

### 6. In-situ characterization of plasma deposited copolymers

#### 6.1. Introduction

It has been shown in Chapter 5 that the external plasma parameters allow to control the chemical character of plasma deposited films. For example, a high degree of retention of the chemical functionality of the monomer was found when low duty cycles, low plasma power, or high monomer flow rates, i.e., “mild” plasma conditions, were employed. An increase in the duty cycle or plasma power reduced the retention of monomer functionality, but it also resulted in a wider range of other functionalities. Duty cycle and plasma power also affected the film's properties in terms of unsaturation, branching and/or cross-linking. Therefore, the duty cycle or plasma power are not ideal variables for controlling the concentration of a certain functional group. Another variable that affects the level of functional group retention is the monomer flow rate. However, this variable also enables considerable side reactions influencing the deposit's properties.

A plasma copolymerization of a functional groups bearing monomer with a “chain extending” hydrocarbon monomer can be a work around. Therefore, plasma copolymerization was used to control the concentration of a selected functionality for plasma deposited films.

In a dedicated study allyl alcohol, or allylamine were used as “functional group bearing” monomers and styrene, or ethylene as “chain extending” monomers. The partial flow rates of the monomers were the only parameter varied during the plasma copolymerization experiments (c.f. Table 3.5). Other external plasma parameters were selected in a way to get *mild* plasma conditions. So, it was expected that the retention of functional groups present in the monomer would be high in the plasma polymer.

Plasma deposited copolymers were investigated mainly in terms of their density of functional groups. Investigation of the structure of the plasma deposited copolymers in terms of unsaturation, branching and/or cross-linking was not as straight forward as in the case of plasma homopolymers. The reason is that the approaches described in section 4.4 for the interpretation of SSIMS data can be used only for organic materials of the same family.

