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## 7. Ageing of plasma deposited polymers

### 7.1. Introduction

It is well known that plasma deposited films undergo certain chemical reactions when they are exposed to atmosphere. Freshly deposited plasma polymers typically contain radicals, which, on exposure to air, rapidly react with in-diffusing oxygen. As a consequence, even when the plasma processing atmosphere itself does not contain oxygen, this element can be detected subsequently, and the incorporation of oxygen can continue for many months after deposition of films.

By using the analytical approaches introduced in section 4.4 the plasma deposited films could be analyzed without air contact, under so called “in-situ” conditions. This provides the possibility to analyze samples without the influence of post-plasma reactions and the possibility to investigate the post-plasma reactions in some detail.

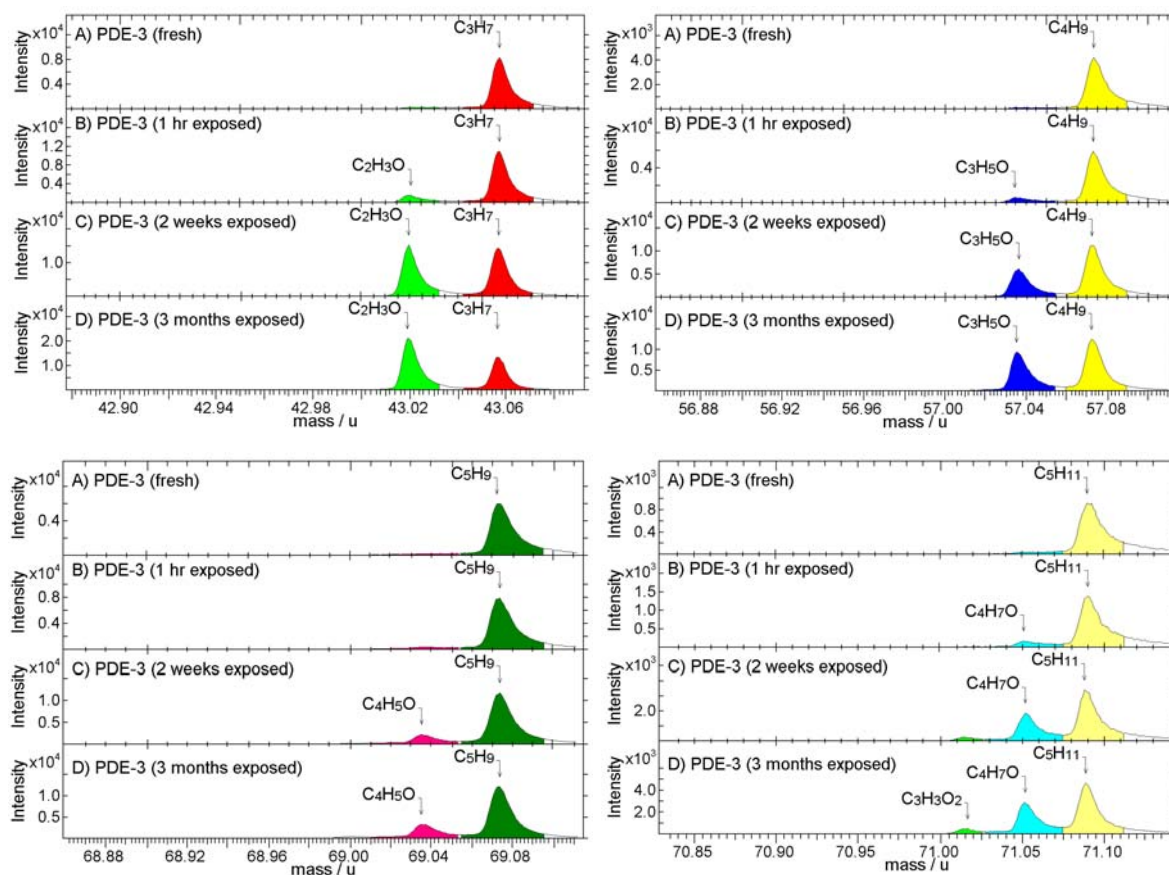
In this chapter, the effect of air exposure, in terms of plasma technology denominated as the “ageing” of plasma deposited films, is investigated. The plasma deposited films were analyzed by means of ToF-SSIMS at different exposure times from hours to several months. The oxygen uptake, the formation of oxygen species due to ageing and the effect of external plasma parameters on the oxygen uptake related changes are the topics of this dedicated study.

Possible reactions assumed to occur during ageing of plasma deposited films are discussed according to the ToF-SSIMS findings reported.

### 7.2. Ageing of plasma deposited films prepared from styrene and ethylene

As the plasma deposited films prepared from styrene and ethylene were exposed to air, oxygen uptake started immediately. This was derived from the increasing intensities of well resolved oxygen containing secondary ions in the positive ToF-SSIMS spectra of all samples. The most dominant oxygen containing secondary ions in the positive ToF-SSIMS spectra of plasma deposited styrene and ethylene films after exposure to air were at  $m/z$  43 ( $C_2H_3O^+$ ), 45 ( $C_2H_5O^+$ ), 55 ( $C_3H_3O^+$ ), 57 ( $C_3H_5O^+$ ), 69 ( $C_4H_5O^+$ ), 71 ( $C_4H_7O^+$ ), and 83 ( $C_5H_7O^+$ ). This will be demonstrated by the variations in the yields of secondary ions at  $m/z$  43, 57, 69, and 71 vs. exposure time for the PDE-3 sample (c.f. Figure 7.1). These secondary ions were also observed with high yields in the positive SSIMS spectra of plasma deposited films made from ethane, ethylene and acetylene, [61] as well as plasma modified polyolefin samples (polypropylene and hexatriacontane, [59]) after exposure to

air. This points to a more common ageing process in ambient air for plasma deposited and modified organics. For this reason the ageing behavior of plasma deposited styrene and ethylene films are presented under the same headline and the common features are highlighted.

