

Quantification of the Functional Groups Present at the Surface of Plasma Polymers Deposited from Propylamine, Allylamine, and Propargylamine

F. FALLY,* C. DONEUX, J. RIGA, and J. J. VERBIST

Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles, 61, B-5000 Namur, Belgium

SYNOPSIS

The surface chemistry of plasma-deposited films created from amine-functionalized saturated (propylamine) and unsaturated (allylamine and propargylamine) precursors has been investigated by high-energy resolution XPS, chemical derivatization, elemental analysis, and HREELS. XPS results show that nitrogen-rich deposits are obtained from unsaturated precursors at low power or at high power in the postdischarge region. Quantitative information on the chemical groups in the polymers is obtained by simulating the XPS C1s and N1s core levels and by performing derivatization reactions. The proportion of primary amine functions deduced from tagging reactions with pentafluorobenzaldehyde in the liquid phase and with 4-trifluoromethylbenzaldehyde in the vapor phase varies between 10 and 33%. These groups are converted into imine (more than 50%) in polypropylamine and polyallylamine, while imine and nitrile functions were found in polypropargylamine. HREELS has allowed us to distinguish between different nitrogen-containing functionalities present at the extreme surface of the polymers. The comparison of the HREELS and TIR spectra shows that the chemical composition at the extreme surface of the samples is representative of that of the bulk. To explain the conversion of the chemical groups in the plasma, polymerization mechanisms are proposed for each of the monomers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Aminofunctionalization is of interest in several applications such as adhesion or for biomaterials. For example, in the field of adhesion, amino groups on surfaces can improve the interfacial bonding between fibers and polymer matrices.¹ These functions play also an important role in improving the biocompatibility of artificial biomaterials or can be used for covalent bonding of bioactive molecules.² Moreover, they are suitable reactants in many derivatizing reactions: postreactions with these primers allow the creation of new functionalities such as sulfonate groups,³ the grafting of molecules such as acrylic

acid,⁴ or the introduction of a Ziegler Natta catalyst at the surface of various materials.⁵

In this article, propylamine ($\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—NH}_2$), allylamine ($\text{CH}_2=\text{CH—CH}_2\text{—NH}_2$), and propargylamine ($\text{CH}\equiv\text{C—CH}_2\text{—NH}_2$) have been polymerized in various conditions in an RF plasma. It is well known that during the plasma deposition of monomers containing amine functions fragmentation reactions leading to the elimination of nitrogen fragments as well as to some transformation of the amino groups into imine and nitrile functions take place.⁶ However, to minimize the transformation of the primary amino groups, unsaturated monomers (allylamine and propargylamine) were chosen: The double or triple bond was expected to be involved in the polymerization process, thereby reducing the fragmentation of the monomer. These films were compared with the films formed from the corresponding saturated monomer: propylamine.

* To whom correspondence should be addressed.

Our previous studies⁷ concerning the plasma polymerization of monomers containing alcohol functions which are known to produce oxygen-deficient films because of their high tendency of fragmentation and ablation⁸ have shown that allyl alcohol and propargyl alcohol can produce, under mild conditions, deposits with a very high oxygen content. Alcohol, ether, and carbonyl functions are present in equivalent quantities in polypropargyl alcohol, but for polyallyl alcohol, the degree of hydroxyl retention is very high. Alcohol functions (53–72%) are found mainly in this last polymer.

Detailed structural information on the polymers formed from monomers containing amine functions were obtained by X-ray photoelectron spectroscopy (XPS), using a Scienta ESCA 300 spectrometer.⁹ The very high energy resolution of this spectrometer (0.25 eV) is helpful to obtain quantitative information on polymers containing nitrogen atoms for which the chemical shifts for various functionalities such as amine, imine, nitrile, or amide functions on the C1s and N1s core levels are very small.¹⁰ The accessibility and the reactivity of the amino groups were studied by means of tagging reactions with pentafluorobenzaldehyde (PFB) in solution¹¹ and with 4-trifluoromethylbenzaldehyde (TFBA) in the vapor phase,¹² followed by XPS analysis. Because many problems concerning the labeling of the primary amine functions are described in the literature, using two different reactions to quantify the proportion of these functions allows some comparison of the values obtained.

The possible errors of the functional group quantification can arise from the lack of specificity of the reaction,¹¹ the dissolution of low molecular weight materials of the polymer surface in the solvent used for the reaction, the incomplete reaction over the whole sampling depth of the polymer analyzed by XPS,¹³ the swelling of the film,⁶ or the adsorption of the labeling compound (without covalent bonding) at the polymer surface.¹⁴ Incomplete reaction can also occur because of steric hindrance.

The quantitative results obtained on the proportion of the primary amino groups introduced on the surface, investigated by applying the liquid-phase reaction with PFB and the vapor phase reaction with TFBA followed by XPS analysis, are therefore compared together to evaluate the reliability of these reactions. Angular-dependent studies are also performed to shed light on the penetration depth of the reagent.

Information on the deposition mechanism was also obtained from the percentage of C=C bonds deduced from their reaction with mercuric trifluo-

roacetate [Hg(TFA)₂]¹¹ as well as from the hydrogen percentage determined by elemental analysis. The quantitative XPS information on the functional groups present in the polymers was compared with qualitative data obtained by transmission infrared spectroscopy (TIR) and high-resolution electron energy loss spectroscopy (HREELS).

Although up to now HREELS has been less commonly used than have XPS and IR to characterize plasma polymers, its extreme surface sensitivity as well as its ability to distinguish between different nitrogen-containing functionalities give very interesting chemical information on such materials. The sampling depth is expected to be below 20 Å for polymer surfaces.¹⁵ This technique is particularly suited for polymer analysis because it is sensitive to the light elements (H, C, N, O, . . .) involved in chemical bonds¹⁶ and because it gives information on the relative orientation of chemical groups at the interface with respect to the outside world.^{17,18} Based on the structure and composition of the films obtained by XPS, elemental analysis, IR, and HREELS, polymerization mechanisms are proposed for the monomers.

EXPERIMENTAL

Chemicals

Propylamine, allylamine, and propargylamine, of 98% purity, were obtained from Aldrich Chemie. Pentafluorobenzaldehyde (98%), 4-trifluoromethylbenzaldehyde (98%), mercuric trifluoroacetate (98%), 2,2,2-trichloroethanol (99%), hexane anhydrous (95%), and benzene (99.9%), used in the derivatization reactions, were also from Aldrich. Au-coated silicon wafers were used as substrates for the deposition and for the XPS and HREELS analysis. KBr windows from Analis were used for infrared measurements.

Films Deposition

Polymers were deposited in an inductively coupled plasma reactor (Fig. 1).⁷ To compare the films formed from the three amino-functionalized precursors at various powers, the other reaction conditions were kept invariant. After a stable argon flow rate was established, [230 cm³(STP)/min], the monomer was introduced in the postdischarge region through a needle valve and polymerized with an RF power adjusted between 10 and 50 W. The total pressure in the plasma chamber during the poly-

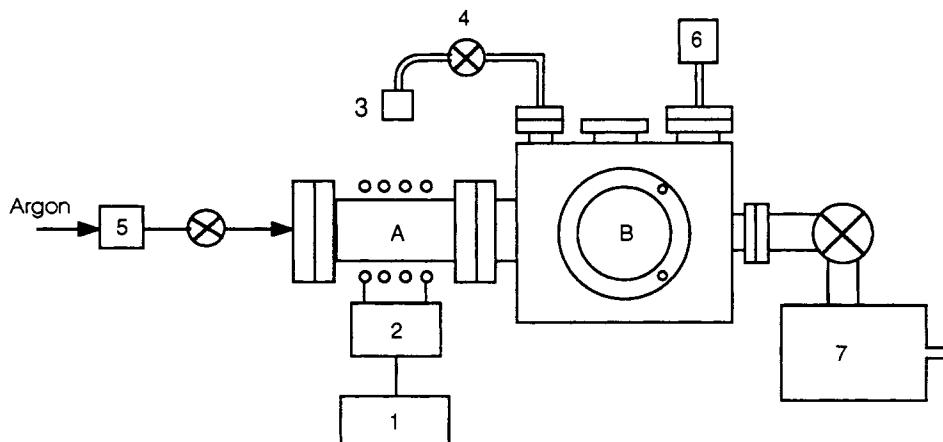


Figure 1 Apparatus for plasma polymerization: (1) rf power; (2) matching network; (3) monomer; (4) needle valve; (5) mass flow controller; (6) capacitance manometer; (7) pumping unit.

merization was kept at 250 mTorr and the flow rates of the monomers were, respectively, 12, 18, and 49 $\text{cm}^3(\text{STP})/\text{min}$ for propylamine, allylamine, and propargylamine.