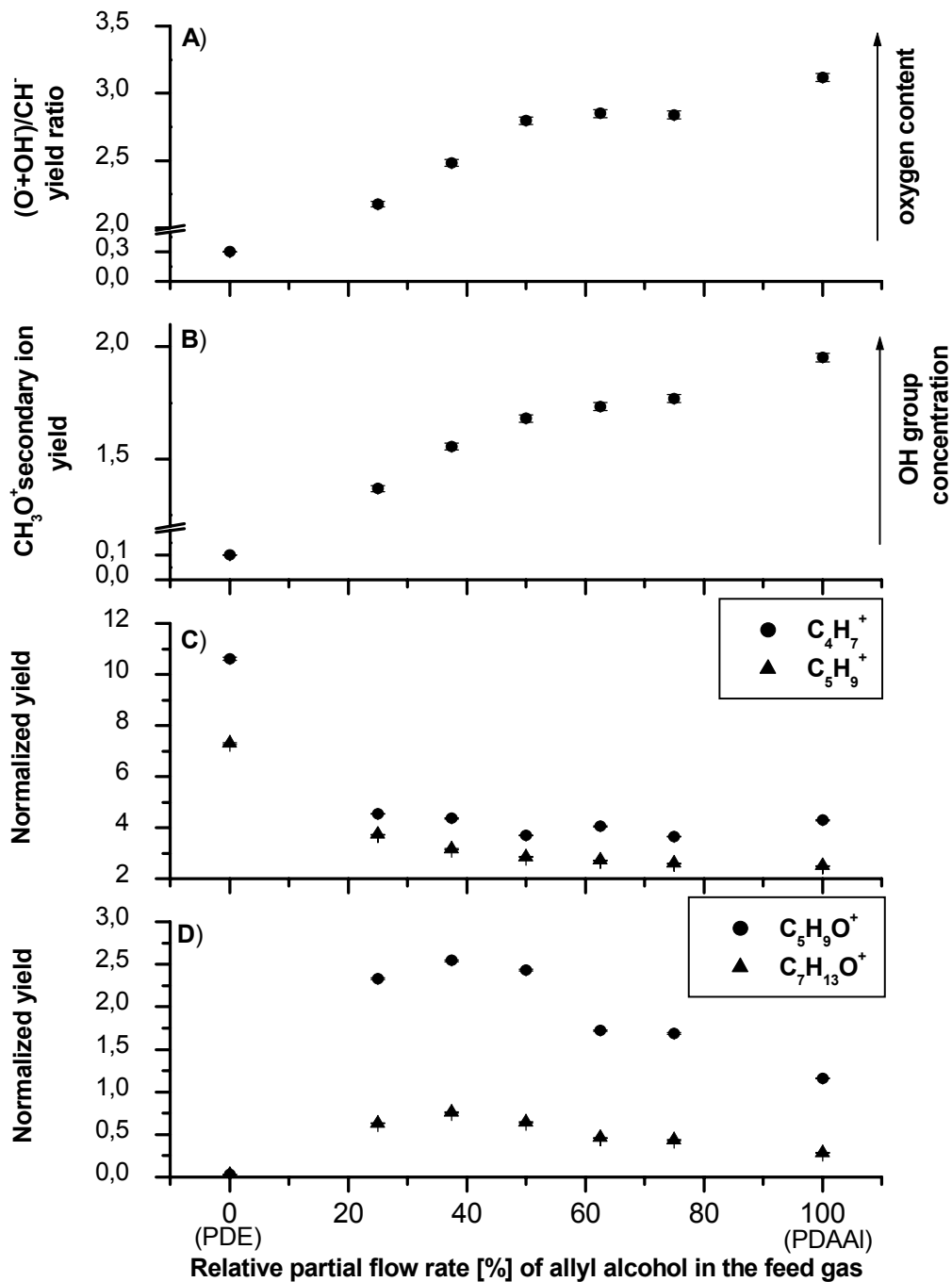
### 6.2. Results

#### 6.2.1. Characterization of plasma deposited ethylene-allyl alcohol copolymers

The positive ToF-SSIMS spectra of the plasma deposited copolymer films prepared from ethylene and allyl alcohol were dominated by the secondary ions that were observed at high yields in the positive ToF-SSIMS spectra of plasma homopolymers prepared from ethylene and allyl alcohol. However, as to be expected the relative yields of these secondary ions were dependent on the composition of the feed gas. As the partial flow rate of allyl alcohol in the feed gas was increased, yields of oxygen containing secondary ions increased, too. This is monitored by the oxygen content of the plasma deposited copolymers, which itself was measured by the  $(O^+OH^-)/CH^-$  yield ratio. Obviously, the oxygen content of the plasma copolymer films increased with increasing the partial flow rate of allyl alcohol in the feed gas (c.f. Figure 6.1.A). It was rather high already at partial flow rate of allyl alcohol of 25 %. However, when the partial flow rate of allyl alcohol reaches 50 %, the oxygen content of the plasma copolymers seems to saturate.

In section 5.2.4.2 it was reported that presence of  $-CH_2-OH$  groups in plasma deposited allyl alcohol films could be derived from the secondary ion at  $m/z$  31 ( $CH_3O^+$ ) in their positive SSIMS spectra. The yield of this secondary ion, normalized to the total secondary ion yield, was used to investigate the relative concentration of the OH groups with respect to the composition of the feed gas (c.f. Figure 6.1.B). Similar to the oxygen content of the plasma copolymer films, the concentration of OH groups increased drastically already when small amounts of the allyl alcohol were introduced into the feed gas. Further increase in the allyl alcohol partial flow rate in the feed gas caused only small additional increases in the  $CH_3O^+$  secondary ion yield.

Considering the yields of hydrocarbon secondary ions, which were the most intense secondary ions in the spectrum of the plasma deposited ethylene film, also changes with respect to the allyl alcohol partial flow rate in the feed gas were observed. As an example the yields of the secondary ions at  $m/z$  55 ( $C_4H_7^+$ ), and 69 ( $C_5H_9^+$ ) were displayed in Figure 6.1.C. The yields of these secondary ions decreased drastically when the allyl alcohol monomer was introduced into the feed gas.



**Figure 6.1.** Reduced SSIMS data of copolymer films plasma deposited from ethylene and allyl alcohol 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). **A)** oxygen content, measured by the  $(O^+OH^-)/CH^-$  secondary ion yield ratio, **B)** OH group concentration measured by  $CH_3O^+$  secondary ion yield. Note that arrows indicate the increase for a selected property. **C)**  $C_4H_7^+$  and  $C_5H_9^+$  secondary ion yields, **D)**  $C_5H_9O^+$  and  $C_7H_{13}O^+$  secondary ion yields.

