

5. In-situ characterization of plasma deposited polymers

5.1. Introduction

In this chapter, the relationship between the basic chemical character of plasma deposited polymer films and the external plasma parameters, plasma power, duty cycle, monomer flow rate, and reaction pressure, is explored. This is achieved by a systematic variation of these parameters. For one selected monomer the plasma conditions are varied from “mild” to “hard”. While mild conditions could be obtained at low duty cycle, low plasma power, and high monomer flow rate, hard conditions are obtained when high duty cycles, high plasma power, and low monomer flow rates are employed.

The basic chemical character of the plasma polymers has been investigated by means of time of flight - static secondary ion mass spectrometry (ToF-SSIMS). From the secondary ion mass spectra, information on the variation of the chemistry, i.e., the unsaturated, branched and/or cross-linked character of the films as well as the retention of the respective monomer functionality was derived. The analysis of the plasma deposited films was performed directly, i.e., without any exposure to air. The approaches for the interpretation of SSIMS data outlined in section 4.4 are used for the evaluation of SSIMS data.

5.2. Results

5.2.1. Plasma deposited styrene films

5.2.1.1. Characterization of a polystyrene reference sample

The static positive ToF-SIMS spectrum of a spin-coated polystyrene reference sample (PS-R), which is in rather good agreement with a spectrum published in the literature [53], is presented in Figure 5.1.A. The structures of characteristic secondary ions of the positive SSIMS spectrum of polystyrene at m/z 51, 63, 77, 91, 103, 105, 115, 128, 152, and 178 were investigated in detail using tandem SIMS techniques [98] and by deuteration of polystyrene [99]. Fig. 5.2 summarizes these interpretations. These characteristic secondary ions must be viewed as results of complex but characteristic rearrangements of moieties sputtered from the polymer surface.

Because of its great stability the most intense peak in the positive secondary ion mass spectrum of polystyrene is the tropylium ion at m/z 91. Between m/z 100 and 200 the secondary ions at m/z 103, 105, 115 and 117 are the most intense ones characterizing polystyrene. Among those, the ion at m/z 105 was discussed to represent two alternative

5. In-situ characterization of plasma deposited polymers

structures: $(m+H)^+$, where m is the molecular weight of the repeat units or a methyl substituted tropylium ion.

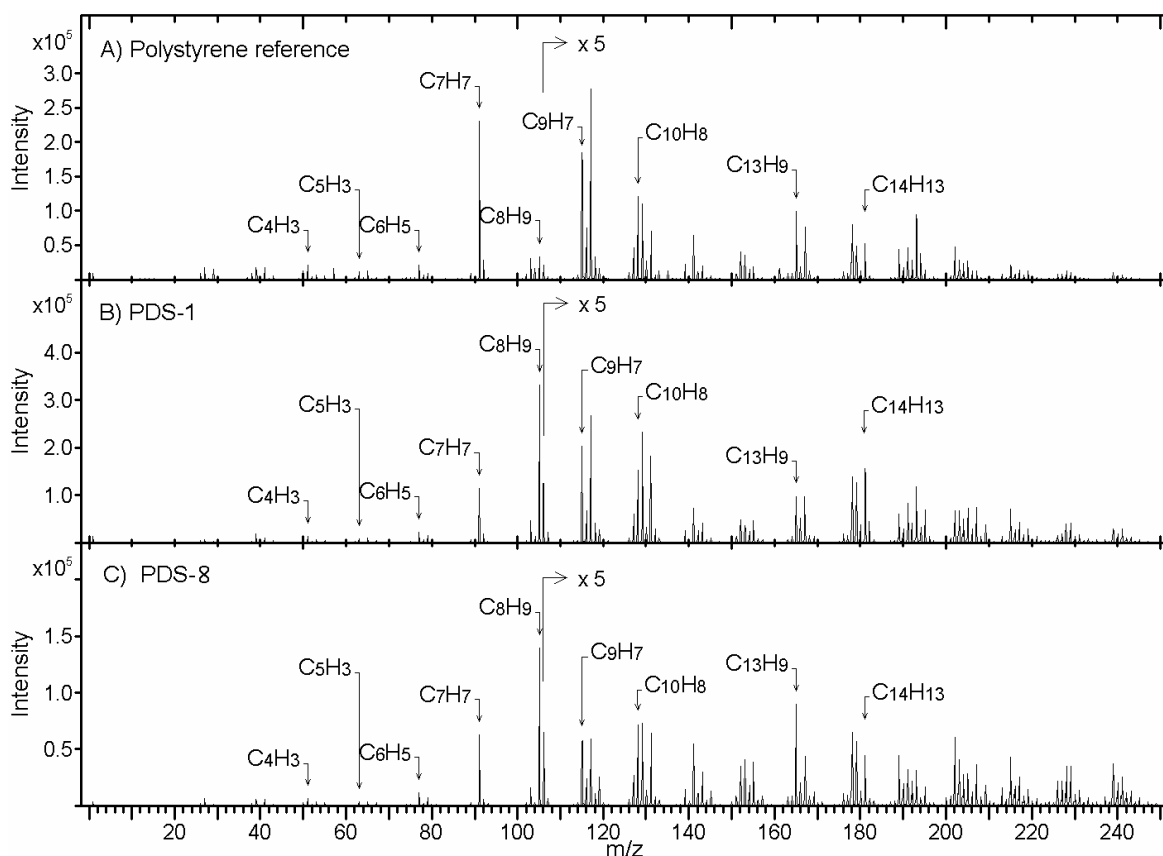


Figure 5.1. Positive ToF- SSIMS spectra of **A)** the polystyrene reference, **B)** the PDS-1 sample (prepared under mildest plasma conditions), and **C)** the PDS-8 sample (prepared under hardest plasma conditions). The external plasma parameters employed for the deposition of plasma polymers are given in see Table 3.1, p. 27.

5.2.1.2. Characterization of the plasma deposited styrene film prepared at mildest plasma conditions

The positive ToF-SIMS spectrum of a plasma deposited styrene film prepared under mildest plasma conditions (PDS-1) is presented in Figure 5.1.B. Comparison of this spectrum with the reference spectrum of PS-R reveals that most of the characteristic secondary ions present in the PS-R spectrum are observed in the spectrum of PDS-1, too.

5. In-situ characterization of plasma deposited polymers

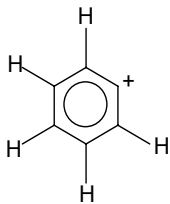
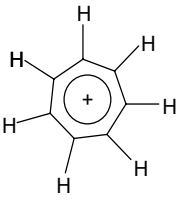
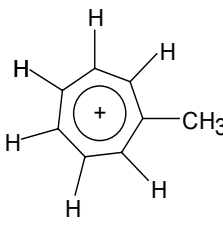
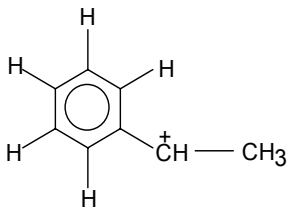
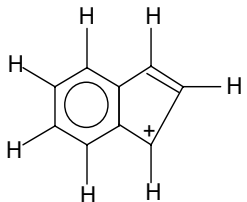
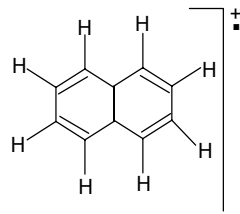
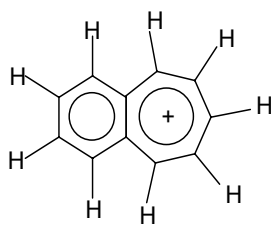
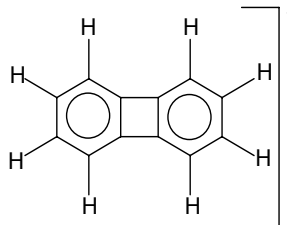
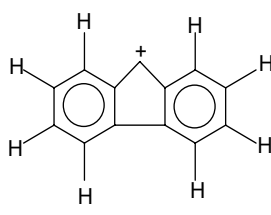
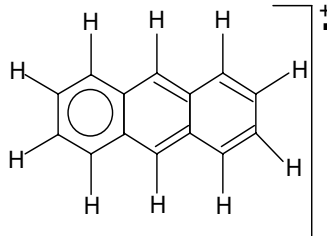
Ion Structure	m/z	Ion Structure	m/z
	77 (C ₆ H ₅ ⁺)		91 (C ₇ H ₇ ⁺)
	105 (C ₈ H ₉ ⁺)	or 	105 (C ₈ H ₉ ⁺)
	115 (C ₉ H ₇ ⁺)		128 (C ₁₀ H ₈ ⁺)
	141 (C ₁₀ H ₆ ⁺)		152 (C ₁₂ H ₈ ⁺)
	165 (C ₁₃ H ₉ ⁺)		178 (C ₁₄ H ₁₀ ⁺)

Figure 5.2. Structure of the characteristic ions in the polystyrene static SIMS spectrum (adapted from Ref. [98]).

5. In-situ characterization of plasma deposited polymers

However, some differences between these two spectra are also obvious. The major difference is related to the relative intensities of the secondary ions at m/z 91 ($C_7H_7^+$) and 105 ($C_8H_9^+$). The secondary ion at m/z 105 is the most intense ion in the PDS-1 spectrum. This ion was also found with high abundance in the positive SSIMS spectra of methyl substituted polystyrenes, e.g., poly(α -methyl styrene) and poly(4-methyl styrene) [99]. For poly(α -methyl styrene) the m/z 105 ion has been postulated to be a methyl substituted tropylium ion. Therefore, addition of an α -methyl group should lead to an increase in the intensity of this spectral feature. A certain degree of methyl substitution during plasma polymerization of styrene has been suggested by Prohaska et al. [100] upon examination of related IR spectra. They suggested that the methyl substitution occurred at α - or β -positions of the backbone. Nevertheless, according to their IR study of plasma and conventionally polymerized polystyrenes, Retzko et al. [101] and Retzko [95] concluded that the number of methyl end-groups is increased in the backbone of the plasma polymer. Considering the positive SSIMS spectrum of PDS-1 the intensity ratio of the peaks at m/z 91 and 105 is similar to that observed for poly(α -methyl styrene) but other secondary ions characterizing poly(α -methyl styrene) at m/z 119, 129, and 143, are less intense. Therefore, it is not very probable that the plasma deposited styrene has a structure like α -methyl substituted polystyrenes.