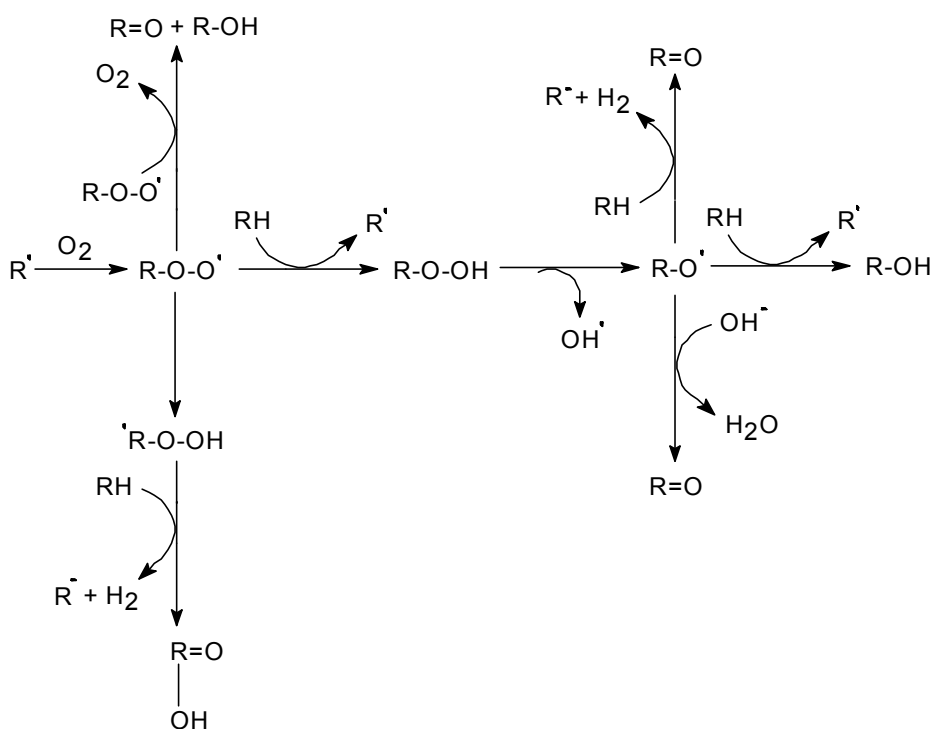


**Figure 7.1.** Variations in yields of the secondary ions at  $m/z$  43 ( $C_2H_3O^+$ ), 57 ( $C_3H_5O^+$ ), 55 ( $C_3H_3O^+$ ), 69 ( $C_4H_5O^+$ ) and 71 ( $C_4H_7O^+$ ) in the positive ToF-SSIMS spectra of the PDE-3 sample vs. time of exposure to ambient air. The mass resolution at  $m/z$  28 was 6000. External plasma parameters employed for the deposition of the PDE-3 sample are given in Table 3.2, p. 28.

The ageing process of plasma deposited and plasma modified organics can be divided into two steps [34]. The primary ageing reaction is that molecular oxygen reacts with C-radical sites. This results in the formation of peroxy radicals ( $C-O-O^\bullet$ ). Decay of these peroxy radicals and formation of different oxygen functionalities are the secondary reaction step in the ageing process. In the case of plasma deposited films made from hydrocarbon monomers, e.g., ethylene and styrene, these peroxy radicals are mainly

converted into hydroperoxides (C-O-OH) by the abstraction of hydrogen from C-H (c.f. Figure 7.2). Hydroperoxides are unstable and may decay or rearrange giving rise to many kinds of oxygen functionalities. This process is well known as *auto-oxidation* [33, 34]. The auto-oxidation process leads to the formation of different oxygen functionalities like C=O and COO as it was observed by XPS studies [104].

The most dominant oxygen containing secondary ions in the positive ToF-SSIMS spectra of plasma deposited styrene and ethylene films after exposure to air are characteristic secondary ions of different oxygen functional groups (c.f. section 4.4). Obviously, after exposure to air several oxygen functional groups are formed on the surface of plasma deposited styrene and ethylene films. However, it is not possible to identify and quantify these different functional groups by ToF-SSIMS. Every species gives rise to an individual fragment pattern superimposing each other in the SSIMS spectra. There is no chance to separate them.

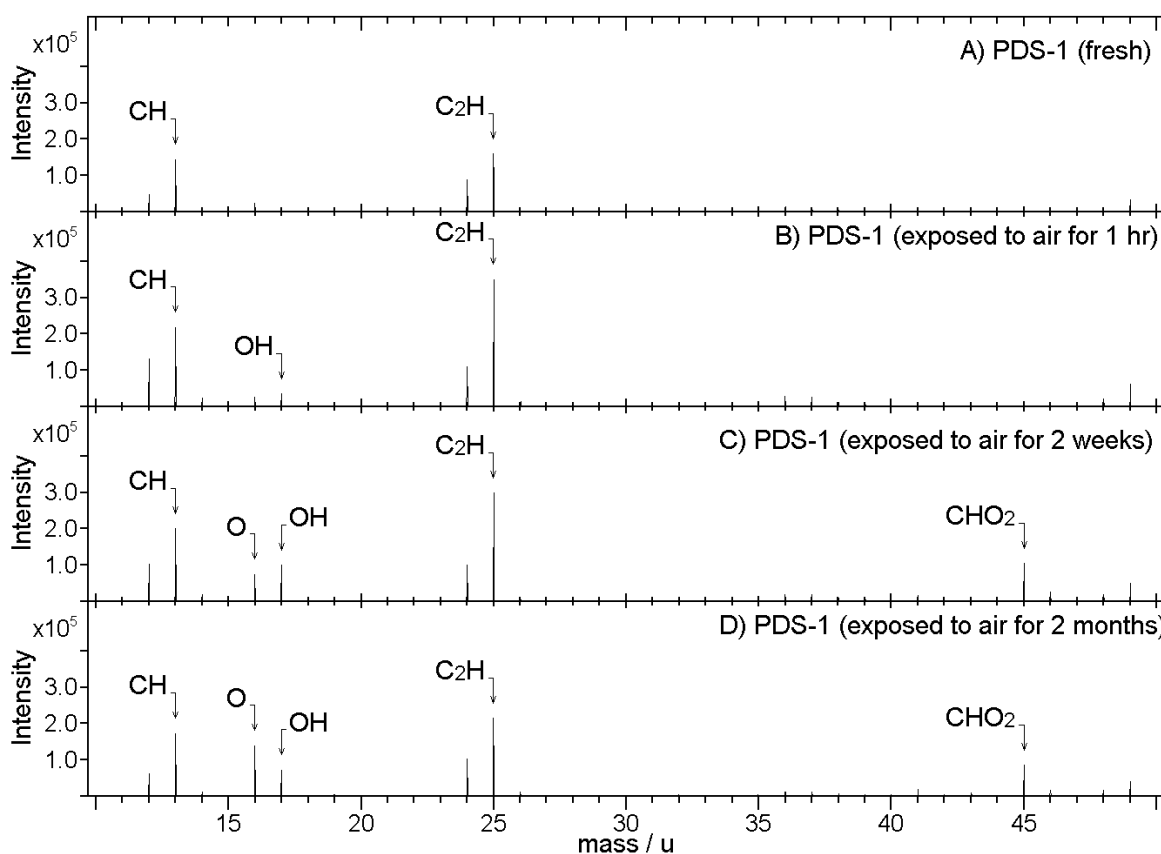


**Figure 7.2.** Reaction scheme of the oxygen uptake and auto-oxidation reactions (adapted from Ref. [34]).

Alternatively the oxygen uptake of plasma deposited styrene and ethylene films could be monitored by measuring the intensities of oxygen and oxygen containing secondary ions in the negative ToF-SSIMS spectra. They are given as an example for the

