

6. In-situ characterization of plasma deposited copolymers

6.1. Introduction

As seen in chapter 5, a considerable control can be exercised over the basic chemical character of the plasma deposited films by the choice of appropriate external plasma parameters like, duty cycle, plasma power and reaction pressure. The chemical properties, that were possible to control to some extent, were the retention of functional groups on the films, the unsaturated character of the films and the cross-linked and branched character of the films. In general, the unsaturated, branched and cross-linked character of the films was found to increase as the duty cycle or power was increased. The increase in these parameters affected the overall energy of the particles in the plasma leading to the decrease in the retention of monomer functionalities and formation of several other functionalities on the surface of the films. Therefore, the duty cycle or plasma power are not ideal variables for controlling the surface concentration of functional groups. However, it was found that a low value of these parameters, i.e. "mild" plasma conditions are effective in obtaining a higher concentration of monomer functionalities e.g. OH groups. To minimize the formation of other functionalities, it would be ideal to deposit plasma polymers at "mild" plasma conditions. At this point another parameter is required such that while operating the plasma at "mild" conditions it is still possible to control the surface concentration of functional groups on the deposited films. Therefore, polymerization of different monomers in one step, i.e. copolymerization of two organic monomers, was developed. One of the comonomers being a "chain extending" hydrocarbon monomer carrying a polymerizable double bond such as ethylene or styrene and another being a functional group carrying monomer such as allyl alcohol or allyl amine. The new external plasma parameter of control is the **partial flow rate (PFR)** of a comonomer in the feed gas. All the other external parameters were kept at "mild" conditions.

This section deals with the XPS and NEXAFS analysis of plasma copolymerized films. The copolymer films studied were:

- (a) The ethylene-allyl alcohol copolymer films,
- (b) The styrene-allyl alcohol copolymer films,
- (c) The ethylene-allylamine copolymer films and
- (d) The styrene-allylamine copolymer films.

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Apart from finding a correlation between the chemical character of the films, such as the extent of functional group retention, unsaturation, branching and cross-linking, with the variation in the PFR of the comonomers, the analysis was also aimed at investigating copolymerization effects. The details of the deposition parameters of the experiments are given in table 3.5 (chapter 3).

6.2. Results and discussion

6.2.1. Characterization of plasma deposited ethylene-allyl alcohol copolymers

XPS characterization: Figure 6.1a shows the C1s photoelectron spectra of three different ethylene-allyl alcohol copolymer films prepared at different conditions. X-Etal1 is prepared at 100% PFR of ethylene, X-Etal2 is prepared at 90% PFR of ethylene and 10% PFR of allyl alcohol and X-Etal6 is prepared at 100% PFR of allyl alcohol. The spectrum of X-Etal2 appears as a superposition of the spectra of X-Etal1 and X-Etal6 pointing to the fact that this spectrum includes contributions from both ethylene as well as allyl alcohol like chemical characters.

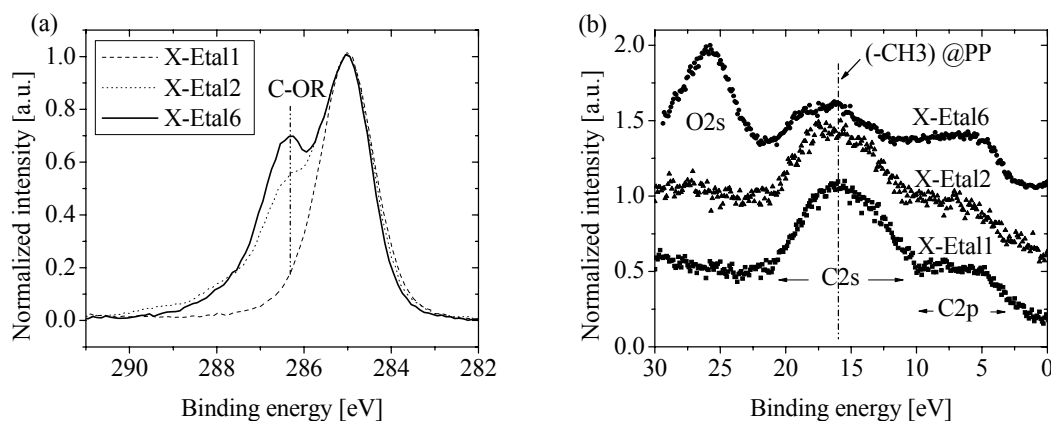


Figure 6.1: XPS vs variation of PFR. (ethylene-allyl alcohol copolymers)(cf. Table 3.5 for deposition parameters). **(a)** XP C1s spectra of X-Etal1 (% PFR of ethylene: 100%), X-Etal2 (% PFR of ethylene: 90%, % PFR of allyl alcohol: 10%) and X-Etal6 (% PFR of allyl alcohol: 100%). **(b)** XPS valence band spectra of X-Etal1, X-Etal2 and X-Etal6.

Figure 6.1b displays the valence band spectra of these copolymer films. The C2s contribution observed in the case of X-Etal1 decreases in intensity with decrease in the PFR of ethylene in the feed gas. As already discussed in section 5.1.1 this C2s feature at binding energy ~ 16 eV is related to branching in the plasma deposited film. A decrease in

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this feature as shown in Figure 6.1b suggests a decreased level of branching in the films. The O2s feature is found to increase with the increase in the PFR of allyl alcohol.

The oxygen surface concentration of the plasma copolymer films was monitored by calculating the O/C atomic ratio (Figure 6.2a) from the XPS survey scan of the films (not shown). The C1s spectra for the copolymer films were individually fitted as already discussed in section 5.2.3 (chapter 5) and the area under the C-OR component curve was compared (Figure 6.2b). As shown in Figure 6.2, with the increase in the PFR of allyl alco-

