

5. In-situ characterization of plasma deposited homopolymers

5.1. Introduction

This chapter explores the relationship between the basic chemical character of plasma deposited homopolymer films and the external plasma parameters, plasma power, duty cycle and reaction pressure. Each of these parameters was studied individually while keeping the other parameters constant. The deposited samples were analyzed "in-situ" or in other words without exposure to air. Analysis of samples after exposure to air was also a part of this study and is discussed in detail in chapter 7.

As discussed earlier in chapter 3, experiments were performed separately for XPS and NEXAFS analysis. Detailed analysis for each sample was done. Only selected spectra are shown in this chapter to describe the features investigated. The results are mainly presented in the form of comprehensive charts and plots.

5.2. Results and discussion

5.2.1. Plasma deposited ethylene films

Table 3.1 (chapter 3) gives the details of the deposition process used for preparing the samples of plasma deposited ethylene for XPS and NEXAFS characterization.

XPS characterization: A typical XP survey scan of a representative plasma deposited ethylene film (X-PDE2) is shown in Figure 5.1a. Since the measurement was done "in-situ" only carbon signal was detected which includes the C1s signal and the Auger peak.

Figure 5.1b displays the C1s photoemission spectra of the polyethylene reference, and a representative plasma deposited ethylene sample (X-PDE2). The absence of a shake-up feature in these C1s spectra points to the fact that the surface concentration of carbon-carbon double bonds is below the detection limit of XPS. The figure shows the broadening in the plasma deposited ethylene samples compared to the polyethylene reference sample. This broadening arises due to the coexistence of several chemical species as well as radicals which lie close in binding energy. The binding energies vary by small amounts, when for instance, a carbon atom is linked to more than two carbon atoms, or in other words the carbon atoms are branched or cross-linked. The FWHM of the C1s spectrum of several polymers as found in literature [97] supports this argument. For example, the C1s FWHM of polymers with increasing extent of branching, i.e. polyethylene, polypropylene and polyisobutylene was found to increase as 0.87, 0.90, 1.01 eV respectively. Therefore,

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the broadening of the C1s spectra is used in this study to probe the extent of branching and cross-linking in the plasma deposited ethylene films. Evidence of branching in the plasma deposited ethylene films can also be observed in the valence band spectra of these films. The valence band spectra of a representative plasma deposited sample (X-PDE2) along with those of the polyethylene ($-\text{[CH}_2\text{-CH}_2\text{]}_n-$) and polypropylene ($-\text{[CH}_2\text{-CH(CH}_3\text{)]}_n-$) references (Figure 5.1c) shows features attributed to the C2s and C2p photoemission [97]. Relying on the binding energy of the $-\text{CH}_3$ related C2s feature measured with the polypropylene reference sample the intense and broad feature in the valence bands of the plasma deposited ethylene samples occurring at around 16 eV can be interpreted to be related to a substantial branching in the plasma deposited samples. The assumption of a branched and cross-linked structure for a plasma deposited film is also validated by a different study of such films by ToF-SSIMS [101].

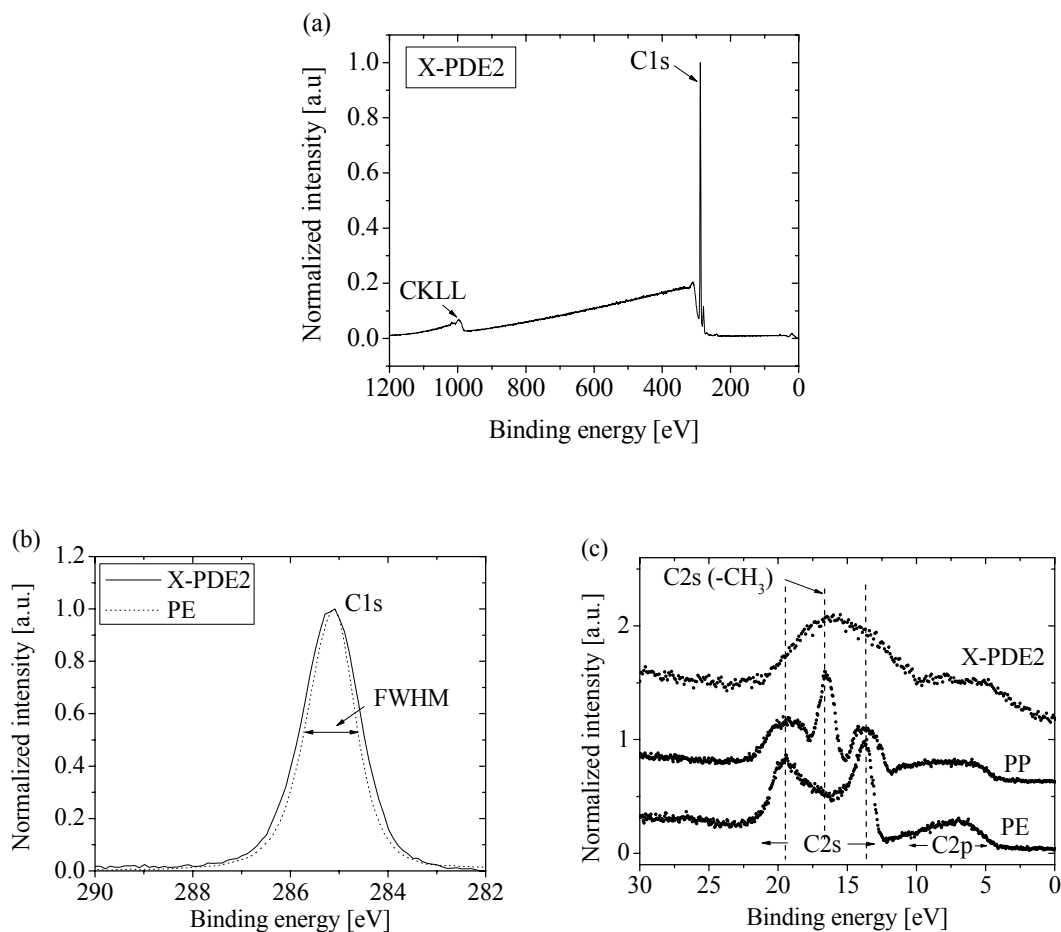


Figure 5.1: XPS of reference and plasma deposited ethylene films (cf. Table 3.1 for deposition parameters). **(a)** XP survey scan of a plasma deposited ethylene film X-PDE2 (20 W, 0.25 duty cycle, 5 Pa, 20 sccm). **(b)** XP C1s spectra of X-PDE2 and a polyethylene (PE) reference. **(c)** XPS valence band spectra of X-PDE2, polyethylene (PE) and polypropylene (PP)[97].

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NEXAFS characterization: Figure 5.2 gives the C K-edge NEXAFS spectra of a polyethylene (PE) reference, a polypropylene (PP) reference, obtained by O. Dhez et al. [102] and a representative plasma deposited ethylene sample (N-PDE1). The principal features seen in the displayed spectrum of the N-PDE1 sample, i.e. a $C1s \rightarrow \pi^*_{(C=C)}$ resonance at 284.8 eV (A), minor shoulder at 286.7 eV (B) possibly due to carbonyl species, a peak at 287.7 eV discussed to represent a $C-H^*$ resonance [102] (C) and different $C1s \rightarrow \sigma^*$ resonances above 292 eV, are representative for all the other plasma deposited samples. As to be expected, the spectra of the references do not show a $C1s \rightarrow \pi^*_{(C=C)}$ resonance because they do not contain any $C=C$ bonds. The splitting of the $C-H^*$ resonance as seen in the PE spectrum is described in the literature for well-defined linear alkane chains [103]. This splitting is absent in the case of polypropylene due to the presence of a methyl group. It is also absent in the plasma deposited ethylene films because they are expected to be branched and cross-linked. The areas under the $C1s \rightarrow \pi^*_{(C=C)}$ reson-

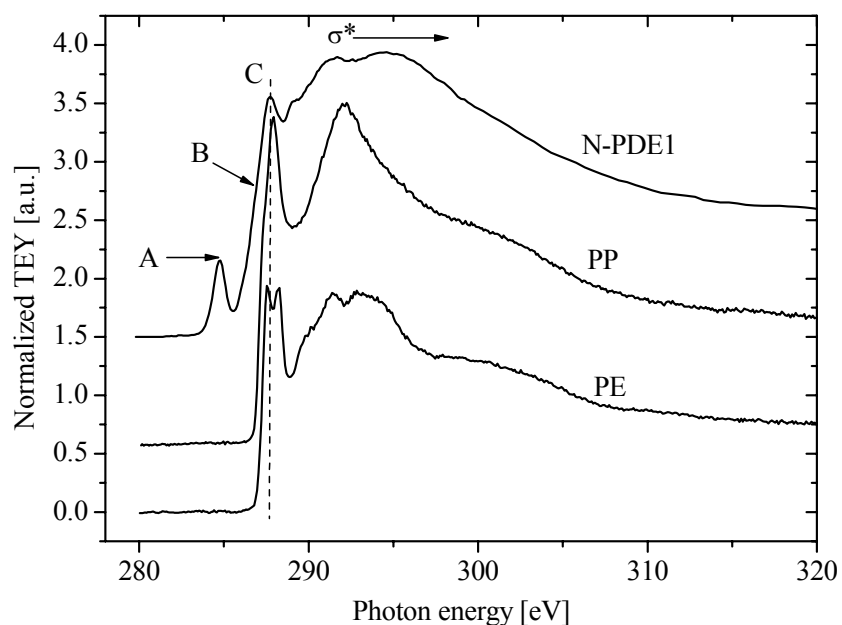


Figure 5.2: NEXAFS C K-edge spectrum of plasma deposited ethylene film N-PDE1 (10 W, 0.1 duty cycle, 5 Pa, 20 sccm) along with polypropylene (PP) and polyethylene (PE) reference spectra [102].