Plasma polymer films were deposited on KBr windows for IR measurements. To minimize the charging effect, conducting silicon wafers covered with gold were used for the XPS and HREELS analysis. We compared the structure of the polymers deposited on the substrates placed in the reactor (A) and in the postdischarge region (B). The films were analyzed directly after preparation to minimize their oxidation upon air exposure.

Film Characterization

X-ray photoelectron spectra are recorded on a Scienta ESCA 300 spectrometer using a high-power rotating anode (4100 rpm) and the monochromatized X-ray $\text{AlK}\alpha$ radiation (1486.7 eV). The spectrometer was operating at a 0.75 mm slit width and a 75 eV pass energy, giving an instrument resolution of 0.25 eV. The X-ray source was run at a power of 2 kW and charge compensation was achieved by the use of a low-energy electron gun. The polymers were analyzed at a 90° takeoff angle and the core levels were calibrated by reference to the first component of the $\text{C}1s$ core level peak (unfunctionalized hydrocarbons) set at 285.0 eV.

The content of primary amino groups in the films was determined by performing derivatization reactions with pentafluorobenzaldehyde (PFB) and 4-trifluoromethylbenzaldehyde (TFBA), followed by XPS analysis. The conditions of the reaction with PFB were described by Everhart and Reilley.¹¹ The

films were dipped in a 0.1M hexane solution of PFB heated at 40°C . After 2 h reaction, the samples were washed in hexane and Soxhlet-extracted with pentane for 6 h. The labeling of the amino groups by TFBA was achieved by exposing the polymers to TFBA vapors for 1 h at 25°C in a sealed vessel.¹² After both derivatization reactions, the polymers were dried overnight in a vacuum desiccator.

To quantify the $\text{C}=\text{C}$ bonds, the films were introduced in a 0.06M benzene solution of mercuric trifluoroacetate $[\text{Hg}(\text{TFA})_2]$ containing 500 μL of 2,2,2-trichloroethanol (TCE). After 2 h reaction at 25°C , the sample were washed with benzene and Soxhlet-extracted for 12 h with pentane.¹¹

The thickness of the films deposited on gold substrates is estimated by XPS, considering the dependence of the electron mean free path on kinetic energy. For higher kinetic energy than 150 eV, the electron mean free path increases as kinetic energy increases ($\lambda = \text{BE}^{1/2}$).¹⁹ Hence, electrons from different gold energy levels have different escape depths from the sample surface. By comparison of the intensities of peaks due to different gold energy levels ($\text{Au } 4d_{5/2}$ and $\text{Au } 4f_{7/2}$), an estimate of the overlayer thickness was obtained using the equation described in Ref. 20.

A Perkin-Elmer 983G infrared spectrometer was used to collect the transmission spectra of the films deposited on KBr windows. The elemental compositions of the films were analyzed with an Heraeus CHN-O-Rapid elemental analyzer in the Central Research Laboratory from Solvay. Only films deposited from propargylamine could be removed from large-size quartz substrates to give enough product for this type of analysis. The deposits were very ad-

herent to the substrate. However, after immersion in water, swelling of the polymers occurred, so that they could easily be removed from the quartz and transformed into powder upon drying *in vacuo*.

The HREEL spectra were recorded with a commercial spectrometer (SEDRA from Riber-ISA) consisting of two electrostatic deflectors, used as the electron monochromator and analyzer, respectively.²¹ The primary electron beam had a kinetic energy E_0 of 5.2 eV and the recording specular geometry was at 45° from the normal for both incident and scattered beams. The full-width at half-maximum (fwhm) of the spectra are 20 and 23 meV for polyallylamine and polypropargylamine, respectively. To minimize the charging effect, relatively thin films (between 100 and 200 Å) were deposited on conducting substrates (gold-covered silicon plates).

RESULTS AND DISCUSSION

IR Characterization

The comparisons of the IR spectra of the polymers obtained at various powers with the spectra of the monomers show that the monomers have undergone an important reorganization during the polymerization process (Fig. 2): Some bands are considerably broadened; new bands appear and some disappear.

The primary amine N—H stretch double-absorption peaks (3380 and 3290 cm^{-1}) that were well resolved in the spectra of the three monomers (A1) are now replaced in plasma polymers by a wide absorption band (3360 cm^{-1}). This band could originate from a primary amine, a secondary amine, or an imine. The second multiple absorption band at 2960, 2940, and 2880 cm^{-1} (C1) is due to the C—H stretching of aliphatic groups. The C—H deformations located at 1460 and 1380 cm^{-1} (C2) rise up mainly for the polymers obtained at high power. The N—H primary bend absorption (A2, 1640 cm^{-1}) observed on the spectra of the three monomers is also present on the spectra of the polymers (I1). It is, however, considerably broadened and includes, certainly, contributions from C=C alkenes or from C=N imine stretches.

A new band appears for some polymers at 2200 cm^{-1} (H1). It is associated with nitrile groups (C≡N stretching vibration) and is not observed for the polymers deposited from allylamine and propylamine, except when this last polymer is deposited at a power of 30 W. In that case, the band is weak but still visible. This peak could also be due to the pres-

ence of alkyne groups (C≡C stretching). The intensity of this band would then probably be higher at low power. As this is not the case (Fig. 3), we suppose that this peak is due to nitrile functions. Figure 3 shows how the intensity ratio of the C≡N stretch band (H1) to the N—H stretch band (A1) varies for polypropargylamine as a function of the rf power. The proportion of nitrile groups increases until the power reaches 30 W. After that, it decreases and finally vanishes at 50 W. Other evidence of the presence of nitrile functions in polypropargylamine will be deduced later from the XPS results.

Krishnamurthy and Kamel²² previously presented IR data on plasma-polymerized allylamine. In the conditions used for their experiments, primary amine groups from the monomer are converted into imine and nitrile functions. The polymerization of allylamine in our reactor seems to proceed with less transformation of the monomer as no nitrile functions were detected on the IR spectra.

The comparison of the monomer spectra with those of the polymers suggests also the transformation of unsaturated groups into saturated ones. Plasma polymers synthesized from allylamine and propargylamine show an extra absorption band at 2960 cm^{-1} due to methyl group stretches (C1) along with C—H aliphatic bend peaks (C2, 1460 and 1380 cm^{-1}).

XPS Characterization

It is well known that when plasma polymers are exposed to the atmosphere residual radicals cause oxidation of the films.²³ Therefore, the films have been analyzed directly after deposition to prevent intensive postoxidation of the samples. For an exposure time lower than 3 min, between 1.5 and 4.0% of oxygen was taken up in the films.

Atomic Ratios

Atomic ratios obtained by XPS analysis depend on the rf power. Under low-power conditions, nitrogen-rich deposits are obtained in the reactor and in the postdischarge region (Fig. 4). Films with a very high nitrogen content can be formed from allylamine and propargylamine. A value of N/C ($\times 100$) of 40 is reached for polyallylamine deposited at 50 W in the postdischarge region. The evolution of the nitrogen content strongly depends on the sample position. In the reactor, high-power values give rise to nitrogen elimination for all monomers, while for polyallylamine and polypropargylamine deposited in the postdischarge region above 20 W, the concentration