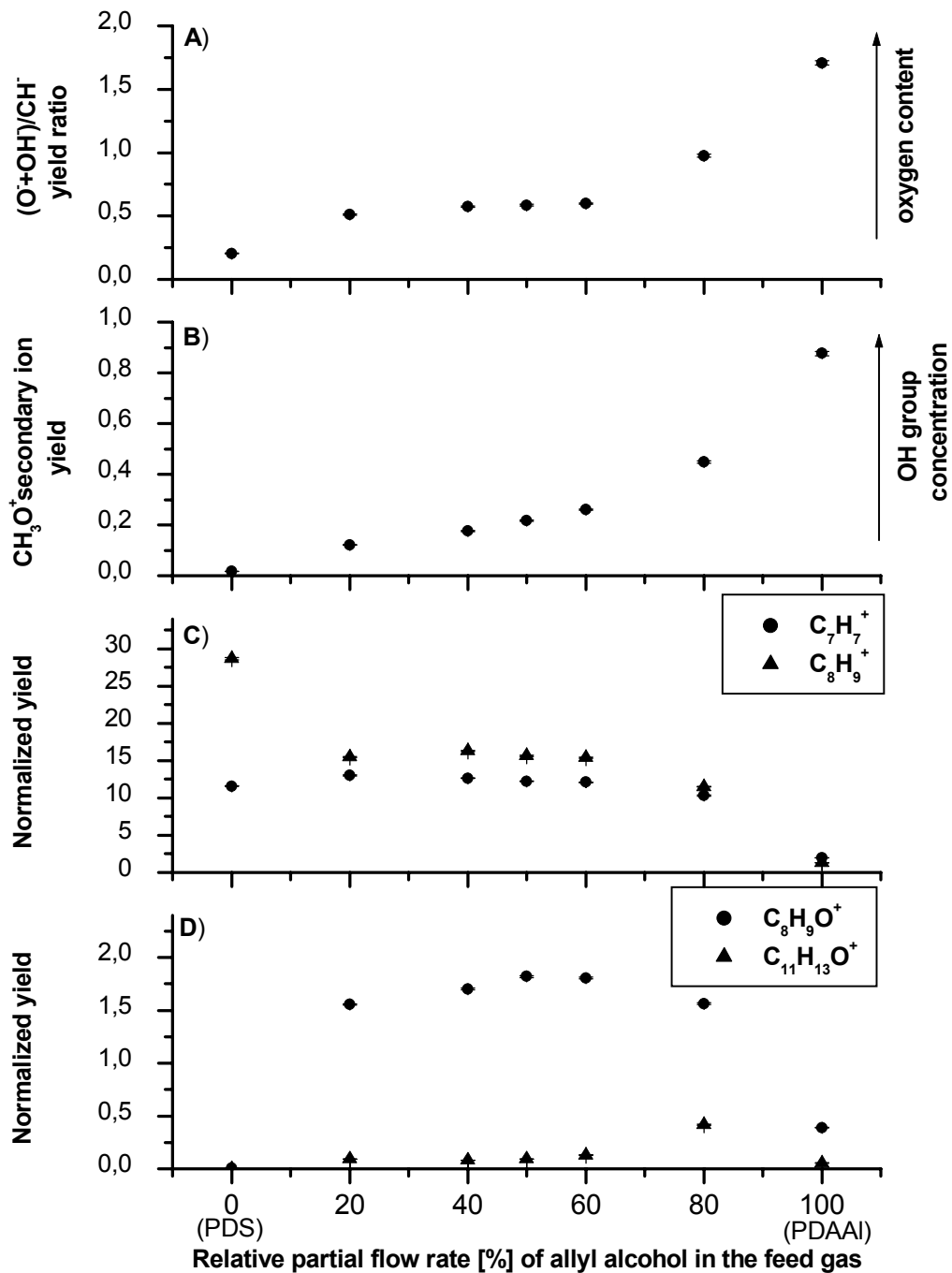
Another important observation was that in the spectra of plasma copolymers several secondary ions are present with yields which were strongly increased in comparison to their yields in the spectra of the respective plasma homopolymers. Examples for this effect are given by the secondary ions at  $m/z$  85 ( $C_5H_9O^+$ ) and 113 ( $C_7H_{13}O^+$ ) (c.f. Figure 6.1.D). The yields of these secondary ions were found to be dependent on the composition of the feed gas. These secondary ions can be taken as characteristic secondary fragment ions for plasma deposited ethylene-allyl alcohol copolymers.

### 6.2.2. Characterization of plasma deposited styrene-allyl alcohol copolymers

The oxygen content and the OH group concentration of the plasma deposited styrene-allyl alcohol copolymer films vs. the feed gas composition are presented in Figure 6.2. A&B, respectively. Actually, when the allyl alcohol was introduced into the feed gas the oxygen content and OH group concentration of the plasma deposited copolymer film increased. However, these increases are relatively small until the partial flow rate of allyl alcohol reached ca. 60%. In the range of 60-100% any further increase in the partial flow rate of allyl alcohol resulted in an efficient increase in oxygen content and OH group concentration.