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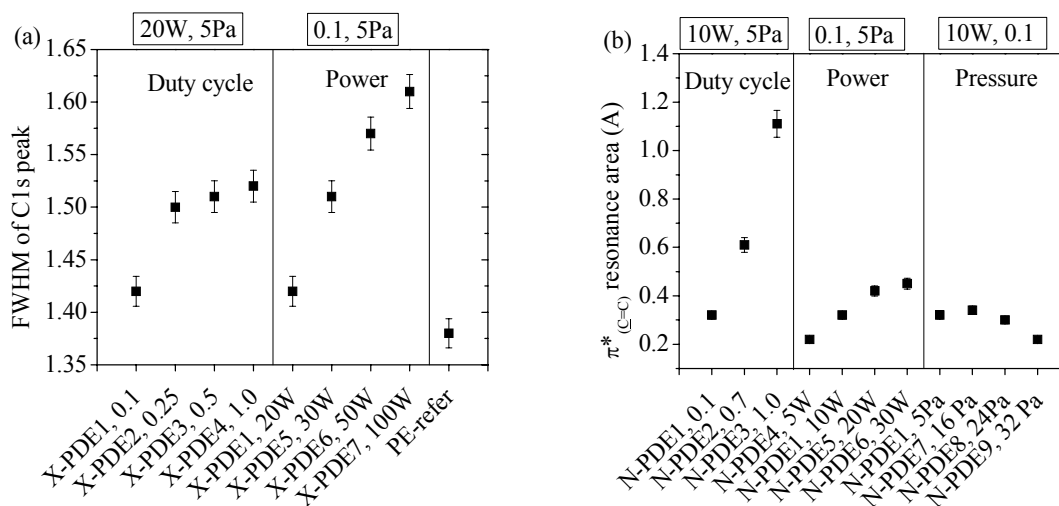


Figure 5.3: XPS and NEXAFS results of plasma deposited ethylene films (cf. Table 3.1 for deposition parameters). **(a)** XP C1s FWHM's of the plasma deposited ethylene (X-PDE) films. **(b)** NEXAFS C1s→π*(C=C) resonance area in the C K-edge spectra of the plasma deposited ethylene (N-PDE) films. Boxes on the top of the figures gives the constraints of the deposition conditions.

ance in the NEXAFS C K-edge spectra of the plasma deposited films prepared under different plasma conditions provides a highly sensitive and specific semi-quantitative measure of the extent of unsaturation in terms of presence of C=C bonds. NEXAFS is obviously much more sensitive compared to XPS in probing the presence of C=C bonds. The low sensitivity of XPS to C=C bonds is also obvious from the C1s spectrum of poly(*cis*-butadiene) [21]. Although 50% of the carbon atoms of poly(*cis*-butadiene) are involved in double bonds, the percentage of the shake-up area of the total C1s area was found to be less than 2.5%.

Results: Figure 5.3a shows the total FWHM of the C1s photoelectron peak for the X-PDE samples. Increase in duty cycle or plasma power, i.e. increase in energy per monomer molecule, provides an increase in the FWHM implying an increase in the branched and cross-linked character of the films. This is expected since a higher degree of monomer fragmentation and subsequent partial recombination of the fragments usually leads to a branched and cross-linked structure. Increase in monomer pressure from 2 Pa to 15 Pa did not show any change in the FWHM of the respective C1s spectra (not shown in Figure 5.3a). Figure 5.3b shows the C1s→π*(C=C) resonance area in the C K-edge spectra for all the N-PDE samples. Increase in duty cycle and power both clearly indicate an increase in

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the concentration of C=C bonds, i.e. the unsaturation of the plasma deposited ethylene films. This is mainly due to newly formed C=C bonds rather than the bonds retained from the monomer molecules. The new C=C bonds are formed due to a higher fragmentation of the monomer molecules and subsequent recombination. An increase in the monomer pressure shows a slight decrease in the concentration of C=C bonds. The increase in monomer pressure leads to a decrease in electron energy resulting in a lower degree of fragmentation and recombination of monomer molecules.

It can be concluded that a higher duty cycle or power employed during deposition of plasma deposited ethylene films leads to a more unsaturated, cross-linked and branched chemical structure. High monomer pressure during deposition was found to introduce a low degree of unsaturation in the films.

5.2.2. Plasma deposited styrene films

Table 3.2 (chapter 3) gives the details of the deposition process used for preparing the plasma deposited styrene samples.

XPS characterization: Figure 5.4a shows a selected XP survey scan of a plasma deposited styrene film (X-PDS2) prepared at “mild” plasma conditions. Along with carbon, traces of oxygen were also detected. The source of oxygen is the anti-polymerizing agent (2,6-di-*tert*-4-methylphenol) present in the styrene monomer. Figures 5.4b & c show the C1s spectra of X-PDS2 and a reference polystyrene (PS-refer) sample, respectively. The similarity in both these spectra is striking and points to the fact that the plasma deposited styrene films have a chemical character very similar to conventionally polymerized polystyrene. A prominent π - π^* shake-up feature is also observed in these C1s spectra which arises due to the presence of aromatic species in the film. As shown, these C1s spectra are first fitted with a background and then fitted with various component peaks representing different species fixed at different energies following the data recommended by Beamsom and Briggs [97] (see caption of Figure 5.4b). The energy positions of the peaks (except the π - π^* shake-up feature) were fixed relative to the “CH aromatic” feature. It is worth mentioning at this point that due to large fitting errors of the component curves “CH aromatic” and “CH_x aliphatic”, the relative areas under these curves could not be used to estimate the aromatic content of the deposited polymers. These fitting errors arise mainly due to a very small binding energy difference (0.24 eV) between these two components. Although there is a strong similarity between the C1s spectra of Figure 5.4b

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and c, it is striking that the area of the $\pi-\pi^*$ shake-up feature in the case of the plasma deposited sample (X-PDS2) compared to the reference polystyrene sample is decreased by about 40%. This decrease depends on the used external plasma parameters and conditions were also found where this decrease was rather small [18]. Hence the area of the shake-up feature relative to that of the total C1s photoelectron peak area can be used as a work around instead of the CH aromatic component to probe the relative aromaticity in the films within the information depth of the method.