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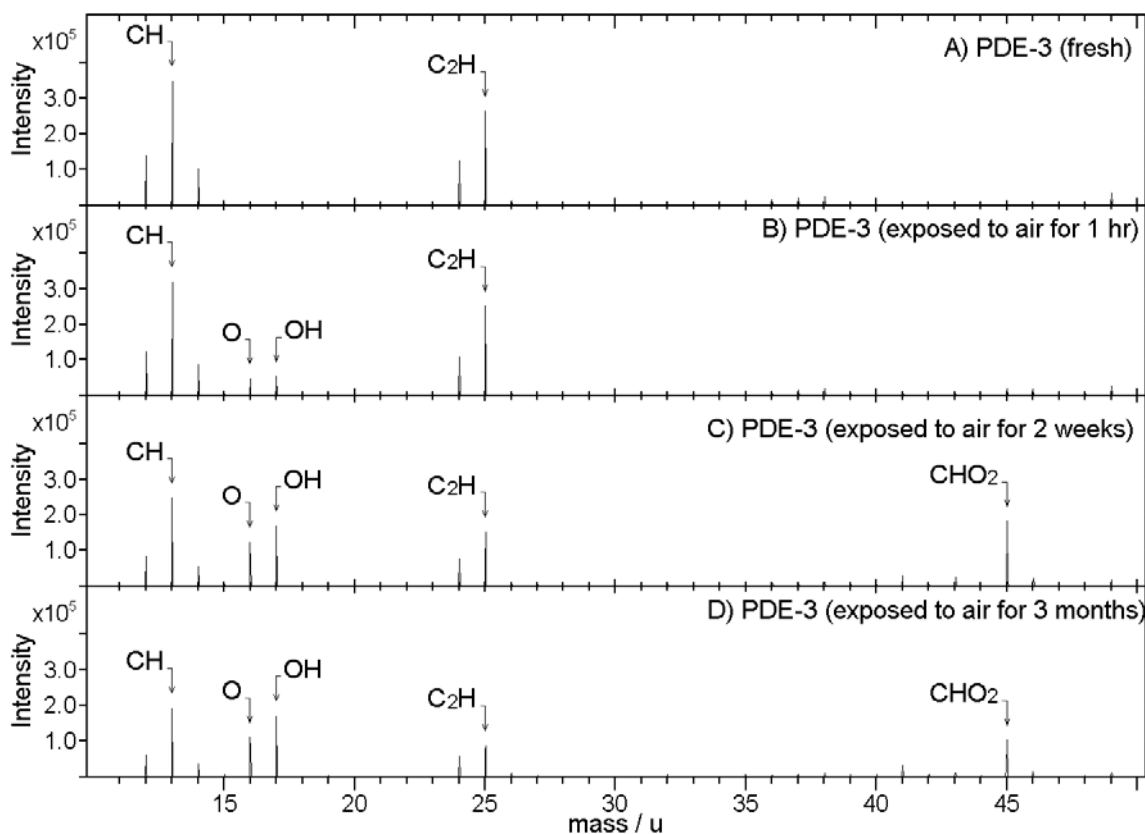
PDS-1 and PDE-3 samples in Figure 7.3 and 7.4, respectively. The most dominant oxygen containing peaks in the negative SIMS spectra of PDS-1 and PDE-3 after exposure to air were at  $m/z$  41 ( $C_2HO^-$ ), 43 ( $C_2H_3O^-$ ), 45 ( $CHO_2^-$ ), and 46 ( $CH_2O_2^-$ ). Among those the peak at  $m/z$  45 ( $CHO_2^-$ ) was found to be the most prominent signal reaching its maximum yield after some days of exposure. After that time of exposure, the yield of this ion decreased slowly. It is highly probable that the secondary ion  $m/z$  45 ( $CHO_2^-$ ) is the key fragment representing the C-O-O $\cdot$  radicals and/or C-O-OH groups. The yield of the  $CHO_2^-$  secondary ion is correlated to the concentration of the C-O-O $\cdot$  radicals and/or C-O-OH groups in the film. The decrease in concentration of these species with increasing exposure time could be explained as a net effect of the different kinetics of the oxygen uptake and auto-oxidation processes.



**Figure 7.3.** Negative ToF- SSIMS spectra of the PDS-1 sample **A)** fresh, **B)** after 1 hr, **C)** after 10 days, and **D)** after 2 months exposure to air. External plasma parameters employed for the deposition of the PDS-1 sample are given in Table 3.1, p. 27.

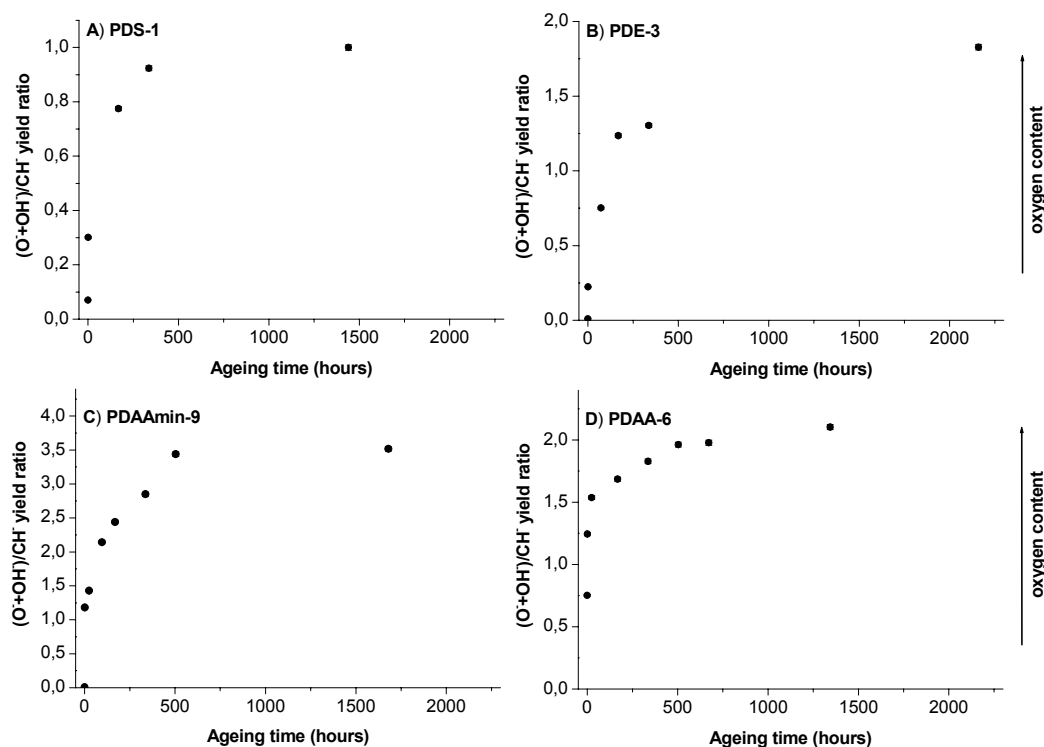
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The oxygen uptake of plasma deposited styrene and ethylene films was also monitored from their oxygen content evaluated by using the  $(O^-+OH^-)/CH^-$  yield ratio at different exposure times. The oxygen uptake of the films was found to be very fast for the first hours of exposure, later on its rate decreased slowly. This behavior of the films is demonstrated by the oxygen uptake of the PDS-1 and PDE-3 samples vs. different exposure times (c.f. Figure 7.5 A&B).