The yields of the secondary ions at  $m/z$  105 ( $C_8H_9^+$ ), and 91 ( $C_7H_7^+$ ), which were the most intense secondary ions in the spectra of plasma deposited styrene films, depend on the composition of the feed gas (c.f. Figure 6.2.C). Introducing the allyl alcohol into the feed gas resulted in a strong decrease in the yield of  $C_8H_9^+$  secondary ion, correlated to the branching and/or cross-linking of the plasma deposited styrene films (c.f. section 5.2.1.2). The yield of  $C_7H_7^+$  secondary ion representing the linear polystyrene structure is only little affected by the addition of allyl alcohol into feed gas. A further increase in the partial flow rate of allyl alcohol until it reached ca. 60 %, caused only a little changes for both yields. However, beginning with 60 % there was a considerable decrease in both yields.

It is interesting to state again that for the spectra of plasma copolymers, several secondary ions, which can be interpreted to be characteristic secondary ions for plasma copolymers, were found to be at higher yields in comparison to the case of the respective plasma homopolymer. For example, the secondary ions at  $m/z$  121 ( $C_8H_9O^+$ ) and 161 ( $C_{11}H_{13}O^+$ ) were observed at higher yields in the spectra of plasma copolymers than in the spectrum of plasma deposited allyl alcohol film (c.f. Figure 6.2.D). In addition, the yields of these secondary ions showed a non-linear dependence on composition of the feed gas.



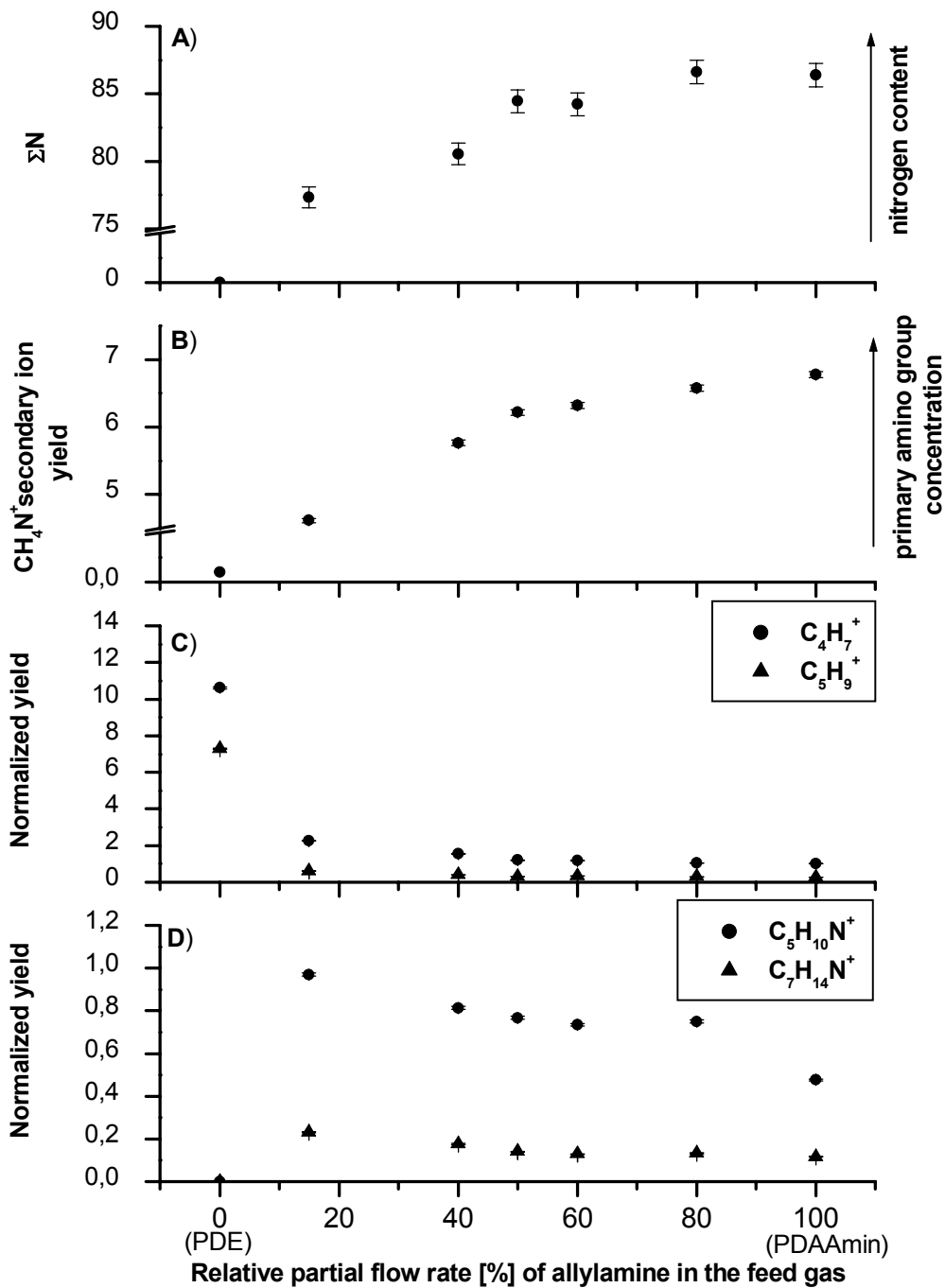
**Figure 6.2.** Reduced SSIMS data of copolymer films plasma deposited from styrene and allyl alcohol vs. relative partial flow rate [%] (partial flow rate/total flow rate) of allyl alcohol (see Table 3.5, p. 31, for the constrained external plasma parameters). **A)** oxygen content, measured by the  $(O^+ + OH^-)/CH^-$  secondary ion yield ratio, **B)** OH group concentration measured by the  $CH_3O^+$  secondary ion yield. Note that arrows indicate the increase for a selected property. **C)**  $C_7H_7^+$  and  $C_8H_9^+$  secondary ion yields, **D)**  $C_8H_9O^+$  and  $C_{11}H_{13}O^+$  secondary ion yields.