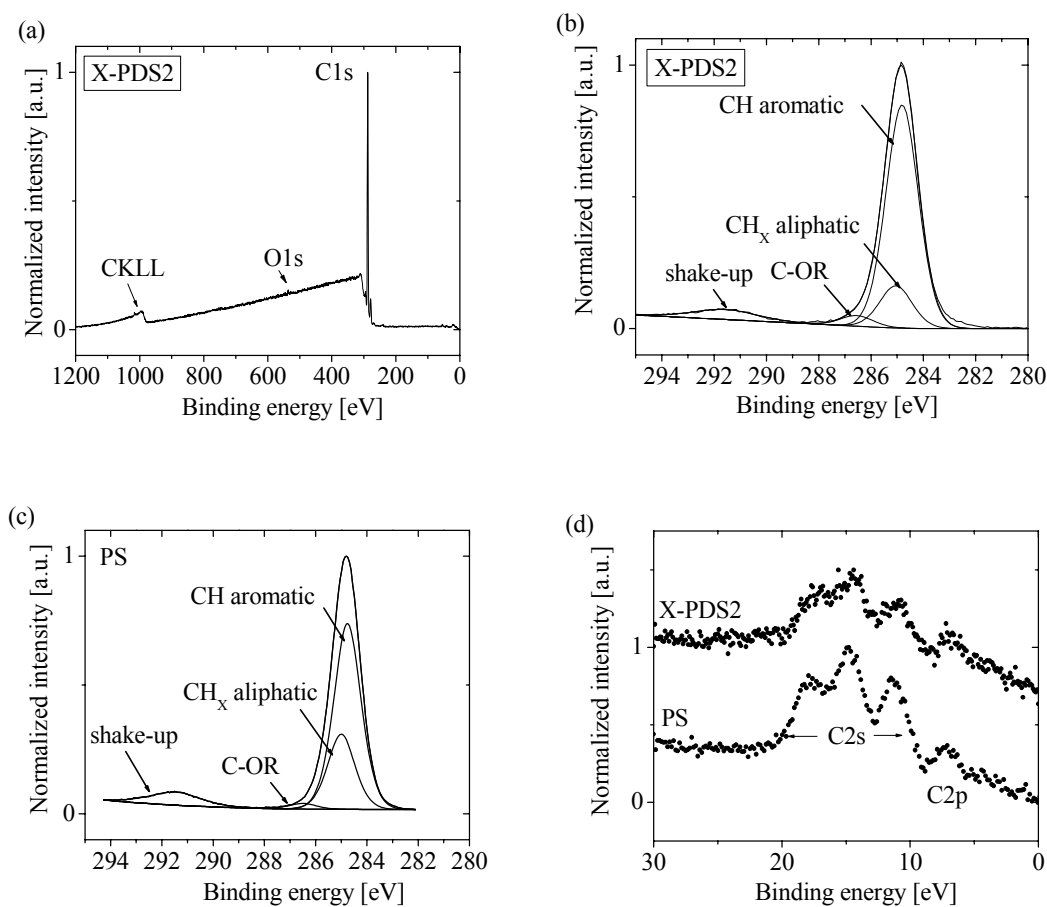


Figure 5.4: XPS of reference and plasma deposited styrene films (cf. Table 3.2 for deposition parameters). **(a)** XP survey scan of the plasma deposited styrene film X-PDS2 (20 W, 0.1 duty cycle, 5 Pa, 20 sccm). **(b)** Fitted XP C1s spectra of X-PDS2 (CH aromatic: 284.76 eV; CH_x aliphatic: 285.00 eV; C-OR: 286.50 eV [97]). **(c)** Fitted XP C1s spectra of reference polystyrene (PS). **(d)** XPS valence band spectra of X-PDS2 and reference polystyrene (PS).

Additionally, it was also found that the FWHM of the C1s spectra for the plasma deposited styrene samples could not be used to estimate the extent of branching and cross-linking in the films as done in the case of plasma deposited ethylene case since the variation in the FWHM was found to be very small for all the plasma deposited samples.

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This may be due to the fact that a higher reactivity of styrene compared to ethylene leads to a more linear character of the deposited films.

The similarity in the chemical character of plasma deposited styrene films and reference polystyrene is emphasized once again in Figure 5.4d which displays the valence band spectra of X-PDS2 and a conventional polystyrene film. However, the features of the X-PDS2 valence band spectra compared to the reference samples are merely broadened. This broadening is due to the co-existence of several species close in binding energy.

NEXAFS Characterization: Figure 5.5 displays the NEXAFS C K-edge spectra of a plasma deposited styrene film (N-PDS2) along with a reference polystyrene sample (PS). The C K-edge of these two spectra displays the following features: C1s→ π^*_{ring} feature (A) at $h\nu = 284.5$ eV, a backbone related peak (B) at 286.8 eV discussed to represent a C-H* resonance [95] or a C3p Rydberg state [104], a second C1s→ π^* resonances, shown as feature C at 288.3 eV, the IP threshold shown as feature D at ~ 289.8 eV and different C1s→ σ^* resonances above 292 eV were observed.

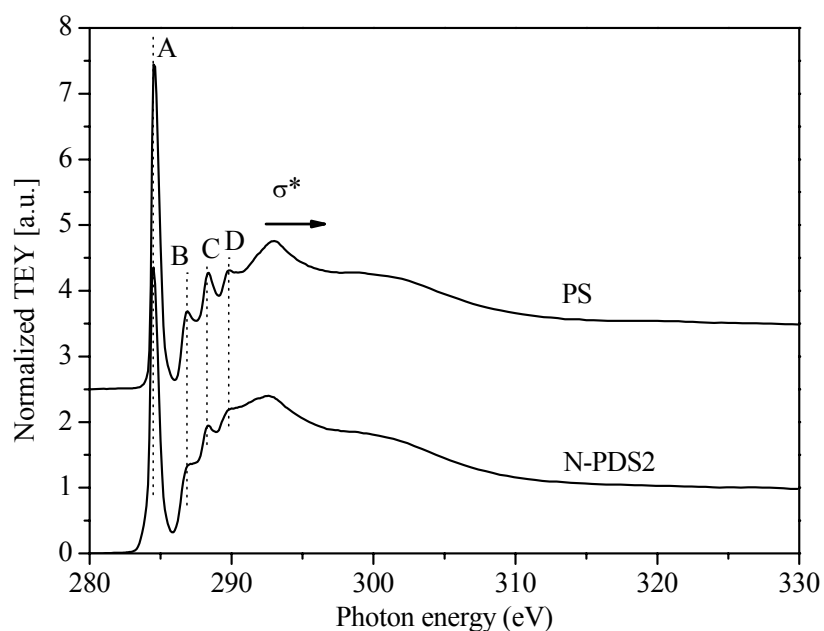


Figure 5.5: NEXAFS C K-edge spectra of the plasma deposited styrene film N-PDS2 (20 W, 0.1 duty cycle, 5 Pa, 20 sccm) and reference polystyrene (PS). Spectral features are explained in the text.

Once again the similarity in these spectra points to the fact that the plasma deposited styrene is very similar to the reference polystyrene sample. The C1s→ π^*_{ring}

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feature in the spectra of the plasma deposited films is broadened by approximately 0.7 eV. This broadening is due to other overlapping resonances or closely separated resonances within the energy range of this feature due to the presence of other unsaturated chemical species on the surface of plasma deposited styrene. $C1s \rightarrow \pi^*$ resonances arising from $C=C$ bonds and double or even multi-substituted aromatic rings contribute to this feature. Evidence of such resonances, which are very close in energy, has also been found in other ToF-SSIMS, XPS and NEXAFS studies [80, 103, 105, 106]. However, a majority of the species that contributes to this feature are of course the aromatic rings. Hence, semi-quantitative information about the presence of aromatic rings or their retention in plasma deposition process can be obtained from the $C1s \rightarrow \pi^*_{ring}$ transitions.

Results: Figure 5.6a displays the variation in the percentage area of the $C1s$ shake-up feature in relation to different X-PDS samples prepared at different plasma conditions. It can be observed that with the increase in applied duty cycle or power a decrease in the shake-up area can be observed. This implies a lower aromatic content in the films prepared at higher power or duty cycle. This fact is successfully cross-checked by Figure 5.6b. This Figure displays the variation in the area of the $C1s \rightarrow \pi^*_{ring}$ resonance (Feature A) in the C K-edge NEXAFS spectra of all the N-PDS samples. A decrease in this area can be observed for samples prepared at high duty cycles or high plasma powers. Hence a lower aromatic content in the plasma deposited samples prepared at high effective powers can be concluded.

The degradation of the aromatic content of the films as observed by both the methods is due to a higher fragmentation of the monomer structure at higher effective powers. An increase in pressure by more than four times did not introduce any significant changes in the shake-up area or the $C1s \rightarrow \pi^*_{ring}$ resonance area. This implies that the parameter “monomer pressure” hardly has any effect on the aromatic content of the plasma deposited styrene films.

It can be concluded that "hard" plasma conditions lead to a loss in the aromatic content on the surface of the plasma deposited styrene films. It was also shown by other investigators [107, 108] that low power per styrene molecule favoured the deposition of a film in which monomer structure is preserved to a high degree.

All the plasma deposited styrene samples were found to show a close resemblance in their chemical character to reference polystyrene samples. This result verifies the work

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done by other researcher e.g. U. Oran [101] who studied similar plasma deposited films by ToF-SSIMS and S. Schelz et. al. [109] who investigated the chemical structure and surface topography of plasma deposited styrene films by photoelectron spectroscopy and scanning force microscopy. The authors found the chemical structure of films to be very similar to the structure of conventional polystyrene films.

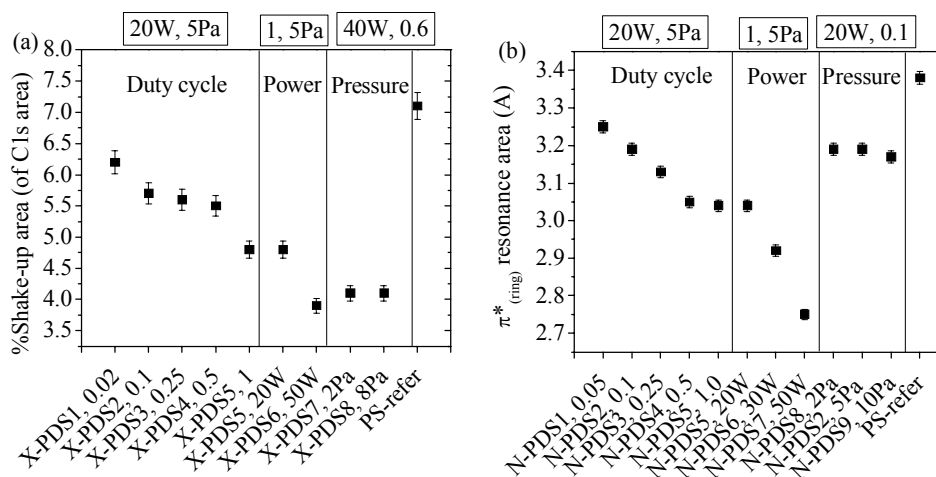


Figure 5.6: XPS and NEXAFS results of plasma deposited styrene films (cf. Table 3.2 for deposition parameters). **(a)** % shake-up area of the total C1s XP spectra of the plasma deposited styrene films (X-PDS). **(b)** NEXAFS C1s $\rightarrow\pi^*$ _(ring) resonance area in the C K-edge spectra of the plasma deposited styrene films N-PDS. Boxes on the top of the figure give the constraints of the deposition conditions.