**Figure 7.4.** Negative ToF- SSIMS spectra of the PDE-3 sample **A)** fresh, **B)** after 1 hr, **C)** after 10 days, and **D)** after 3 months exposure to air. External plasma parameters employed for the deposition of the PDE-3 sample are given in Table 3.2, p. 28.

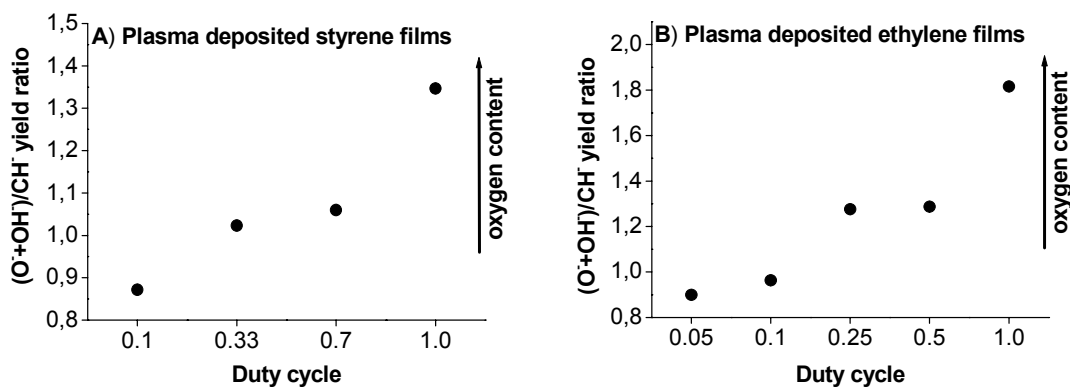
These data reflect the kinetics (including saturation) of the reaction of radicals with ambient air as measured by ToF-SSIMS. Similar data were also measured with XPS in parallel experiments using the same plasma set-up [104]. The prompt and high increase in the oxygen content of the plasma polymers within the first hours of exposure is characteristic of the ageing process. It is explained by the quenching of radicals in the freshly deposited films by oxygen from the ambient air [34].



**Figure 7.5.** Oxygen content of the fresh and aged **A)** PDS-1, **B)** PDE-3, **C)** PDAAmin-9, and **D)** PDAAI-6 samples, measured by the  $(O+OH)/CH^-$  yield ratio vs. different exposure time. External plasma parameters employed for the deposition of the samples are given in Tables 3.1 – 3.4, p. 27 – 30, respectively.

When the plasma deposited films from styrene and ethylene were exposed to air for equal times, it was observed that the oxygen uptake of the samples was different. It was found to be dependent on the external plasma parameters employed for their deposition. As an example, in Figure 7.6 the results for a variation of the duty cycle are given. As the duty cycle increases the oxygen uptake of the plasma deposited styrene and ethylene films increases. This is due to the higher amount of surface radicals of the samples prepared at higher duty cycle values. A higher duty cycle results in the formation of more radicals because the fragmentation of monomer molecules in the plasma is increased. Additionally a higher duty cycle provides higher ion, electron and plasma ultra violet photon bombardment producing higher radical concentrations in the films (c.f. section 2.2.5). Similarly, it was observed that the oxygen up-take of the plasma deposited films increased with increasing plasma power. Again this can be understood in terms of increasing radical concentration. It is clear that the oxygen uptake can be viewed to be controlled by the

external plasma parameters used for the film deposition. Thus, these ToF-SIMS results support the rule proposed by Retzko [95] that “harder plasma conditions result in higher oxygen uptake and vice versa. The higher the regularity of a plasma polymer is, the lower is the oxygen uptake”.



**Figure 7.6.** Oxygen uptake of the plasma deposited films prepared from **A)** styrene and **B)** ethylene, evaluated by taking the  $(O^+OH^-)/CH^-$  yield ratio, after 10 days of exposure vs. duty cycle. External plasma parameters employed for the deposition of the plasma deposited styrene and ethylene films are given in Tables 3.1, p. 27, and Table 3.2, p. 28, respectively.

### 7.3. Ageing of plasma deposited allylamine films

Similar to the SSIMS approach used for the cases of plasma deposited films prepared from ethylene and styrene, the oxygen uptake of plasma deposited allylamine films can be investigated.

The oxygen uptake of plasma deposited allylamine films was again derived from the increasing intensities of the oxygen and oxygen containing secondary ions in their negative ToF-SSIMS spectra. Their oxygen uptake was also evaluated by using the  $(O^+OH^-)/CH^-$  yield ratio. The oxygen uptake was found to be very fast for the first hours of exposure and then its rate decreased slowly. This result reflects the kinetics of the reaction of radicals with ambient air, which were also measured by XPS in parallel experiments using the same plasma set-up [106]. This behavior of the films is demonstrated, for example, by the oxygen uptake of the PDAmin-9 sample vs. different exposure times (c.f. Figure 7.5.C). In comparison to the styrene and ethylene cases, ToF-SSIMS data suggest a higher oxygen uptake for plasma deposited allylamine films.

In the case of aged plasma deposited films made from styrene and ethylene the  $\text{CHO}_2^-$  secondary ion, which was attributed to the formation and decay of peroxy radicals and hydroperoxides, was found at high yields (c.f. section 7.2). In the case of plasma deposited allyl amine films the  $\text{CNO}^-$  secondary ion was one of the most prominent signals in the negative ToF-SSIMS spectra (c.f. for example the PDA Amin-9 SSIMS data in Figure 7.7). Gengenbach et. al. [128, 129], investigated the ageing behavior of plasma deposited films prepared from n-heptylamine [128] and 1,3-diaminopropane [129] by XPS. They found that, as the density of amino groups increases in plasma polymers made from n-heptylamine to 1,3-diaminopropane, oxygen incorporation to sites adjacent to nitrogen containing functional groups (c.f. Figure 7.8) increases. The formation of oxidized groups, which are characteristic of the oxidation of hydrocarbon structures, e.g., esters, hydroxyls, ketones, etc., decreases parallel to this effect. It seems that for plasma deposited allylamine films also most of the oxygen incorporated due to ageing is fixed at  $\alpha$ -positions, i.e., sites adjacent to nitrogen containing functional groups. On the other hand, the presence of  $\text{C}_x\text{H}_y\text{O}^+$  type secondary ions in the positive and  $\text{CHO}_2^-$  secondary ions in the negative ToF-SSIMS spectra of aged plasma deposited allylamine films points to the formation of oxidized groups, e.g., hydroxyls and ketones, which are formed to be characteristic of the oxidation process of hydrocarbon plasma polymers. Obviously formation of these oxidized groups is a minor process.