### 6.2.3. Characterization of plasma deposited ethylene-allylamine copolymers

As to be expected both hydrocarbon and nitrogen containing secondary ions were observed in the positive ToF-SSIMS spectra of the plasma deposited copolymer films prepared from ethylene and allylamine. The relative yields of these secondary ions were found to be dependent on the composition of the feed gas. The yields of nitrogen containing secondary ions, contributing to the parameter,  $\Sigma N$  (c.f. section 5.2.3.3), increased with increasing allylamine partial flow rate in the feed gas. The nitrogen content of the plasma deposited copolymer films is correlated to the parameter,  $\Sigma N$ . As shown in Figure 6.3.A, the nitrogen content of the plasma copolymers increased drastically when allylamine was introduced into the feed gas. Further increase in the partial flow rate of allylamine in the feed gas resulted in a relatively slight increase in the nitrogen content of the plasma copolymers (c.f. Figure 6.3.A). Actually, when the partial flow rate of allylamine reaches ca. 80%, the nitrogen content of the plasma copolymers seems to saturate by reaching the pure plasma deposited allylamine value.

Similar to the nitrogen content of the plasma copolymer films, the concentration of primary amino groups derived from the normalized yields of the secondary ion at  $m/z$  30 ( $\text{CH}_4\text{N}^+$ ) (c.f. section 5.2.3.3) increased substantially when the allylamine was introduced into the feed gas (c.f. Figure 6.3.B). Further increase in the partial flow rate of allylamine in the feed gas continuously caused an increase in the concentration of primary amino groups.

Additionally, with increasing partial flow rate of allylamine in the feed gas, the yields of the hydrocarbon secondary ions, which were the most intense secondary ions in the spectrum of plasma deposited ethylene film decreased. This is demonstrated by the variations in the yields of secondary ions at  $m/z$  55 ( $\text{C}_4\text{H}_7^+$ ), and 69 ( $\text{C}_5\text{H}_9^+$ ) with respect to the feed gas composition (c.f. Figure 6.3.C). The yields of these secondary ions decreased drastically when the allylamine was introduced as a second monomer into the reaction chamber. Further increase in the allylamine partial flow rate in the feed gas caused only relatively small decreases in the yields of these secondary ions.



**Figure 6.3.** Reduced SSIMS data of copolymer films plasma deposited from ethylene and allylamine 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). **A)** nitrogen content, measured by the parameter  $\Sigma N$ , **B)** primary amino group concentration measured by the  $\text{CH}_4\text{N}^+$  secondary ion yield. Note that arrows indicate the increase for a selected property. **C)**  $\text{C}_4\text{H}_7^+$  and  $\text{C}_5\text{H}_9^+$  secondary ion yields, **D)**  $\text{C}_5\text{H}_{10}\text{N}^+$  and  $\text{C}_7\text{H}_{14}\text{N}^+$  secondary ion yields.