5.2.3. Plasma deposited allyl alcohol films

Table 3.3 (chapter 3) gives the details of the deposition process used for preparing the samples of plasma deposited allyl alcohol for XPS and NEXAFS characterization.

XPS characterization: A typical XP survey scan of plasma deposited allyl alcohol film X-PDA3, prepared at “mild” conditions, is shown in Figure 5.7a. Carbon and oxygen were detected along with traces of nitrogen. The O/C atomic ratio is used to estimate the surface concentration of oxygen. A reference film could not be obtained. The reason is that allyl alcohol monomers are too low in reactivity to allow sufficient polymerization by chain propagation. The allylic radicals, which are formed are rather stable and undergo terminati-

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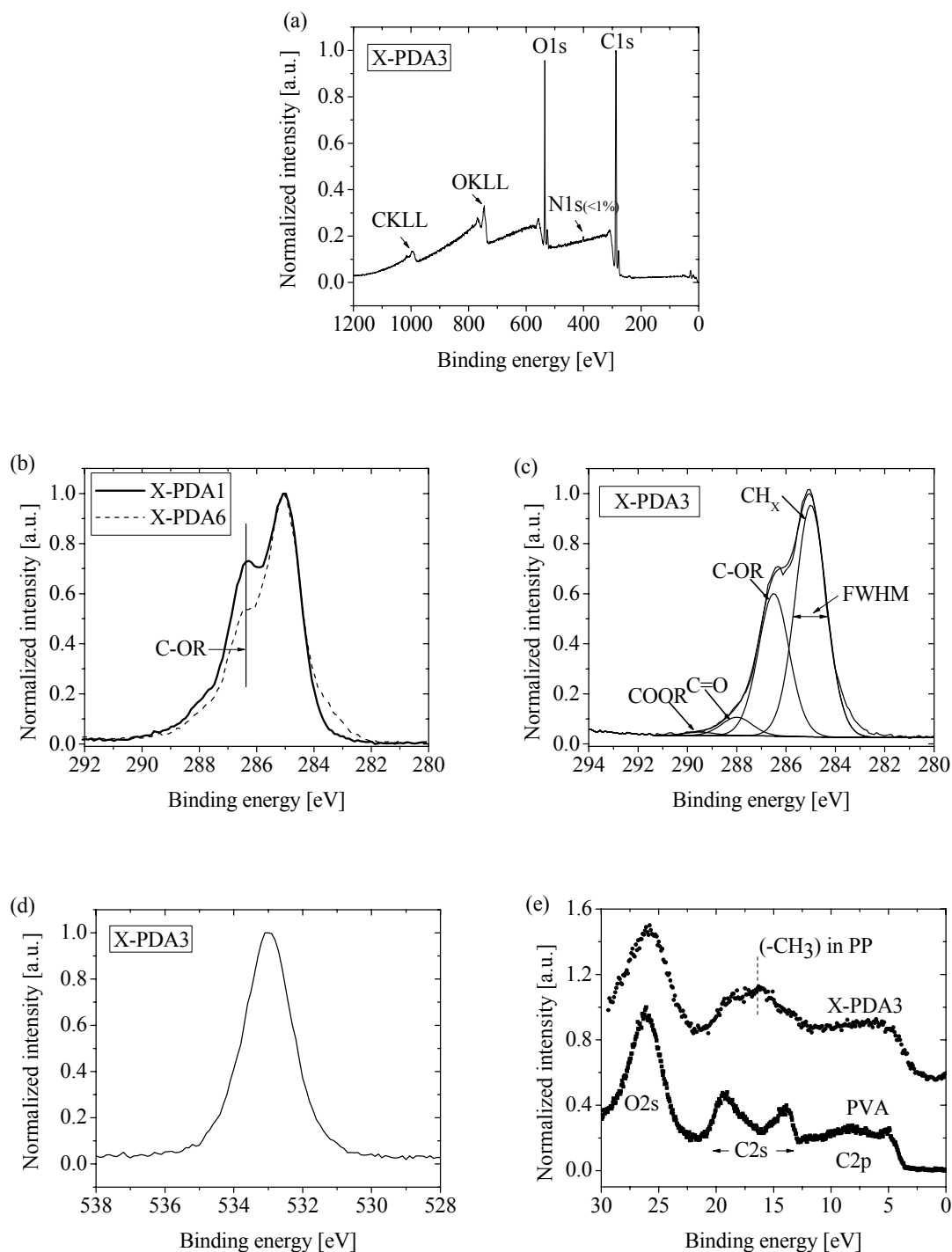


Figure 5.7: XPS of plasma deposited allyl alcohol films (cf. Table 3.3 for deposition parameters). **(a)** XP survey scan of the plasma deposited allyl alcohol film X-PDA3 (20 W, 0.1 duty cycle, 5 Pa, 20 sccm). **(b)** XP C1s spectra of X-PDA1 (5 W, 0.1 duty cycle, 5 Pa, 20 sccm) and X-PDA6 (30 W, 0.1 duty cycle, 5 Pa, 20 sccm). **(c)** Fitted XP C1s spectrum of X-PDA3 (CH_x aliphatic: 285.0 eV; C-OR: 286.5 eV; C=O: 288.0 eV; COOR: 289.5 eV) [97]. **(d)** XP O1s spectrum of X-PDA3. **(e)** XPS Valence band spectra of X-PDA3 and poly(vinyl alcohol) (PVA) [97].

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on by reaction with each other, or with propagating radicals [110]. Therefore for comparison, Figure 5.7b shows only C1s photoelectron spectra of two plasma deposited films prepared at “mild” (X-PDA1) and “hard” (X-PDA6) conditions. There is a significant difference arising from different surface concentrations of C-OR functional groups at the films. The variation in this feature was studied in detail by first fitting the C1s spectra with a Shirley background [111] and then fitting the spectra with various component peaks representing different species (see fitting of X-PDA3 in Figure 5.7c) fixed at different energies using the data recommended by Beamson and Briggs [97]. It is worth mentioning at this point that the C-OR component curve includes the relevant major contribution from C-OH groups. However, XPS cannot distinguish between C-OR and C-OH.

Similar to the case of plasma deposited ethylene films, the FWHM of the CH_x component curve (not the total C1s FWHM) can be used to estimate the branching and cross-linked character of the plasma deposited allyl alcohol films. O1s photoelectron spectra for the films were also measured and a representative spectrum of X-PDA3 is shown in Figure 5.7d. This spectrum can also be principally used to determine the C-OH and C-OR species in the sample. However, the energy difference required to fit these two species is ~0.3 eV and this results in large fitting errors. Hence these oxygen spectra are not really useful for a detailed discussion.

A comparison of the valence band spectra of X-PDA3 and poly(vinyl alcohol) [97] is shown in Figure 5.7e. The broad C2s feature in the case of X-PDA3 indicates substantial branching in the film (cf. section 5.1.1). This comparison also points to the fact that plasma deposited allyl alcohol films are similar to conventionally polymerized films.

NEXAFS characterization: Figure 5.8a gives the C K-edge NEXAFS spectra of poly(vinyl alcohol), [102], poly(vinyl methyl ketone), (PVMK) [102] and a representative plasma deposited allyl alcohol sample, N-PDE4 prepared at “mild” plasma conditions. The principal features seen in the displayed spectrum of N-PDE4 sample are representative for all the other plasma deposited allyl alcohol films. An important feature (A) in the spectrum of plasma deposited sample is the presence of a C1s→π*(C=C) resonance at $h\nu=284.9$ eV, characteristic for the presence of C=C bonds. Similar to ethylene and styrene the comparison of the area under this feature also provides a specific semi-quantitative measure of the surface concentration of C=C bonds in samples prepared under different plasma conditions. A comparison with the spectra of PVA and PVMK