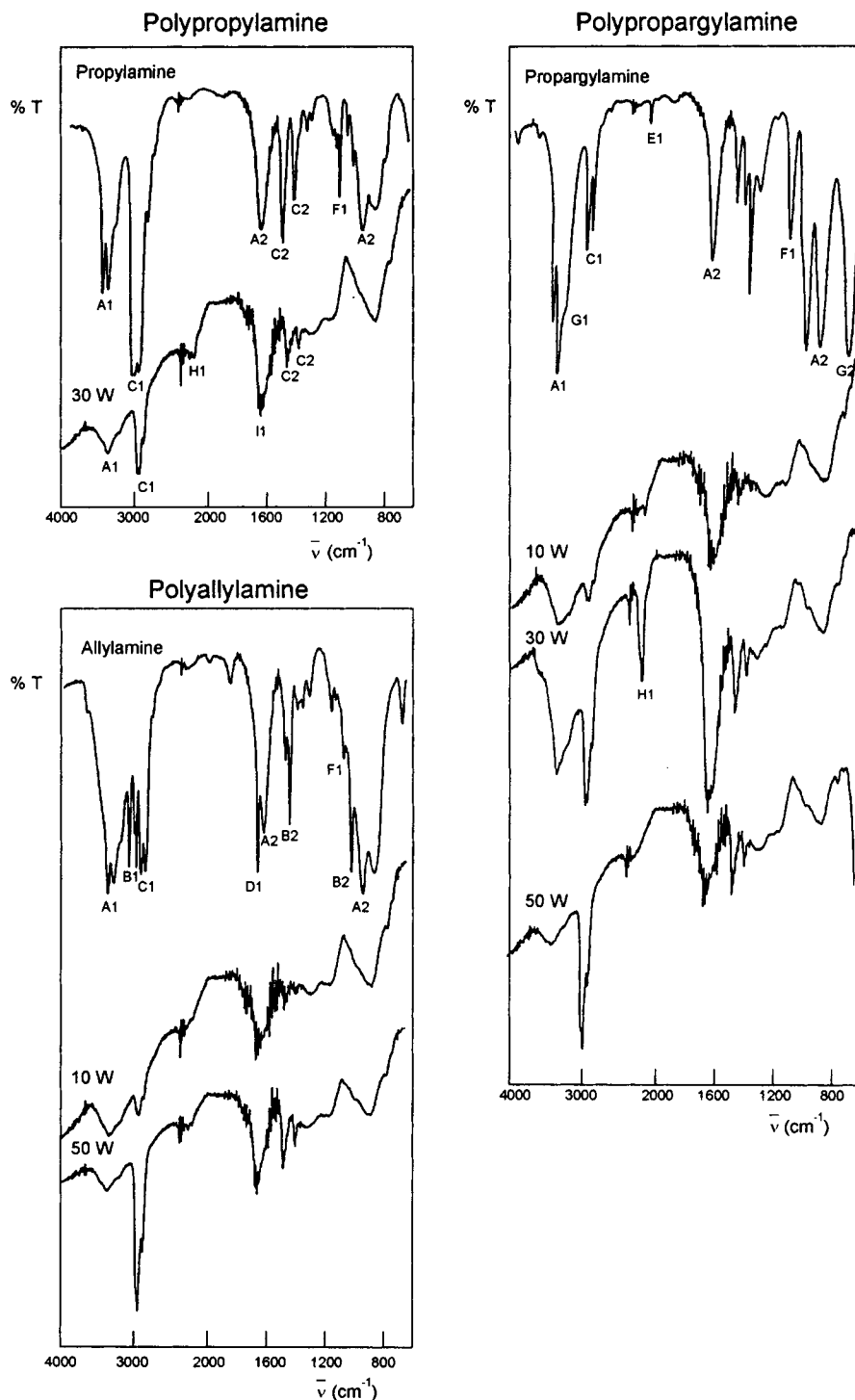


Figure 2 IR spectra of monomers and polymers obtained in the reactor.

of nitrogen increases as a function of power. For the polypropylamine deposited in the postdischarge-region, a decrease of the N/C ratio is observed when the power increases.

These opposite evolutions of the nitrogen content vs. power, for polyallylamine and polypropargylamine, with the sample positions have previously been observed during the polymerization of allyl alcohol

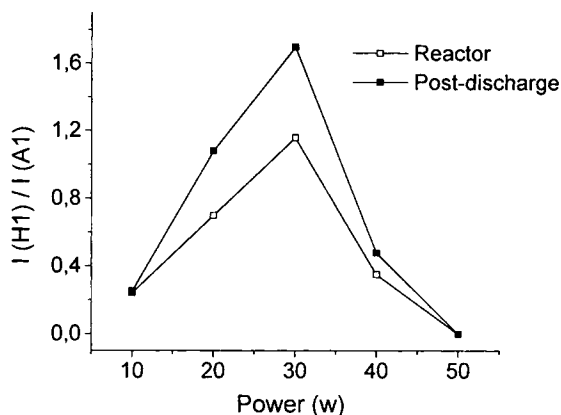


Figure 3 Intensity ratio of the C≡N stretch band (H1) with respect to the N—H stretch band (A1) for polypropargylamine as a function of power.

and propargyl alcohol.⁷ Two hypotheses are proposed to explain the important differences, at high power, between the films formed in the reactor and those deposited in the postdischarge region.

For high-energy input, the important electron temperature and electron density led to numerous fragmentations of the monomer. It is possible that some nitrogen fragments, relatively stable, do not react directly in the reactor. These species could then react on their way to the pump. So, more nitrogen would be fixed on substrates placed in the postdischarge region. The other explanation could be that the polymerization mechanism at high power, in the postdischarge region, is similar to that occurring in the reactor at low power. Actually, the low electron temperature and electron density in the plasma at low power or at high power in the postdischarge region would allow the polymerization to proceed with less fragmentation of the monomer.²⁴ It is also possible that phenomena mentioned above are both involved.

The comparison of the atomic ratio evolution for the three monomers seems to indicate that the double and triple bonds are involved in the polymerization mechanisms of allylamine and propargylamine, respectively (Fig. 4). So, the nitrogen content is higher in the films formed from the unsaturated monomers. The stoichiometry of these polymers formed under mild conditions is also closer to that of the precursor. The higher tendency of nitrogen elimination for propylamine is probably due to the fact that the polymerization cannot proceed via the opening of unsaturations but can only be initiated by bond breakings (N—H, C—N, or C—H). This explanation is supported by the comparison of the deposition rates for the three monomers (Fig. 5).

Deposition Rates

The deposition rate increases with the number of unsaturations: Propargylamine polymerizes more rapidly than does allylamine, which has a higher deposition rate than does the saturated monomer (Fig. 5). This supports the role played by the double and triple bonds in the deposition mechanism. Figure 5 shows also that thicker films are obtained on substrates placed in the reactor where the electron temperature and electron density are higher.²⁴ For the three polymers and the two regions, the deposition rate increases with power. This shows that the polymerization reactions predominate over the ablation reactions. These evolutions are different from those observed for the corresponding alcohol functions containing monomers (allyl alcohol and propargyl alcohol) for which an increase in deposition rate vs. power was followed by a drastic decrease due to numerous ablation reactions.⁷ This lower tendency of ablation in the case of the amino groups containing monomers explains why the nitrogen elimination is less pronounced than is the oxygen

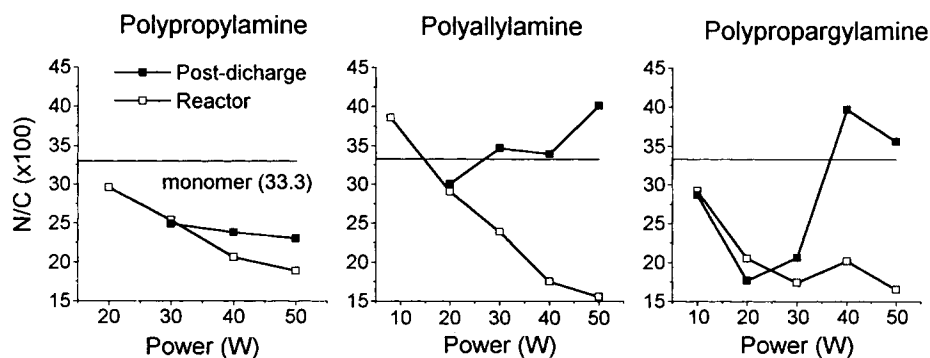


Figure 4 XPS N/C atomic ratios ($\times 100$) of polypropylamine, polyallylamine, and polypropargylamine deposited at different values of rf power.

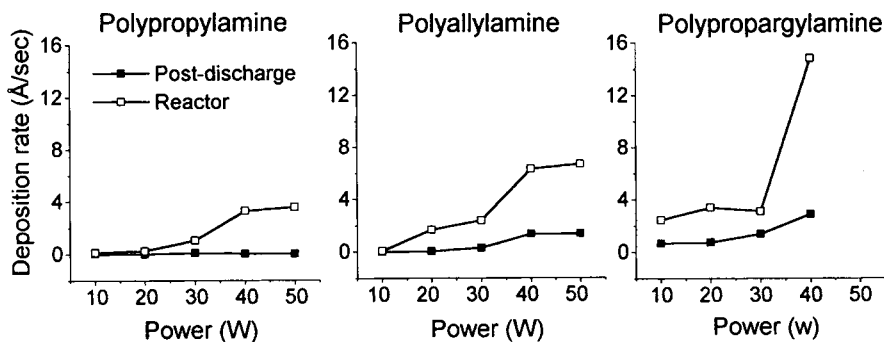


Figure 5 Deposition rates ($\text{\AA}/\text{s}$) of polypropylamine, polyallylamine, and polypropargylamine for different values of rf power.

elimination during the polymerization under hard conditions. For the three monomers used in this study, the N/C ratios ($\times 100$) of the deposits formed at high power in the reactor remain higher than 15, while O/C ratios ($\times 100$) between 6 and 8 were found for polyallyl alcohol and poly(propargyl alcohol) deposited in the same conditions.