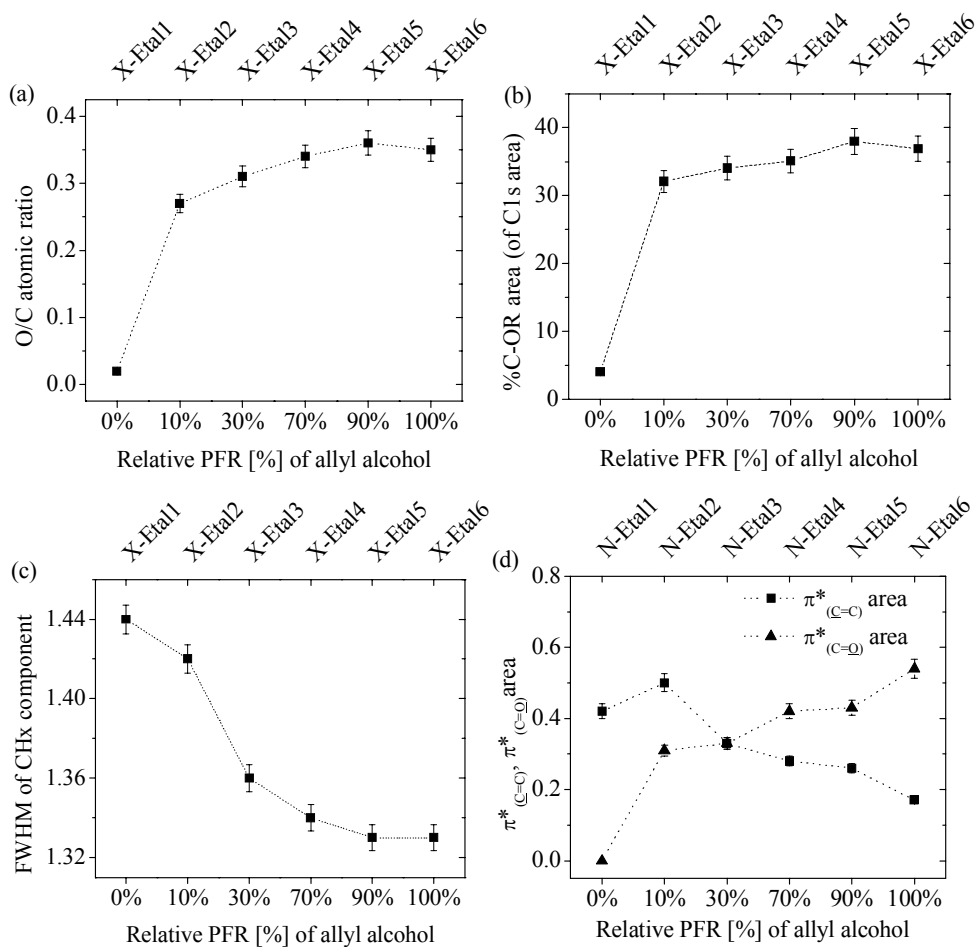


Figure 6.2: XPS and NEXAFS results for ethylene-allyl alcohol copolymer (cf. Table 3.5 for deposition parameters). (a) XPS O/C atomic ratio. (b) C1s percentage area of C-OR component. (c) XP C1s FWHM's of the X-Etal films. (d) NEXAFS C1s $\rightarrow \pi^*_{(C=C)}$ and O1s $\rightarrow \pi^*_{(C=O)}$ resonance area of the N-Etal films.

hol there is an increase in the oxygen surface concentration and the percentage of C-OR area. Since mild plasma conditions were used the majority of the C-OR functionalities is

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assumed to be hydroxyl groups. Both the O/C atomic ratio and the C-OR concentration are found to increase in non-linear way with increase in the PFR of allyl alcohol. The FWHM's of the CH_x component of the fitted XPS C1s spectra of the copolymer films were also monitored (Figure 6.2c). It was found to decrease with decrease in the PFR of ethylene. This once again points to the fact that branching in the copolymer films decreases with decrease in the PFR of ethylene. This result was also verified from the ToF-SIMS analysis of ethylene-allyl alcohol copolymer films [101].

NEXAFS characterization: The extent of unsaturation in the films was studied using NEXAFS spectroscopy as discussed before in chapter 5 (section 5.1.3). The $\text{C}1s \rightarrow \pi^*_{(\text{C}=\text{C})}$ resonance area was found to decrease with a decrease in the PFR of ethylene (Figure 6.2d) while the $\text{O}1s \rightarrow \pi^*_{(\text{C}=\text{O})}$ resonance area was found to increase with an increase in the PFR of allyl alcohol.

Discussion: It can be concluded that a higher PFR of ethylene in the feed gas introduces more unsaturation in terms of C=C bonds, branching and cross-linking while higher PFR of allyl alcohol in the feed gas introduces higher oxygen contents, higher hydroxyl concentrations and unsaturation in terms of C=O bonds. However, as it can be seen from Figure 6.2b the increase in the concentration of OH groups is not linear with the increase in PFR of allyl alcohol. Due to its higher reactivity compared to ethylene after fragmentation [18], allyl alcohol dominates the chemical character of the plasma copolymers. This leads to a higher concentration of hydroxyl groups on the surface of the films. Additionally, it is worth noting that in the case of plasma copolymers the concentration of the C=O bonds is found to be much smaller as compared to the plasma deposited allyl alcohol films and the concentration of C=C bonds is found to be much smaller as compared to plasma deposited ethylene films as shown in chapter 5. It can be argued that there exists a certain copolymerization effect or an interaction between the comonomers, ethylene and allyl alcohol that leads to the formation of films with a lesser degree of unsaturation and a higher degree of retention of hydroxyl functionality, as compared to the films formed by the respective plasma homopolymers.

6.2.2. Characterization of plasma deposited styrene-allyl alcohol copolymers

XPS characterization: Figure 6.3a shows a representative C1s photoelectron spectrum of a plasma deposited styrene-allyl alcohol copolymer film (X-Stal4). This spectrum was fitted with component curves as earlier discussed in section 5.1.2. The valence band spectra of three different copolymer films are shown in Figure 6.3b. X-Stal1 is prepared at 100% PFR of styrene, X-Stal4 is prepared at 10% PFR of styrene and 90% PFR of allyl alcohol and X-Stal5 is prepared at 100% PFR of allyl alcohol.