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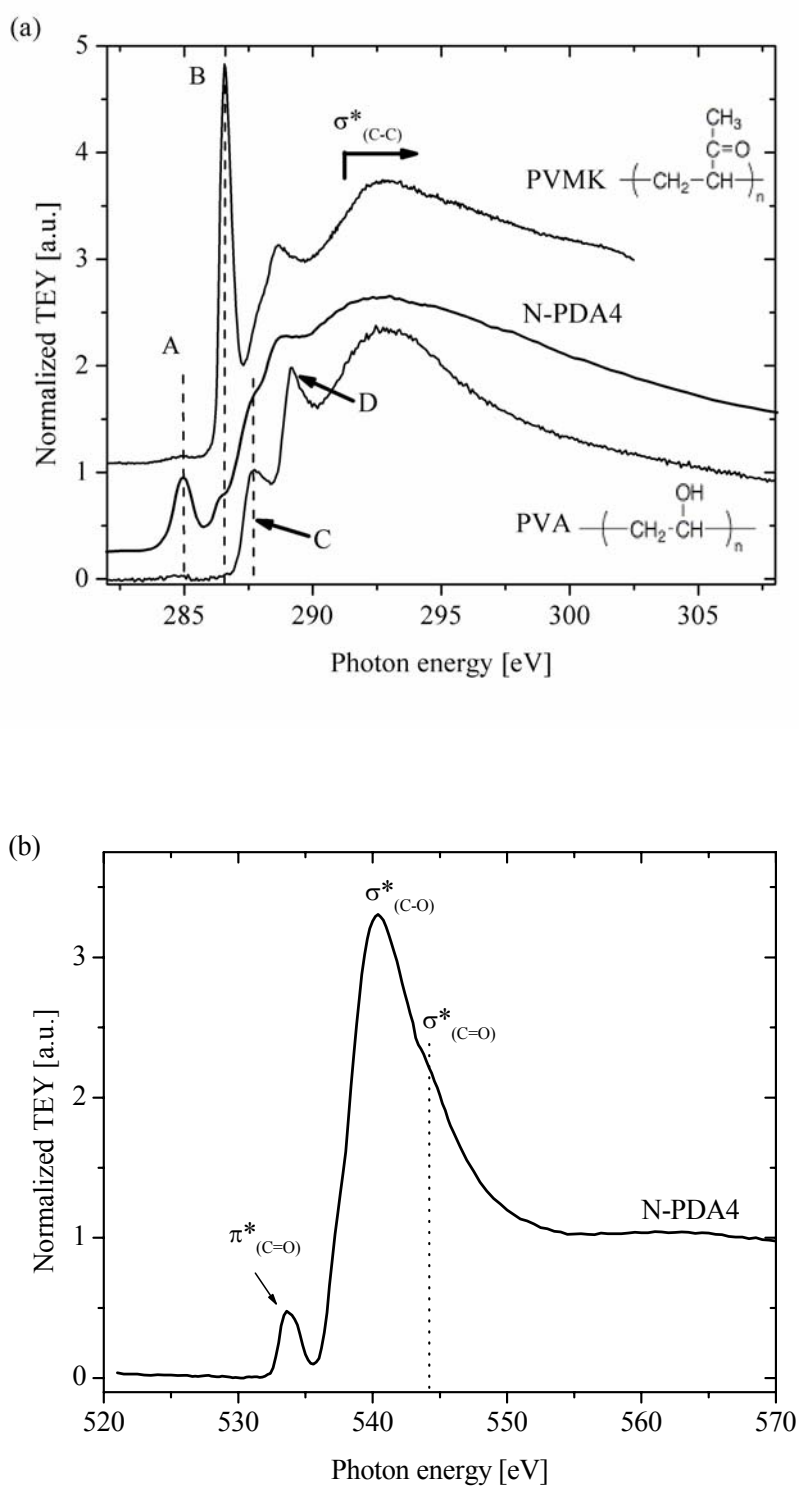


Figure 5.8: (a) NEXAFS C K-edge spectra of the plasma deposited allyl alcohol film N-PDA4 (20 W, 0.1 duty cycle, 5 Pa, 20 sccm), poly (vinylmethyl ketone) (PVMK) and poly (vinyl alcohol) (PVA) references [102]. (b) NEXAFS O K-edge spectrum of N-PDA4. Spectral features are explained in the text.

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highlights some other features in the C K-edge NEXAFS spectrum of N-PDA4: A shoulder at ~ 286.7 eV representing a $C1s \rightarrow \pi^*_{(C=O)}$ resonance (B), another shoulder at ~ 287.6 eV representing a C-H* resonance (C), a $C1s \rightarrow \sigma^*_{(C-O)}$ resonance at ~ 289 eV (D) and $C1s \rightarrow \sigma^*_{(C-C)}$ resonances above 292 eV were observed. The O K-edge NEXAFS spectra of the plasma deposited samples were also measured (cf. Figure 5.8b) to obtain information on the presence of C=O species. The spectral feature at $h\nu=533.6$ eV represents the $O1s \rightarrow \pi^*_{(C=O)}$ resonance and can be used to obtain specific semi-quantitative information on the surface concentration of C=O bonds in the plasma deposited samples. This spectrum also shows a $\sigma^*_{(C-O)}$ resonance at 540 eV and a shoulder representing the $\sigma^*_{(C=O)}$ resonance at 544 eV. A $C1s \rightarrow \pi^*_{(ROC=O)}$ resonance or a $O1s \rightarrow \pi^*_{(ROC=O)}$ resonance is not seen in the NEXAFS analysis of these samples because of a low surface concentration of these species as already measured by XPS (cf. Figure 5.7c).

Results: Figure 5.9a and b show the variation in the O/C atomic ratio and C-OR intensity for all the X-PDA samples prepared at different plasma conditions. With the increase in duty cycle or power the O/C atomic ratio and the surface concentration of C-OR species were found to decrease. A significant observation here is that, compared to the expected value of O/C atomic ratio (0.33) for the allyl alcohol monomer, higher values were observed for plasma deposited films prepared at ‘mild’ deposition conditions. To explain this the plasma polymerization process itself should be discussed. There are different simultaneous processes. One of them is the “polymerization” of the excited monomer molecules that leads to the retention of C-OH groups in the film, here called as Process A. Another one is the fragmentation of the monomer molecules and the subsequent recombination of these fragments (Process B). The excess of oxygen observed in the films can be related to Process B which can also result in the formation of additional C-OR bonds. Process B also leads to the formation of other species such as C=O and COOR. However, as shown in Figure 5.7c the surface concentration of these species is rather small. According to the XPS analysis, the average percentage component area for C=O species was less than 5% and for COOR species less than 1%.

A change in the monomer pressure from 2 Pa to 7 Pa did not produce any significant difference in the O/C atomic ratio or C-OR species on the surface of the film. The FWHM of the CH_x component in the fitted C1s spectra of all of the X-PDA samples is displayed in Figure 5.10. An increase in the FWHM can be observed for samples prepared

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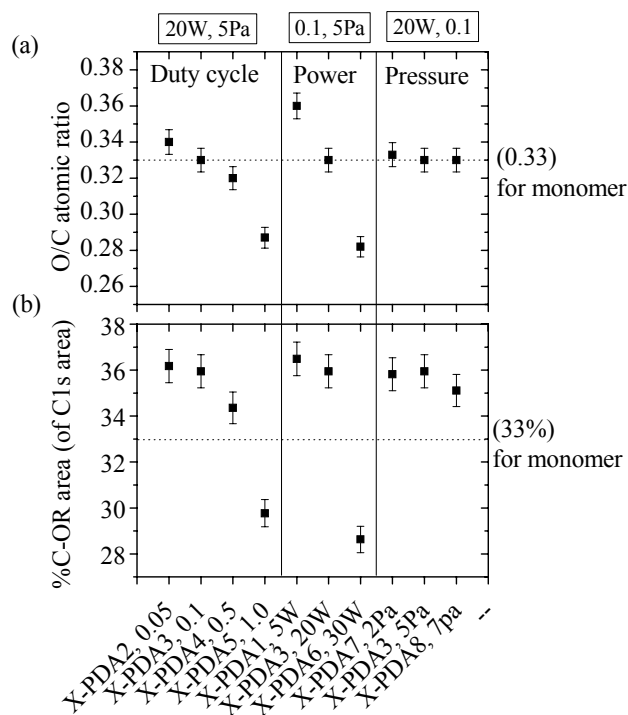


Figure 5.9: XPS results of plasma deposited allyl alcohol films (cf. Table 3.3 for deposition parameters). **(a)** XPS O/C atomic ratio. **(b)** %C-OR area of the total XP C1s area of the plasma deposited allyl alcohol X-PDA films. Boxes on the top of the figure gives the constraints of the deposition conditions.

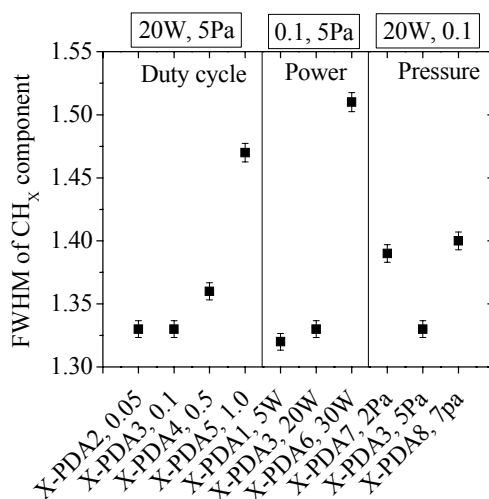


Figure 5.10: XPS results of plasma deposited allyl alcohol films (cf. Table 3.3 for deposition parameters). FWHM 's of the XP C1s spectra of the plasma deposited allyl alcohol X-PDA films. Boxes on the top of the figure gives the constraints of the deposition conditions.

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at high duty cycle or power. This indicates an increase in branching and cross-linking in the deposited films with an increase in effective power. This was also supported by the valence band spectra (Figure 5.7e) and by a ToF-SSIMS study of plasma deposited allyl alcohol samples [101]. An increase in monomer pressure did not show any particular trend in the FWHM. The variation in the area under the $O1s \rightarrow \pi^*_{(C=O)}$ resonance and the $C1s \rightarrow \pi^*_{(C=C)}$ resonance (A) observed for different plasma deposited samples is presented in Figure 5.11a and b. With an increase in duty cycle or power an increase in the unsaturated character in terms of C=C and C=O bonds is observed. For samples prepared at “mild” deposition conditions, i.e. at low duty cycle and power, it can be argued that the Process A (see above) is dominant and therefore the concentration of C=C bonds is low. Such a mechanism of plasma polymerization through opening of carbon-carbon double bonds has been suggested in various studies for different monomers [15, 17, 19, 32, 112].