Legget et al. [56] suggested that the secondary ion at m/z 105 ($C_8H_9^+$) is indicative of cross-linking in the plasma polymerized styrene. This suggestion is well accepted and it is also probably true for our PDS-1 sample because branching and/or cross-linking in the plasma deposited polystyrene films prepared by using the same experimental set-up has been previously reported according to their NEXAFS, FTIR and XPS analysis [95, 101, 102]. This can be additionally supported by the fact that in the positive SSIMS spectrum of the PDS-1 sample the intensities of high mass ions, especially above m/z 200, are higher and the intensities of the low mass ions below m/z 80 are lower in comparison to the polystyrene reference spectrum. Higher yields of high mass ions were usually interpreted as a result of a higher degree of branching and/or cross-linking.

To evaluate the structure of the PDS-1 on a more common level its aromatic content is compared with that of the polystyrene reference. The aromatic content of PS-R and PDS-1 was compared by investigating the 91/55 ($C_7H_7^+/C_4H_7^+$) intensity ratio (c.f. section 4.4). In these experiments, this ratio evaluated for both samples was quite similar. The conclusion is that the aromatic content of these two samples is almost equal. Similar

results were reported by Retzko [95] and Swaraj et al. [102] according to their NEXAFS analysis of plasma deposited styrene films prepared by using the same experimental set-up.

ToF-SSIMS spectra suggest that the aromatic contents of PS-R and PDS-1 are rather similar but the PDS-1 sample is more irregular in structure due to branching and/or cross-linking.

5.2.1.3. Effect of external plasma parameters on the chemical character of plasma deposited styrene films

The influence of the external plasma parameters, duty cycle and plasma power, on the secondary ion mass spectra of plasma deposited polystyrene films was investigated. Details of the different experiments are given in Table 3.1. From the SSIMS spectra, information on the variation of the basic chemical character of the plasma deposited styrene films was derived.

It was observed that the differences in the positive ToF-SSIMS spectra of plasma deposited films prepared at different plasma conditions were rather subtle. This is demonstrated by comparing the positive SSIMS spectrum of PDS-1, prepared at mildest plasma conditions, and that of PDS-8, prepared under hardest plasma conditions, in Figures 5.1.B and 5.1.C, respectively. However, differences between the samples in terms of branching and/or cross-linking, and retention of aromaticity could be obtained by detailed analysis of the spectra.

Investigation of the branched and/or cross-linked character

The effect of variation of external plasma parameters on the branched and/or cross-linked character of plasma deposited styrene films was investigated by taking total secondary ion yields of each sample into consideration (c.f. section 4.4). It was observed that both increasing the duty cycle or the plasma power caused a decrease in the total secondary ion yield (cf. Figure 5.3.A). Obviously, this increase in duty cycle or plasma power increases the branching and/or cross-linking of the plasma deposited styrene films.

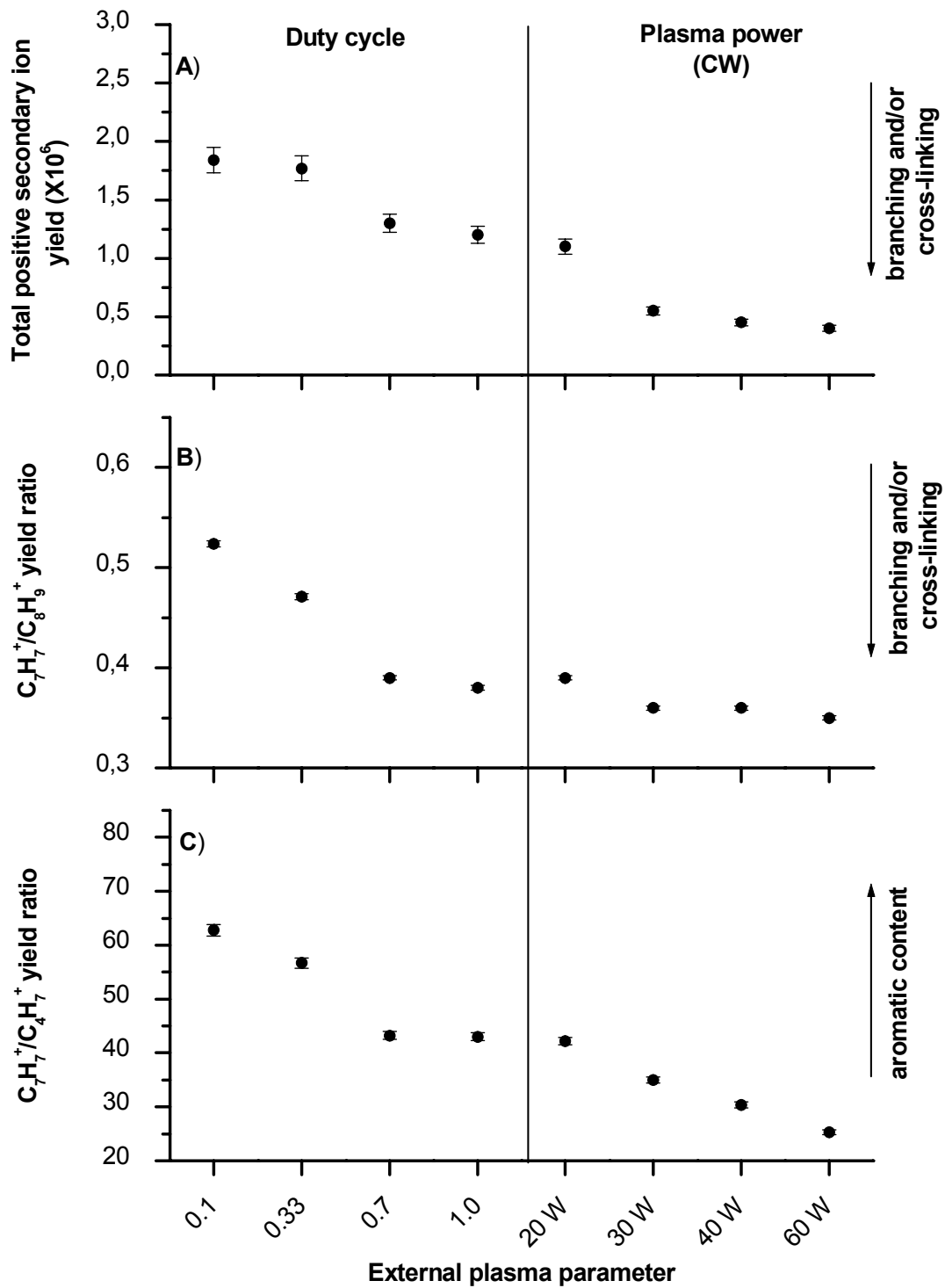


Figure 5.3. Reduced SSIMS data of plasma deposited styrene films prepared at different plasma conditions (see Table 3.1, p. 27, for the constrained external plasma parameters). **A)** the total positive secondary ion yields, **B)** ($C_7H_7^+/C_8H_9^+$) yield ratios, and **C)** ($C_7H_7^+/C_4H_7^+$) yield ratios. Note that arrows indicate the increase for a selected property.

5. In-situ characterization of plasma deposited polymers

A similar result was obtained when the ratio of the yields of secondary ions at m/z 91 ($C_7H_7^+$) and 105 ($C_8H_9^+$) was investigated. It was previously shown that the secondary ions at m/z 91 and 105 were the most intense secondary ions in the positive ToF-SIMS spectra of linear polystyrene and plasma deposited polystyrene, respectively. So, while the first secondary ion could be attributed to the linear polystyrene structure, the other one could be attributed to the branching and/or cross-linking of the plasma deposited styrene films. For these reasons, the ($C_7H_7^+/C_8H_9^+$) yield ratio could be taken as a measure of branching and/or cross-linking in plasma deposited polystyrene films. As presented in the Figure 5.3.B, this ratio decreases with increasing duty cycle or plasma power, i.e., the branching and/or cross-linking in the plasma deposited styrene films increases.

Investigation of the retention of aromatic character

The integrity of the aromatic system of the different plasma deposited styrene films was monitored by using the m/z 91/55 ($C_7H_7^+/C_4H_7^+$) yield ratio values (c.f. Fig. 5.3.C). Obviously an increase in duty cycle or plasma power results in an increase in the intensity of the low mass fragment at m/z 55. This is to be expected because increase in any of these external plasma parameters increases the monomer fragmentation in the plasma and results in a decrease in the aromatic content of the deposited films [95, 100-102].

5.2.2. Plasma deposited ethylene films

5.2.2.1. Characterization of a polyethylene reference sample

The static positive ToF-SSIMS spectrum of a spin-cast polyethylene reference sample (PE-R), which is in good agreement with a spectrum published in the literature [53], is presented in Figure 5.4.A. The identities of the characteristic secondary ions of the positive SSIMS spectrum of polyethylene were investigated in detail using tandem SIMS techniques [103]. These secondary ions were found to have $C_nH_x^+$ type structures, where $n = 1-7$ and $n \leq x \leq 2n + 1$.

5.2.2.2. Characterization of the plasma deposited ethylene film prepared at mildest plasma conditions

When the positive ToF-SSIMS spectrum of PE-R was compared to the spectrum of the plasma deposited ethylene film prepared at mildest plasma conditions (PDE-1), some significant differences were observed (Figure 5.4.A&B). The structure of PDE-1 must be rather different from that of PE-R. The most striking spectral differences are found for the

5. In-situ characterization of plasma deposited polymers

intensities of high mass secondary ions above m/z 100 as well as secondary ions with aromatic character at m/z 77, 91, 105, 115, 128, 141, 165. The presence of high mass secondary ions can be taken as an overall indication of branching and/or cross-linking (c.f. section 4.4). On the other hand, the presence of secondary ions with aromatic character in the positive ToF-SSIMS spectrum of PDE-1 can be attributed to its unsaturated character (c.f. section 4.4).