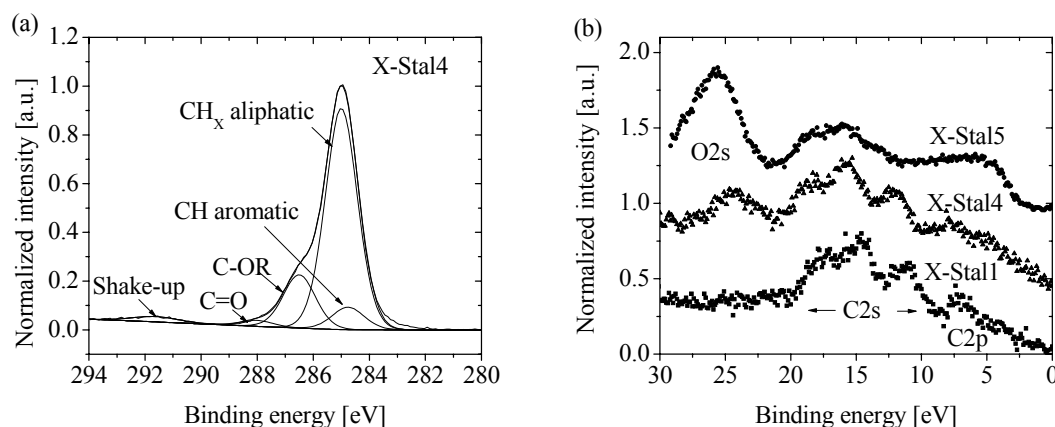


Figure 6.3: XPS of styrene-allyl alcohol copolymer films (cf. Table 3.5 for deposition parameters). **(a)** XP C1s spectra of X-Stal4 (%PFR of styrene: 10%, %PFR of allyl alcohol: 90%). **(b)** XPS valence band spectra of X-Stal1 (%PFR of styrene: 100%), X-Stal4 (%PFR of styrene: 10%, %PFR of allyl alcohol: 90%) and X-Stal5 (%PFR of allyl alcohol: 100%).

The area under the C-OR component curve of the C1s spectra was found to increase vs PFR of allyl alcohol (Figure 6.4a). This increase was sharp after the percentage of allyl alcohol in the feed gas was more than 50%. The increase in the C-OR component area was found to follow the trend in the change in the XPS O/C atomic ratio of the copolymer film surface. It increased with the increase in the PFR of allyl alcohol as shown in Figure 6.4b. This increase in the oxygen surface concentration of the films can also be observed in the valence band spectra (Figure 6.3b). The presence of a O2s feature increases in intensity from X-Stal4 to X-Stal5. The shake-up area observed in the C1s spectra, reflects the aromatic character of the deposited films and was found to decrease with decrease in the PFR of styrene (Figure 6.4c).

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NEXAFS characterization: The extent of unsaturation in terms of aromatic character as well as the presence of C=C or C=O bonds was monitored by using NEXAFS spectroscopy. Figure 6.5a and b show the C K-edges and the O K-edges of the plasma deposited copolymer films. The area under the $C1s \rightarrow \pi^*_{(C=C)}$ or $C1s \rightarrow \pi^*_{(ring)}$ resonance decreases with decrease in the PFR of styrene (Figure 6.6a). The energy difference between these resonances is small (0.3 eV) and therefore it is not possible to differentiate these two resonances in the spectrum. The decrease in the total area of these resonances

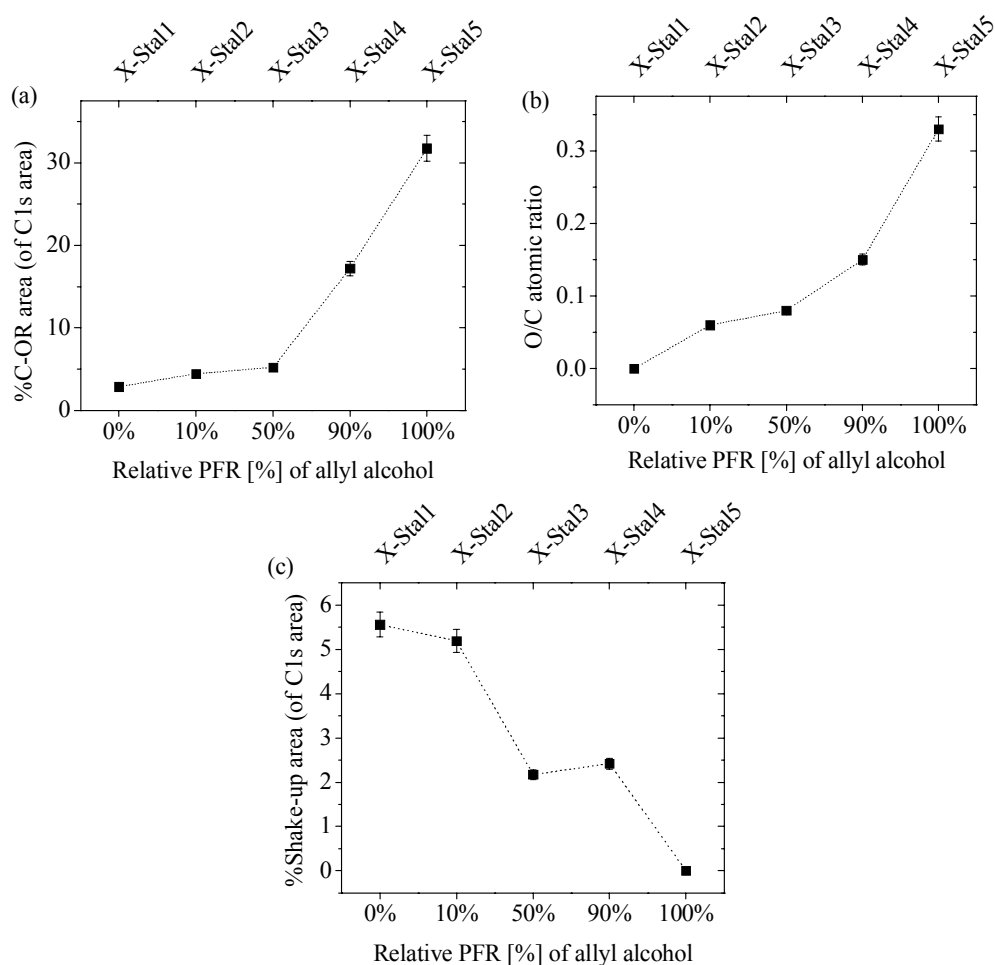


Figure 6.4: XPS of styrene-allyl alcohol copolymer films (cf. Table 3.5 for deposition parameters). **(a)** Percentage area of C-OR component in the XPS C1s spectra. **(b)** XPS O/C atomic ratio. **(c)** Percentage area of the shake-up component in the C1s spectra of the X-Stal films.

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indicates an overall decrease in unsaturation in the films with the decrease in the PFR of styrene. On the other hand, the area under the $O1s \rightarrow \pi^*_{(C=O)}$ resonance increased with increase in the PFR of allyl alcohol (Figure 6.6b) indicating an increased unsaturation with increase in the PFR of allyl alcohol in terms of formation of $C=O$ bonds.

