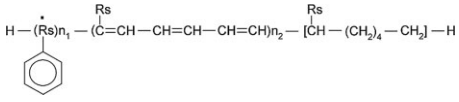
Chemically Polymerization Mechanism of Aromatic Compounds under Atmospheric Pressure Plasma Conditions

Mihai Asandulesa, Ionut Topala,* Valentin Pohoata, Yves Marie Legrand, Marius Dobromir, Marian Totolin, Nicoleta Dumitrascu*

The multitude of chemically reactive species that are involved in plasma polymerization process make difficult to anticipate how the polymer will look like. In order to prepare polymerized films with imposed properties a good control over the plasma polymerization reaction should be done. In this paper, we investigate plasma polymerization reactions of aromatic compounds using a cold atmospheric pressure glow discharge working in helium. The structure of polymerized films was determined using infrared spectroscopy, X-ray photoelectron spectroscopy, and nuclear magnetic resonance spectroscopy. Furthermore, the results of spectroscopic analyses allowed us to develop a polymerization mechanism from a chemical point of view related to formation of plasma-polymerized films.



1. Introduction

Plasma polymerization involves complex physico-chemical reactions, very different from classical polymerization methods. In plasma, organic molecules can be activated, fragmented, or functionalized and some of these newly created reactive species randomly recombine into highly branched and crosslinked structures.[1] Final compounds are conventionally called plasma polymer films.[2] Organic coatings developed by plasma polymerization are characterized by physical properties that make them unique in the polymers field.[3,4] Such films are mechanically and thermally stable, they can be pinhole-free and adherent to different substrates in terms of nature and shape. They can be deposited as thin layers with controllable thickness and a wide range of starting precursors can be used in the synthesis process.[5] Due to these excellent properties, plasma polymers are employed as technological solution in some important applications ranging from optical devices, biomaterials, protective coatings, electrical insulators, conductive, or permselective membranes etc.[6–11]

A serious drawback that still blocks the extension of plasma thin polymer films applications is the control of polymer structure.[12] Due to the complexity of plasma molecular processes and the multitude of plasma generated reactive species, it is difficult to control the final chemical composition of plasma polymerized-films. Challenges to obtain regular polymer-like structures using plasma-assisted synthesis, have led to the development of various modes to control and characterize the plasma polymerization process. Related to this aspect, Neiswender proposed an energy-related factor in order to identify different regimes of plasma polymerization reactions.[13]

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His idea was improved by Yasuda,[14] who evaluated a composite parameter, *W/FM*, were *W* is the discharge power, *F* the monomer flow rate, and *M* is the molecular weight of monomer. The discharge power per unit of molecule is considered to be proportional with the concentration of activated species in plasma. Hegemann developed a macroscopic approach to control plasma polymerization processes. He considers an active plasma zone, where organic molecules are activated and fragmented into reactive species and a passive zone where the reaction intermediates form stable compounds at the surfaces in contact with plasma.[15,16]

Regarding the plasma polymerization mechanisms and its relations with the plasma polymers one can find limited information in the literature. Stille et al.[17] identified the intermediary reactions of benzene in plasma, Tibbitt et al.[18] investigated the structure of plasma-polymerized ethylene, Kaplan and Dilks[19] suggested a model for chemical reactions of aromatic compounds etc.

This paper aims to describe the plasma polymerization mechanism of selected aromatic precursors: benzaldehyde, benzyl alcohol, styrene, and benzyl chloride. They are used as solvents and as precursors to other organic compounds with applications ranging from pharmaceutics to plastics industry. Benzyl alcohol and benzyl chloride polymerize only in presence of catalysts and up to our best knowledge, no report is available concerning the plasma polymerization reactions of these two compounds.

The polymerized films were investigated by Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and proton nuclear magnetic resonance (^{1}H NMR). The plasma polymerization mechanism of aromatic precursors combines the results of all spectroscopic analysis: we identified the possible activation and fragmentation reactions, oxidation reactions, and polyrecombination of reactive species into randomly structures like three-dimensional polymeric networks.

