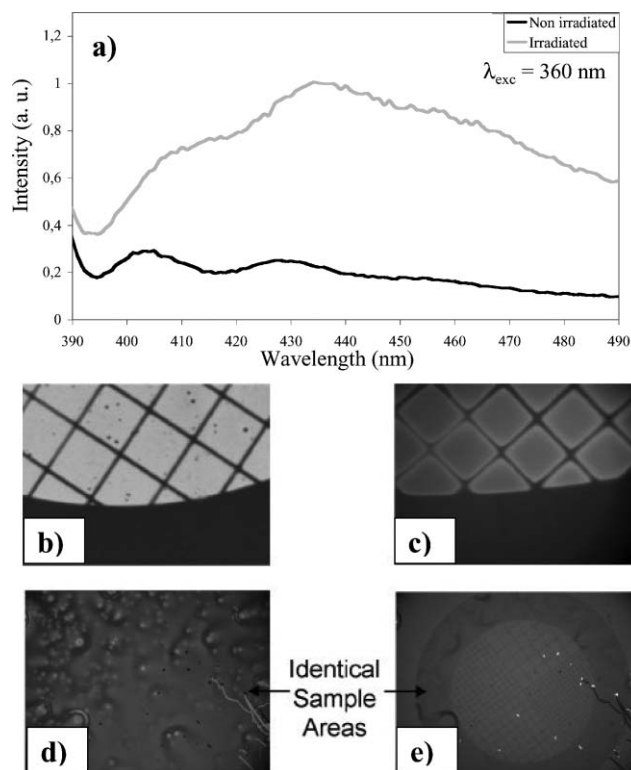
**Fig. 5** Excimer fluorescence ( $\lambda_{\text{exc}}$ : 260 nm) of native polystyrene (a), after VUV-irradiation (b, irradiation time: 10 min, distance: 4 mm), after VUV-irradiation and washing with acetonitrile (c).

- (i) Oxidation of the aromatic entities and consequent decrease of the concentration of fluorescent centers.
- (ii) Quenching of electronically excited aromatic units or of excimers by groups formed by the VUV-photochemically initiated oxidation.
- (iii) Filter effect by the products of VUV-photochemically initiated oxidation deposited on the surface.

After washing the irradiated samples with acetonitrile, the excimer fluorescence intensity increased when compared to that obtained before washing (Fig. 5c). Nevertheless, the intensity never reached the original value of the native polystyrene. By removing the oxidation products from the polymer surface, most of the filter and quenching effects were apparently eliminated, the decrease of the fluorescence with respect to the native polystyrene being primarily due to the quenching effects of remaining HO- and C=O-groups bound to the polymer chain.

But VUV-irradiated PS also exhibits a red-shifted emission at wavelengths  $> 400$  nm (Fig. 6a). Fig. 6b and 6c show optical and fluorescence microscopy images of samples irradiated for 10 min under nitrogen or under ambient conditions.

Under ambient conditions, the mask is clearly visible on the irradiated sample (Fig. 6b, see also Fig. 2), and the fluorescent image was obtained at  $\lambda_{\text{exc}}$ : 370 nm (Fig. 6c); it may be attributed to products generated during VUV-photolysis. It is, however, interesting to note that a similar image was obtained for samples irradiated under nitrogen (Fig. 6e), hence, this new fluorescence cannot arise from any oxygenated product. C-centered radicals produced by VUV-photochemical homolysis might be trapped by molecular oxygen, and might lead to cross-linking, but might also react by disproportionation yielding conjugated double bonds on the aliphatic chain of the polymer. Such chromophors had been proposed for a broad band emission at wavelengths in the



**Fig. 6** Fluorescence of VUV-irradiated polystyrene with  $\lambda_{\text{exc}}$ : 360 nm and  $\lambda_{\text{em}} > 400$  nm. a) Fluorescence spectra of native and VUV-irradiated (10 min, 4 mm) polystyrene. Polystyrene irradiated under normal atmosphere (10 min, 4 mm). b) Optical microscopic image of the irradiated surface. c) Fluorescence microscopic image of the same surface ( $\lambda_{\text{exc}}$ : 370 nm and  $\lambda_{\text{em}} > 400$  nm). Polystyrene irradiated under nitrogen. d) Optical microscopic image of the irradiated surface. e) Fluorescence microscopic image of the same surface ( $\lambda_{\text{exc}}$ : 370 nm and  $\lambda_{\text{em}} > 400$  nm).

range of 400 to 700 nm.<sup>6,17</sup> This observation further supports the mechanistic hypothesis of the VUV-photochemical homolysis as an important reaction path during the oxidative functionalization of polystyrene surfaces.