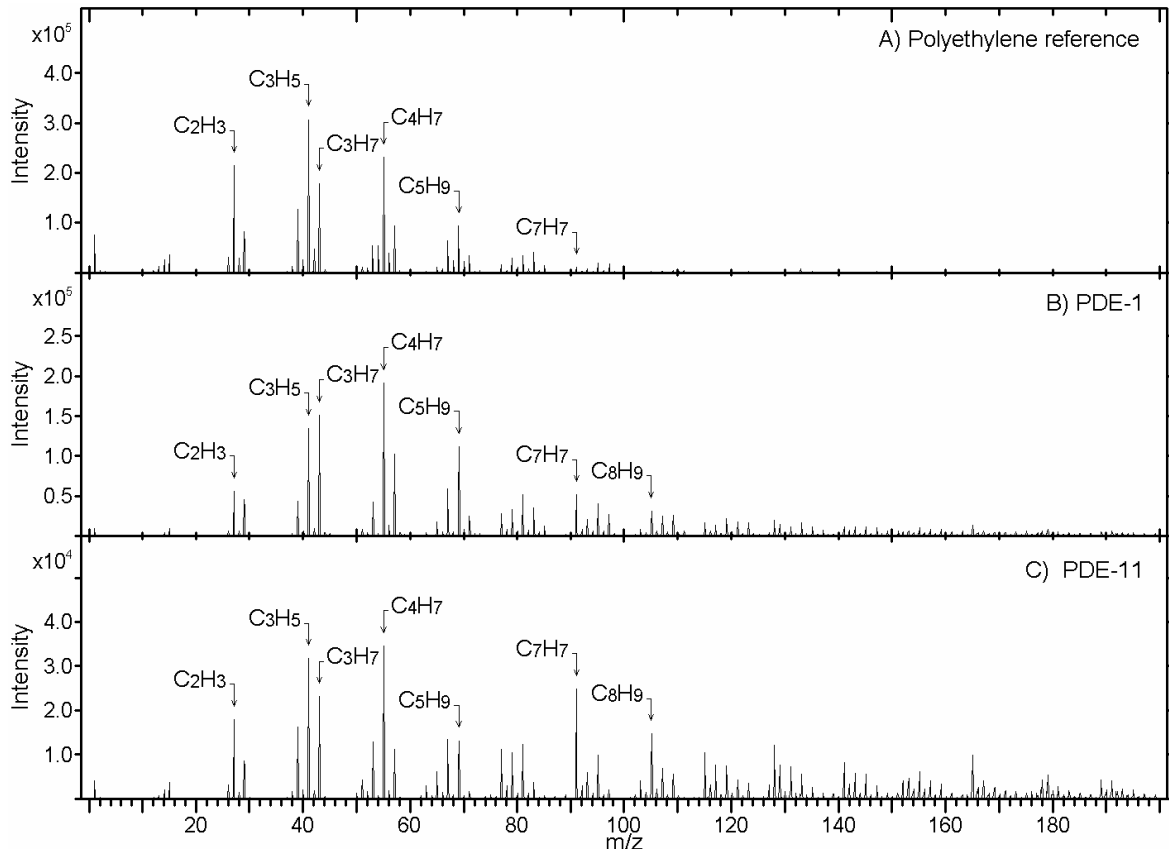


Figure 5.4. Positive ToF- SSIMS spectra of **A)** the polyethylene reference, **B)** the PDE-1 sample (prepared under mildest plasma conditions), and **C)** the PDE-11 sample (prepared under hardest plasma conditions). The external plasma parameters employed for the deposition of plasma polymers are given in see Table 3.2, p. 28.

Also the relative intensities of the low mass secondary ions below m/z 100 were rather different. For example, in the positive ToF-SSIMS of PE-R the most intense secondary ions were m/z 41 ($C_3H_5^+$), 55 ($C_4H_7^+$) and 27 ($C_2H_3^+$). On the contrary, in the positive ToF-SSIMS of PDE-1 the most intense secondary ions were at m/z 55 ($C_4H_7^+$), 43 ($C_3H_7^+$) and 69 ($C_5H_9^+$).

5.2.2.3. Effect of external plasma parameters on the structure of plasma deposited ethylene films

The chemical character of the plasma deposited ethylene films was investigated again with respect to a variation of the external plasma parameters, plasma power, duty cycle, reaction pressure, and the monomer flow rate (c.f. Table 3.2).

The overall effect of external plasma parameter variation can be easily observed when the ToF-SSIMS spectra of the plasma deposited ethylene films prepared at mildest (PDE-1) and hardest (PDE-11) plasma conditions are compared (c.f. Figure 5.4 B&C). There are significant changes; most striking are the variations of the relative yields of the high mass cluster secondary ions above m/z 100 and of the yields of secondary ions with aromatic character. These differences between the spectra of plasma deposited ethylene films were analyzed now in terms of their basic chemical characters.

Investigation of the unsaturated character

A variation in the unsaturated character of plasma deposited ethylene films with respect to external plasma parameters can be derived from the changes in the relative yields of the secondary ions within each carbon $C_nH_x^+$ cluster pattern (c.f. section 4.4). As the plasma conditions are varied from mild to hard, almost in each $C_nH_x^+$ cluster pattern for $n \leq 5$ yields of higher mass secondary ions with higher H contents decrease but the respective yields of the lower mass ions increase. This is demonstrated by an investigation of the individual yields of the $C_5H_x^+$ cluster ions vs. variations of duty cycle (c.f. Table 5.1). Within that cluster patterns, the yields of the secondary ions between $C_5H_2^+$ and $C_5H_5^+$ increase and those of the secondary ions between $C_5H_8^+$ and $C_5H_{12}^+$ decrease. Relying on the approach described in section 4.4, the unsaturation increases vs. duty cycle.

Alternatively, the relative unsaturation of the plasma deposited ethylene films was monitored by the negative yield ratio m/z 12/14 (C^-/CH_2^-) (c.f. section 4.4). This ratio was found to vary from 1.22 to 3.2 in correlation to the external plasma parameters employed (Figure 5.5.A). Bearing in mind that the mean value of this ratio for saturated polymers was 1.0 [85], the conclusion is that the plasma deposited ethylene films must be unsaturated to some extent. Any increase in duty cycle or plasma power results in an increase of the unsaturated character. Similarly, an increase in the external plasma parameter “reaction pressure” caused an increase in the unsaturated character of the films. Additionally, when the flow rate of the monomer was increased from 10 sccm to 40 sccm the unsaturated character was decreased (c.f. Figure 5.5.A). Ameen et al. [19] also

5. In-situ characterization of plasma deposited polymers

investigated flow rate effects in the case of the plasma polymerization of allyl alcohol. They reported a similar result.

Table 5.1. Variations in the normalized and averaged secondary ion yields of the $C_5H_x^+$ cluster ions in the positive ToF-SIMS spectra of plasma deposited ethylene films vs. duty cycle. (Constrained plasma parameters: plasma power: 20 W, monomer pressure in reactor: 5.1 Pa, flow rate of the monomer: 20 sccm).

Ion(s)	Duty cycle					% statistical scatter
	0.05	0.1	0.25	0.5	1.0	
$C_5H_2^+$	0.03	0.03	0.04	0.05	0.07	2.17
$C_5H_3^+$	0.21	0.21	0.27	0.32	0.39	0.92
$C_5H_4^+$	0.06	0.06	0.07	0.08	0.10	1.98
$C_5H_5^+$	0.72	0.70	0.80	0.87	0.93	0.14
$C_5H_6^+$	0.22	0.21	0.23	0.24	0.24	1.39
$C_5H_7^+$	2.91	2.87	3.12	3.17	3.00	0.01
$C_5H_8^+$	0.26	0.26	0.23	0.22	0.21	2.23
$C_5H_9^+$	7.58	7.30	6.12	5.24	4.40	0.34
$C_5H_{10}^+$	0.48	0.49	0.36	0.31	0.26	2.67
$C_5H_{11}^+$	1.31	1.29	0.96	0.78	0.63	0.82
$C_5H_{12}^+$	0.11	0.12	0.06	0.05	0.04	1.71

As discussed in section 4.4, the unsaturated character of the plasma deposited ethylene films can also be monitored by the parameter Σ_{Arom} . Obviously, the values of the parameter Σ_{Arom} increases with increasing duty cycle, plasma power or reaction pressure or with decreasing monomer flow rate (c.f. Figure 5.5.B). A presence of secondary ions with aromatic character in the positive ToF-SSIMS spectrum of PDE-1 can be attributed to its unsaturated character because it was shown previously by FTIR analysis that there were no aromatic rings in pulsed plasma deposited ethylene films [95, 101]. These films were prepared at mild plasma conditions in the same reactor system used in this study. However, in the case of the PDE-11 sample aromatic rings might be present since the formation of aromatics by CW plasma polymerization of ethylene at high plasma power was reported earlier by Tibbitt et al. [9] and Tsai et al. [61]. From the data presented in this study it is

5. In-situ characterization of plasma deposited polymers

difficult to come to a conclusion about whether the PDE-11 contains aromatic rings or not. However, in any case it is obvious that the PDE-11 is the most unsaturated sample.

Information on the relative degree of the unsaturated character of the plasma deposited ethylene films were cross-checked by three different SSIMS based approaches outlined in section 4.4. All these methods provided equal results. Obviously, the SSIMS based approaches though developed for an interpretation of SSIMS spectra of aliphatic hydrocarbons, can be used for the evaluation of SSIMS data of plasma deposited ethylene films, too.

The unsaturated character was also cross-checked by NEXAFS analysis of the plasma deposited ethylene films prepared by using the same experimental set-up. It was observed that the C 1s $\rightarrow\pi^*$ resonance feature which represents the presence of C=C bonds was increased when the duty cycle or plasma power was increased and also when the monomer flow rate was decreased [104].