2. Experimental Section

2.1. Atmospheric Pressure Plasma Polymerization

The atmospheric pressure plasma is generated using the principles of dielectric barrier discharge. Details of the experimental set-up can be found in our previous work.[20] It consists on two plane-parallel electrodes separated by 1 mm thick glass dielectrics. In this study, the gap was fixed to 5 mm. Helium (Messer Romania Gas SRL) with spectral purity of 99.999% was used as working gas in order to obtain a homogenous discharge. Organic vapors from liquids monomers are introduced in the discharge by gas bubbling. The precursor flow rate is maintained constant at $4\,\mu L \cdot min^{-1}$ and the discharge environment is helium, with fixed flow rate of $2.5\,L \cdot min^{-1}$.[21] The plasma is driven by 6 kV amplitude square high-voltage pulses, 250 μs width, 2 kHz frequency. This leads to individual current on the increasing and decreasing flanks of the each voltage pulse, of microsecond order duration. The deposition time was 10 min.

2.2. Precursors

The chemical compounds studied in this paper are: benzaldehyde, benzyl alcohol, styrene, and benzyl chloride (reagents for synthesis from Merk) with purity of ≥99%. All these aromatic organic precursors consist of a phenyl group with a different alkyl radical attached (Scheme 1).

2.3. Polymer Characterization

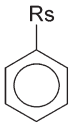
The chemical structure of plasma-polymerized films was investigated by FT-IR technique using a Bomem MB Series 104 spectrometer in the range of 4 000–600 cm^{-1}. Infrared spectra were recorded in transmittance mode and the data were analyzed using GRAMS GALACTIC software. In order to obtain the FT-IR spectra, plasma polymers were deposited onto NaCl windows which are transparent in the infrared range in the above mentioned domain.

XPS analyses were performed to resolve the chemical composition of plasma films. The XPS spectra were obtained on a 5000 VersaProbe spectrometer (physical Electronics), equipped with a monochromatic Al Kα X-ray source ($h\upsilon = 1.486$ keV). During measurements, the pressure in the analysis chamber was maintained at 5.9×10^{-8} Pa and the photoelectron take-off angle relative to the sample surface was 45°. The binding energy was calibrated by the peak energy of C 1s (284.6 eV) as reference and the resolution of the XPS analyzer is 0.85 eV for organic materials. The full width at half maximum is around 2 eV and the XPS data were analyzed using PHI Summit software for peak deconvolution.

Complementary analyses of polymeric films were performed by means of NMR spectroscopy. ^{1}H NMR spectra were recorded at 400 MHz with dimethyl sulfoxide-d_6 (DMSO) as solvent, on a Bruker Avance DRX 400 spectrometer in the range of 11–0 ppm. The chemical shift was determined relative to tetramethylsilane (TMS) signal, assigned as reference.

3. Results and Discussion

In this section, the chemical composition of polymer films is discussed. From the observed FT-IR, XPS, and ^{1}H NMR data, a possible chemical mechanism during plasma polymerization process is suggested.



Scheme 1. Structural formula of the aromatic compounds; Rs is the general alkyl radical that could be of aldehyde type (HC=O from benzaldehyde), alcohol type (H_2C-OH from benzyl alcohol), vinyl type ($HC=CH_2$ from styrene) and methylene chloride type (H_2C-Cl from benzyl chloride).

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3.1. Analysis of Benzaldehyde-Based Plasma Polymer Film

FT-IR spectrum of benzaldehyde used as precursor contains absorption bands corresponding to aromatic CH stretching between 3 100 and 3 000 cm^{-1}, CH from aldehyde (HC=O) between 2 910 and 2 670 cm^{-1}, carbonyl C=O stretching from aldehyde at 1 695 cm^{-1}, C=C linkage into ring at 1 600 and 1 453 cm^{-1}, the aromatic CH in-plane deformations between 1 330 and 1 000 cm^{-1} and aromatic CH out-of-plane vibrations between 900 and 650 cm^{-1} (Figure 1).[22]