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In section 6.2.1 it was observed that in the positive ToF-SSIMS spectra of the plasma deposited ethylene-allyl alcohol copolymer films secondary ions, which were thought to be characteristics of the plasma copolymers, were at higher yields in comparison to the pure plasma deposited allyl alcohol case. The yields of these secondary ions were found to be dependent on composition of the feed gas. Considering the positive ToF-SSIMS spectra of the plasma deposited ethylene-allylamine copolymers, secondary ions, e.g.,  $C_5H_{10}N^+$  and  $C_7H_{14}N^+$ , were also observed at higher yields in comparison to the spectrum of plasma deposited allylamine (c.f. Figure 6.3.D). The yields of these secondary ions showed a dependence on partial flow rate of allylamine in the feed gas.

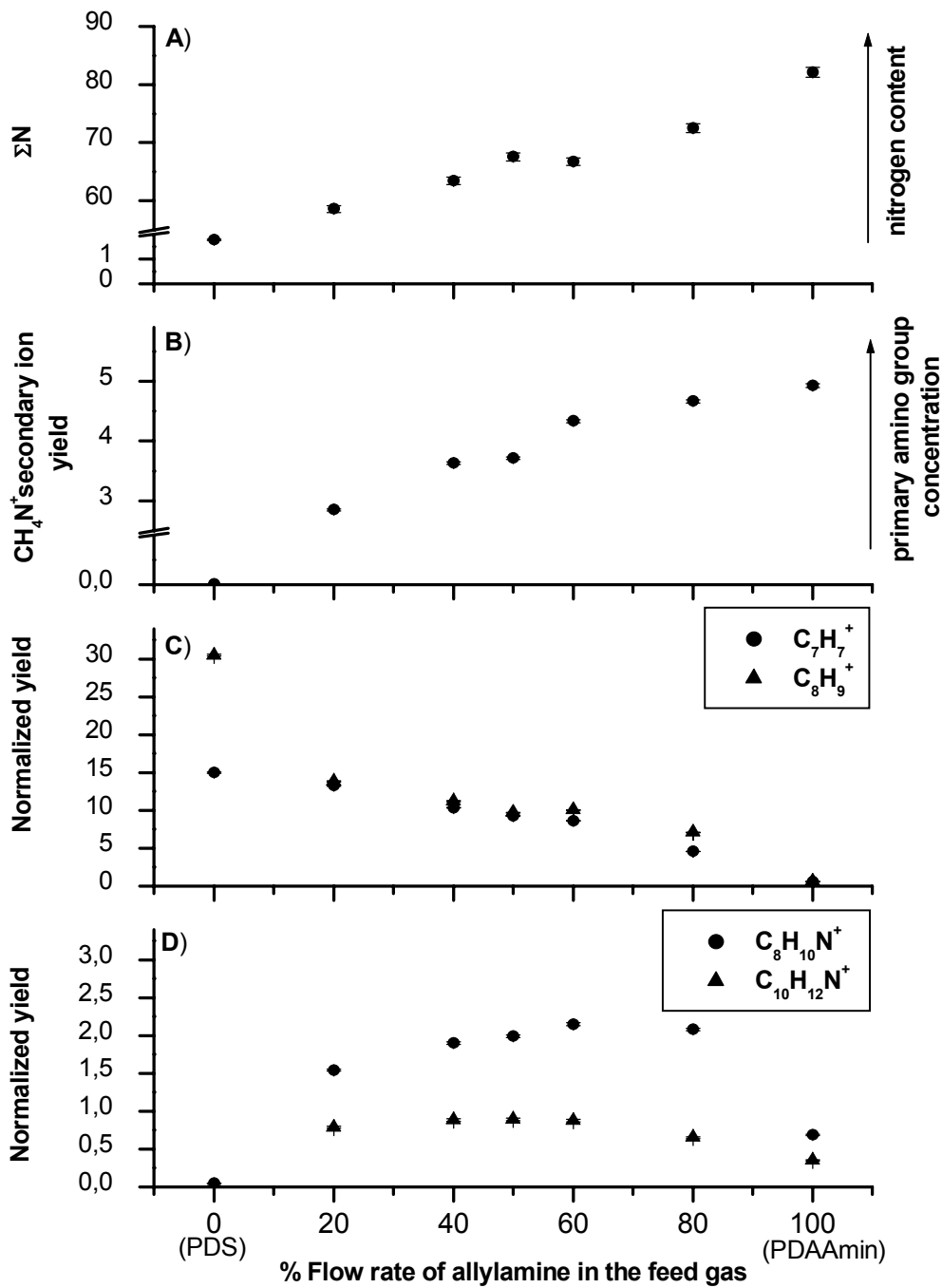
### 6.2.4. Characterization of plasma deposited styrene-allylamine copolymers