Evolution of the C1s Core Level Spectra

The C1s core level spectra of polyallylamine obtained at different powers is shown in Figure 6. For the films

deposited in the reactor, the shoulder, located at higher binding energy and due to carbon atoms bonded to nitrogen atoms, decreases vs. power. On the other hand, for the postdischarge position, increasing the power gives rise to a decrease of this shoulder followed by an increase at higher values. Similar trends were observed for polypropargylamine.

Simulation of the C1s and N1s Core Levels

Obtaining quantitative information from the simulation of the XPS C1s or N1s signals on the func-

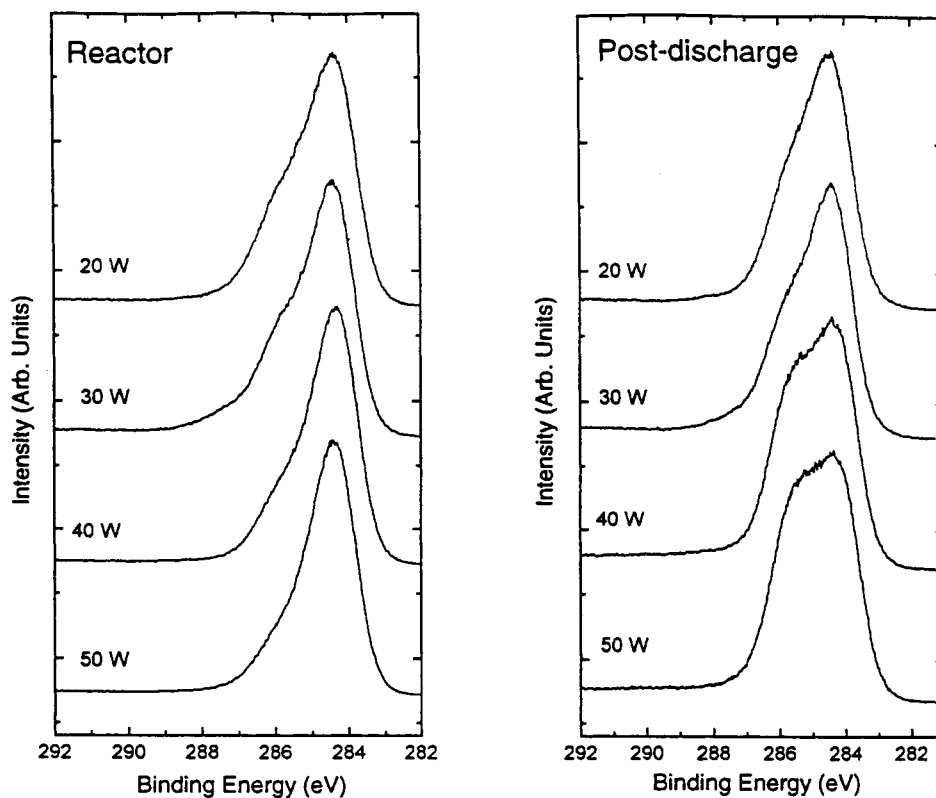


Figure 6 XPS C1s core levels spectra of polyallylamine deposited at different values of rf power in the reactor and in the postdischarge region.

tional groups (amine, imine, nitrile, amide, . . .) present in multifunctional nitrogen-containing polymers is not easy. One reason is that the chemical shifts between the different functionalities are rather small. However, due to the good resolution of the Scienta XPS spectrometer, the reconstruction of the core levels of some polymers gives several distinct components that can be attributed to different chemical environments. Several nitrogen-containing polymers used as reference materials have been analyzed by Beamson and Briggs on the same spectrometer, giving the C1s and N1s chemical shifts induced by the presence of different nitrogen functionalities.¹⁰ However, some functions such as imine groups are not found among the commercial polymers.

Theoretical calculations can also be very helpful for identifying chemically shifted atoms in different chemical environments. For example, Naves de Brito et al.²⁵ solved a controversy in the assignment of the components of the C1s of polyacrylonitrile. They used proper calculations on model molecules such as acetonitrile, propionitrile, and acrylonitrile and extrapolated their results to the case of polyacrylonitrile. This theory correctly predicts the chemical shifts on the C1s core level of the polymer. However, these types of theoretical calculations have been performed mainly in order to be correlated with the experimental spectrum of commercial well-defined polymers.

Quantitative information on the nitrogen functional groups in the polymer structure have been obtained from the simulation of the C1s only for polypropylamine and polyallylamine. Four components are needed for simulating the spectra [Fig. 7(a) and Table I]. For these types of plasma polymers, the assignment of the components is simpler because no nitrile functions have been detected by IR spectroscopy (Fig. 2). The first component due to unfunctionalized hydrocarbons (CH_x environment) (a) was positioned at 285.0 eV, while the second one appearing at 285.9 eV (b) is attributed to carbon atoms singly bonded to nitrogen ($\text{C}-\text{NH}_2$, $\text{C}-\text{NH}-\text{C}$, $\text{C}-\text{N}=\text{C}$, . . .). This component has been assigned by reference to the values given by Beamson and Briggs for polyethyleneimine (commercial polymer containing secondary amine functions).¹⁰

As only amine and imine functions were detected by IR spectroscopy, the third important component, located at 286.8 eV (c), can only be due to the presence of imine groups ($\text{C}=\text{N}$). The last component (d) (288.0 eV), of low intensity, is due to the small oxygen contamination in the films (carbonyl functions, amide functions, . . .). The presence of these

different functions (amine, imine, amide . . .) in the polymers leads to a broad N1s core level peak (fwhm = 1.8 eV) appearing at 399.5 eV.

Knowing that component (c) is only due to carbon atoms doubly bonded to nitrogen ($\text{C}=\text{N}$), the proportion of imine functions can be calculated from the comparison of the percentage of component (c) with the N/C ($\times 100$) ratio. For example, for polyallylamine deposited at 30 W in the reactor, the N/C ($\times 100$) ratio is 23.9. As carbon atoms from the imine groups ($\text{C}=\text{N}$) represent 14.9% from the carbon atoms, we can deduce that 62.3% of the nitrogen atoms are imine functions.

Figure 8 shows that for all values of power the imine functions are the main functions (more than 50%) in polypropylamine and polyallylamine. For the films deposited in the reactor, the percentage of imine functions is higher for increased values of power. It seems also that more imine functions are formed in polypropylamine: up to 82% for the films obtained at 50 W in the reactor. For polypropylamine deposited at 30 W in the reactor, the percentage of imine functions was not calculated because of the weak absorption band due to the presence of nitrile functions on the IR spectrum.

These values have been compared to those obtained from the reconstruction of the broad N1s core levels [Fig. 7(a)]. The three components used for the simulation, appearing at 398.8, 399.7, and 400.7 eV, respectively, assigned to amine functions, imine, and oxidized species (Table I). For polyallylamine deposited at 30 W in the reactor, component (b) arising from imine functions represents 61.5% of the nitrogen atoms. This value is close to that obtained from the reconstruction of the C1s core level.

These results show that the primary amine groups have a very high tendency to be transformed into imine groups in the plasma; even at very low power, more than 50% imine groups are found in the polymers. The tendency of transformation into imine functions seems higher at high power.

Four components appearing approximately at the same energy positions are needed for simulating the C1s of polypropargylamine (Table I). In that case, as absorption bands due to nitrile groups are present on the IR spectra, component (c) due to imine functions ($\text{C}=\text{N}$) includes also carbon atoms from the nitrile groups ($\text{C}\equiv\text{N}$) as well as carbon atoms in the α position from the nitrile group ($\text{C}-\text{C}\equiv\text{N}$).¹⁰ This overlap hinders any quantitative information.