In contrast, FT-IR spectrum of plasma benzaldehyde film shows a broad band around 3 300 cm^{-1} corresponding to hydroxil groups. Thus, the chemical structure of polymerized films contains alcohol type groups, R−OH, as the effect of oxidation during plasma polymerization. The aldehydic region from 2 910 to 2 670 cm^{-1} is shifted up to 3 000 cm^{-1} suggesting that CH group from HC=O is now of aliphatic type, due to aldehyde reduction in plasma environment. New bands at 1 265 and 1 068 cm^{-1} are specific to C−O and C−O−C, respectively, which confirms that carbon–oxygen π bond from aldehyde is broken. Also, the new bands from 1 495 to 1 024 cm^{-1} are specific to aliphatic C−C and CH, respectively, which are formed probably due to benzaldehyde fragmentation.

Analysis of plasma benzaldehyde XPS spectrum indicates the presence of 84.8% carbon (C 1s at 284.6 eV) and 15.2% oxygen (531.6 eV). The fitted C 1s signal contains five distinctive components (Figure 2a) assignable to CH, C−C and C=C (284.6 eV), ether C−O−C and alcohol C−OH groups (286 eV), carbonyl C=O type bonds (287.1 eV), esters −O−C=O (287.7 eV) and O−CO−O of carbonate type (288.5 eV). O 1s cover contains two peaks (Figure 2b) associated with single (532.3 eV) and double (531.3 eV) type bonds containing oxygen.[23]

Typical ^{1}H NMR spectrum of benzaldehyde precursor (Figure 3) provides strong signal at 10.02 ppm specific to aldehydic HC=O proton and a broad strong signal at 8.1–7.4 ppm characteristic to aromatic protons.[22,24]

In the case of pure benzaldehyde containing six protons, the ^{1}H NMR spectrum is composed of only four peaks due to the symmetry of the molecule whereas in the corresponding plasma polymer spectrum, there is a huge increase of the peak number indicating a loss of symmetry in the final

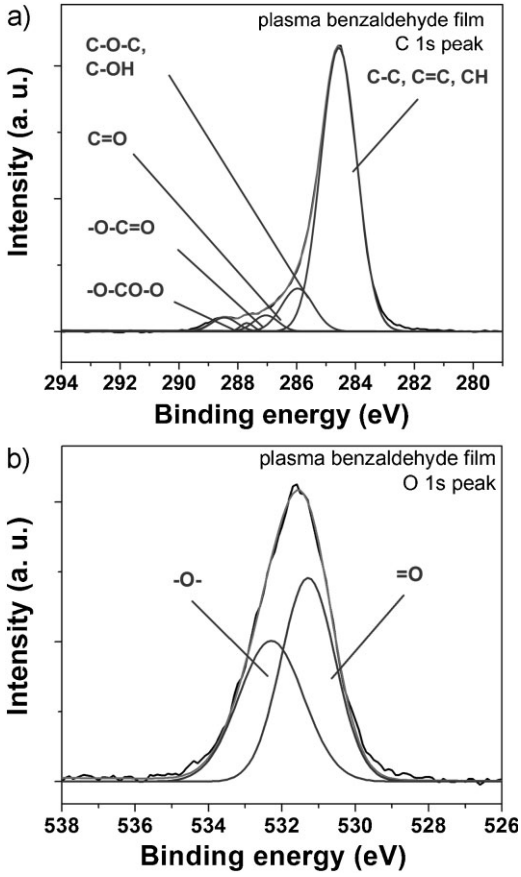


Figure 2. (a) Deconvoluted C 1s peak of plasma benzaldehyde film. (b) Deconvoluted O1s peak of plasma benzaldehyde film.

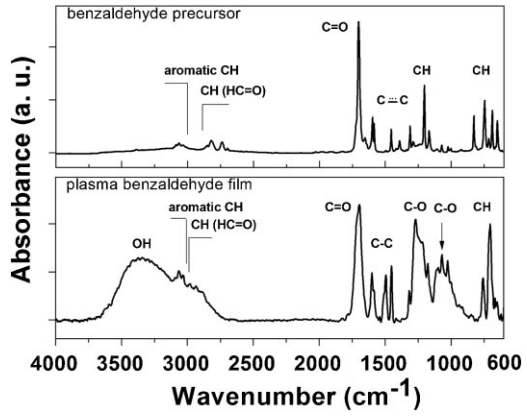


Figure 1. FT-IR spectra of benzaldehyde precursor and plasma benzaldehyde film.