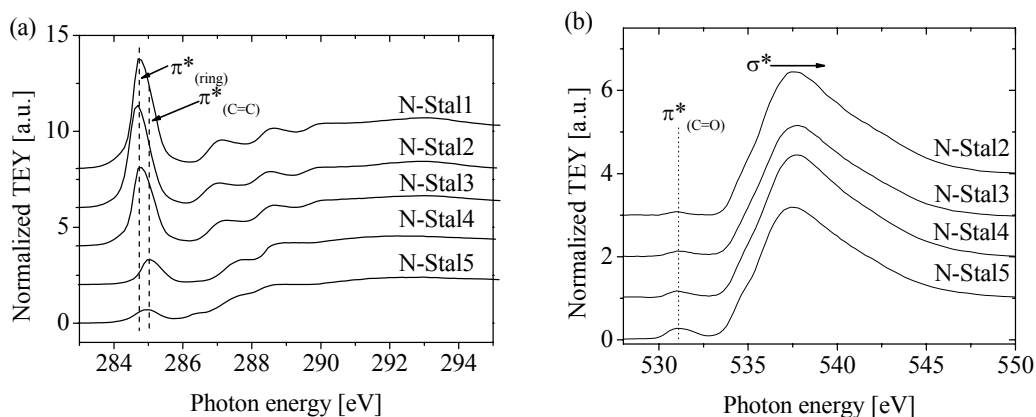


Figure 6.5: NEXAFS of styrene-allyl alcohol copolymer films (cf. Table 3.5 for deposition parameters). N-Stal1: 0% PFR of allyl alcohol, N-Stal2: 10% PFR of allyl alcohol, N-Stal3: 50% PFR of allyl alcohol, N-Stal4: 90% PFR of allyl alcohol, N-Stal5: 100% PFR of allyl alcohol (a) C K-edge (b) O K-edge of N-Stal copolymer films.

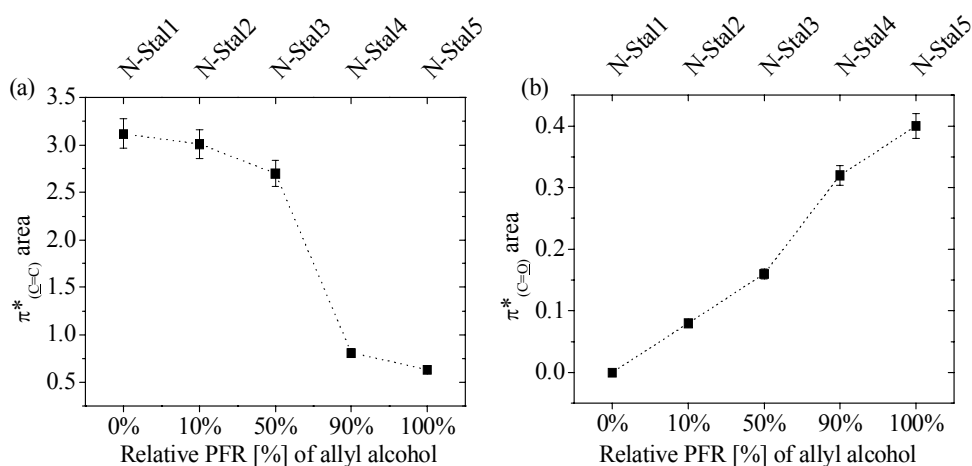


Figure 6.6: NEXAFS results of styrene-allyl alcohol copolymer films (cf. Table 3.5 for deposition parameters). (a) NEXAFS $C1s \rightarrow \pi^*_{(C=C)}$ resonance area (b) NEXAFS $O1s \rightarrow \pi^*_{(C=O)}$ resonance area of N-Stal films

Discussion: It can be concluded that the aromatic character and the unsaturation in terms of C=C bonds was found to decrease systematically with the decrease in the PFR of styrene. The unsaturation due to C=O species increased with increase in the surface concentration of oxygen in the feed gas as the PFR of allyl alcohol in the feed gas is increased. A high PFR of allyl alcohol also leads to a higher concentration of hydroxyl groups in the films. In this case it was found that there was a sharp increase in the XP C1s C-OR after the percentage of allyl alcohol in the feed gas was more than 50%. In this case allyl alcohol takes over the chemical character at a higher PFR than in the case of ethylene-allyl alcohol copolymer. This is primarily due to different interaction or copolymerization effects arising from a higher reactivity [18] and deposition rate [118] of styrene compared to allyl alcohol.

6.2.3. Characterization of plasma deposited ethylene-allylamine copolymers

XPS characterization: Figure 6.7a gives the fitted XP C1s spectrum of a representative ethylene-allyl amine copolymer (X-Etam3). As discussed earlier in chapter 5, due to the superposition of various species in the C1s spectra, it could not be used for the discussion of a retention of the primary amines on the films. However, the survey scan can be used to

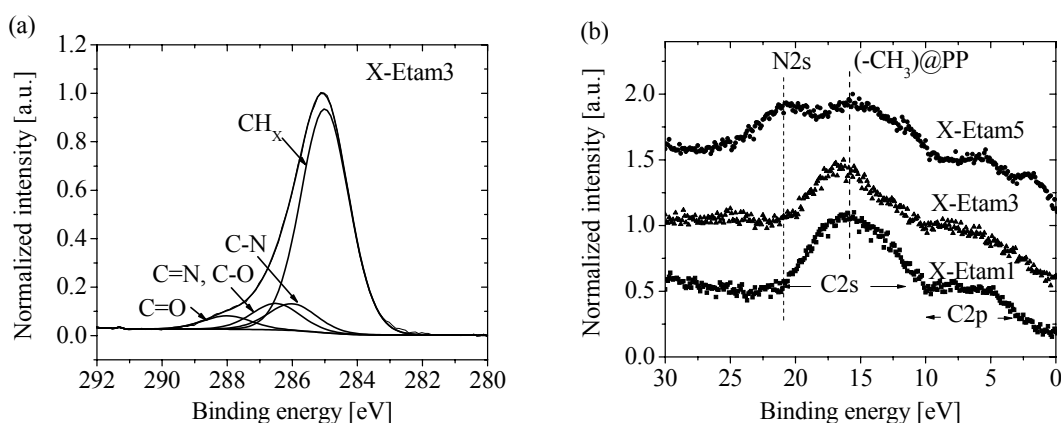


Figure 6.7: XPS of ethylene-allylamine copolymer films (cf. Table 3.5 for deposition parameters). **(a)** XP C1s spectra of X-Etam3 (PFR of ethylene: 50%, PFR of allylamine: 50%) **(b)** XPS valence band spectra of X-Etam1 (PFR of ethylene: 100%), X-Etam3 (PFR of ethylene: 50%, PFR of allylamine: 50%) and X-Etam5 (PFR of allylamine: 100%).