Investigation of the branched and/or cross-linked character

Considering the variation of the parameter which was derived from the ratio of the total yield of C₆H_x-C₈H_x hydrocarbon secondary ion clusters to the total yield of C₂H_x - C₈H_x clusters [$\Sigma(C_6-C_8) / \Sigma(C_2-C_8)$] (c.f. section 4.4), it can be found that increasing the duty cycle or plasma power cause an increase in branching and/or cross-linking of the plasma deposited ethylene films (c.f. Figure 5.5.C). Similar results were observed when the monomer flow rate was decreased (c.f. Figure 5.5.C). This conclusion was underpinned from the respective analysis of the total secondary ion yields (Figure 5.5.D). Any increase in duty cycle or plasma power and any decrease in the monomer flow rate resulted in a decrease in the total secondary ion yields of the plasma deposited films which indicates an increasing level of branching and/or cross-linking. On the contrary, the branched and/or cross-linked character of the plasma deposited films is nearly unaffected from the variations in reaction pressure.

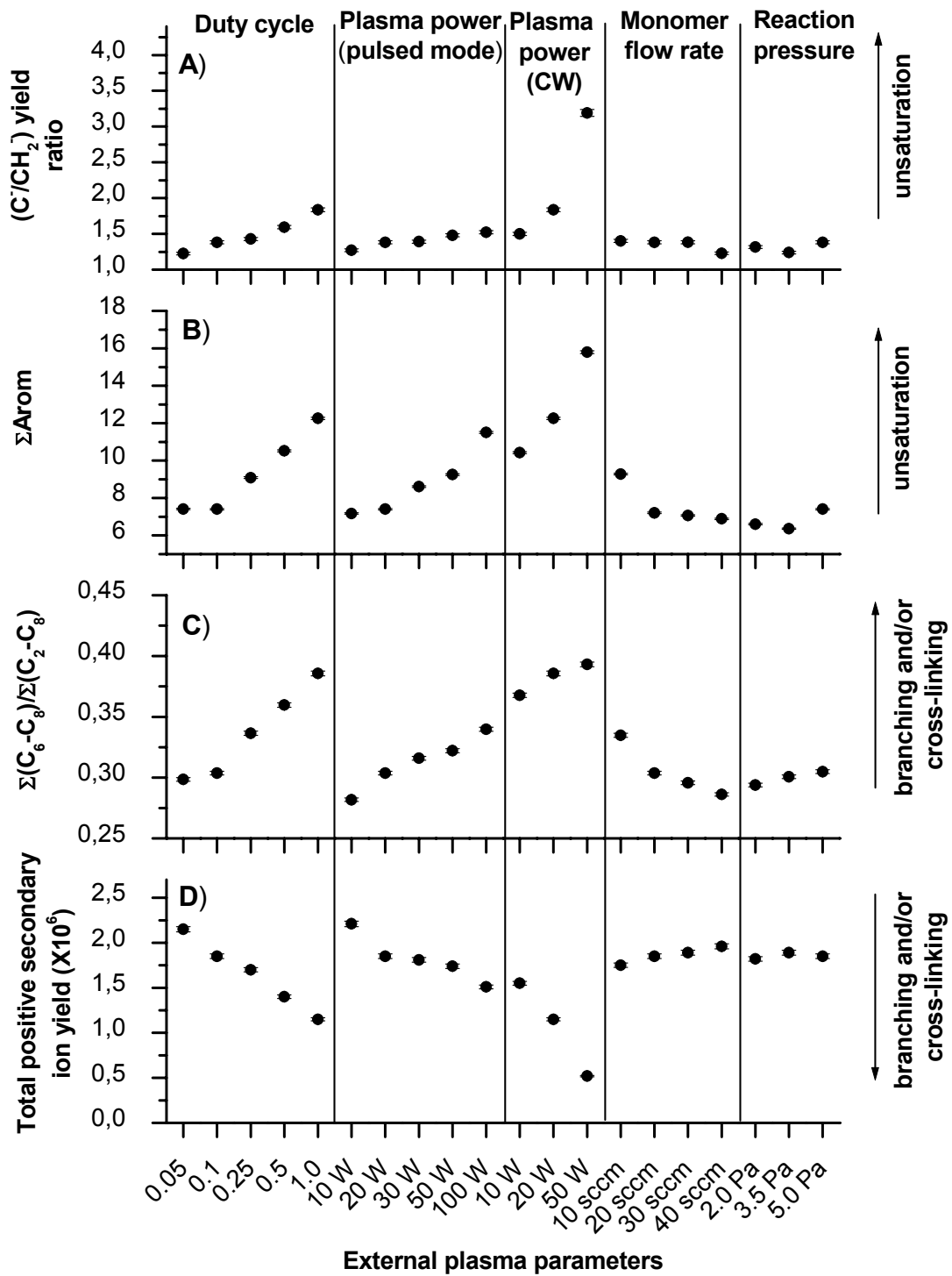


Figure 5.5. Reduced SSIMS data of plasma deposited ethylene films prepared at different plasma conditions (see Table 3.2, p. 28, for the constrained external plasma parameters). **A)** m/z 12/14 (C^+/CH_2^+) yield ratios, **B)** the parameter Σ_{Arom} , **C)** the parameter $[\Sigma(C_6-C_8)/\Sigma(C_2-C_8)]$, and **D)** the total positive secondary ion yields. Note that arrows indicate the increase for a selected property.

5.2.3. Plasma deposited allylamine films

5.2.3.1. Characterization of a poly(allylamine) reference sample

The positive ToF-SSIMS spectrum of a spin-cast poly(allylamine) reference sample (PAAmin-R) is presented in Figure 5.6.A. The most dominant nitrogen containing hydrocarbon secondary ions in this SSIMS spectrum are the ones at m/z 30 (CH_4N^+), 56 ($\text{C}_3\text{H}_6\text{N}^+$), and 70 ($\text{C}_4\text{H}_8\text{N}^+$). Possible fragments providing these secondary ions are presented in Figure 5.7. Formation of CH_4N^+ secondary ions requires only a single C-C bond scission and it is mainly a result of direct emission of the $-\text{CH}_2-\text{NH}_2$ side chain fragment. However, unimolecular reactions of high mass metastable secondary ions can also contribute to the formation of CH_4N^+ secondary ions at a certain but much smaller extent. In any case the CH_4N^+ ion directly represents the $-\text{CH}_2-\text{NH}_2$ group. This secondary ion can be taken as a key fragment for primary amino groups and its yield can be used to investigate the relative primary amino group concentration related to the $-\text{CH}_2-\text{NH}_2$ side chain groups at the surface of plasma deposited allylamine films.

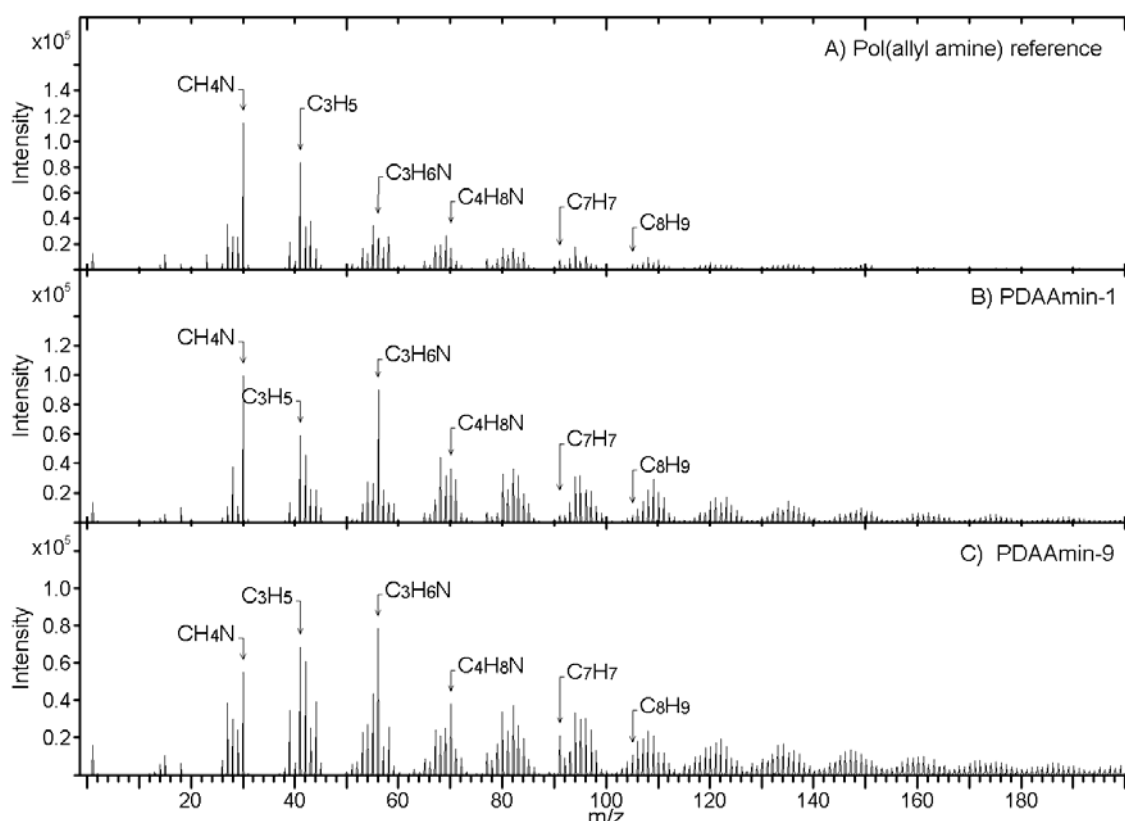


Figure 5.6. Positive ToF- SSIMS spectra of **A)** the poly(allylamine) reference, **B)** the PDAmin-1 sample (prepared under mildest plasma conditions), and **C)** the PDAmin-9 sample (prepared under hardest plasma conditions). The external plasma parameters employed for the deposition of plasma polymers are given in see Table 3.3, p. 29.

5. In-situ characterization of plasma deposited polymers

On the other hand, the secondary ions at 56 ($C_3H_6N^+$), and 70 ($C_4H_8N^+$) are mainly due to scissions in the backbone of poly(allylamine). At least two C-C bonds must be broken in that case. That is probably the reason why the CH_4N^+ secondary ion yield is higher.