However, the comparison of the percentage of component (c) with the N/C ($\times 100$) ratio seems to confirm the presence of nitrile groups in the polymers (Table II). Table II shows that when the rel-

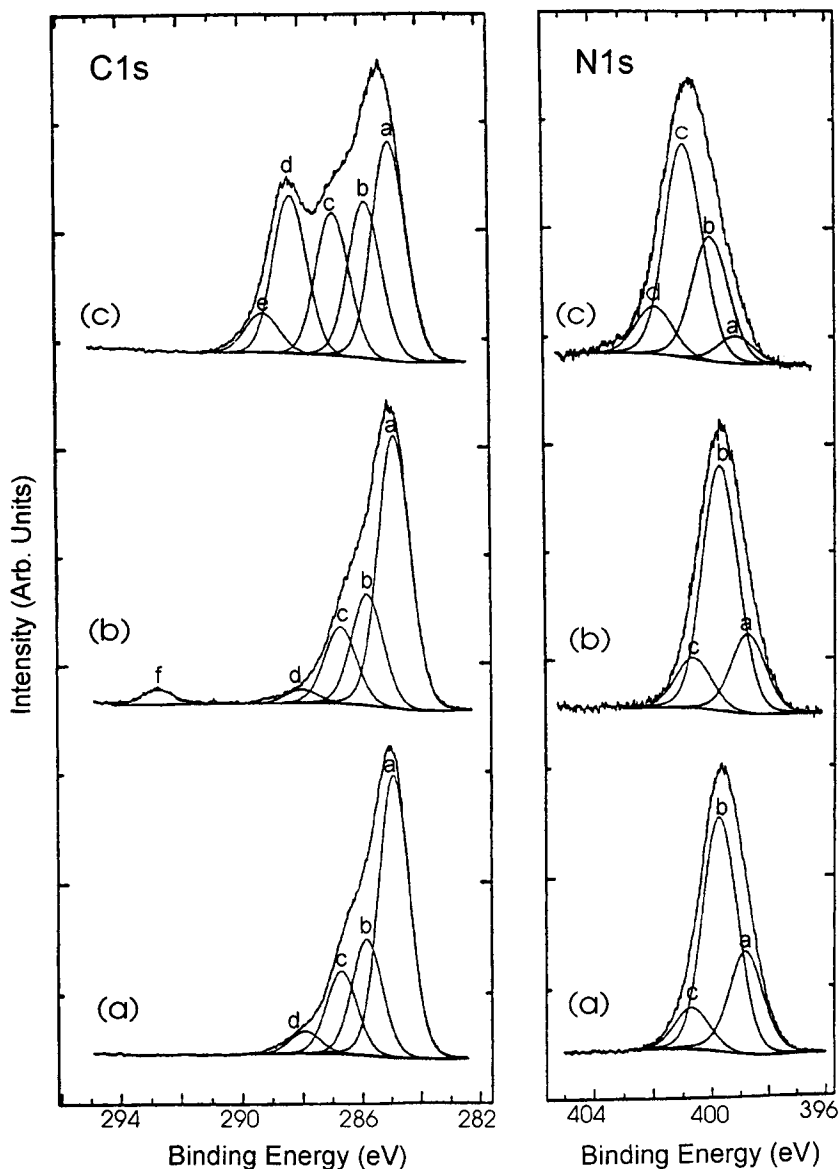


Figure 7 Simulation of the XPS C1s and N1s signals for polyallylamine deposited at 30 W in the reactor (a) before and after derivatization with (b) TFBA and (c) PFB.

ative intensity of the $C\equiv N$ stretch band (H1) with respect to the intensity of the N—H stretch band (A1) is high the percentage of component (c) is close to the N/C ($\times 100$) ratio and even higher for the polypropargylamine deposited at 20 W (postdischarge region) and at 30 W. This is an indication of the presence of nitrile functions. Since for one nitrogen from a nitrile group two carbon atoms are shifted to relatively high binding energy [component (c)], the presence of nitrile functionalities can lead to a higher percentage of component (c) compared to the N/C ($\times 100$) ratio. These results confirm that

the IR absorption band appearing at 2200 cm^{-1} is mainly due to nitrile functions.

Primary Amine Derivatization

The accessibility and reactivity of primary amino groups were deduced from tagging reactions with pentafluorobenzaldehyde (PFB) in the liquid phase¹¹ and with 4-trifluoromethylbenzaldehyde (TFBA) in the vapor phase,¹² followed by XPS analysis [Fig. 9(a) and (b)]. Table III gives atomic percentages for polyallylamine deposited at 30 W

Table I Corrected C1s and N1s Binding Energies (Eb), Percentages, and Attributions of the Components Obtained from Peak Fits for Polypropylamine (PPP), Polyallylamine (PAA), and Polypropargylamine (PPA) Deposited at 30 W in the Reactor as Well as for the PFB and TFBA-derivatized Polyallylamine Samples (PAA-TFBA and PAA-PFB).

Sample	C1s Core Level: Eb (eV) and (%)						N1s Core Level: Eb (eV) and (%)					
	a	b	c	d	e	f	a	b	c	d	FIs	
	$\underline{\text{C}}\text{H}_x$	$\underline{\text{C}}-\text{NH}_2$ $\underline{\text{C}}-\text{NH}$ $\underline{\text{C}}-\text{N}=\text{C}$	$\underline{\text{C}}-\underline{\text{C}}=\text{N}$ $\underline{\text{C}}-\underline{\text{C}}\equiv\text{N}$	$\underline{\text{C}}\text{O}-\text{NH}$ $\underline{\text{C}}=\text{O}$ $\underline{\text{C}}-\text{F}$	$\underline{\text{C}}(\text{O})\text{O}$ (1)	$\underline{\text{C}}\text{F}_3$	$\underline{\text{C}}-\underline{\text{N}}$	$\underline{\text{C}}=\underline{\text{N}}$ $\underline{\text{C}}\equiv\text{N}$	(2)	NH^+	Eb (eV)	
PPP	285.0 54.6%	285.9 22.4%	286.7 21.5%	288.0 1.5%	—	—	398.9 17.0%	399.7 76.0%	400.9 7.0%	—	—	
PAA	285.0 53.0%	285.9 27.0%	286.8 14.9%	288.0 5.1%	—	—	398.8 28.0%	399.7 61.5%	400.7 10.9%	—	—	
PPA	285.0 52.0%	285.9 27.0%	286.8 18.7%	288.2 2.2%	—	292.8 3.0%	398.9 20.9%	399.7 70.2%	401.0 8.7%	—	—	
PAA-TFBA	285.0 55.7%	285.9 22.5%	286.8 15.6%	288.1 2.8%	—	—	398.5 21.2%	399.4 65.2%	400.4 13.4%	—	688.3	
PAA-PFB	285.0 31.3%	285.8 22.1%	286.8 19.6%	288.3 21.7%	289.2 5.3%	—	398.8 6.8%	399.7 29.9%	400.5 51.6%	401.5 11.6%	688.4	

(1) $\text{NH}-\underline{\text{C}}(\text{O})\text{O}$; (2) $\text{NH}-\text{C}(\text{O})\text{O}$.

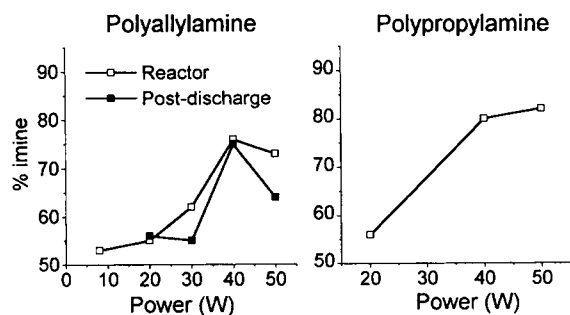


Figure 8 Proportion of imine functions obtained by XPS analysis for polypropylamine and polyallylamine as a function of power.

in the reactor (TOA = 90°) before and after derivatization. The derivatized sample with PFB and TFBA contain, respectively, 10 and 6% fluorine. Knowing the stoichiometry of the reactions, the NH₂ proportion in the films is easily calculated from the F/N ratios.

Different values are obtained for the two tagging reactions. The proportion of primary amine functions deduced from the reactions with PFB is 18%, while a value of 11% is obtained for the TFBA reaction. These differences underline the difficulty of quantification of the primary amino groups.

The atomic percentages (Table III) show that the PFB-derivatized samples contain a large amount of oxygen, close to the nitrogen one. From the comparison of the C1s core levels, it seems that both reactions proceed well, as new components (f) due to carbon atoms from the CF₃ group and (d) due to carbons singly bonded to fluorine appear, respectively, after derivatization with TFBA and PFB (Table I and Fig. 7).

The N1s core level of the polymers before and after derivatization with TFBA appears approximately at equivalent binding energy (399.5 eV), while the N1s of the PFB-derivatized sample is shifted by approximately 0.9 eV to higher binding energy (Fig. 7). The reconstruction of the N1s core levels shows that for the polymers and the TFBA-derivatized samples the (b) component (399.4–399.7 eV) due to imine or nitrile functions is the major component (Table I). This component is of lower intensity in the PFB-derivatized samples for which nitrogen atoms appearing at 400.5 eV [component (c)] are in a higher proportion. It is possible that the imine functions formed after reaction of the primary amine functions with PFB appear at higher binding energy [component (c)] due to a withdrawing effect of the fluorine-substituted phenyl rings. However, as only 18% of the nitrogen atoms have

reacted with PFB, to explain the high intensity of component (c), other types of nitrogen atoms such as NH-C(O)O must be present in the polymers. Component (c) can thus be correlated to the oxygen contamination of the samples. The additional component (d) needed for fitting the N1s core level spectra of the PFB-derivatized samples could be due to still more oxidized species or NH⁺-type nitrogen atoms.