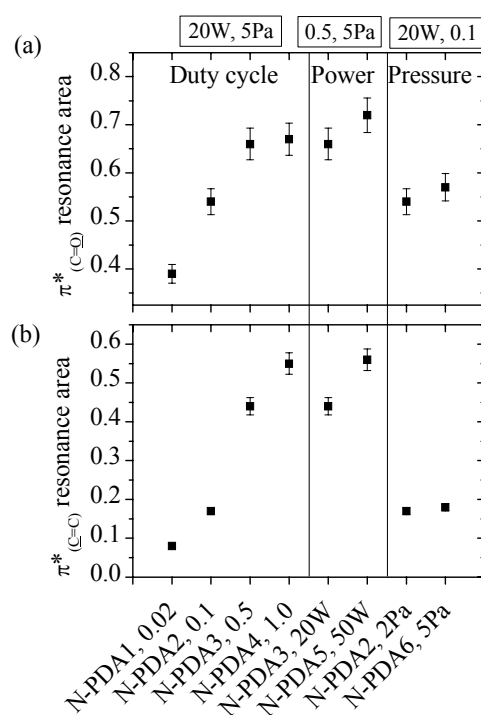


Figure 5.11: NEXAFS results of plasma deposited allyl alcohol films (cf. Table 3.3 for deposition parameters). **(a)** NEXAFS $O1s \rightarrow \pi^*_{(C=O)}$ resonance area in the O K-edge spectra. **(b)** NEXAFS $C1s \rightarrow \pi^*_{(C=C)}$ resonance area in the C K-edge spectra of the plasma deposited allyl alcohol N-PDA films. Boxes on the top of the figure gives the constraints of the deposition conditions.

For samples prepared at “hard” deposition conditions, i.e., at high duty cycle and power, the fragmentation of the monomer molecules and the recombination of these

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fragments increases (Process B). This explains the higher concentration of C=C bonds in the case of samples prepared at "hard" plasma conditions because new carbon double bonds are efficiently formed by the plasma. The same process will also produce other double bonds, e.g. carbonyls. Consequently, Figure 5.11a shows an increase in the concentration of C=O double bond species vs. plasma conditions becoming harder. The deposition parameter "monomer pressure" did not produce any definite effect on the unsaturation of the surface.

Assuming that almost all of the C-OR species present in the C1s spectra are due to hydroxyl groups it can be concluded that a high retention of hydroxyl groups is observed for plasma deposited allyl alcohol samples prepared at "mild" plasma conditions. Similar results, i.e. of high retention of hydroxyl groups in the case of plasma deposited allyl alcohol samples studied by XPS and IR spectroscopy are found in literature [15, 18, 19, 30, 101].

5.2.4. Plasma deposited allylamine films

Table 3.4 (chapter 3) gives the details of the deposition process used for preparing the samples of plasma deposited allylamine for XPS and NEXAFS characterization.

XPS characterization: Figure 5.12a displays an XP survey scan of a representative plasma deposited allylamine film (X-PDAm3) prepared at "mild" plasma conditions. Carbon and nitrogen along with traces of oxygen were detected on the surface of the film. The source of oxygen is an anti-polymerizing agent used for the storage of the allylamine monomer. The N/C atomic ratio obtained from the survey scan can be used to obtain a quantitative measure of the nitrogen surface concentration of the films. The C1s photoelectron spectrum of the X-PDAm3 sample is displayed in Figure 5.12b. The spectrum is fitted by fixing the binding energies according to data found in the literature [113]. The presence of nitrogen along with oxygen requires the consideration of the components C-N, C=N, C-OR and C=O. The binding energy difference between the components C-N and C-OR as well as C=N is small (0.5 eV). This introduces high uncertainty in the results derived from these component curves. Therefore it is not possible to rely on the C-N component area to estimate the surface concentration of amines on the films. Figure 5.12c gives the N1s spectrum of two different plasma deposited amine films prepared at extreme deposition conditions. X-PDAm1 was prepared at "mild" conditions while X-PDAm6 was prepared at "hard" conditions. A broadening by ~0.3 eV

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of the total FWHM in the case of X-PDAm6 can be observed. This broadening occurs due to the presence of several species very close in binding energy. The anticipated presence of multiple species however, did not show any structure in the N1s spectra. Figure 5.12d additionally supports the presence of multiple species in the plasma deposited allylamine samples. It shows the valence band spectra of X-PDAm2 along with those of poly(ethyleneimine), PEI, ($[-\text{CH}_2-\text{CH}_2-\text{NH}-]_n$) and poly(acrylonitrile), PAN, ($[-\text{CH}_2-\text{CH}(\text{CN})-]_n$) references [97]. The N2s feature is clearly observed in the spectra of the reference samples. In the case of plasma deposited samples this feature is broadened suggesting the presence of C-N as well as $\text{C}\equiv\text{N}$ species.

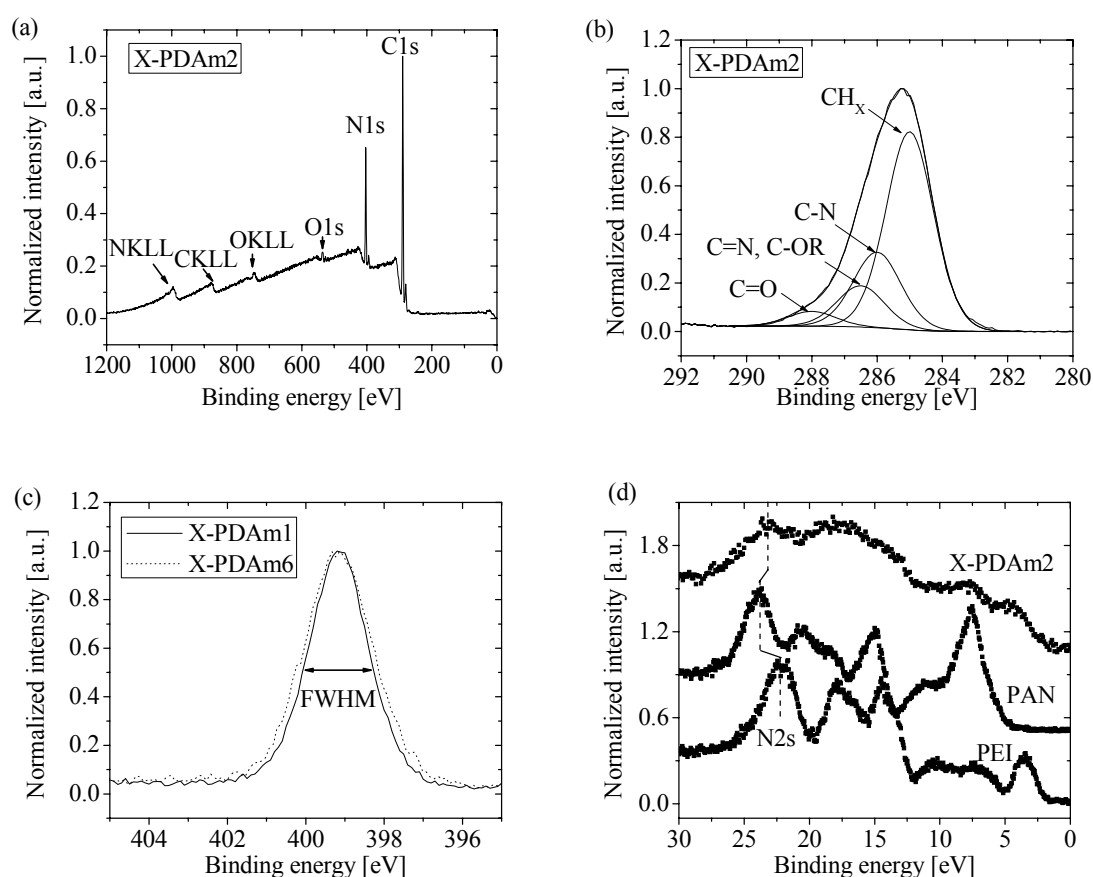


Figure 5.12: XPS of reference plasma deposited allylamine films (cf. Table 3.4 for deposition parameters). (a) XP survey scan of plasma deposited allylamine sample X-PDAm2 (20 W, 0.1 duty cycle, 5 Pa, 20 sccm). (b) Fitted XP C1s spectrum of X-PDAm2 (CH_x aliphatic: 285.0 eV; C-N: 286.0 eV; C=N, C-OR: 286.5 eV; C=O: 288.0 eV) [113]. (c) XP N1s spectra of X-PDAm1 (20 W, 0.1 duty cycle, 5 Pa, 20 sccm) and X-PDAm6 (50 W, 1.0 duty cycle, 5 Pa, 20 sccm). (d) XPS valence band spectra of X-PDAm2 along with references poly(ethyleneimine) (PEI) and poly(acrylonitrile) (PAN) [97].