The positive ToF-SSIMS spectra of the plasma deposited copolymer films prepared from styrene and allylamine were dominated by the secondary ions that were also observed at high yields in the spectra of the respective plasma homopolymers. The relative yields of these secondary ions were dependent on the composition of the feed gas. When the flow rate ratio of allylamine in the feed gas was increased,  $C_nH_xN_y^+$  fragment yields increased whereas the yields of hydrocarbon secondary ions observed at high yields in the spectrum of plasma deposited styrene, e.g., at  $m/z$  105 ( $C_8H_9^+$ ) and 91 ( $C_7H_7^+$ ), decreased (c.f. Figure 6.4.A&C).

The nitrogen content ( $\Sigma N$ ) and the primary amino group concentration ( $CH_4N^+$  yield) of the plasma deposited styrene-allylamine copolymer films enhanced with increasing the partial flow rate of allylamine in the feed gas (Figure 6.4.A&B). When the allylamine is introduced into the feed gas the nitrogen content and primary amino group concentration of the plasma deposited copolymer film increased drastically. A further increase in the partial flow rate of allylamine in the feed gas resulted in a straight increase in the nitrogen content and concentration of primary amino groups.

Comparison of the ToF-SSIMS spectra of plasma deposited copolymers with the spectrum of plasma deposited allylamine film revealed that several secondary ions, which could be attributed to the characteristics of plasma copolymers, were at higher yields. The yields of these secondary ions showed a dependence on the composition of the feed gas. This is demonstrated by the  $C_8H_{10}N^+$  and  $C_{10}H_{12}N^+$  secondary ions yields in Figure 6.4.D.





**Figure 6.4.** Reduced SSIMS data of copolymer films plasma deposited from styrene and allylamine 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). **A)** nitrogen content, measured by the parameter  $\Sigma N$ , **B)** primary amino group concentration measured by the  $CH_4N^+$  secondary ion yield. Note that arrows indicate the increase for a selected property. **C)**  $C_7H_7^+$  and  $C_8H_9^+$  secondary ion yields, **D)**  $C_8H_{10}N^+$  and  $C_{10}H_{12}N^+$  secondary ion yields.

### 6.3. Discussion of results of in-situ analysis of plasma deposited copolymers

Ethylene or styrene as “chain extending” monomers were plasma copolymerized with allyl alcohol or allylamine as carrier monomers for hydroxyl and amino groups, respectively. Then, the composition of the feed gas was systematically varied and the plasma copolymers were preferentially analyzed in terms of their density of functional groups.

It was observed that generally the density of functional groups in the plasma copolymers was varying non-linearly with respect to the partial flow rates of the monomers in the feed gas. Such non-linear behaviors are also typical for chemical copolymerization process [10]. Friedrich et al. also reported similar results by IR and XPS analysis [10, 15]. They argued that under *mild* plasma conditions obtained by employing pulsed plasma, the ability of chemical copolymerization, i.e., reactivity, of each monomer becomes important because the chemical radical polymerization in the gas phase or in an adsorption layer is enhanced during plasma-off periods. It seems that under the deposition conditions employed in this work the copolymerization phenomenon is initiated by plasma and the different reactivities of the monomers are responsible for the observed non-linear variations. Table 6.1 gives for the respective anticipated reactivity of monomers in radical gas phase polymerization during the plasma-off period in a pulsed plasma polymerization. It must be also mentioned that these reactivities of the monomer depend on the external plasma parameters, e.g., duty cycle values and composition of the feed gas. It can be concluded that control of the concentration of the functional groups requires a careful selection of the monomer pairs and the external plasma parameters.

**Table 6.1.** Proposed reactivity of monomers in radical gas phase polymerization during the plasma-off period in a pulsed plasma polymerization (adapted from Ref. [15]).