Several hypotheses can be suggested to explain the high oxygen content in these derivatized samples. First, the nonspecific adsorption of PFB which contains oxygen could be responsible for it and would lead to an overestimation of the primary amine calculated concentration. Another possibility is that some water produced by the reaction is trapped in the films. Tougas and Collier²⁶ also suggested that the ring is susceptible to undergoing a nucleophilic attack by an oxygen species. Such an attack could explain the oxidation and would result in the formation of F⁻ as a leaving group. The primary amine calculated yield would then be too low. However, all these hypotheses cannot explain the shift on the N1s core level, which probably results from the oxidation of the polymer in the solution used for the reaction.

To obtain information on the penetration depth of the reagents, the derivatized samples have been analyzed by XPS at different electron takeoff angles (TOA). For the PFB-derivatized samples, the atomic percentages show little difference [Fig. 10(b)]. This suggests that the reaction proceeds over the full sampling depth analyzed by XPS. On the other hand, for the TFBA-derivatized samples, the fluo-

Table II N/C Ratios (×100) and Percentages of Component (c) Resulting from the Simulation of the XPS C1s Core Levels of Polypropargylamine for Different Values of rf Power

Power (W)	I(H1)/I(A1)	N/C (×100)	% (c)
Reactor			
10	0.2	29	20
20	0.7	20	19
30	<u>1.2</u>	<u>17</u>	<u>19</u>
50	—	16	9
Postdischarge			
10	0.2	29	23
20	<u>1.1</u>	<u>18</u>	<u>21</u>
30	<u>1.7</u>	<u>19</u>	<u>20</u>
50	—	36	24

I(H1)/I(A1): relative intensity of the C≡N stretch band with respect to the N—H stretch band obtained by IR analysis.

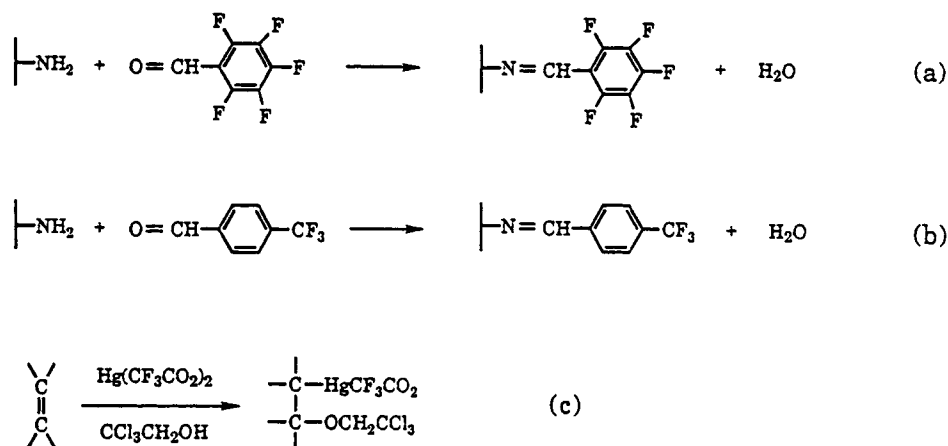


Figure 9 Amino and double bonds derivatization reactions with (a) pentafluorobenzaldehyde (PFB), (b) 4-trifluoromethylbenzaldehyde (TFBA), and (c) mercuric trifluoroacetate [$\text{Hg}(\text{TFA})_2$] and 2,2,2-trichloroethanol (TCE).

rine content increases and the nitrogen content decreases when the sampling depth analyzed by XPS decreases (smaller TOA) [Fig. 10(a)]. This can be explained by the incomplete reaction of TFBA over the sampling depth. Compared to the reaction with PFB in the liquid phase, the penetration of TFBA in the films is probably more difficult because the reaction was performed in the vapor phase. Moreover, according to the experimental protocol proposed by Terlingen et al.,¹² the temperature used for the reaction (25°C) was also lower. These different compositions obtained for various TOA could also be due to a preferential orientation of the CF_3 groups at the surface of the polymers.

To favor the penetration of TFBA in the films, derivatization reactions have been performed at higher temperatures (35 and 45°C). A similar evolution of the atomic ratios with TOA has been observed. It is therefore probable that these different compositions obtained for various TOA are not due to an incomplete penetration of TFBA over the sampling depth analyzed by XPS but to a preferential orientation of the CF_3 groups at the surface of the polymers.

This variation of the stoichiometry of the TFBA-derivatized samples, determined by XPS for various TOA, leads to some errors when the primary amine function content in the films is calculated from the atomic ratios. If these variations are due to a preferential orientation of the CF_3 groups at the surface of the samples, the better estimations of the amine content in the films are obtained at 90° TOA (higher sampling depth analyzed by XPS).

The XPS analyses of PFB- and TFBA-derivatized samples have therefore shown peculiar prob-

lems for both reactions. Important oxidation occurs during the first reaction while variations of the atomic ratios with TOA is observed for the second one. Moreover, these reactions are not entirely specific to the primary amine functions. By performing these reactions on polyethyleneimine (polymer containing secondary amine functions), we observed that both reagents react partially with the secondary amine functions: 46.5 and 40.2% of the nitrogen atoms of this polymer, respectively, react with PFB and TFBA.

Despite the errors due to the problems described above, the proportion of primary amine functions—probably overestimated because of the reaction with part of the secondary amine functions—were deduced from the intensities of the F1s and N1s core levels spectra (Table IV). The percentage of primary amine functions in the films varies between 10 and 33%. These very low values are in agreement with the information obtained from the simulation of the core levels which have shown the high tendency of transformation of the primary amine groups into imine or nitrile functions.

Double Carbon–Carbon Bond Derivatization

The proportion of $\text{C}=\text{C}$ bonds in the three polymers formed in the reactor at 30 W was determined from the reaction with mercuric trifluoroacetate [$\text{Hg}(\text{TFA})_2$] and 2,2,2-trichloroethanol (TCE) [Fig. 9(c)].

Table V shows the atomic ratios of the derivatized samples. The low Cl/Hg ratios can be due to the fact that the mercury detected in the samples does not result only from the reaction of the $\text{C}=\text{C}$ bonds

Table III XPS Atomic Percentages of Polyallylamine Deposited at 30 W in the Reactor (TOA = 90°) Before and After Derivatization Reactions

	Before Derivatization	Derivatization (PFB)	Derivatization (TFBA)
% C	85	69	72
% N	13	11	18
% O	2	10	4
% F	—	10	6

with $\text{Hg}(\text{TFA})_2$ and TCE: Some complexation reactions can occur between $\text{Hg}(\text{TFA})_2$ and nitrogen functionalities. Considering the reaction proposed in Figure 9(c), the proportion of $\text{C}=\text{C}$ bonds in the samples can be deduced from the $\text{Cl}2p$ core level intensities.

Quantitative information was obtained by comparing the atomic ratios $\text{Cl}/3\text{N}$ of the derivatized samples with the N/C^* ratios of the polymers before derivatization (Table V). The atomic ratios $\text{Cl}/3\text{N}$ give information on the proportion of $\text{C}=\text{C}$ double bonds per nitrogen atoms. Knowing the proportion of nitrogen atoms per carbons in the samples before derivatization, the number of double bonds per carbon atoms was estimated. Polyallylamine deposited at 30 W in the reactor contains one double bond for 198 carbon atoms. This shows that for this monomer the double bonds are saturated in the plasma. During the polymerization of polypropargylamine, some

triple bonds can be transformed into double bonds, leading to some more $\text{C}=\text{C}$ bonds (1 $\text{C}=\text{C}$ for 73 C) compared to polyallylamine. However, the proportion of unsaturations remain still very low. The saturated monomer (propylamine) forms a polymer with 1 $\text{C}=\text{C}$ for 114 C.

Elemental Analysis

The elemental compositions of polypropargylamine deposited in the reactor under different values of power have been obtained with a Heraeus CHN-O-Rapid elemental analyzer and compared to the XPS atomic ratios (Table VI). This technique allows the determination of the hydrogen percentages that cannot be reached by XPS. The values obtained by both analysis for the N/C ratios are relatively close. However, the percentages of nitrogen found by elemental analysis are a little higher than those calculated from the XPS results. This could be due to some surface contamination by hydrocarbons, leading to an underestimation of the N/C atomic ratios by a surface-sensitive technique such as XPS.