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NEXAFS characterization: Figure 5.13a gives the NEXAFS C K-edge spectrum of a representative plasma deposited allylamine film (N-PDAm1). This spectrum displays feature A (284.9 eV) due to a $C1s \rightarrow \pi^*_{(C=C)}$ resonance, feature B (285.5 eV) due to a $C1s \rightarrow \pi^*_{(C=N)}$ resonance, a shoulder (C) at ~ 287.5 eV probably due to a $C1s \rightarrow \pi^*_{(C=N)}$ resonance and various σ^* resonances above 292 eV. These features are assigned by a comparison with spectra of nitrogen-incorporated tetrahedral amorphous carbon films found in literature [114, 115]. The features (A) and (B) are rather broad and do not show a large variation for all the different plasma deposited films while feature (C) is not useful because it appears only as a shoulder. For further information we rely on the NEXAFS N K-edge spectrum of these films. Figure 5.13b displays a N K-edge spectrum of the N-PDAm1 sample representative for all the other samples.

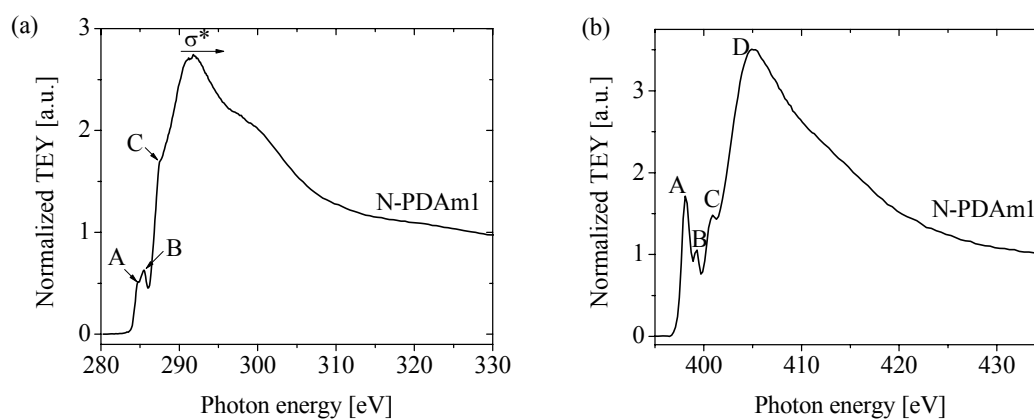


Figure 5.13: (a) NEXAFS C K-edge spectrum of plasma deposited allylamine film, N-PDAm1 (20 W, 0.1 duty cycle, 5 Pa, 20 sccm). (b) NEXAFS N K-edge spectrum of N-PDAm1. Spectral features are explained in the text.

Several prominent features can be seen in this spectrum. While feature C (400.9 eV) is discussed to be σ^* resonance arising due to bound nitrogen in the film [115] and feature D (405.1 eV) is widely accepted to be a $\sigma^*(C-N)$ resonance [116], in the literature very different spectral assignments have been reported for features (A) at 398.1 eV and (B) at 399.3 eV [115, 116]. To obtain reasonable assignments of these features the following argument is put forward. As shown in Figure 5.14a & b feature (B) is observed to vary to a large extent compared to feature (A) with the variation in the plasma deposition parameters, “duty cycle” and “power”. In a similar study of plasma deposited allylamine films Shard et. al. [116] observed that at “hard” plasma conditions the probability of formation of nitriles was higher compared to those of imines. They suggested a gas-phase

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reaction mechanism of formation of nitriles with imine intermediates (Figure 5.15) in the plasma. Assuming a similar mechanism is in place during deposition of our plasma films, it is appropriate to assume that feature (B) is the $N1s \rightarrow \pi^*_{(C \equiv N)}$ resonance and feature (A) is the $N1s \rightarrow \pi^*_{(C=N)}$ resonance. The Intensities of both these resonances are a measure of unsaturation of the deposited films. Since a direct measure of the surface concentration of amine species is not available through either XPS or NEXAFS, it is reasonable to assume that a lower concentration of $C=N$ and $C \equiv N$ species as detected by NEXAFS would imply a higher surface concentration of amine groups on the surface of the films. FTIR measurements of plasma deposited allylamine films studied by Zhang et. al. [117] also showed similar inverse relationship between the concentration of unsaturated nitrogen species and amine groups.

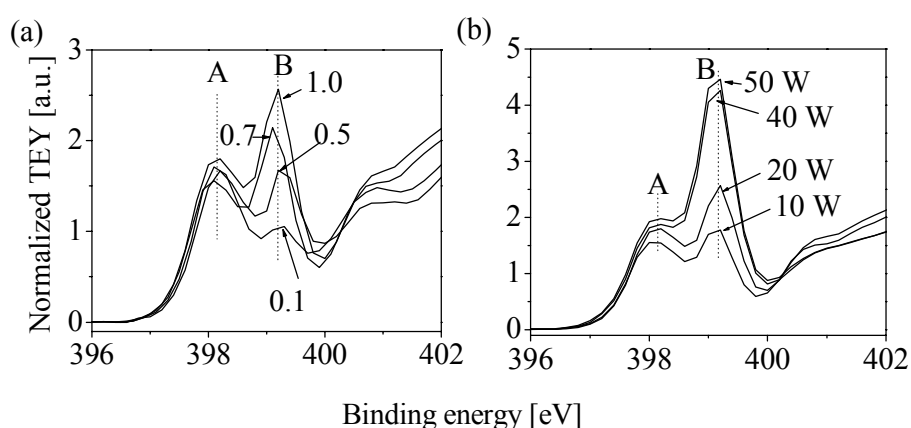


Figure 5.14: Expanded NEXAFS N K-edge spectra of the plasma deposited allylamine (N-PDAm) films studied for (a) duty cycle variation and (b) power variation. (cf. Table 3.4 for deposition parameters).

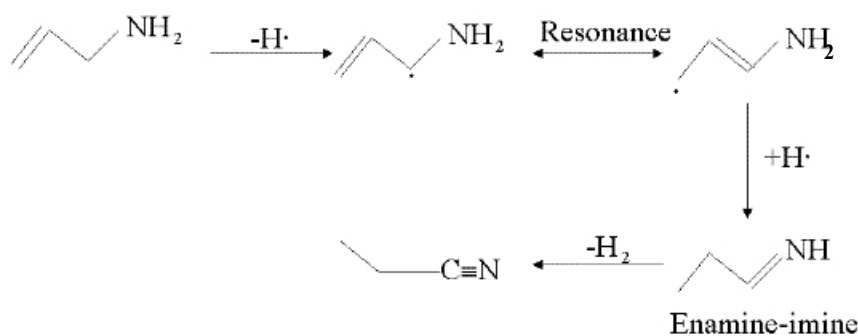


Figure 5.15: Suggested mechanism for the formation of nitriles from allylamine in the gas phase [adapted from ref. 116].

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Results: Figure 5.16a displays the total FWHM of XP N1s spectra for the plasma deposited allylamine samples. Similar to the results for ethylene and allyl alcohol, it can be observed that the FWHM increases with increase in duty cycle or power. It implies an increase in the formation of new coexisting species. This is due to a higher degree of fragmentation and subsequent recombination of monomer molecules in the plasma. Increase in monomer pressure from 2 Pa to 15 Pa did not produce any definite effect on the FWHM of the N1s spectrum (not shown in Figure 5.16a). Figure 5.16b displays the N/C atomic ratio obtained for the X-PDAm samples. An increase in duty cycle or power leads to a decrease in this ratio. Due to a high degree of fragmentation of the monomer molecules, the nitrogen containing functional groups are lost. Figure 5.17 displays the sum of $\pi^*_{(C=N)}$ and $\pi^*_{(C=N)}$ maximum intensities for NEXAFS N K-edge spectra for plasma deposited allylamine samples prepared for NEXAFS studies. An increase in this sum can

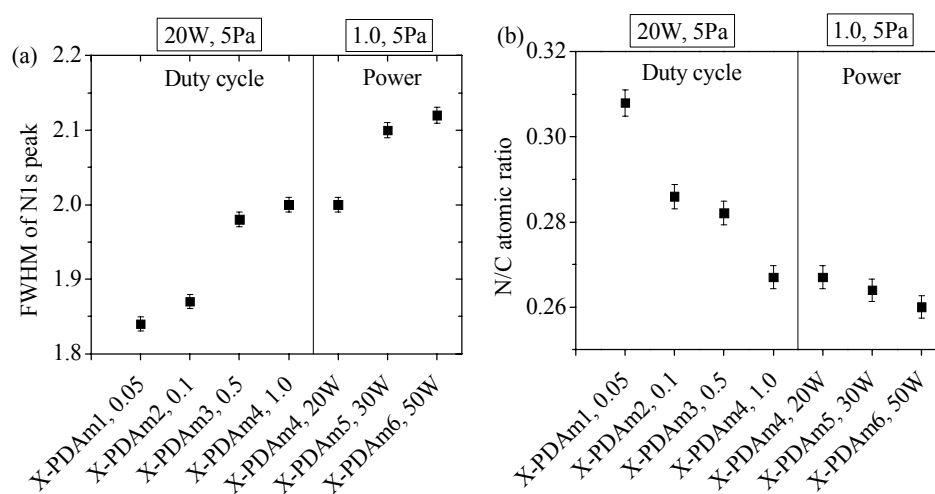


Figure 5.16: XPS results of plasma deposited allylamine films (cf. Table 3.4 for deposition parameters). **(a)** FWHM's of XPS N1s spectra. **(b)** XP N/C atomic ratio of XP N1s spectra of plasma deposited allylamine (X-PDAm) films. Boxes on the top of the figure gives the constraints of the deposition conditions.