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obtain information about the surface concentration of nitrogen in the films by calculating the N/C atomic ratio and the variation in the N1s FWHM can be used to obtain information regarding the multiplicity of species. Additionally information regarding the branching can be obtained from the valence band spectrum. Figure 6.7b displays the valence band spectra of X-Etam1 (100% PFR of ethylene), X-Etam3 (50% PFR of ethylene, 50% PFR of allyl amine) and X-Etam5 (100% PFR of allyl amine). The $(-\text{CH}_3)\text{C}_2\text{s}$ feature observed in the case of X-Etam1 decreases in intensity with decrease in the PFR of ethylene. The decrease in this feature hints a decreased branching in the deposited films. This was also verified by ToF-SIMS studies [101].

Figure 6.8a gives the variation in the N1s FWHM of the copolymer films. A higher multiplicity of species can be concluded in films with higher PFR of ethylene. On the other hand an increase in nitrogen content can be concluded from the increase in N/C atomic ratio (Figure 6.8b) with an increase in the PFR of allylamine.

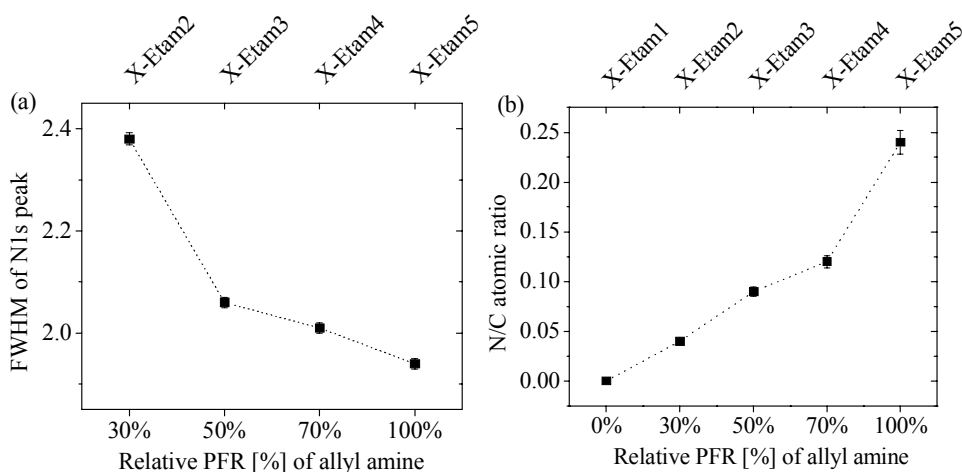


Figure 6.8: XPS results of ethylene-allyl amine copolymer films (cf. Table 3.5 for deposition parameters). (a) XP N1s FWHM's (b) XPS N/C atomic ratio of the X-Etam films.

NEXAFS characterization: To investigate the unsaturated character of the films NEXAFS C K-edge and N K-edge spectra of the samples were studied. Figure 6.9a displays the C K-edge of the different copolymer films. The various features of these spectra are discussed in chapter 5 (section 5.1.4). There is a broadening in the energy range of resonances $\text{C}1\text{s} \rightarrow \pi^*_{(\text{C}=\text{C})}$ and $\text{C}1\text{s} \rightarrow \pi^*_{(\text{C}=\text{N})}$ with increase in the PFR of allylamine

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indicating superimposed peaks arising due to unsaturated species like C=C or C=N. While the resonance $C1s \rightarrow \pi^*_{(C=C)}$ was found to be prominent in spectra with high PFR of ethylene, the resonance $C1s \rightarrow \pi^*_{(C=N)}$ was completely absent. Additionally the C-H* resonance can only be observed in N-Etam1. However, these spectra did not provide any useful semi-quantitative information.

The $N1s \rightarrow \pi^*_{(C=N)}$ and $N1s \rightarrow \pi^*_{(C \equiv N)}$ resonance features in the N K-edge spectra of the copolymer films (Figure 6.9b) were more specific compared to the features of C K-edge. As in the case of allylamine homopolymers the sum of maximum intensities of these

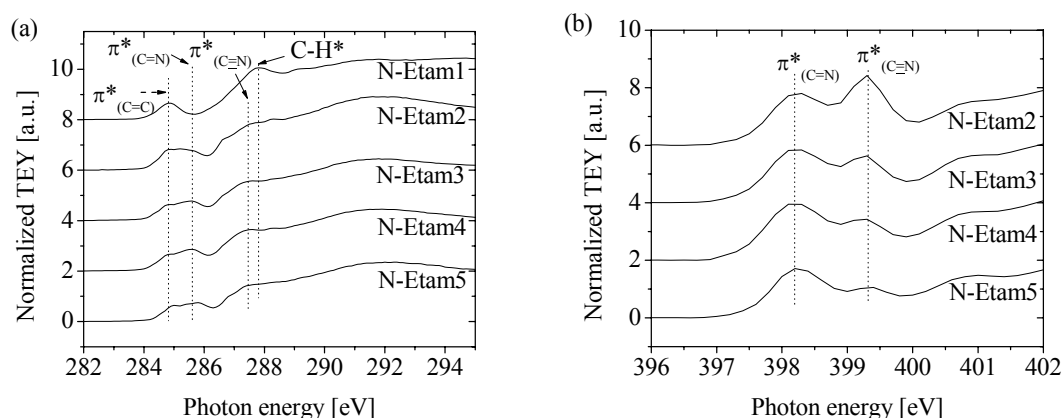


Figure 6.9: NEXAFS of ethylene-allylamine copolymer films (cf. Table 3.5 for deposition parameters). N-Etam1: 0% PFR of allylamine, N-Etam2: 30% PFR of allylamine, N-Etam3: 50% PFR of allylamine, N-Etam4: 70% PFR of allylamine, N-Etam5: 100% PFR of allylamine. **(a)** NEXAFS C K-edge. **(b)** NEXAFS N K-edge of N-Etam films.

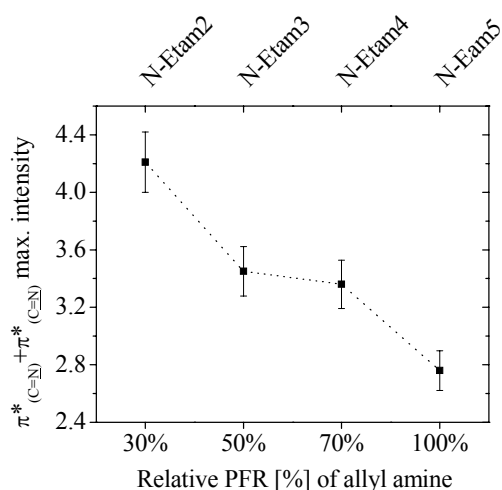


Figure 6.10: NEXAFS results of ethylene-allylamine copolymer films (cf. Table 3.5 for deposition parameters). Sum of NEXAFS $N1s \rightarrow \pi^*_{(C=N)}$ resonance and $N1s \rightarrow \pi^*_{(C \equiv N)}$ resonance maximum intensities.