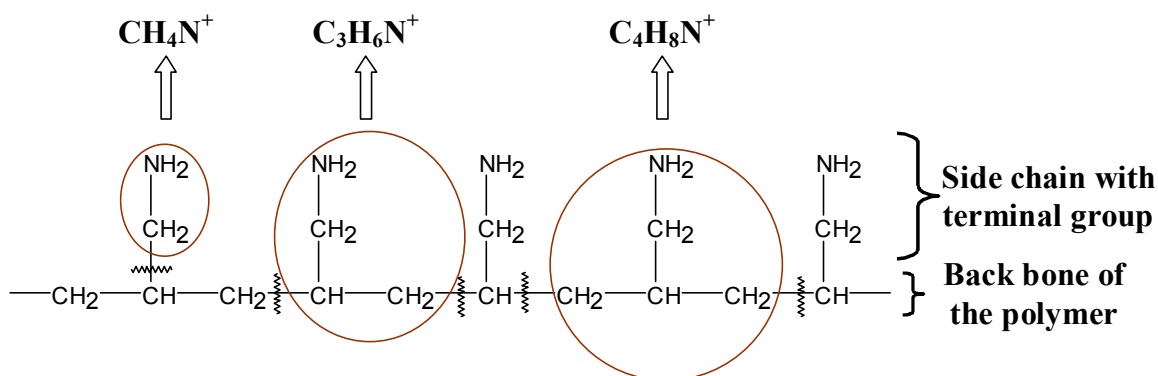


Figure 5.7. Possible fragments providing secondary ions at m/z 30 (CH_4N^+), 56 ($C_3H_6N^+$), and 70 ($C_4H_8N^+$) from the surface of the poly(allylamine) reference sample.

5.2.3.2. Characterization of the plasma deposited allylamine film prepared at mildest plasma conditions

The positive ToF-SSIMS spectrum of the plasma deposited allylamine polymer prepared at mildest plasma conditions (PDA Amin-1) is presented in Figure 5.6.B. Comparison of this spectrum with that of the poly(allylamine) reference sample reveals significant differences. In the positive SSIMS spectrum of PDA Amin-1, the total yields of the hydrocarbon secondary ions, especially these between m/z 1 – 100, are lower but the yields of secondary ions at masses above m/z 100 are higher. Generally, the relative yields of the low mass secondary ions are found to be different. For the PDA Amin-1 sample the yield of the secondary ion at m/z 30 (CH_4N^+) is lower but the yields of the secondary ions at m/z 56 ($C_3H_6N^+$) and 70 ($C_4H_8N^+$) are higher in comparison to the spectrum of PAAmin-R (c.f. Figure 5.6 A&B). As discussed in the previous section the CH_4N^+ secondary ion represents the primary amino groups involved in the $-CH_2-NH_2$ side chain group. Whereas, the $C_3H_6N^+$ and $C_4H_8N^+$ secondary ions can be due to both primary and secondary amino groups. It follows that PDA Amin-1 contains less primary amino groups but more secondary or even tertiary amino groups than PAAmin-R. Differences were also observed when the respective negative ToF-SSIMS spectra are compared (c.f. Figure 5.8 A&B). The most significant secondary ions in the negative SSIMS spectrum of

5. In-situ characterization of plasma deposited polymers

poly(allylamine) are at m/z 12 (C^-), 13 (CH^-), 24 (C_2^-), 25 (C_2H^-), and 26 (CN^-). For the PDA Amin-1 the relative yields of the $C_nH_x^-$ type secondary ions are lower but the relative yield of the CN^- secondary ion is much higher. CN^- was found to be formed in organic SSIMS strongly by nitriles ($C\equiv N$), less by imines ($C=N$) and much less by amines [105]. A high yield of CN^- probably indicates a presence of other functionalities like nitrile and/or imine in addition to amine in the PDA Amin-1 plasma polymer. Presence of signals originating from $C=N$ or $C\equiv N$ species observed in the respective NEXAFS results supports this conclusion [106]. Re-organization of the allylamine monomer during its plasma polymerization and partially transformation of primary amino groups into imine and nitrile functionalities was observed by other researchers [10, 15, 28, 107-114]. It was argued that fragmentation and plasma phase reactions in the allylamine plasma are complex and this may explain why plasma deposits predominantly containing only one nitrogen functional group, i.e. primary amino, can not be prepared [108, 110]. It is obvious that the structure of PDA Amin-1 must be more complex than that of PDA Amin-R due to unsaturation, branching and/or cross-linking, and other nitrogen functionalities in addition to primary amino groups.

5.2.3.3. Effect of external plasma parameters on the structure of plasma deposited allylamine films

By a systematic variation of the duty cycle, plasma power, and the monomer flow rate (Table 3.3), changes in the chemical character of the plasma deposited allylamine films were investigated.

The overall influence of the external plasma parameters on the ToF-SSIMS data of plasma deposited allylamine films is demonstrated in Figure 5.6 B&C. Comparison of the spectra of plasma polymerized allylamine prepared under mildest (PDA Amin-1) and hardest plasma conditions (PDA Amin-9) reveals characteristic differences. The relative yields of the high mass hydrocarbon secondary cluster ions and these of secondary ions of aromatic character are affected. Additionally, variations in the relative yields of CH_4N^+ , $C_3H_6N^+$ and $C_4H_8N^+$ secondary ions are obvious.

5. In-situ characterization of plasma deposited polymers

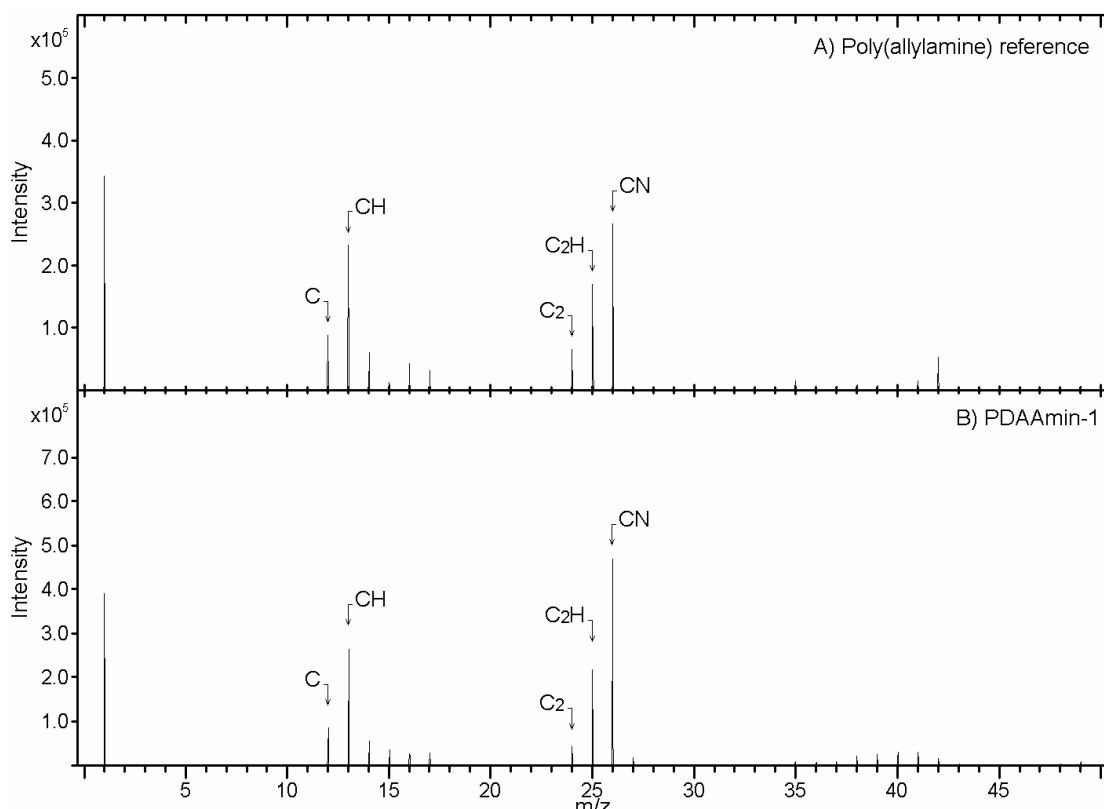


Figure 5.8. Negative ToF- SSIMS spectra of **A)** the poly(allylamine) reference, **B)** the PDA Amin-1 sample (prepared under mildest plasma conditions). The external plasma parameters employed for the deposition of plasma polymer are given in see Table 3.3, p. 29.

As already known, information on unsaturated and branched and/or cross-linked character of plasma deposited allylamine films can be derived from the interpretation of their respective SSIMS data. Additionally, the influence of the external plasma parameters on the nitrogen and primary amino group concentration of the films was investigated.

Investigation of the unsaturated character

Considering the plasma deposited allylamine films it was found that the values of Σ_{Arom} increase with increasing duty cycle or plasma power (c.f. Figure 5.9.A). This indicates that the plasma deposited films become more unsaturated as the duty cycle or plasma power is increased. Additionally, when the flow rate of the monomer is decreased the values of Σ_{Arom} and, hence, the unsaturated character of the films increases (c.f. Figure 5.9.A).

5. In-situ characterization of plasma deposited polymers

By adapting the approaches described in section 4.4, variations in the unsaturated character of the plasma deposited allylamine films vs. external plasma parameters could be derived from the relative yields of the nitrogen containing hydrocarbon secondary ions within a $C_nH_xN^+$ cluster series. The yields of the unsaturated secondary ions like $C_3H_2N^+$ (52), $C_4H_2N^+$ (64), $C_5H_2N^+$ (76), $C_6H_6N^+$ (92), and C_7H_6N (104) increase with increasing duty cycle or plasma power or decreasing monomer flow rate. This can be taken as an indication of higher degree of unsaturation at harder plasma conditions.

Obviously, the unsaturation and therefore, the irregularity of the plasma deposited allylamine films increases as the plasma conditions become harder. These trends were cross-checked by NEXAFS results obtained in similar experiments [106]. Similarly Shard et al. [109] observed from their NEXAFS examination that the unsaturation in allylamine plasma polymers increased with plasma power and was mainly due to carbon-nitrogen double and triple bond formation.