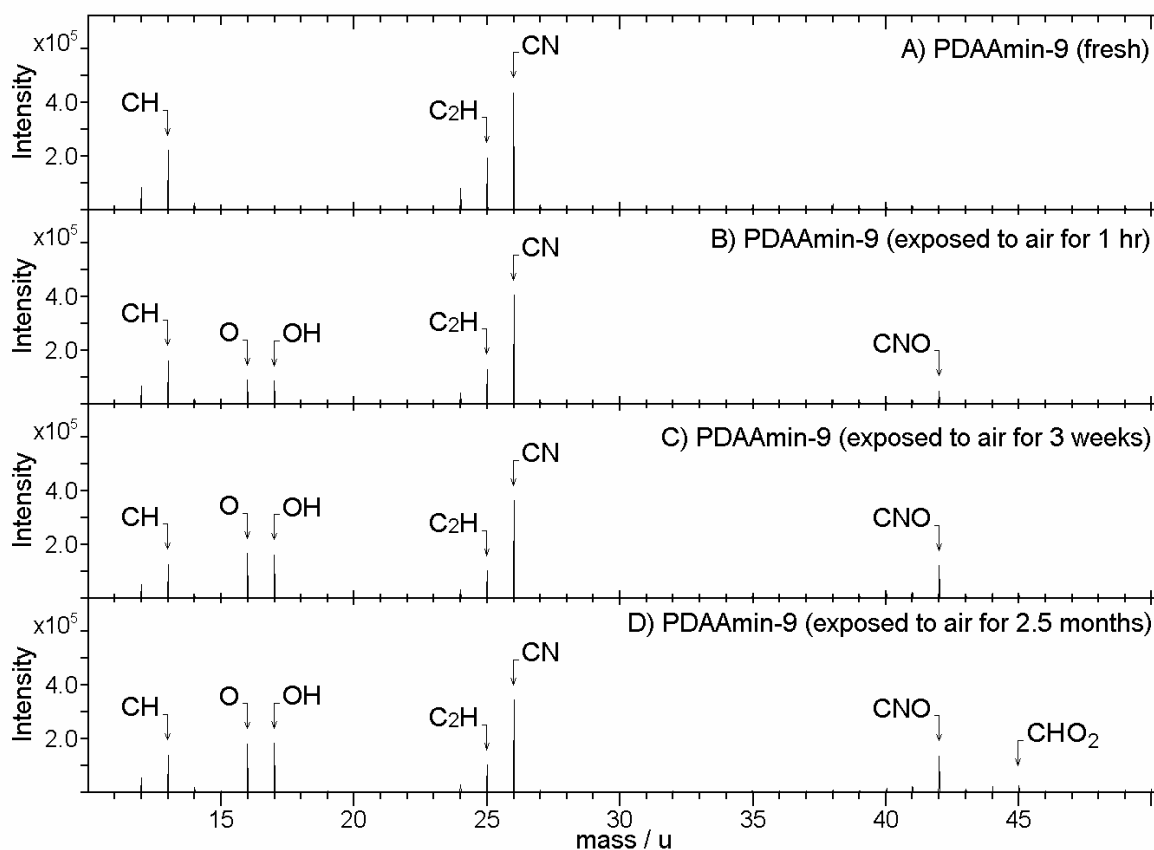
Additionally, Gengenbach and Griesser, [129] concluded that, different from the ageing of hydrocarbon plasma polymers, where the abstraction of hydrogen from C-H was a major ageing reaction, in the case of the 1,3-diaminopropane plasma polymer the main secondary reactions were the recombinations of peroxy radicals leading to the formation of mainly amides and similar groups (c.f. Figure 7.8). Formation of amide and similar groups during the ageing of amino group bearing plasma polymers has been concluded also in other studies [109, 113, 130, 131]. On the other hand, different from the free radical mechanism originally proposed by Gengenbach and Griesser [129], according to their NEXAFS studies Shard et. al., [109] argued that hydrolysis of the nitrile functionalities present in the structure of allylamine plasma polymers could be also a major source for the formation of amide and similar groups.

Unfortunately, neither from positive nor from negative ToF-SSIMS spectra of aged plasma deposited allylamine films any unequivocal evidence related to the formation and decay of peroxy radicals (as in the case of plasma deposited films made from styrene and ethylene, c.f. section 7.2) or formation of amide or similar groups were obtained. Oxidation



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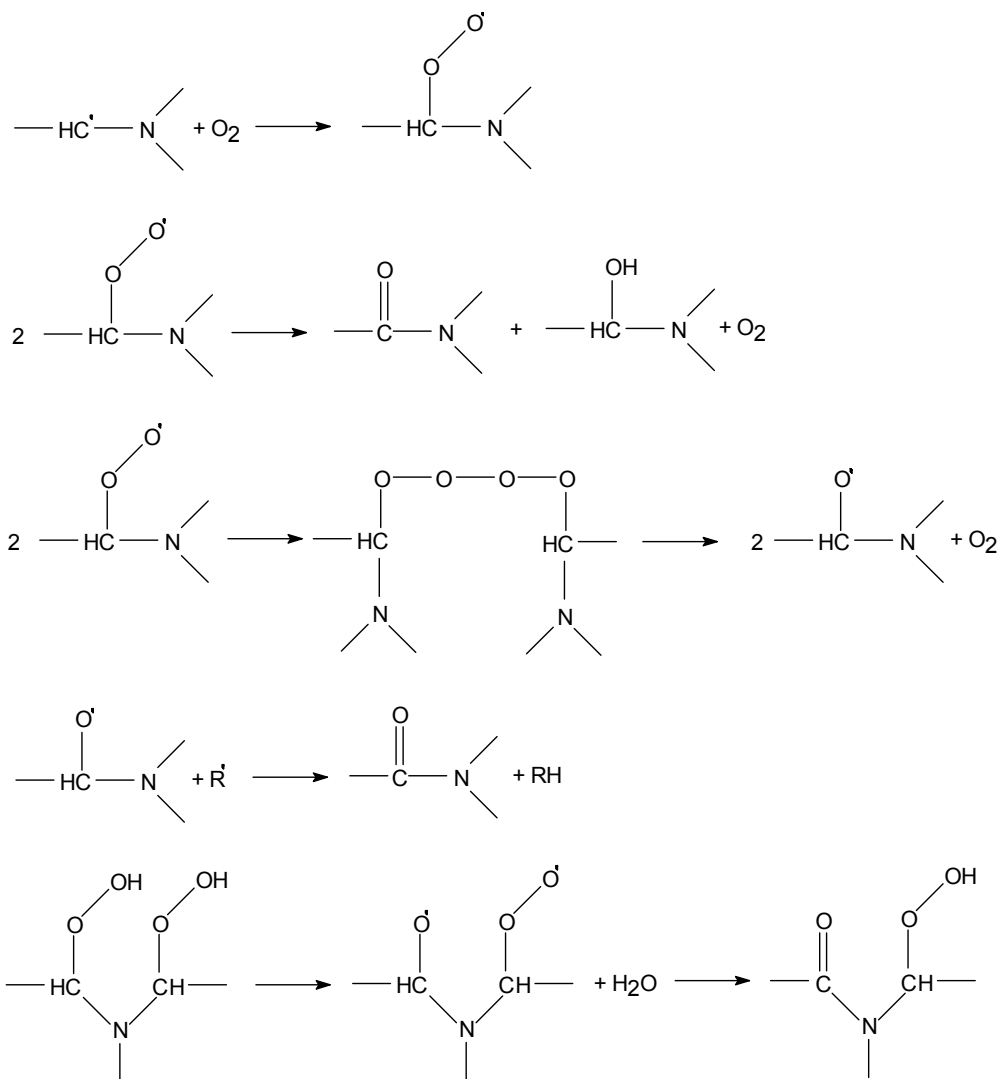
of the allylamine plasma polymers resulted in the formation of the  $C_xH_yNO$  type secondary ions in their positive and negative SSIMS spectra. The yields of these secondary ions were found to vary linearly with respect to the amount of oxygen incorporated during the ageing process.