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two features are used to investigate the overall unsaturated character of the plasma deposited ethylene-allylamine copolymer films. Figure 6.10 indicates a decrease in the overall unsaturated character of the films with decrease in the PFR of ethylene. It is also observed from Figure 6.9b that the maximum intensity of the $N1s \rightarrow \pi^*_{(C \equiv N)}$ resonance is higher in the case of films deposited at low PFR of allylamine. This intensity is found to decrease with an increase in the PFR of allylamine. It is also obvious that ethylene promotes the formation of $C \equiv N$ species.

Discussion: It can be concluded that a higher PFR of ethylene introduces a higher unsaturation and branching in the copolymer films while a higher PFR of allylamine introduces a higher nitrogen surface concentration. Similar to the case of the plasma deposited allylamine homopolymers films, indirect evidence was used to obtain conditions favorable for a high surface concentration of amine groups on the surface of the films. It is argued that a low surface concentration of nitriles and imines and a low degree of cross-linking on the surface of the deposited films are indications of a high concentration of amine groups on the film. Similar to the ethylene-allyl alcohol copolymer films, the unsaturation of the ethylene-allylamine copolymer films, in terms of the presence of $C=N$ and $C \equiv N$ was found to decrease with the decrease in the PFR of ethylene. Additionally there was an increase in the nitrogen surface concentration of the copolymer films with the increase in the PFR of allylamine. These factors indirectly imply a higher surface concentration of amine groups in the samples deposited at high PFR of allyl amine. The decrease in the PFR of ethylene also leads to a decrease in multiplicity of species and the branched and cross-linked character of the films. It was observed that there was relatively small variation in the concentration of $C=N$ bonds compared to $C \equiv N$ bonds (Figure 6.9b). This is attributed to the plasma chemical mechanism suggested in chapter 5 (Figure 5.15), that explains the formation of nitriles with imines as intermediates. Moreover, the changes observed in the extent of unsaturation, nitrogen surface concentration and multiplicity of species were found to be linear without any abrupt changes indicating the lack of any copolymerization effect.

6.2.4. Characterization of plasma deposited styrene-allylamine copolymers.

XPS characterization: Figure 6.11a shows a representative $C1s$ photoelectron spectrum of a plasma deposited styrene-allylamine copolymer (X-Stam3). This spectrum was fitted

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with component curves as discussed in section 5.1.2. As already discussed this spectrum cannot be used to estimate the amine content of the films. However, the shake-up area in the C1s spectra is used to investigate the aromatic character of the deposited films. Additionally, the survey scan (not shown here) can be used to obtain information about the nitrogen surface concentration of the films by calculating the N/C atomic ratio and the variation in the N1s FWHM can be used to obtain information about the multiplicity of species in the films. Figure 6.11b displays the valence band spectra of X-Stam1 (100% PFR of Styrene), X-Stam3 (70% PFR of Styrene and 30% PFR of allylamine) and X-Stam6 (100% PFR of allylamine). The characteristic polystyrene $(-\text{CH}_3)\text{C}2\text{s}$ features observed in the case of X-Stam1 decrease in intensity and are broadened with decrease in the PFR of styrene. The broadening of this feature reflects the contributions from both the monomers.

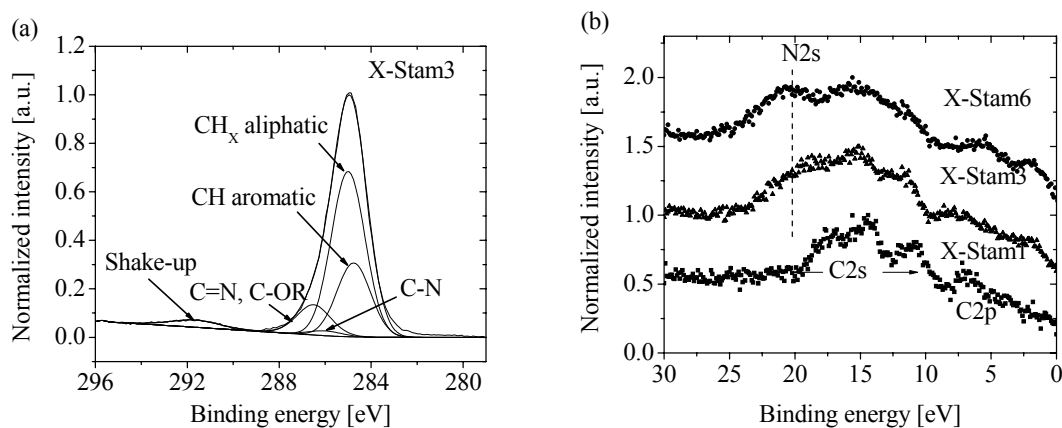


Figure 6.11: XPS of styrene-allylamine copolymer films (cf. Table 3.5 for deposition parameters). **(a)** XP C1s spectra of X-Stam3 (%PFR of styrene: 70%, %PFR of allylamine: 30%). **(b)** XPS valence band spectra of X-Stam1 (%PFR of styrene: 100%), X-Stam3 (%PFR of styrene: 70%, %PFR of allylamine: 30%) and X-Stam6 (%PFR of allylamine: 100%).

Figure 6.12a displays the N/C atomic ratio of the films. An increase in this ratio is observed with an increase in the PFR of allylamine. On the other hand Figure 6.12b shows a decrease in the N1s FWHM of the films with increase in the PFR of allylamine, indicating a decrease in the multiplicity of species and branched and cross-linked character of the films. This was also supported by a separate ToF-SIMS investigation of styrene-allylamine copolymer films [101]. The aromatic character of the films, monitored by the shake-up area of the XP C1s spectra, was found to decrease with the decrease in the PFR of styrene (Figure 6.12c).