Monomer	Chemical reactivity
Ethylene	Low
Styrene	High
Allyl alcohol	Moderate
Allylamine	Moderate

In the SSIMS spectra of all plasma deposited copolymer films several characteristic secondary ions, e.g., the  $C_5H_9O^+$  and  $C_7H_{13}O^+$  secondary ions in the case of plasma

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ethylene-allyl alcohol copolymers, were observed at higher yields in comparison to the spectra of the respective plasma homopolymers. It is highly probable that the reasons for these observations are interactions and/or recombination reactions taking place between monomer molecules either in the gas phase or during the deposition process. For example, the secondary ion at  $m/z$  85 ( $C_5H_9O^+$ ) might represent a fragment ( $m_{\text{ethylene}} + m_{\text{allyl alcohol}} - H$ )<sup>+</sup>, where  $m_{\text{ethylene}}$  and  $m_{\text{allyl alcohol}}$  are the molecular weights of the monomer molecules for ethylene and allyl alcohol, respectively. Similarly, the secondary ion at  $m/z$  113 ( $C_7H_{13}O^+$ ) can be attributed to  $(2m_{\text{ethylene}} + m_{\text{allyl alcohol}} - H)^+$ . Considering other plasma copolymers, characteristic secondary ions emphasized in previous section can be explained in similar ways.

These results can be interpreted as that the structure of the plasma copolymers are partially different than the structure of plasma homopolymers, i.e., the nature of plasma copolymers might not be straightforwardly predicted by a detailed knowledge of the structure of the plasma homopolymers. Additional supports to this conclusion can be derived when the relative yields of the most intense secondary ions observed in the spectra of plasma homopolymers are investigated with respect to the feed gas composition. For example, dependence of the yields of secondary ions at  $m/z$  55 ( $C_4H_7^+$ ), and 69 ( $C_5H_9^+$ ), which are the most intense ions in the spectrum of the plasma deposited ethylene film, on the feed gas composition were different. As the functional group bearing monomers, e.g., allyl alcohol or allylamine, is introduced into feed gas, a stronger decrease is observed in the ( $C_4H_7^+$ ) yield (c.f. Figure 6.1.C & 6.3.C). Similar results were observed when the yields of the secondary ions at  $m/z$  105 ( $C_8H_9^+$ ), and 91 ( $C_7H_7^+$ ), which were the most intense secondary ions in the spectra of plasma deposited styrene films vs. the feed gas composition were investigated (c.f. Figure 6.2.C & 6.4.C). It seems that the interactions and/or recombination reactions, which take place between the different monomers, result in a plasma copolymer structure partially different from the structure of the respective plasma homopolymers. Several researchers discussed such interactions between the monomer molecules, too. Golub et al. [120] investigated the plasma copolymerization of ethylene and tetrafluoroethylene (TFE) by IR spectroscopy. A “positive” (productive) interaction was noted between ethylene and TFE, i.e., the rates of plasma copolymer deposition for all compositions of the feed gas exceeded those expected on the basis of non-interactions between those monomers. On the contrary, according to deposition rates of plasma deposited homopolymers and copolymers, “negative” interaction was concluded for vinyl acetate/styrene [121] and hexamethyldisiloxane (HMDSO)/TFE [122]. Moreover,

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Urrita et al. [121] reported that there was no interaction in the respective plasma copolymerization of HMDSO/methyl methacrylate (MMA).

However, the nature of these interactions has not been fully understood. Shirafiji et al. [123, 124] investigated the gas phase plasma of TFE and HMDSO by In-Situ FTIR Spectroscopy. They reported that there was an interaction between the TFE and HMDSO in the plasma, which resulted in formation of  $\text{SiF}_4$ . They concluded that this interaction resulted in a higher decomposition rate of the HMDSO monomer in the plasma. However, they did not observe any  $\text{SiF}_4$  species in the plasma copolymers. Different from that Beck et al. [30] studied the gas phase plasma of styrene and propenoic acid by plasma mass spectrometry. They found that there was little or no interaction between both monomers in the plasma. However, they observed that oxygen and COOR group yield in the copolymers, measured by XPS, were increasing with an increase in the propenoic acid concentration in the feed gas. They concluded that the absence of reactions between two monomers in the plasma gas phase implies that cross-linking reactions between the styrene and propenoic acid monomers and/or oligomers occur only on the surface or in the bulk of the forming plasma polymer.

It seems that the interactions and/or recombination reactions between the monomer molecules in the plasma polymerization process can take place either in the plasma gas phase or during the deposition process. According to XPS analysis of the plasma copolymerization of tetramethyltin and perfluorobenzene, Munro and Till [125] reported that such interactions affect the structure of the plasma deposited copolymer films. These interactions were also found to be dependent on the monomers used [10] and the external plasma parameters employed like plasma power [126], and monomer flow rate [127].

The final conclusion is that the structures of the plasma deposited copolymer films can not be easily anticipated from the structure of the respective plasma homopolymers due to interactions and/or recombination reactions between monomer molecules during their respective plasma copolymerization process. This is monitored also by the fragment pattern in the respective ToF-SSIMS spectra.