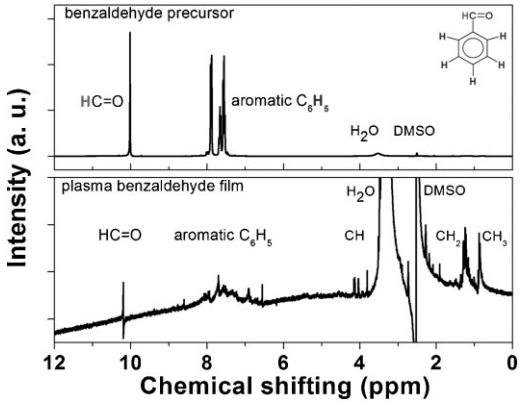


Figure 3. ^{1}H NMR spectra of benzaldehyde precursor and plasma benzaldehyde film.

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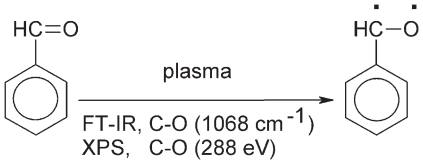
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structure. The ^{1}H NMR spectrum of plasma benzaldehyde film includes the signal specific to aldehydic proton and a broad band corresponding to aromatic protons. These signals have a smaller intensity and the aromatic protons are more dispersed causes overlap of the signals. New peaks of aliphatic protons are detected in the ^{1}H NMR spectrum. Thus, the signal at 1.24 ppm is specific to methylene CH_2 protons and the 0.88 peak corresponds to methyl CH_3 protons of aliphatic type. The two peaks around 4.1 ppm are specific to CH protons of aliphatic type.

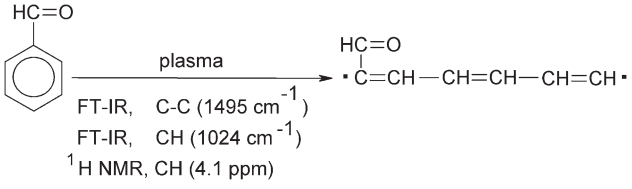
If we combine the experimental results from FT-IR, XPS, and ^{1}H NMR spectra we can anticipate some intermediary reactions during plasma polymerization of benzaldehyde. FT-IR and XPS spectra reveal the presence of C–O type groups in the polymeric film which suggest that plasma polymerization reactions of benzaldehyde are initiated by breaking the π bonds from aldehyde (Scheme 2). FT-IR and ^{1}H NMR spectra provide strong signals specific to aliphatic type groups, probably obtained from aromatic ring breakage (Scheme 3). ^{1}H NMR spectrum of polymer contains two signals assigned to aliphatic CH_2 and CH_3 protons that are organized into hydrocarbons probably due to hydrogenation reactions (Scheme 4).

The reactive species can randomly recombine as below (Scheme 5).

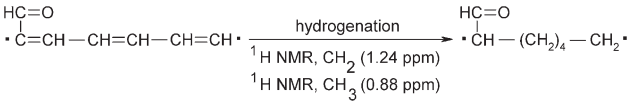
During film growth, the reactive species could be also oxidized. FT-IR and XPS spectra reveal the presence of ethers, alcohol, esters, and carbonate units into chemical composition of polymeric film that can be obtained by radical oxidation during plasma polymerization reactions (Scheme 6).



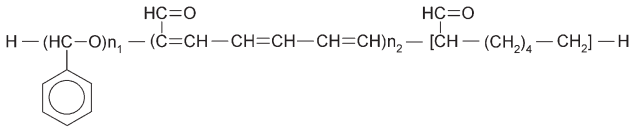
Scheme 2. Benzaldehyde radical generation by π bond breakage bond from aldehyde.



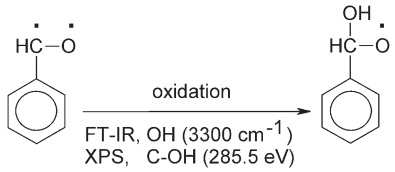
Scheme 3. Aliphatic chain production by aromatic ring breakage.