**Figure 7.7.** Negative ToF- SSIMS spectra of the PDA Amin-9 sample, **A)** fresh, **B)** after 1 hr, **C)** after 4 days, and **D)** after 10 weeks exposure to air. External plasma parameters employed for the deposition of the PDA Amin-9 sample are given in Table 3.3, p. 29.

Earlier results showed that when the deposition conditions become harder, the oxygen uptake of the plasma deposited films increases because the amount of radicals available for post-plasma reactions with ambient air increases. Here it was observed that when the plasma deposited allylamine films were exposed to air for 3 weeks, their oxygen contents were quite similar. This behavior of the films was re-tested by investigating the ageing of PDA Amin-3 and PDA Amin-9 samples (c.f. Table 3.3 for plasma conditions) at different exposure times. It was found that starting from the first hours of exposure, the amount of oxygen incorporated to these two films were rather similar. This could be

possible only if both films had similar radical density because within the 1 hour of exposure the most dominant reaction mechanism for the oxygen uptake is the rapid oxidation of surface radicals. It seems that in addition to the external plasma parameters, the nature of the monomer also play an important role for the formation of radicals in the plasma polymers.



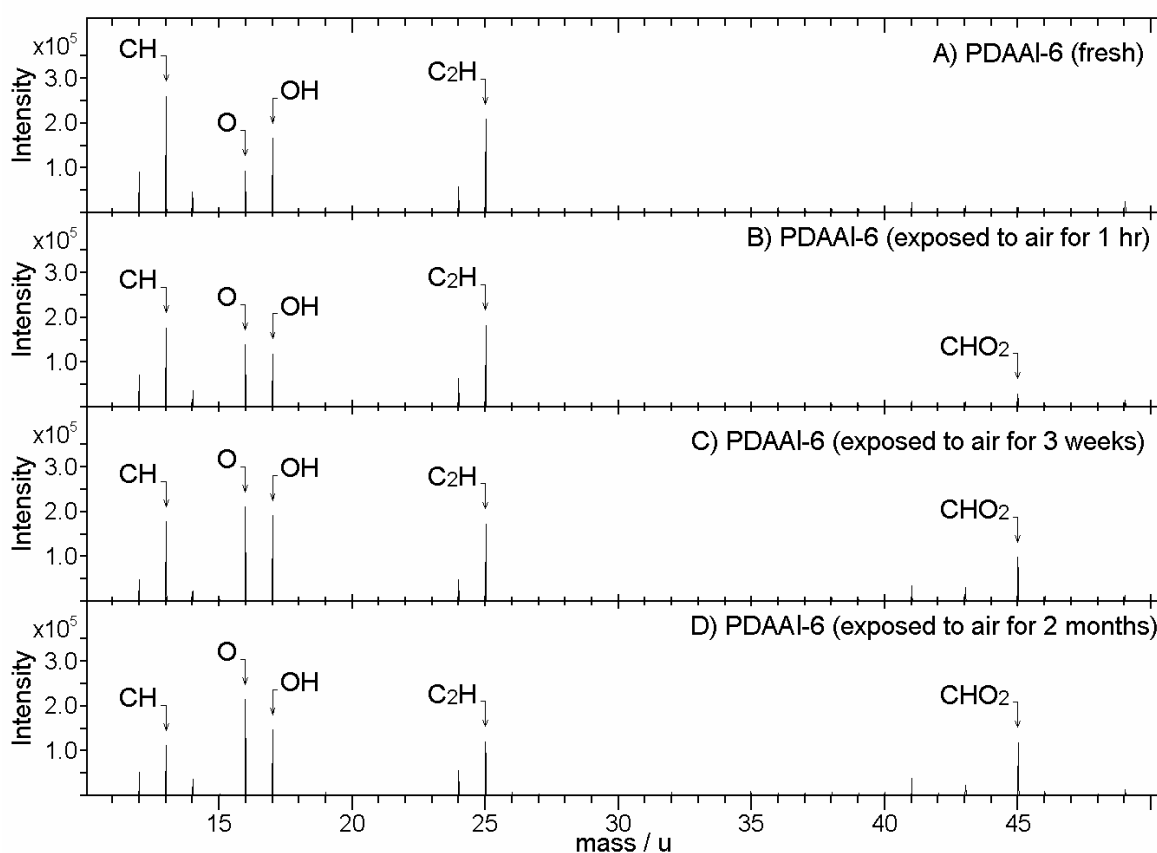
**Figure 7.8.** Reaction scheme of the oxygen uptake and auto-oxidation reactions for plasma deposited 1,3-diaminopropane film (adapted from Ref. [129]).

#### 7.4. Ageing of plasma deposited allyl alcohol films

After exposure to ambient air oxygen was incorporated into plasma deposited allyl alcohol films. This could be derived from the increasing intensities of well resolved oxygen containing secondary ions at  $m/z$  43 ( $\text{C}_2\text{H}_3\text{O}^+$ ), 45 ( $\text{C}_2\text{H}_5\text{O}^+$ ), and 55 ( $\text{C}_3\text{H}_3\text{O}^+$ ) in their positive ToF-SIMS spectra.