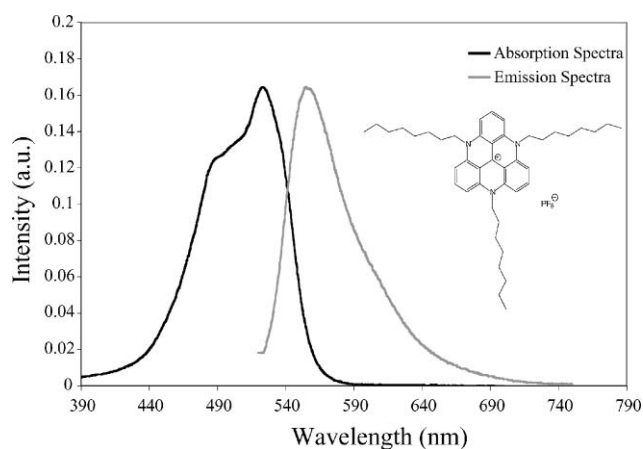
### Fluorescence analysis of oxidative functionalization

So far, the results of a rather large range of experiments support the mechanistic hypothesis of an oxidative fragmentation due to photochemical homolysis of backbone C–C-bonds and subsequent radical trapping by molecular oxygen. An extended mechanistic hypothesis would foresee, that formation of hydroxyl and carbonyl groups at the organic surface (oxidative functionalization) implies primarily hydrogen abstraction by reactive oxygen species produced in the gas phase. It remains now to present evidence for such a mechanistic differentiation.

It was found that the *N,N,N*-tridodecyl-triaza-triangulenium (TATA) cation (Fig. 7) is adsorbed strongly to polar functionalized surfaces and might therefore serve to quantify the extent of oxidative functionalization of PS surfaces by fluorescence analysis.

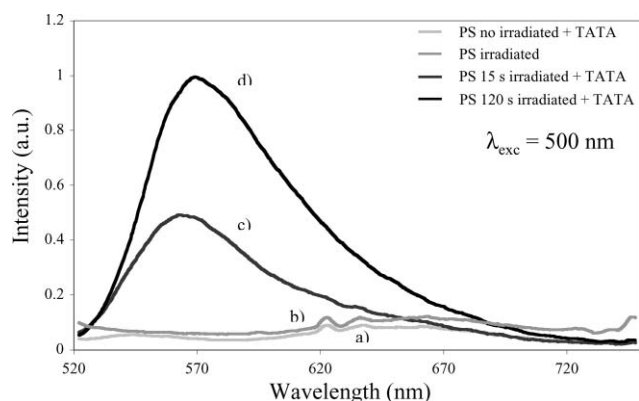
The absorption and fluorescence spectra of TATA are shown in Fig. 7; the cation exhibits an  $\lambda_{\text{max}}$  at 500 nm and a very strong fluorescence in the region between 550 and 750 nm.

Secondary functionalization was performed by submerging irradiated PS films into a  $5 \times 10^{-5}$  M solution of TATA in



**Fig. 7** Molecular structure of *N,N,N*-tridodecyl-triaza-triangulenium (TATA) cation. Absorption (black line) and fluorescence ( $\lambda_{\text{exc}}$ : 500 nm) (grey line) spectra in acetonitrile.