Scheme 4. Hydrogenation of the aliphatic chain.



Scheme 5. The recombination process between benzaldehyde radicals and aliphatic chains (n_1 and n_2 are the number of benzaldehyde radicals and aliphatic chains, respectively).



Scheme 6. Benzaldehyde radical oxidation under plasma conditions.

3.2. Analysis of Benzyl Alcohol-Based Plasma Polymer Film

Typical FT-IR spectrum of benzyl alcohol precursor (Figure 4) contains absorption bands assigned to OH groups from alcohol type (H_2C–OH) in the 3 550–3 110 cm^{-1} spectral region, aromatic CH stretching between 3 110 and 3 000 cm^{-1}, CH from alcohol between 3 000 and 2 760 cm^{-1}, C=C vibrations type from benzene at 1 592, 1 495, and 1 453 cm^{-1}, ether C–O–C groups at 1 069 cm^{-1}, CH in-plane deformation bending of aromatic ring between 1 330 and 1 000 cm^{-1} and aromatic CH out-of-plane deformation bending of aromatic ring between 900 and 650 cm^{-1}.[22]

Superimposed on precursor spectrum, plasma benzyl alcohol spectrum shows an enhanced band between 3 670 and 2 770 cm^{-1}. This region contains also the aromatic CH stretching and the CH stretching vibrations from alcohol bonded to benzene. The absorption band assigned to CH

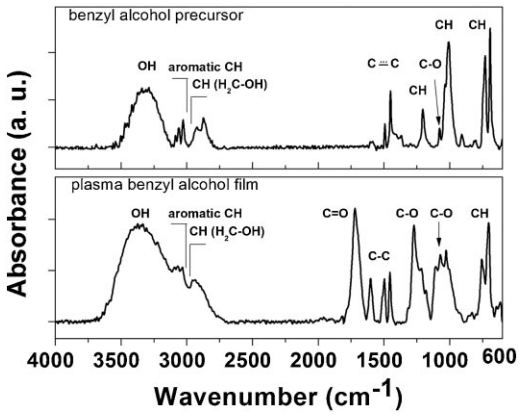


Figure 4. FT-IR spectra of benzyl alcohol precursor and plasma benzyl alcohol film.

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from alcohol is shifted up to 3 000 cm^{-1} assuming that the hydroxyl group could be detached from initial molecule. The FT-IR spectrum reveal the presence of an intense band at 1 717 cm^{-1} assigned to the stretching of the carbonyl C=O groups and one at 1 069 cm^{-1} characteristic to the ether C–O–C groups. The bands from 1 600 to 1 024 cm^{-1} are specific to aliphatic C–C and CH, respectively, which are formed probably due to aromatic ring breakage.

Survey XPS spectrum of plasma benzyl alcohol film reveals the presence of carbon (C 1s at 284.6 eV) and oxygen (O 1s at 532 eV). Quantitative analysis of XPS spectrum shows the presence of 61.8% carbon and 38.2% oxygen.[23]

The curve fitting of C 1s region indicates the presence of four distinctive peaks. Taking into consideration the chemical formula of benzyl alcohol, the resulted peaks can be assigned to C–C, C=C, and CH type groups (284.5 eV), ether C–O–C linkage type and alcohol C–OH groups (286 eV), carbonyl (C=O) type bonds (287.4 eV), and –O–C=O units from esters (288.7 eV; Figure 5a). The O 1s peak is decomposed in two peaks corresponding to –O– (532.6 eV) and =O (531.6 eV) oxygen type bonds (Figure 5b).