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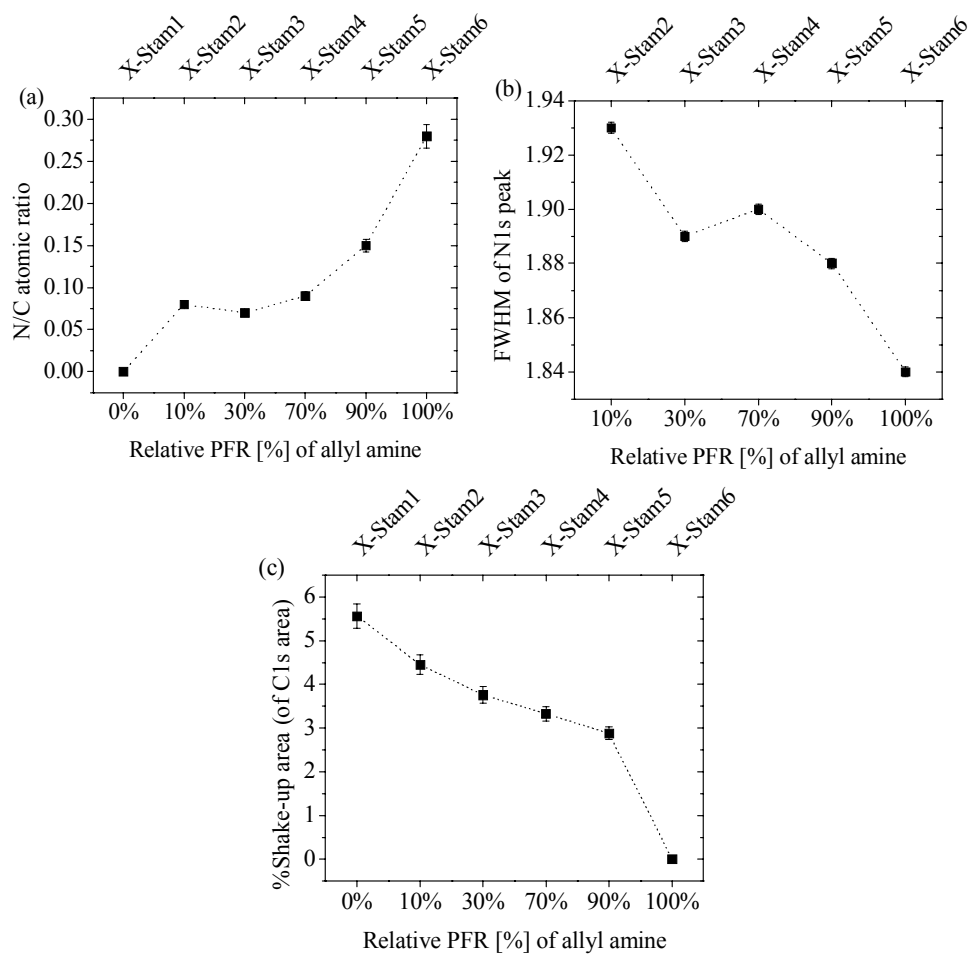


Figure 6.12: XPS results of styrene-allylamine copolymer films (cf. Table 3.5 for deposition parameters). **(a)** XPS N/C atomic ratio. **(b)** XP N1s FWHM's. **(c)** Percentage area of the shake-up component of the C1s spectra of the X-Stam copolymer films.

NEXAFS characterization: The NEXAFS C and N K-edges of these films were also investigated (Figure 6.13). The features of the C and N-K-edge spectra (Figure 6.13a & b) are already discussed in the respective homopolymers cases.

The area under the resonance $C1s \rightarrow \pi^*_{ring}$ (C K-edge), plotted in Figure 6.14a, is found to decrease with the decrease in the PFR of styrene. This indicates a decrease in the overall unsaturation of the deposited films. However, in the case of N K-edge the unsaturation (sum of $N1s \rightarrow \pi^*_{(C=N)}$ and $N1s \rightarrow \pi^*_{(C=N)}$ resonance maximum intensities) first increased with the increase in the PFR of allylamine and then decreased (Figure 6.14b).

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The increase was observed as long as there was a sufficient styrene concentration in the feed gas (up to 30% PFR) and then found to decrease.

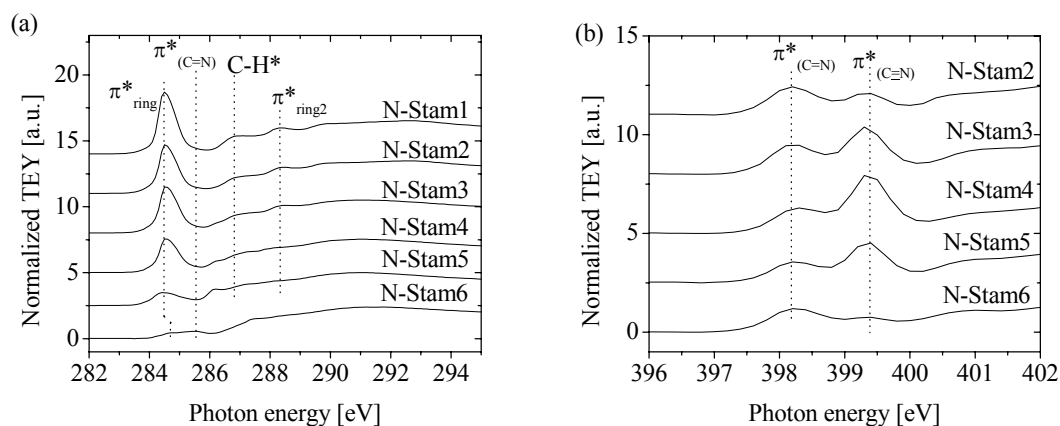


Figure 6.13: NEXAFS of styrene-allylamine copolymer film (cf. Table 3.5 for deposition parameters). N-Stam1: 0% PFR of allylamine, N-Stam2: 10% PFR of allylamine, N-Stam3: 30% PFR of allylamine, N-Stam4: 70% PFR of allylamine, N-Stam5: 90% PFR of allylamine, N-Stam6: 100% PFR of allylamine. **(a)** NEXAFS C K-edge spectra **(b)** NEXAFS N K-edge spectra of N-Stam films.