Investigation of the branched and/or cross-linked character

Variations in the branched and/or cross-linked character of the plasma deposited allylamine films with respect to external plasma parameters are derived from the parameter $[\Sigma(C_6-C_8)/\Sigma(C_2-C_8)]$ (c.f. section 4.4). As monitored by Figure 5.9.B, the $[\Sigma(C_6-C_8)/\Sigma(C_2-C_8)]$ parameter increases with respect to increasing duty cycle or plasma power and it decreases with increasing monomer flow rate.

The total positive secondary ion yields of the plasma deposited allylamine films decreased slightly as the deposition conditions became harder. This is again interpreted as an indication for an increase in the branched and/or cross-linked character of the films. The yields of the secondary ions and, therefore, the total secondary ion yield, too, could be influenced by the nitrogen surface concentration, thus providing a matrix effect in SSIMS. As the plasma deposition conditions become harder, the nitrogen content of the films deposited from allylamine decreases to some extent (cf. Figure 5.9.C). For this reason, the slight decrease of the total secondary ion yields could be a result of an increased branched and/or cross-linked character and/or a decreasing nitrogen surface concentration.

Investigation of the nitrogen content

To investigate the influence of the external plasma parameters on the nitrogen content of the films, a parameter, ΣN , which is given by summing up the yields of all nitrogen containing positive secondary ions, can be defined.

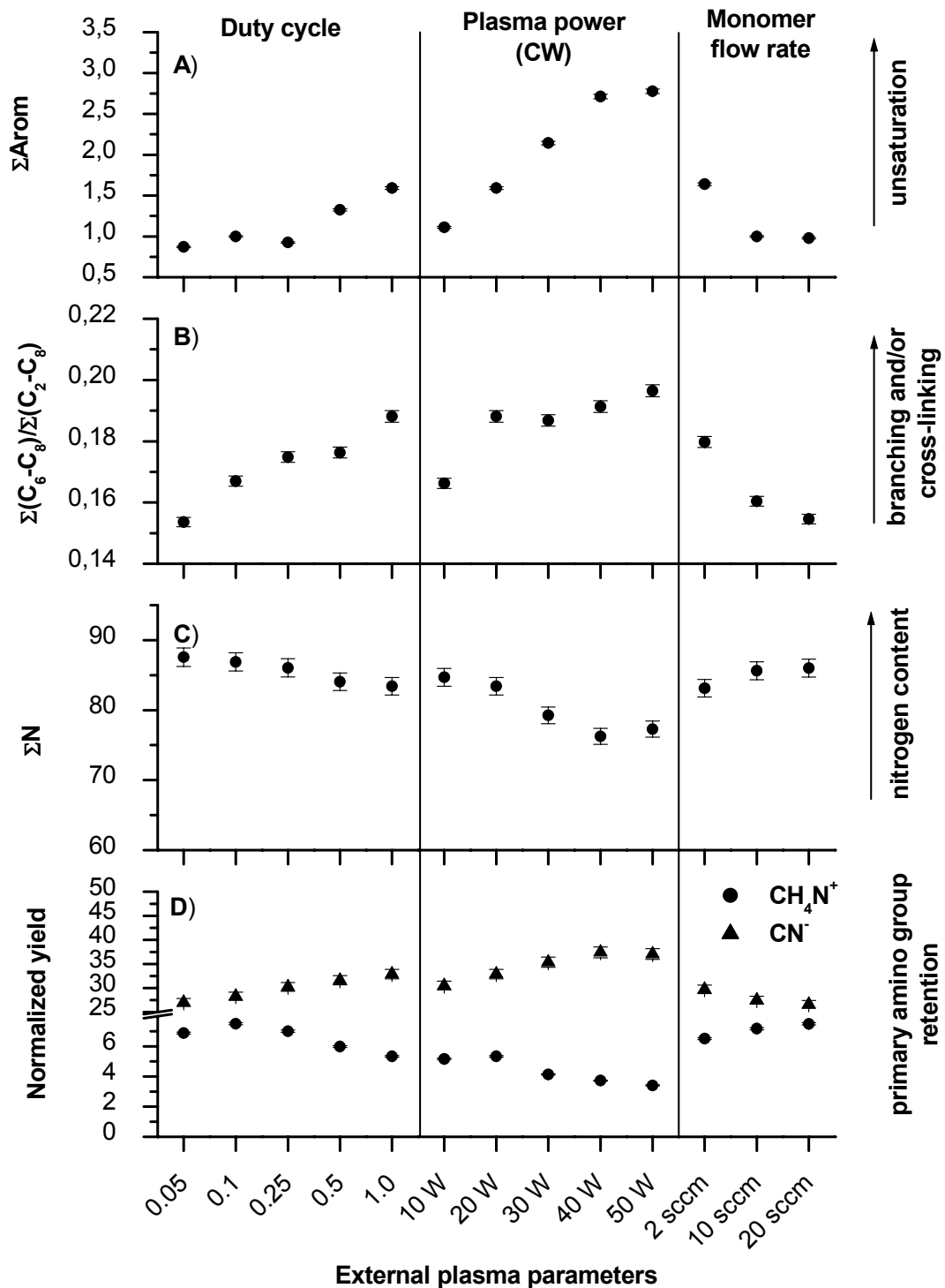


Figure 5.9. Reduced SSIMS data of plasma deposited allylamine films prepared at different plasma conditions (see Table 3.3, p. 29, for the constrained external plasma parameters). **A)** the parameter Σ_{Arom} , **B)** the parameter $[\Sigma(C_6-C_8)/\Sigma(C_2-C_8)]$, and **C)** the parameter ΣN (Note that arrows indicate the direction of increase for the described property). **D)** normalized secondary ion yields of CH_4N^+ and CN^- secondary ions.

5. In-situ characterization of plasma deposited polymers

The investigation of the positive SSIMS spectra of the plasma deposited allylamine films showed that as the plasma conditions become harder, the parameter, ΣN , decreases to some extent (c.f. Figure 5.9.C). This is cross-checked by the XPS N/C surface concentration ratio in parallel XPS experiments using the same experimental set-up [106]. A similar decrease in the nitrogen content of the plasma polymerized allylamine films was also observed by other researchers as the external plasma parameters become harder [28, 107-110, 113, 115]. This effect was attributed to the loss of low molecular weight nitrogen species by increasing fragmentation in the plasma.

Investigation of the retention of primary amino groups

Information on the retention of primary amino groups in plasma polymerized allylamine films is derived from the CH_4N^+ secondary ion yield. The yield of this ion was normalized according to the total yields of nitrogen containing secondary ions because any variation in the nitrogen content of the films affects the yield of this secondary ion. Increasing duty cycle or plasma power or decreasing the monomer flow rate resulted in a decrease in the CH_4N^+ yield (c.f. Figure 5.9.D). It seems that conversion of the primary amino groups originally present in the allylamine monomer into other nitrogen functionalities in the plasma was emphasized as the plasma conditions were varied from mild to hard. This conclusion was underpinned by the higher CN^- secondary ion yields at harder plasma conditions (c.f. Figure 5.9.D). The conclusion is that during its plasma polymerization, the allylamine monomer is re-organized and primary amino groups are partially transformed into other nitrogen functionalities like imine or nitrile. This conversion of primary amino groups increases vs. increasing duty cycle or plasma power or decreasing monomer flow rate. Increasing of the intensity of signals originating from $C=N$ or $C\equiv N$ species observed in the respective NEXAFS spectra supports this conclusion [106].

5.2.4. Plasma deposited allyl alcohol films

5.2.4.1. Characterization of the plasma deposited allyl alcohol film prepared at mildest plasma conditions

A poly(allyl alcohol) reference sample could not be obtained. The reason is that allyl alcohol monomers are simply too low in reactivity to allow a sufficient chain propagation. The allylic radicals, which are formed are rather stable and undergo termination by reaction with each other, or with propagating radicals [116]. Instead of a

5. In-situ characterization of plasma deposited polymers

“classic” reference polymer the plasma deposited allyl alcohol film prepared at mildest plasma conditions (PDAAI-1) is taken as a reference for further comparisons.

The positive ToF-SSIMS spectrum PDAAI-1 sample is presented in Figure 5.10.A. Similar to the case of films plasma deposited from ethylene and allylamine, high mass ions above m/z 100, which are thought to represent branching and/or cross-linking, are observed in the positive SSIMS of PDAAI-1. In addition, secondary ions with aromatic character at m/z 77, 91, 105, 115, 128, 141, 165 are observed at significant yields. They indicate the significant degree of unsaturation of the PDAAI-1 film. Ameen et al. [19] also attributed the presence of secondary ions of aromatic character in the positive SIMS spectrum of plasma deposited allyl alcohol to its unsaturated structure.