To obtain further information on molecular structure, ^{1}H NMR spectra of the benzyl alcohol and plasma benzyl alcohol film were recorded (Figure 6). The ^{1}H NMR of benzyl alcohol shows a broad strong signal of the protons into 7.5–7.2 ppm range, the signal of OH proton at 5.28 ppm and the proton signal in methylene group at 4.6 ppm.[22,25,26]

Compared to the precursor spectrum, the plasma benzyl alcohol spectrum shows chemical shifting of the aromatic protons into a larger range (7.7–6.9 ppm). This fact indicates the presence of the aromatic ring into the polymeric film. The multitude of peaks in the range of 8–7 ppm indicates that the aromatic cycle is substituted with different chemical groups. Meanwhile, new peaks in aliphatic region can be detected between 1.26 and 0.85 ppm. Interestingly enough is the appearance in the spectrum of the signals characteristic to the methyl (triplet, 0.85 ppm) and methylene (multiplet, 1.23 ppm) aliphatic protons that suggest the presence of aliphatic chains in the polymeric film, which could form by aromatic ring breackage. The new peaks around 4.1 ppm are specific to CH protons of aliphatic type. Also, the new peak from 10.1 ppm corresponds to aldehyde groups that could be formed during plasma polymerization reactions of benzyl alcohol.

Taking into account the data of all spectroscopic analysis, some conclusions can be drawn. FT-IR, XPS, and ^{1}H NMR spectra indicate the presence of aromatic rings and aliphatic chains in the chemical composition of plasma benzyl alcohol film. FT-IR spectrum indicates that plasma polymerization reactions of benzyl alcohol are initiated by OH group detachment from initial molecule (Scheme 7). The FT-IR and ^{1}H NMR spectra of polymeric film suggest the aromatic ring breakage (Scheme 8). The methyl (triplet, 0.85 ppm) and methylene (multiplet, 1.23 ppm) aliphatic

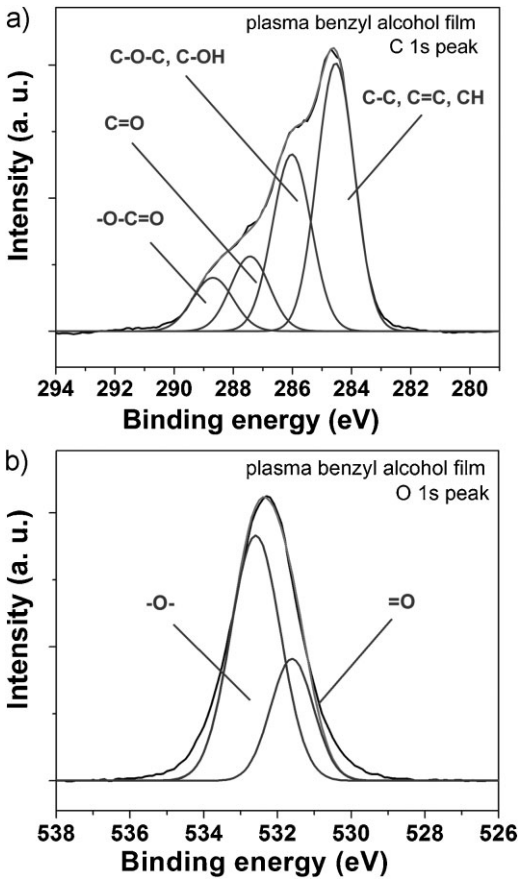


Figure 5. (a) C 1s peak deconvolution of plasma benzyl alcohol film. (b) O1s peak deconvolution of plasma benzyl alcohol film.

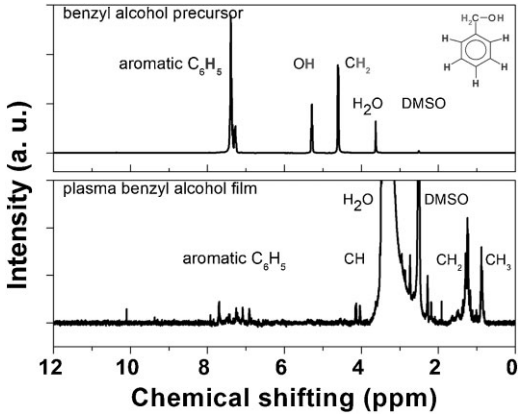


Figure 6. ^{1}H NMR spectra of benzyl alcohol and plasma benzyl alcohol film.