## 7. Ageing of plasma deposited polymers

Additionally, the oxygen uptake of the films was monitored from the increasing intensities of the oxygen and oxygen containing secondary ions in their negative SSIMS spectra. This is demonstrated by the negative ToF-SSIMS spectra of the PDAAI-6 sample measured at different exposure times (c.f. Figure 7.9). From Figure 7.9 it can be followed that the yield of the  $\text{CHO}_2^-$  secondary ion, which was found to be the most prominent signal in the negative ToF-SSIMS spectra of aged plasma deposited ethylene and styrene films, increases with increasing exposure time. This points again to the presence of peroxy radicals and hydroperoxides on the surface of aged plasma deposited allyl alcohol films.



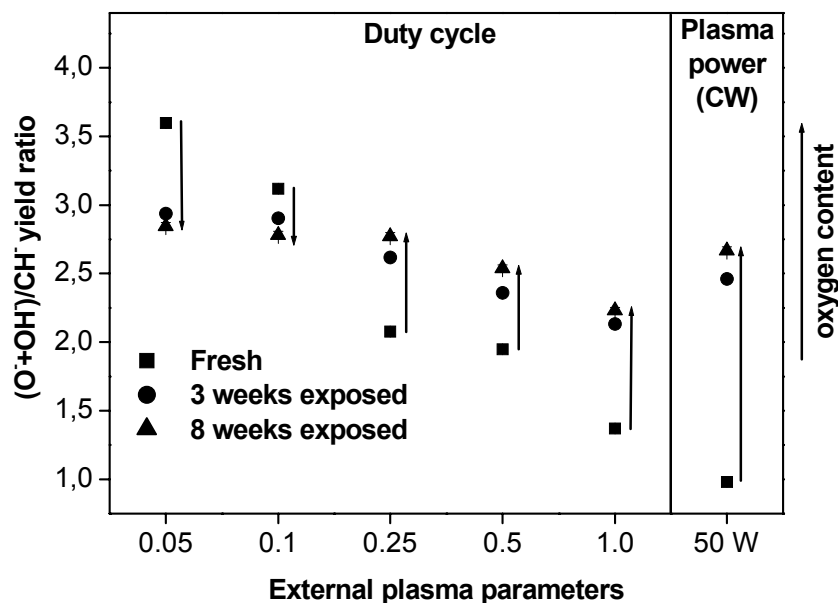
**Figure 7.9.** Negative ToF- SSIMS spectra of the PDAAI-6 sample, **A)** fresh, **B)** after 1 hr, **C)** after 3 weeks, and **D)** after 2 months exposure to air. External plasma parameters employed for the deposition of the PDAAI-6 sample are given in Table 3.4, p. 30.

The oxygen uptake of plasma deposited the PDAAI-6 sample was also monitored from its oxygen content evaluated by using the  $(\text{O}^- + \text{OH}^-)/\text{CH}^-$  yield ratio at different exposure times. Similar to other plasma polymers studied, the oxygen uptake of the PDAAI-6 sample was found to be very fast for the first hours of exposure, later on its rate

decreased slowly (c.f. Figure 7.5 D). It seems that the kinetics of the reaction of radicals with oxygen from ambient air is similar for all plasma deposited films studied.

In the case of plasma deposited ethylene and styrene films it was observed that when they were aged in air at a fixed exposure time, their oxygen content varied with respect to the external plasma parameters employed for their deposition. This is also investigated for plasma deposited allyl alcohol films. The  $(O^-+OH^-)/CH^-$  yield ratio was used to measure the oxygen content of selected plasma deposited allyl alcohol films during their ageing (c.f. Figure 7.10). While the oxygen content at the surface of the films deposited at duty cycle values of 0.05 and 0.1 *decreases with storage on air*, the oxygen surface content of the other samples deposited at harder plasma conditions increases. Similar results were observed in the XPS analysis of plasma deposited allyl alcohol films before and after exposure to air [117]. These results show that, in addition to an oxygen uptake process, which increases the oxygen surface concentration of the plasma polymer, there should be another process, which may cause a decrease in the oxygen content of the analyzed surface.

Fallyl et. al. [48] studied plasma deposited allyl alcohol films by XPS, IR spectroscopy and high resolution electron energy loss spectroscopy. They concluded that the hydroxyl groups are mainly pointing to the bulk of the plasma polymer films due to high chain mobility. They observed that the efficiency of the re-distribution process was inversely proportional to the cross-linked character of the plasma polymer. Different from that, Gerenser [132] investigated the ageing effect on oxygen plasma modified polymer surfaces. Using XPS he observed that the surface concentration of oxygen decreases with time of exposure to air and he attributed this to the diffusion of low-molecular weight oxidized species into the bulk of the polymer. Similarly, Qiseth et al. [133] concluded that the ageing of oxygen plasma treated polyethylene films in air is a two step process with (i) the adsorption of atmospheric oxygen by the radicals and (ii) the re-organization of the surface by diffusion of low molecular weight oxidized species into the bulk and macromolecular motions which re-orient polar groups away from the surface.



**Figure 7.10.** Oxygen content of fresh and aged plasma deposited allyl alcohol films measured by the  $(O^-+OH^-)/CH^-$  secondary ion yield ratio at different exposure times vs. external plasma parameters. External plasma parameters employed for the deposition of the plasma deposited allyl alcohol films are given in Table 3.4, p. 30.

It is highly probable that in the case of plasma deposited allyl alcohol films these competing processes, i.e. the oxygen uptake and the diffusion of low molecular weight oxidized species into the bulk together with re-orientations of oxygen functional groups, are responsible for the observed results displayed in Figure 7.10. For the samples prepared at mild plasma conditions, i.e., these deposited at duty cycle values of 0.05 and 0.1, the re-orientation and the diffusion of low molecular weight oxidized species is more effective than the oxygen uptake process because the samples are less cross-linked and the amount of radicals is comparably low. For that reason the oxygen content of the surface of films may decrease with exposure time. On the other hand, for the samples prepared at harder plasma conditions, cross-linking and the amount of surface radicals are increased and the oxygen uptake becomes the dominant process. This results in an increase in the surface oxygen content of the films.