By contrast, the O/C atomic ratios are quite different. Although the surface of the polymer is normally more oxidized than is the bulk polymer, more oxygen contamination is present in the samples analyzed by elemental analysis (Table VI). This can be explained by a longer exposure time to the atmosphere: The samples were analyzed by XPS directly after their preparation, while the elemental analysis were performed only 2 months after de-

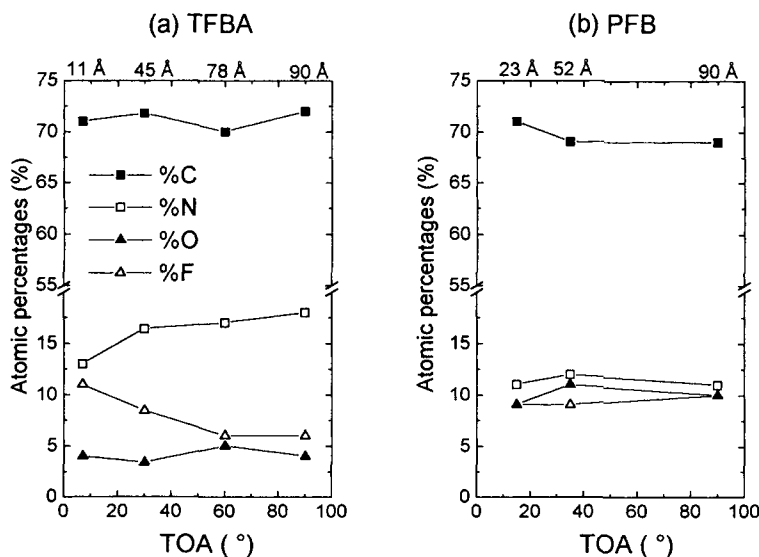


Figure 10 Atomic percentages obtained by XPS analysis with different TOA for (a) TFBA and (b) PFB derivatized polyallylamine (30 W reactor).

Table IV Proportion of Primary Amine Functions (%) for Plasma Polymers Deduced from the Reactions with Pentafluorobenzaldehyde (PFB) and [4-trifluoromethylbenzaldehyde (TFBA)]; Samples Analyzed at 90° TOA

Power (W)	Polypropylamine		Polyallylamine		Polypropargylamine	
	Reactor	PD	Reactor	PD	Reactor	PD
10	—	—	[33]	[24]	—	—
20	10	—	18	16	28	—
30	11	26	18 [11]	14 [31]	—	—
40	—	—	—	11	14	—
50	22	19	17	—	—	—

PD: postdischarge region.

position. This can also be due to the method used to collect the polymers for the elemental analysis. As the films were very adherent to the substrate, in order to remove the polymers from it, they were immersed in distilled water. The water permeates the film and allows its detachment from the substrate. Afterward, the samples were dried under vacuum. The high concentration of oxygen detected in the samples after drying could therefore arise from the reaction between water and the radicals trapped in the films.

Compared to the monomer ($C_1H_{1.66}N_{0.33}$), the polymers are hydrogen-deficient (Table VI). This hydrogen removal is more pronounced at high power and can be correlated to the elimination of nitrogen-containing fragments as well as to the transformation of the amine groups into imine and nitrile functionalities.

Evolution of the Samples upon Air Exposure

The stability upon storage in air of polypropargylamine deposited at 30 W in the reactor was investigated by means of XPS angular analysis. It is well known that when the plasma polymers are exposed to atmosphere residual trapped radicals react

with oxygen.²⁷ This leads to oxygen incorporation in the films. Table VII sums up the variation of the atomic ratios with the takeoff angle for polypropargylamine directly analyzed after polymerization. The oxygen concentration is higher at the surface. On the other hand, at a TOA of 20°, the N/C ratio is smaller. This could be due to some hydrocarbon contamination at the surface of the polymer. To suppress the errors that can arise from this contamination, to study air oxidation, we followed the evolution of the O/N ($\times 100$) ratio with the time exposure to the atmosphere. Figure 11 shows that the oxygen concentration increases rapidly with time and that this oxidation is more pronounced at the surface of the polymer. After 36 h air exposure, the oxygen percentage at the surface of the polymer is almost equal to the nitrogen percentage.

For Gengenbach et al.,²⁸ the diffusion of oxygen in the films cannot explain the preferential oxidation at the surface of the polymer. Oxygen penetrates rapidly on the whole sampling depth of the polymer analyzed by XPS. It is therefore not easy to explain the slower evolution of the oxidation more deeply into the polymer. The authors have proposed an oxidation mechanism similar to that observed in the case of radical-induced oxidation of conventional

Table V Atomic Ratios Cl/Hg, Cl/3N, N/C*, and Proportion of Double Bonds for Polypropylamine, Polyallylamine, and Polypropargylamine Derivatized with Mercuric Trifluoroacetate (30 W Reactor)

	Cl/Hg	Cl/3N	N/C*	Proportion of C=C Bonds
Polypropylamine	0.19	0.035	0.25	1 C=C for 114 C
Polyallylamine	0.22	0.021	0.24	1 C=C for 198 C
Polypropargylamine	0.39	0.080	0.17	1 C=C for 73 C

N/C*: atomic ratios of the polymer before derivatization.

polyolefins.²⁹ The primary peroxy radicals which are metastables decompose with time to give rise to various very complicated oxidative chain reaction pathways, which, in turn, produce secondary radicals. While some reactions quench radicals, others lead to chain branching with the generation of two new radicals. Thus, the oxidative process continues for an extended period of time. Therefore, following the formation of initial peroxides, very complex chain oxidative reactions occur.

The slower progression of the oxidative processes more deeply into the polymer compared to the extreme surface could be explained by this complex mechanism. The oxidation rate could be limited by the decay rate of the metastable hydroperoxides, which decay to produce further radicals.

HREELS Characterization

The HREEL spectrum of polyallylamine is shown in Figure 12. It has a resolution of 20 meV (measured as the fwhm of the elastic peak). Despite the relative poor resolution of this spectrum, compared to the IR spectrum, some bands or shoulders are clearly discernible and can be easily identified. Their positions are approximately the same as for the bulk infrared spectrum of the polymer. The bands due to hydrocarbon groups which are always present on the HREEL spectra of polymers³⁰ appear at 2950 cm^{-1} (C—H stretching) and 1400 cm^{-1} (C—H bending). The band at 3370 cm^{-1} (N—H stretching) can be due to the presence of primary amine, secondary amine, or imine functionalities. Because of the very high sensitivity of this technique to the extreme surface, the presence of this band shows that some functionalities which contain N—H bonds are present in the top 0–20 Å of the polymer. The shoulder at 1640 cm^{-1} can include C=C or C=N stretching vibrations as well as N—H deformations. As a very high concentration of imine functionalities have been detected by XPS, an important contribution of these functionalities to the shoulder is expected.

Table VII Atomic Ratios N/C ($\times 100$) and O/C ($\times 100$) Obtained by XPS Analysis with Different TOA for Polypropargylamine Deposited at 30 W in the Reactor

TOA	80°	50°	20°
N/C ($\times 100$)	22	22	19
O/C ($\times 100$)	2	3	6

The comparison of the HREEL spectra of polyallylamine and polypropargylamine (Fig. 13) shows that a new band which could be due to C \equiv N or C \equiv C stretching vibrations appears at 2220 cm^{-1} for polypropargylamine. This extra band had also been detected by IR and had been assigned to nitrile functionalities.

The comparison of the XPS, IR, and HREELS results are in very good agreement. It seems, therefore, that the chemical composition at the extreme surface is representative to that of the bulk.

DISCUSSION

This multitechnique characterization of plasma-deposited films of amine function-containing monomers has shown the difficulty in quantifying the chemical functions present in such polymers. However, by using several techniques (high-energy resolution X-ray photoelectron spectroscopy, chemical derivatization, infrared, . . .), apparently consistent quantitative results have been obtained.

In the reactor at high plasma power, nitrogen elimination as well as important transformations of the primary amine functions into imine or nitrile functions occur during the polymerization. These important reorganizations of the monomers are due to numerous bond breakings (C—C, C—N, C—H, N—H, . . .) resulting from the high electron density and electronic temperature in such plasmas.