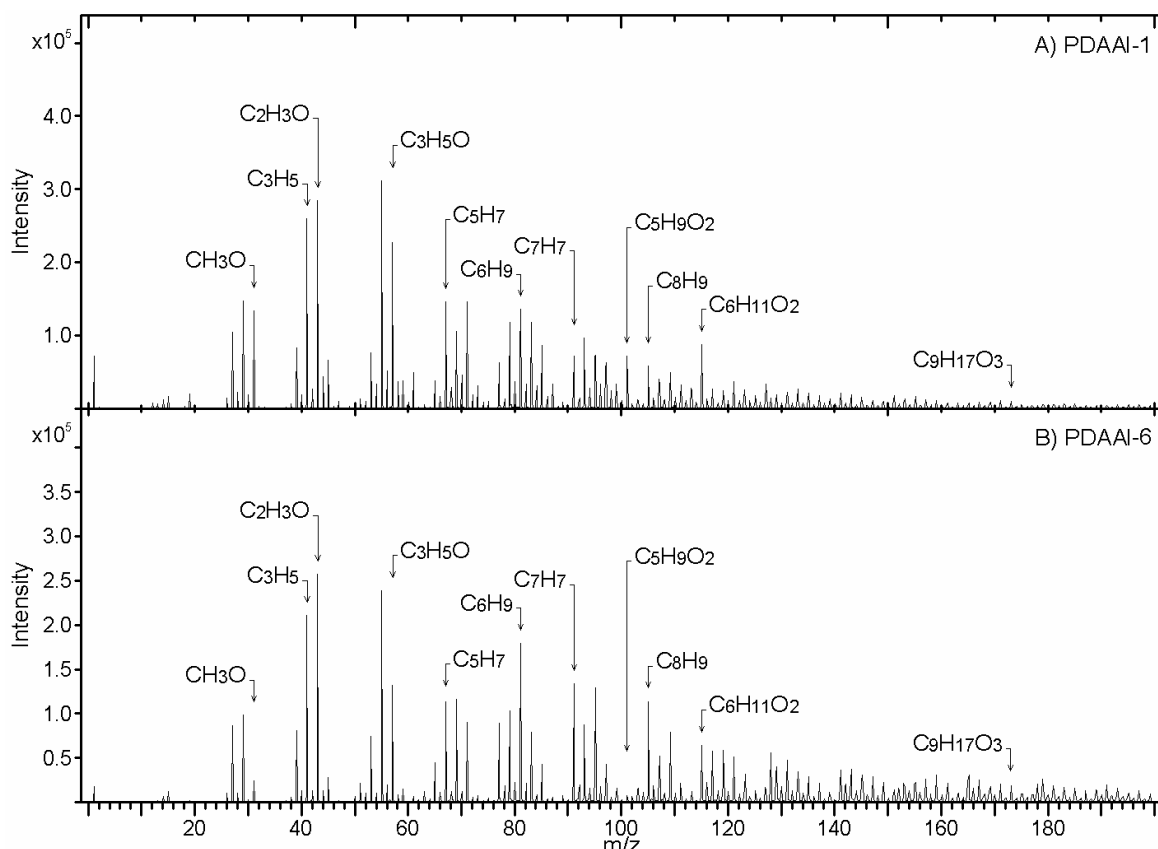


Figure 5.10. Positive ToF- SSIMS spectra of **A)** the PDAAI-1 sample (prepared under mildest plasma conditions), **B)** the PDAAI-6 sample (prepared under hardest plasma conditions). The external plasma parameters employed for the deposition of plasma polymer are given in see Table 3.4, p. 30.

5.2.4.2. Effect of external plasma parameters on the structure of plasma deposited allyl alcohol films

The structure of plasma deposited allyl alcohol films vs. variations in duty cycle, plasma power or monomer flow rate were investigated (c.f. Table 3.4). Influences of these external plasma parameters on the ToF-SSIMS spectra of the plasma deposited allyl alcohol films are demonstrated by comparing the spectrum of PDAAI-1, the film deposited at mildest plasma conditions, to that of PDAAI-6, the film deposited at hardest plasma conditions (c.f. Figure 5.10 A&B). The most significant differences between these two spectra are the relative intensities of the high mass secondary ions above m/z 100 and the relative yields of the oxygen containing secondary ions, e.g., $C_3H_5O^+$, $C_5H_9O_2^+$.

Investigation of the unsaturated character

Considering plasma deposited allyl alcohol films it was found that the values of Σ_{Arom} increased with increasing duty cycle or plasma power (Figure 5.11.A). A similar increase in this parameter was also observed when the flow rate of the monomer was decreased. This indicates that the plasma deposited films become more unsaturated as the plasma conditions become harder. Similarly Ameen et al. [19] reported that, as employing a lowered monomer flow rate, the concentration of unsaturated moieties, which give rise to secondary ions of aromatic character in the SIMS, increases.

The presence of these secondary ions with aromatic character in the positive SSIMS spectra of plasma deposited allyl alcohol films has to be attributed exclusively to their unsaturated character because previously IR and XPS studies proved that even plasma deposited allyl alcohol film prepared at rather hard conditions (300 W, CW plasma) did not contain aromatic species [15, 25]. This conclusion was cross-checked by NEXAFS results obtained in similar experiments. Here, it also was found that the $C\ 1s \rightarrow \pi^*_{C=C}$ resonance intensities grow as the deposition conditions become harder [117].

5. In-situ characterization of plasma deposited polymers

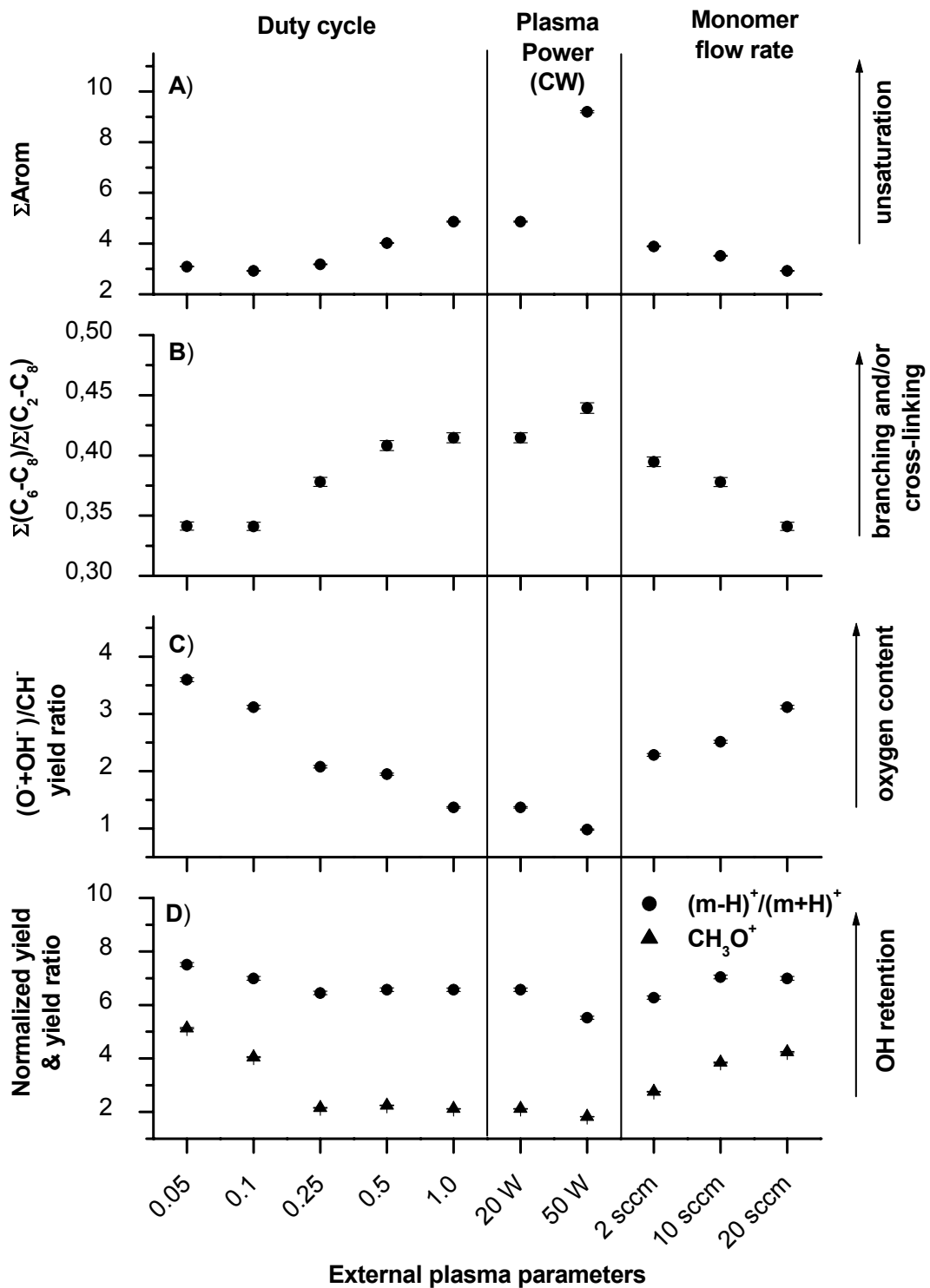


Figure 5.11. Reduced SSIMS data of plasma deposited allyl alcohol films prepared at different plasma conditions (see Table 3.4, p.30, for the constrained external plasma parameters). **A)** the parameter Σ_{Arom} , **B)** the parameter $[\Sigma(C_6-C_8)/\Sigma(C_2-C_8)]$, **C)** $(O^-+OH^-)/CH^-$ yield ratios, and **D)** $(m-H)^+/(m+H)^+$ yield ratios and the normalized yields of CH_3O^+ secondary ions. Note that arrows indicate the increase for a selected property.

5. In-situ characterization of plasma deposited polymers

Investigation of the branched and/or cross-linked character

Variations in the branched and/or cross-linked character of the plasma deposited allyl alcohol films vs. external plasma parameters were derived from the parameter $[\Sigma(C_6-C_8)/\Sigma(C_2-C_8)]$ (c.f. section 4.4). In these experiments, as presented in Figure 5.11.B, the parameter $[\Sigma(C_6-C_8)/\Sigma(C_2-C_8)]$ increases with increasing duty cycle or plasma power. Decreasing the monomer flow rate also causes a similar increase in this parameter. The conclusion here is that plasma deposited allyl alcohol films become more branched and/or cross-linked as the plasma conditions become harder.

The well known oxygen induced matrix effect has to be considered when the variations in the cross-linked character of plasma deposited allyl alcohol films are derived from the total secondary ion yields. As the plasma deposition conditions become harder, the oxygen content of the films deposited from allyl alcohol decreases (cf. Figure 5.11.C). For this reason, both the decreasing oxygen content and the increased cross-linked character will cause a decrease in the total secondary ion yields. Because it is not possible to differentiate between both effects an argumentation based on total secondary ion yields is not straightforward in the given case.

Investigation of the oxygen content

The yields of oxygen containing secondary ions were found to be at maximum in the positive SSIMS spectrum of PDAAI-1 and at minimum in the spectrum of PDAAI-6 (c.f. Figure 5.10 A&B). This should correlate to the oxygen surface concentration.

Alternatively to that simple observation, the oxygen content of the films was evaluated by using the $(O^-+OH^-)/CH^-$ yield ratio. This ratio was found to correlate with the O/C surface concentration ratio measured by XPS [118, 119]. As shown in Figure 5.11.C, the $(O^-+OH^-)/CH^-$ yield ratio, i.e. the oxygen content, of the films decreases with increasing duty cycle or plasma power. The oxygen content of the films was also found to depend on the monomer flow rate and it decreases with decreasing flow rate.