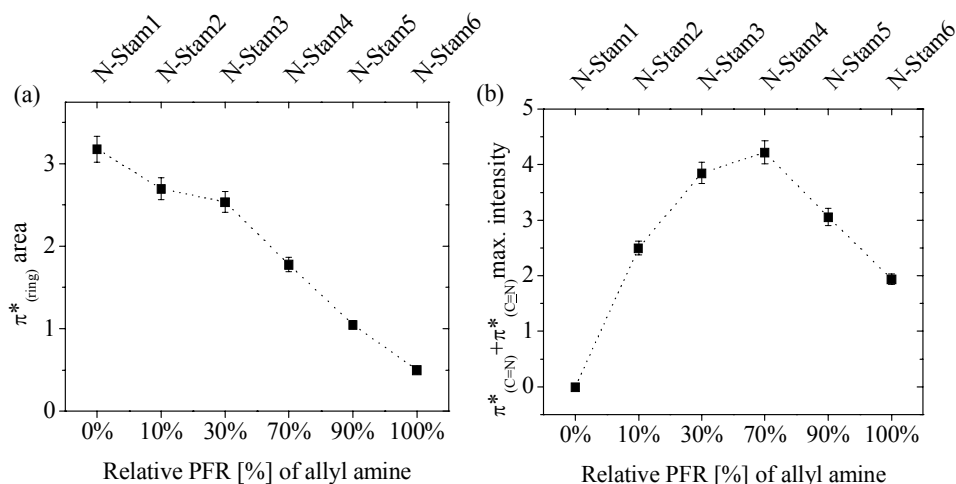


Figure 6.14: NEXAFS results of styrene-allylamine copolymer film (cf. Table 3.5 for deposition parameters). **(a)** NEXAFS C1s \rightarrow π^* resonance area. **(b)** Sum of NEXAFS N1s \rightarrow π^* _(C=N) and N1s \rightarrow π^* _(C≡N) resonance maximum intensities of N-Stam films.

Discussion: In the case of styrene-allylamine copolymer the nitrogen surface concentration of the films was found to increase with increase in the PFR of allylamine. The aromatic

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content of the films decreased with the decrease in the PFR of styrene. However, the variation in the unsaturation in terms of the $C\equiv N$ and $C=N$ bonds was not linear as observed in the case of ethylene-allylamine copolymers films. Styrene along with a sufficient concentration of allylamine favors the formation of unsaturated CN bonds such as nitriles and imines. This leads to the increase in unsaturation till the % PFR of allylamine was 70% as shown in Figure 6.14b. This increase in the extent of unsaturation does not continue further because there is insufficient styrene to favor the formation of unsaturated CN bonds. This result implies a higher level of unsaturation in the copolymer films as compared to the respective homopolymers. The difference in the behavior of plasma deposited styrene-allylamine and ethylene-allylamine copolymer films arises mainly due to the difference in the chemical reactivity of the "chain extending" monomer and also the difference in the mutual "interactions" or the copolymerization effects of the comonomers.

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

Plasma deposited films of ethylene-allyl alcohol, styrene-allyl alcohol, ethylene-allylamine and styrene-allylamine were prepared and analyzed without exposure to air by XPS and NEXAFS. The films were deposited under "mild" plasma conditions and the composition of the feed gas was varied systematically.

It was observed that a considerable control could be exercised on the chemical nature of the copolymer films by the variation in the partial flow rates (PFR) of the comonomers. The chemical aspects of the deposited films that could be controlled were, the density of functional groups, the unsaturation, branching and cross-linking. In general these aspects of the deposited films were not found to vary linearly with respect to the variation in the partial flow rates of the comonomers but were found to depend also on the nature of the monomers involved and the anticipated interactions between them in the plasma phase.

Similar results were also reported by Friedrich et al. when they studied copolymer films of ethylene-allyl alcohol and butadiene-allyl alcohol by IR and XPS analysis [8, 18, 31]. It is argued that under "mild" plasma conditions employed such as in this study, the reactivity of each monomer i.e. the ability of polymerization becomes important because the conventional radical polymerization in the gas phase seems to define the film chemistry during plasma-off periods. Table 6.1 gives the anticipated relative reactivities of the

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monomers used in this study in radical gas phase polymerization during the plasma-off period in a pulsed plasma polymerization.

Table 6.1: Relative reactivity of monomers in radical gas phase polymerization during the plasma-off period in a pulsed plasma polymerization (adapted from ref [18]).

Monomer	Reactivity
Ethylene	Low
Styrene	High
Allyl alcohol	Moderate
Allylamine	Moderate

Several studies have been reported wherein interactions between comonomer molecules have been observed. Golub et al. [119] investigated the plasma copolymerization of ethylene and tetrafluoroethylene by IR spectroscopy. They observed that the rates of plasma copolymer deposition for all compositions of the feed gas exceeded those expected on the basis of a non-interaction between those monomers. This interaction was termed as a "positive" or productive interaction. On the basis of deposition rates, "negative" interactions between comonomer molecules such as vinyl acetate/styrene [120] and hexamethyldisiloxane/tetrafluoroethylene [121] have also been reported. For the copolymers investigated in this study, a similar "positive" interaction can be stated in the case of ethylene-allyl alcohol copolymers on the basis of surface concentration of hydroxyl groups, C=C and C=O bonds. A "negative" interaction can also be stated in the case of styrene-allylamine copolymer films where a higher unsaturation was observed as compared to the unsaturation in the respective homopolymers films. The nature of these interactions has not been fully understood, even though it has been shown that these interactions play an important role either in the plasma gas phase [122], or during the deposition process [123]. These interactions were also found to be dependent on external plasma parameters such as plasma power [124] and monomer flow rate [125].

It can be concluded that a detailed knowledge of the chemical reactivity of the comonomers may lead to a better control of copolymer film properties. However, at the given level of understanding it was already possible to control the chemical character of the copolymer films to a large extent as shown in this study. Table 6.2 summarizes the effects of the comonomers on the chemical character of the deposited films.

6. In-situ characterization of plasma deposited copolymers

Table 6.2: Summary of the effect of the comonomers on the chemical character of the plasma deposited copolymer films.

Copolymer	Monomer 1	Monomer 2	Effects of monomer 1	Effects of monomer 2
Ethylene-Allyl alcohol	Ethylene	Allyl alcohol	<ul style="list-style-type: none"> • Promotes branching, cross-linking • Promotes C=C bonds 	<ul style="list-style-type: none"> • Promotes oxygen surface concentration • Promotes C-OR species • Promotes C=O bonds
Styrene-Allyl alcohol	Styrene	Allyl alcohol	<ul style="list-style-type: none"> • Promotes aromatic rings. 	<ul style="list-style-type: none"> • Promotes oxygen surface concentration • Promotes C=O bonds
Ethylene-Allylamine	Ethylene	Allylamine	<ul style="list-style-type: none"> • Promotes branching, cross-linking • Promotes unsaturation in terms of CN bonds. 	<ul style="list-style-type: none"> • Promotes nitrogen surface concentration
Styrene-Allylamine	Styrene	Allylamine	<ul style="list-style-type: none"> • Promotes surface concentration of aromatic rings • Favors the formation of nitriles and imines 	<ul style="list-style-type: none"> • Promotes nitrogen surface concentration