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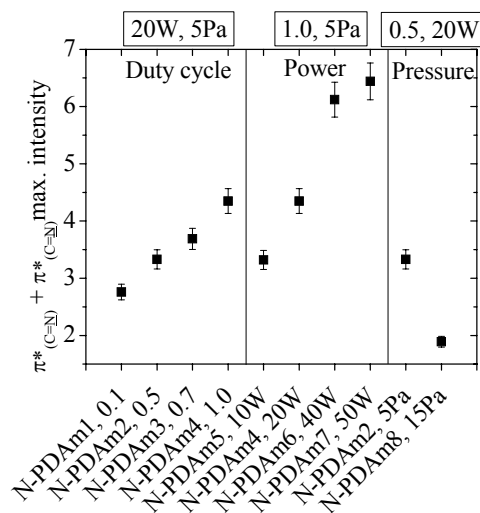


Figure 5.17: NEXAFS results of plasma deposited allylamine films (cf. Table 3.4 for deposition parameters). Sum of $\pi^*_{(C=N)}$ and $\pi^*_{(C\equiv N)}$ maximum intensities for NEXAFS N K-edge spectra for the plasma deposited allylamine (N-PDAm) samples. Boxes on the top of the figure gives the constraints of the deposition conditions.

be observed for samples prepared at high duty cycle or power. This increase in the surface concentration of C=N and C≡N bonds is again directly related to a higher degree of fragmentation and subsequent partial recombination of monomer molecules at high effective powers. A decrease in this sum of intensities was also observed at high pressures. The degree of fragmentation and recombination is reduced with increased pressures due to a lower electron energy (cf. section 2.2).

It can be concluded that for films prepared at "mild" conditions such as low duty cycle and low power there is a relatively lower degree of multiple species on the films. It is also concluded that at "mild" plasma conditions a low degree of unsaturation is observed. A low unsaturation also implies a high retention of amine groups on the surface of the plasma deposited films. However, a direct determination of the amine groups was not possible by XPS or NEXAFS. In a related work ToF-SSIMS was able to obtain information about the surface concentration of primary amino groups derived from the CH_4N^+ secondary ion yield [101]. The surface concentration of primary amines was found to be high at samples prepared at "mild" plasma conditions. Additionally the amine concentration was found to vary inversely with the surface concentration of C=N and C≡N bonds.

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

XPS and NEXAFS were found to be powerful tools in investigating the basic chemical properties of plasma deposited films. It was possible to obtain complimentary information as well as cross-checking information obtained by one method with the other. For the plasma deposited films prepared in this study, Figure 5.18 presents the measuring capabilities of these two methods in obtaining a variety of information.

It was also observed that certain chemical properties of plasma deposited films can be effectively controlled by an appropriate choice of external plasma parameters such as duty cycle, power and reaction pressure. Table 5.1 gives the details of the effect of these parameters introduced in the plasma deposited films prepared in this study.

In general high duty cycles and high powers were found to introduce a high degree of unsaturation, branching and cross-linking in the film. A loss of the monomer functional group was also observed at these deposition conditions. These general trends can be explained by the fact that at high duty cycles or powers the effective plasma power is high which subsequently increases the energy of the plasma particles. This increase in energy of the particles leads to increased levels of fragmentation of monomer molecules and subsequent partial recombination of the fragments.

An increase in the deposition parameter “monomer pressure” leads to a decrease in unsaturation and a higher retention of monomer functional groups (as seen in the case of allylamine). This parameter, however, in most of the cases did not show any specific effect. This might be due to the fact that there are multiple effects brought about in the plasma by a change of pressure. An increase in pressure decreases the electron energy in the plasma resulting in a decrease in the fragmentation of the monomer molecules. In addition, increase in pressure also increases the collision rate of the molecules and plasma particles resulting in an increase in the fragmentation of the monomer molecules. These 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.

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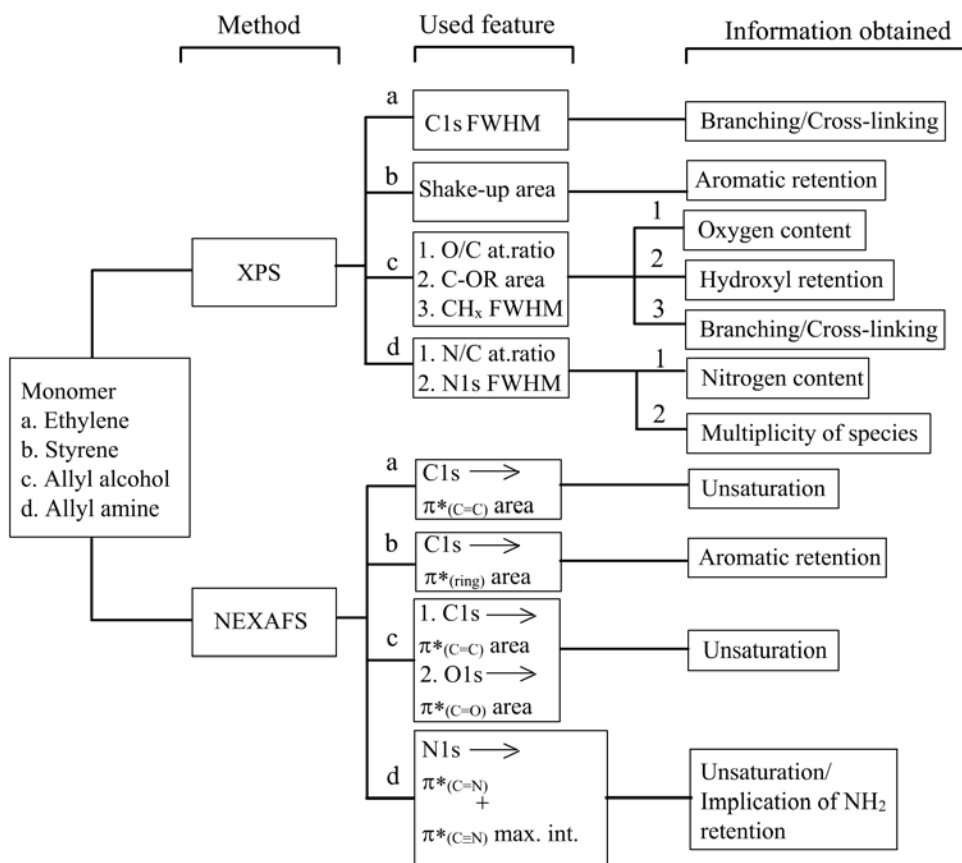


Figure 5.18: Summary of measuring capabilities of XPS and NEXAFS to analyze the plasma deposited films investigated in this study.

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Table 5.1: Summary of the effect of plasma deposition parameters on the chemistry of the plasma deposited films.

Monomer	Duty cycle	Power	Pressure
Ethylene	<ul style="list-style-type: none"> • Branching,cross-linking \propto duty cycle. • Unsaturation \propto duty cycle. 	<ul style="list-style-type: none"> • Branching,cross-linking \propto Power • Unsaturation \propto Power. 	<ul style="list-style-type: none"> • No effect detected on Branching,cross-linking • Unsaturation \propto 1/Pressure.
Styrene	<ul style="list-style-type: none"> • Aromatic retention \propto 1/duty cycle. 	<ul style="list-style-type: none"> • Aromatic retention \propto 1/power. 	<ul style="list-style-type: none"> • No effect detected.
Allyl alcohol	<ul style="list-style-type: none"> • Oxygen content \propto 1/duty cycle. • Hydroxyl retention \propto 1/duty cycle. • Branching,cross-linking \propto duty cycle. • Unsaturation \propto duty cycle. 	<ul style="list-style-type: none"> • Oxygen content \propto 1/Power. • Hydroxyl retention \propto 1/ Power. • Branching,cross-linking \propto Power. • Unsaturation \propto Power. 	<ul style="list-style-type: none"> • No effect detected.
Allylamine	<ul style="list-style-type: none"> • Nitrogen content \propto 1/duty cycle. • Branching,cross-linking \propto duty cycle. • Unsaturation \propto duty cycle. • Amine retention \propto 1/duty cycle. 	<ul style="list-style-type: none"> • Nitrogen content \propto 1/ Power. • Branching,cross-linking \propto Power. • Unsaturation \propto Power. • Amine retention \propto 1/ Power. 	<ul style="list-style-type: none"> • No effect on Nitrogen content or branching,cross-linking. • Unsaturation \propto 1/Pressure. • Amine retention \propto Pressure.