The SSIMS analysis of the oxygen content was successfully cross-checked by XPS. As shown in Table 5.2, the respective XPS O/C surface concentration ratios decreases vs. increasing duty cycle. A similar decrease in the oxygen content of the plasma polymerized allyl alcohol films as the plasma conditions become harder was observed by other researchers using XPS or FTIR spectroscopy [15, 19, 25, 60]. O'Toole et al. [60] investigated allyl alcohol r.f. plasmas operated at low (1 W) and high (8 W) plasma power

5. In-situ characterization of plasma deposited polymers

using gas phase mass spectrometry. They observed that there was a fragmentation of the allyl alcohol monomer even at a rather low plasma power of 1 W. Additionally, the yields of the low mass fragments at m/z 18 (H_2O^+), 26 (C_2H_2^+), 28 (CO^+ or C_2H_4^+) and 42 (C_3H_6^+) were found to increase with increasing plasma power [60]. It seems to be highly probable that the elimination of water or CO from the monomer is responsible for the observed oxygen deficiency in the plasma deposited allyl-alcohol films found by SSIMS or XPS.

Table 5.2. Results of XPS analysis of selected plasma deposited allyl alcohol films measured after two weeks of exposure to ambient air.

Sample	Duty cycle	O/C
PDAAI-1	0.05	0.38
PDAAI-2	0.1	0.37
PDAAI-5	1.0	0.26

Investigation of the retention of hydroxyl groups (OH)

The degree of retention of hydroxyl groups in the structure of plasma deposited allyl alcohol films is a rather important issue. In this section, it will be shown how SSIMS may contribute to a discussion of this retention of hydroxyl groups.

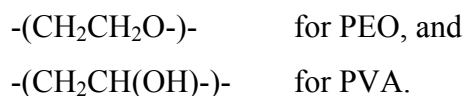
In section 5.2.3.1 it was reported that the secondary ion at m/z 30 (CH_4N^+) may be attributed to the direct emission of the $-\text{CH}_2-\text{NH}_2$ side chain group. Though there was no poly(allyl alcohol) reference sample investigated, it can be argued that the presence of $-\text{CH}_2-\text{OH}$ side chain groups in the plasma deposited allyl alcohol films can be derived from the secondary ion at m/z 31 (CH_3O^+) in their positive SSIMS spectra. This secondary ion represents the alcohol structure (c.f. Table 4.1) and its yield can be used to investigate the relative surface concentration of the OH groups involved in the of $-\text{CH}_2-\text{OH}$ side chain group.

The CH_3O^+ yields, which are normalized to the respective total yields of oxygen containing secondary ions, vs. external plasma parameters are presented in Figure 5.11.D. As the plasma conditions become harder, the normalized CH_3O^+ yields and the related retention of the OH groups decreases, too.

Ameen et al. [19] proposed another approach to investigate the retention of hydroxyl groups in plasma polymerized allyl alcohol films. They compared the positive

5. In-situ characterization of plasma deposited polymers

ToF-SSIMS spectra of poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO). For PVA and PEO the stoichiometry and molecular weight of the repeat units (m) of these polymers are the same, but the bonding differs:



The authors observed that, while $(m\text{-H})^+$ was the most intense secondary ion in the spectrum of PVA, $(m\text{+H})^+$ was found to be the most intense one in the spectrum of PEO. By taking these facts into consideration they argued that, if the hydroxyl retention decreases for the plasma deposited allyl alcohol films and, instead of this, the oxygen is more involved in the backbone, e.g. as ether bridges, the yield of $(m\text{-H})^+$ should decrease and that of $(m\text{+H})^+$ should increase. Actually the relative yields of the ions at m/z 57, $(m\text{-H})^+$, and 59, $(m\text{+H})^+$, in the positive ToF-SIMS spectra of plasma deposited allyl alcohol films were sensitive to an external plasma parameter variation. In detail, they observed that, with decreasing monomer flow rate, the yields of $(m\text{+H})^+$ increase while the yields of the $(m\text{-H})^+$ decrease. The authors attributed this to a decrease in the hydroxyl group retention effect.

Instead of the individual relative yields of the secondary ions at m/z 57, $(m\text{-H})^+$, and 59, $(m\text{+H})^+$, their yield ratio $(m\text{-H})^+ / (m\text{+H})^+$ is used to monitor the hydroxyl group retention in this study. This ratio was found to be much more sensitive.

It was found that the $(m\text{-H})^+ / (m\text{+H})^+$ yield ratio decreased from 7.50 to 5.52 when the plasma conditions were varied from the mildest to the hardest (c.f. Figure 5.11.D). The variations in these $(m\text{-H})^+ / (m\text{+H})^+$ yield ratios vs. external plasma parameters are rather similar to the variations in the normalized CH_3O^+ yields. However, a rather strong variation of the external plasma parameters results in comparable small changes (c.f. Figure 5.11.D). This means that there was probably a saturation of conversion of the monomer's hydroxyl groups to other oxygen functionalities like ether groups in the plasma. These results can be interpreted as that under these circumstances a good retention of the hydroxyl groups in the plasma deposited allyl alcohol films could be obtained. This idea can be also supported by the presence of secondary ions at m/z 57 $(m\text{-H})^+$, 101 $(2m\text{-CH}_3)^+$, 115 $(2m\text{-H})^+$ and 173 $(3m\text{-H})^+$ in the positive SSIMS spectra. These secondary ions are also characteristic of the plasma phase mass spectra obtained by extraction of particles from allyl alcohol plasma into a mass spectrometer. They were due to oligomerization reactions in the plasma through the addition of m to $(m\text{-H})^+$ [60]. It has been argued that at low plasma power these oligomers are mainly responsible for the deposition of allyl

5. In-situ characterization of plasma deposited polymers

alcohol films. It seems that the positive secondary ions at m/z 57 ($C_3H_5O^+$), 101 ($C_5H_9O_2^+$), 115 ($C_6H_{11}O_2^+$) and 173 ($C_9H_{17}O_3^+$) can be used as characteristic fragments to prove the retention of hydroxyl groups in the plasma deposited allyl alcohol films, too. Actually, in these experiments, the maximum yields of these secondary ions were found for PDAAI-1 and the lowest yields for PDAAI-6 (c.f. Figure 5.10 A&B). The final conclusion here is, that at the given plasma parameters an effective hydroxyl group retention is obtained at the mildest plasma condition. Similar conclusions were derived by Friedrich et al. [10] by using XPS with trifluoroacetic anhydride labeling of hydroxyl groups.

5.3. Discussion of results of in-situ analysis of plasma deposited homopolymer films

In-situ ToF-SSIMS was successfully applied to investigate the chemical character of plasma deposited films prepared from styrene, ethylene, allylamine, and allyl alcohol. It was found to be a useful tool to obtain information about basic chemical properties as unsaturation, branching and/or cross-linking, and the aromatic and/or aliphatic contents. Additionally, information on the retention of the relevant structure groups was obtained.

The chemical character of the plasma polymers was found to depend on the external plasma parameters applied for their deposition.

When the plasma power or the duty cycle is increased the unsaturated character of the plasma deposited films from ethylene, allylamine and allyl alcohol increases. Investigating the unsaturation in the “backbone” of plasma polymerized styrene films by SSIMS using the interpretation approaches outlined in section 4.4 was impossible due to the presence of aromatic groups. Additionally, duty cycle and plasma power control the branched and/or cross-linked character of the plasma deposited polymers. It increases with increasing any of these external plasma parameters. Finally, it was observed that with increasing the duty cycle or plasma power the retention of the relevant structure groups, e.g., aromatic rings in the case of styrene and side chain groups in the case of allylamine and allyl alcohol plasma polymers, decreases. However, it should be noted that in the case allyl alcohol plasma polymers there was probably a saturation of conversion of the side chain groups to other species in the plasma. This emphasizes that the influence of the duty cycle and the plasma power on the structure of plasma polymers seems to depend also on the nature of the monomers themselves. These general trends can be explained by the fact that an increase in duty cycle or plasma power increases the energy of the plasma particles. Fragmentation and re-arrangement of the monomer molecules are promoted in that way (c.f. section 2.2.2).

5. In-situ characterization of plasma deposited polymers

A decrease in the monomer flow rate provides similar changes in the structure and character of plasma deposited films. A decrease in the monomer flow rate results in an increase in the unsaturated, branched and/or cross-linked character of the plasma polymers. Moreover, retention of the respective monomer functionality decreases with decreasing monomer flow rate. This is to be expected because if the flow rate of the monomer is decreased, its retention time in the plasma chamber increases. Thus monomer molecules are subjected to more collisions, which results in more fragmentations and re-arrangements in the plasma (c.f. section 2.2.2).

It can be concluded that the chemical composition of the formed plasma polymers is strongly influenced by the magnitude of the plasma power and the monomer flow rate. As Yasuda proposed by defining the parameter W/FM , an increase in plasma power or a decrease in monomer flow rate results in an increase in the apparent input energy per monomer molecule (c.f. section 2.2.2). This promotes the fragmentations and re-arrangements in the plasma.

Investigation of a variation of the external plasma parameter “reaction pressure” in the case of plasma deposited ethylene films showed that when the reaction pressure is increased the unsaturated character of the films increases, too. However, branching and/or cross-linking is nearly unaffected from the variations in reaction pressure. These observations may point to the higher complexity of this case, which is due to competing effects. An increase in reaction pressure decreases the electron energy in the plasma but increases the collision rate of the molecules and plasma particles. While the first process causes a decrease in the fragmentation of the monomer molecules, the later one causes its increase. Such competing processes make the reaction pressure a rather complex external plasma parameter, which does not provide a simple control on the chemistry of the plasma polymers. To achieve an exact control on the chemistry of plasma deposited films internal plasma parameters should be controlled.

The final conclusion here is that at circumstances of this study less unsaturated, branched and/or cross-linked plasma polymers with a high functional group retention is obtained at rather mild plasma conditions, which could be obtained at low duty cycles, low plasma power, and high monomer flow rates.