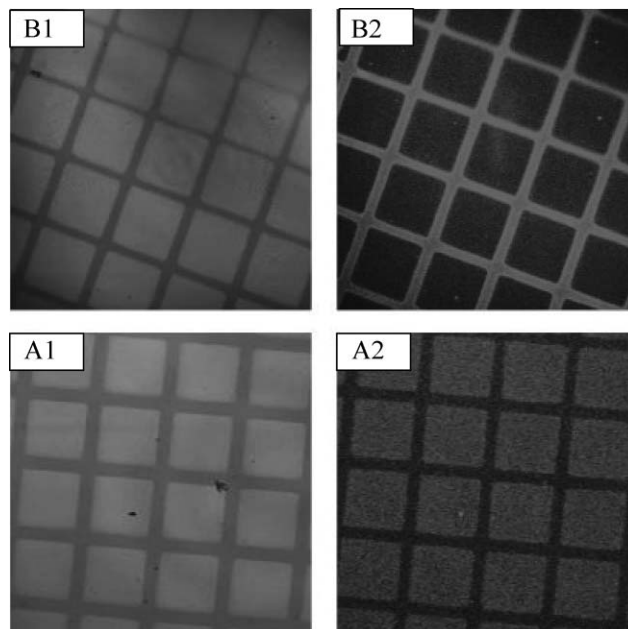
acetonitrile for 5 min. Subsequently, the samples were washed in acetonitrile for 1 min. In Fig. 8, examples of fluorescence spectra are presented. No emission was detected for VUV-irradiated PS that was not functionalized with TATA (Fig. 8b) as well as for a non-irradiated sample subsequently submerged into a TATA solution (Fig. 8a), the latter revealing that TATA is not adsorbed to the surface of the native polymer. However, the two VUV-irradiated and subsequently TATA-functionalized samples emit the typical TATA fluorescence, the emission of the sample irradiated for 120 s being stronger (Fig. 8d) than the emission of the sample that was only irradiated for 15 s (Fig. 8c). For limited surface concentrations, the fluorescence is clearly depending on the amount of cation adsorbed on the surface of irradiated polystyrene, and, hence, on the overall polarity of the VUV-irradiated PS-surface. TATA fluorescence analysis might therefore be applied to obtain some semi-quantitative information on the extent of the VUV-initiated oxidative functionalization of the polymer surface.<sup>18</sup>



**Fig. 8** Fluorescence spectra of non-irradiated (b) and VUV-irradiated (15 s (c) and 120 s (d)) PS-surfaces submerged into a  $5 \times 10^{-5}$  M solution of TATA in acetonitrile for 5 min, and of a VUV-irradiated PS-surface without secondary (TATA) functionalization (a).

Given the fact that the functionalization of PS-surfaces with TATA is only possible if polar surface functionalization was performed, this method of analysis might be used to differentiate

between oxidized and non-oxidized surfaces. Polystyrene samples were irradiated through a TEM net and treated with TATA solution, and the image of the mask was in all cases visible by fluorescence microscopy. Surprisingly, the zones of most intense fluorescence were those covered by the mask, the emission signal increasing with increasing reaction time (Fig. 9).



**Fig. 9** Reflection (A1, B1) and fluorescence microscopic imaging of VUV-irradiated polystyrene films through a TEM net for 30 s (A2) and 3 min (B2), respectively, and subsequently treated with TATA (see text).

The result is clearly indicating that oxidative functionalization is principally achieved *via* the attack of reactive oxygen species produced in the gas phase and capable of diffusing to the non-irradiated parts of the PS-surface. The polarity of the non-irradiated surface increased with increasing reaction time, and, consequently, a higher surface concentration of adsorbed TATA resulted in a more intense fluorescence.

For the irradiated parts of the PS-surface, the working hypothesis proposes an attack of reactive oxygen containing species produced in the gas phase as well as the electronic excitation of the substrate. The latter leading to an oxidative fragmentation of the backbone, a layer of low-molecular weight oxidation products is formed preventing further oxidative functionalization of the polymer surface (decrease of fluorescence intensity) but allowing for its electronic excitation as well as for the mineralization of the low-molecular weight debris by all possible reaction pathways.

## Conclusion

VUV-photochemically initiated oxidation was shown to be a very efficient and fast process for introducing microstructures on PS-surfaces and for oxidative functionalization of these substrates. Under normal atmosphere and at short distance between the radiation source and the substrate surface, oxidative fragmentation of the polymer takes place permitting the imprinting of microstructures on the surface (photolithography).

Hydroxyl- and carbonyl-groups of appropriate surface concentrations may be introduced at the polymer surface (oxidative functionalization) by VUV-irradiation under normal atmosphere, at longer irradiation distances and with appropriate periods of irradiation. Oxidative functionalization is also achieved by ozonization.

Evidence is given that oxidative fragmentation is the consequence of a VUV-electronic excitation of the polymer surface leading to C–C-bond homolysis and subsequent trapping of the C-centered radicals by molecular oxygen yielding peroxy radicals. The latter trigger a manifold of oxidation reactions leading *via* intermediate oxidation products to the mineralization of the organic fragments. The generation of the primary polymer radicals was confirmed by cross-linking and disproportionation reactions in the absence of molecular oxygen.

Secondary functionalization with *N,N,N*-tridodecyl-triazatriangulenium (TATA) cation and analysis by fluorescence microscopy supports the mechanistic hypothesis that oxidative functionalization is mainly due to the attack of reactive oxygen species (hydroxyl radicals, atomic oxygen, ozone) on the polymer surface initiating oxidation by hydrogen abstraction or electrophilic addition.

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