Table VI Atomic Ratios Obtained by Elemental and XPS Analysis of Polypropargylamine Deposited in the Reactor

10 W	Elemental analysis	C ₁	H _{1.35}	N _{0.31}	O _{0.15}
	XPS analysis	C ₁			
20 W	Elemental analysis	C ₁	H _{1.28}	N _{0.25}	O _{0.12}
	XPS analysis	C ₁			
30 W	Elemental analysis	C ₁	H _{1.24}	N _{0.21}	O _{0.08}
	XPS analysis	C ₁			

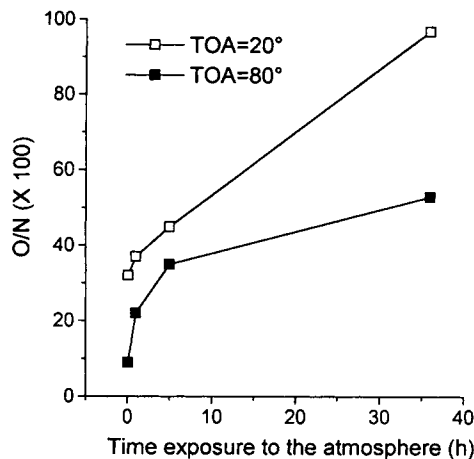


Figure 11 Atomic ratios O/N ($\times 100$) obtained by XPS analysis of polypropargylamine (30 W reactor) upon time exposure to the atmosphere.

However, at low power or at high plasma power in the postdischarge region, nitrogen-rich polymers can be deposited from the unsaturated monomers (allylamine, propargylamine). For these two monomers, the opening of the double or triple bond detected by IR spectroscopy and chemical derivatization with mercuric trifluoroacetate is probably involved in the deposition mechanism. This participation of the unsaturations is also suggested by the increase of the deposition rate with the number of unsaturations. However, even at low power where little fragmentation of the monomer was expected, most of the primary amine functions were transformed into imine or nitrile functions.

These transformations can result from the breaking of molecular bonds [Fig. 14(1)–(4)]. The

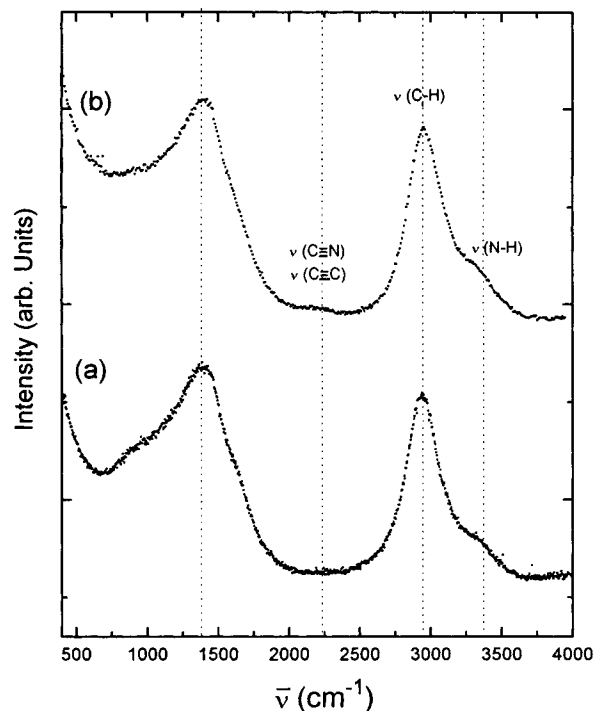


Figure 13 Comparison between the HREEL spectra of (a) polyallylamine (20 W reactor) and (b) polypropargylamine (30 W reactor).

higher deposition rates for the unsaturated monomers are related to the presence of the double or triple bonds which could enhance the possibilities of initiation of the polymerization [(5) and (6)] or which could also act as reaction sites for radicals [(7) and (8)]. For the unsaturated monomers, the contribution of the propagation steps is probably dominant compared to initiation steps.

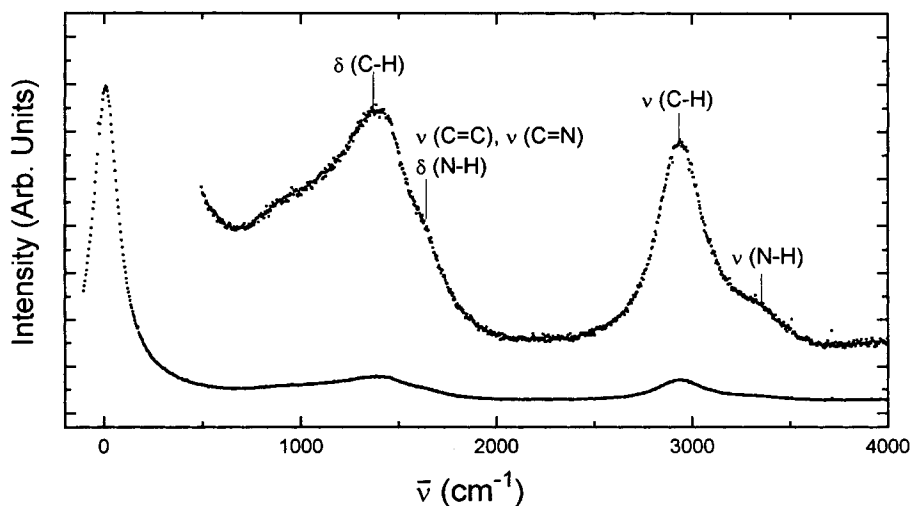
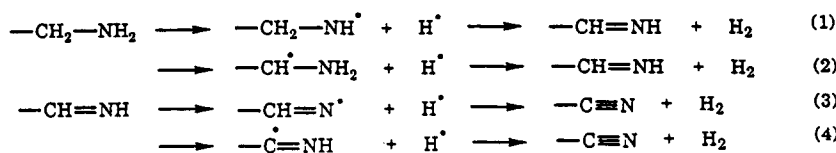


Figure 12 HREEL spectrum of polyallylamine deposited at 20 W in the reactor.

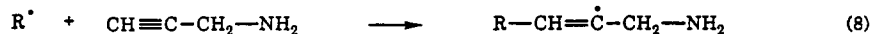
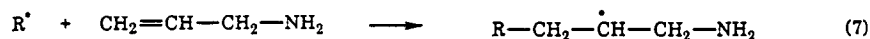
Reactions leading to the formation of imine or nitrile functions.



Initiation reactions via the unsaturations.



Propagation reactions via the unsaturations.



Reactions of the primary amine with radicals.

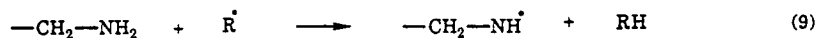


Figure 14 Possible reactions in the plasma.

Comparing the deposition rates at low power of the unsaturated monomers with that of propylamine, it appears that reactions such as (5)–(8) would play a more significant role in the deposition mechanisms than reactions leading to bond breaking. Since these reactions imply the incorporation of primary amine functions in the films, one would expect that the nitrogenated functions of polymers deposited from unsaturated monomers would essentially be primary amines. To account for the significant transformation of primary amines during the low-power polymerization of allylamine and propargylamine, other reactions must occur in the plasma, such as the reaction of primary amines with radicals (9).

CONCLUSION

Films have been plasma-deposited from propylamine, allylamine, and propargylamine. Detailed structural information on the polymers was obtained by using high-energy-resolution XPS, chemical derivatization, infrared, elemental analysis, and HREELS. In the reactor, at high plasma power, elimination of nitrogen fragments takes place during the polymerization process. To obtain nitrogen-rich plasma polymers, unsaturated monomers must be deposited at low power or at high power in the post-

discharge region. IR analysis, chemical derivatization, and the evolution of the deposition rates suggest that in these conditions the double or triple bonds are involved in the deposition mechanisms.

Quantitative information on the proportion of functional groups in the polymers have been obtained by XPS from the simulation of the C1s and N1s core levels and by using chemical derivatization reactions. During the polymerization, the primary amino groups have a very high tendency to be transformed into imine or nitrile groups. Even at low power, more than 50% imine groups were found in polypropylamine and polyallylamine. Nitrile functions were detected by IR and HREEL spectroscopies for polypropargylamine.

The proportion of remaining primary amino groups in the polymers was deduced from tagging reactions with pentafluorobenzaldehyde (PFB) in the liquid phase and with 4-trifluoromethylbenzaldehyde (TFBA) in the vapor phase, followed by XPS analysis. The percentages of primary amine functions calculated vary between 10 and 33%.

Even if the values obtained are in agreement with the results from the simulation of the XPS core levels, we have shown the difficulty to quantify the proportion of primary amine functions by using derivatization reactions. Problems have been observed for both reactions: Oxidation occurs during the reaction with PFB, while for the TFBA-derivatized

samples, the fluorine and nitrogen percentages measured by XPS vary with TOA. Moreover, the reactions are not entirely specific to the primary amine functions; reactions with secondary amine functions have been observed.

We have also shown that HREELS can be useful to characterize the extreme surface of plasma polymers. This technique has allowed us to distinguish between different nitrogen functionalities.

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