### 7.5. Ageing of plasma deposited copolymers

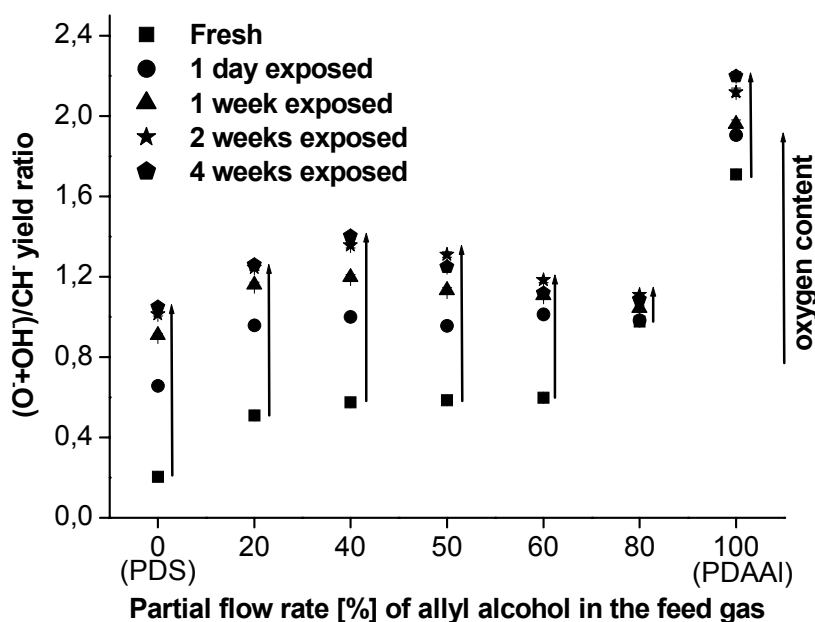
#### 7.5.1. Introduction

The ageing behavior of plasma deposited copolymer films was investigated only by taking the plasma deposited styrene-allyl alcohol and styrene-allylamine copolymer films into consideration. The reasons for this are multiple. In-situ characterization of plasma copolymerization of ethylene with functional group bearing monomers, allyl alcohol and allylamine, showed that the chemical reactivity of ethylene was the lowest (c.f. section 6.3). This resulted in plasma copolymer structures closer to these of plasma deposited homopolymer films made from allyl alcohol and allylamine. So, it is reasonable to assume that the ageing behavior of these plasma copolymers should be rather similar to that of plasma deposited homopolymer films made from allyl alcohol and allylamine. Additionally, if any differences in their ageing behavior arise, for example, due to their partially different structures from the respective plasma homopolymers, these differences should be also observed in the case of ageing of plasma deposited styrene-allyl alcohol and styrene-allylamine copolymer films.

#### 7.5.2. Ageing of plasma deposited styrene-allyl alcohol copolymers

Similar to the respective plasma homopolymers, oxygen uptake started immediately when the plasma copolymer films made from styrene and allyl alcohol were exposed to air. This could be derived from the increasing yields of oxygen containing secondary ions in both their positive and negative ToF-SSIMS spectra. It was found that the primary ageing reactions of the plasma deposited copolymer films, i.e., reaction of molecular oxygen with C-radical sites and formation of peroxy radicals, and secondary ageing reactions, i.e., auto-oxidation process leading to formation of different oxidized groups like hydroxyls, ketones, etc., were rather similar to these in the case of respective plasma homopolymers. However, the ageing behavior of the plasma copolymer films, derived from their oxygen uptake, was dependent on the composition of the feed gas (c.f. Figure 7.11). For example, the oxygen uptake of the plasma deposited copolymer film was minimum when the allyl alcohol partial flow rate in the feed gas was ca. 80 %. This can be interpreted as that the structure of plasma deposited copolymer films are partially different from the structure of the respective plasma homopolymers and dependent on the feed gas composition. The investigation of the ageing behavior of the respective plasma homopolymers already showed that there was a correlation between the structure of the plasma polymers and their

ageing behavior. The same conclusion was also derived from the in-situ characterization of the plasma deposited copolymer films (c.f. section 6.2.2).



**Figure 7.11.** Oxygen content of fresh and aged plasma deposited styrene-allyl alcohol copolymer films measured by the  $(O^+OH^-)/CH^-$  yield ratio at different exposure times vs. relative partial flow rate [%] (partial flow rate/total flow rate) of allyl alcohol (see Table 3.5, p.31, for the constrained external plasma parameters).

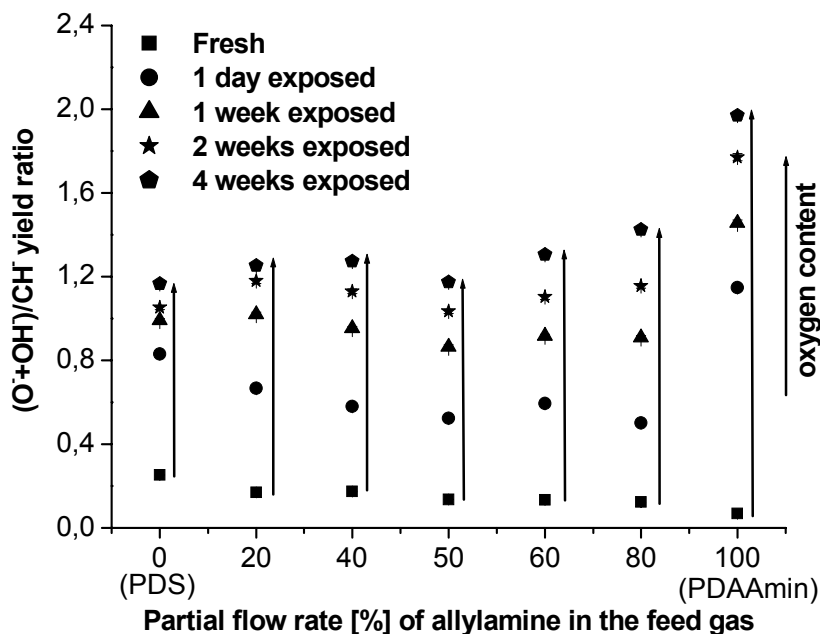
### 7.5.3. Ageing of plasma deposited styrene-allylamine copolymers

Exposure of plasma deposited copolymer films prepared from styrene and allylamine to ambient air resulted in an increase in their oxygen content. In both their positive and negative ToF-SSIMS spectra oxygen containing secondary ion yields increased with increasing exposure time.

Oxygen uptake and formation of oxygen species due to ageing of the plasma deposited copolymer films was found to proceed through primary and secondary reactions of ageing as observed in the case of the respective plasma homopolymers. As the concentration of amino groups increased in plasma copolymers with increasing partial flow rate of allylamine in the feed gas, oxygen incorporated at  $\alpha$ -positions increased and the formation of oxidized groups, which are formed to be characteristic of the oxidation of hydrocarbon plasma polymers, e.g., esters, hydroxyls, ketones, etc., decreased. Additionally, the composition of the feed gas was found to have an influence on the ageing

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behavior of the plasma styrene-allylamine copolymers (c.f. Figure 7.12), e.g., the oxygen surface contents of the plasma homopolymer and copolymer films after 1 day of exposure were rather different. These results again can be attributed to the partially different structures of plasma deposited homopolymer and copolymer films.



**Figure 7.12.** Oxygen content of fresh and aged plasma deposited styrene-allylamine copolymer films measured by the  $(O+OH)/CH$  yield ratio at different exposure times vs. relative partial flow rate [%] (partial flow rate/total flow rate) of allylamine (see Table 3.5, p. 31, for the constrained external plasma parameters).