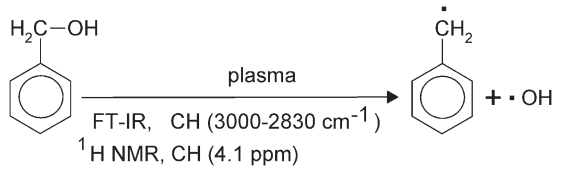
protons reveal the presence of aliphatic chains which could be formed by hydrogenation of aliphatic chains (Scheme 9).

The radicals resulted from benzyl alcohol can recombine as below (Scheme 10):

During recombination of reactive species and their deposition on the substrates in contact with plasma, the

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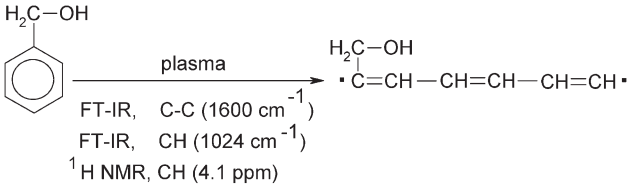


Scheme 7. The possibility of benzyl radical formation from benzyl alcohol molecule.

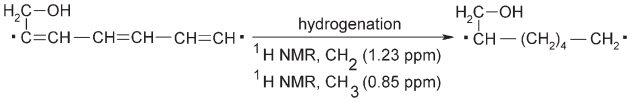
polymeric film is exposed to oxidation processes. Therefore, the FT-IR and XPS data reveal the presence of a carbonylic compound (>C=O), while the presence of aldehydic hydrogen in ^{1}H NMR clearly indicate that this carbonylic compound is an aldehyde (Scheme 11). XPS data indicate the formation of ether C—O—C and alcohol C—OH units that could be obtained from oxidation processes, FT-IR spectrum of plasma benzyl alcohol confirm their existence (Scheme 12).

3.3. Analysis of Styrene-Based Plasma Polymer Film

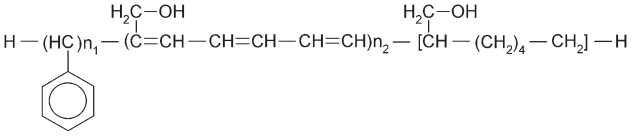
Typical infrared spectrum of styrene (Figure 7) contains absorbance bands assigned to aromatic CH stretching between 3 150 and 3 000 cm^{-1} spectral region, methylene



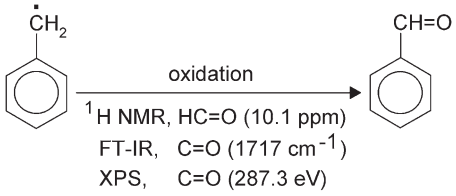
Scheme 8. Aliphatic chains production by aromatic ring breakage.



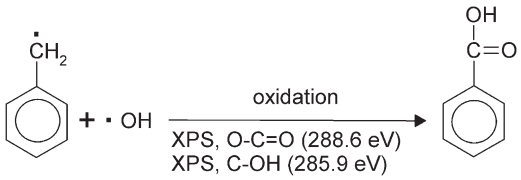
Scheme 9. The hydrogenation reaction of aliphatic chains.



Scheme 10. The recombination process between benzyl radicals and aliphatic chains (n_1 and n_2 are the number of benzyl radicals and aliphatic chains, respectively).



Scheme 11. Benzaldehyde production by oxidation processes.



Scheme 12. Benzyl radical oxidation during plasma polymerization reactions.

CH stretching between 3 000 and 2 850 cm^{-1}, aliphatic C—C from vinyl group at 1 627, aromatic C=C stretching (in-ring) at 1 600, 1 576, 1 494, 1 448, and 1 412 cm^{-1}, aromatic CH in-plane deformation bending at 1 203, 1 083, 1 020, and 991 cm^{-1} and aromatic CH out-of-plane deformation bending at 908, 775, and 695 cm^{-1}.[27,28]

The infrared absorption spectrum of plasma styrene film reveals that the aromatic/aliphatic CH ratio is drastically reduced. It clearly indicates that under plasma influence, part of aromatic rings from styrene vapors are broken into fragments and corresponding IR signals are presented in the aliphatic region (3 000–2 750 cm^{-1}). The aromatic ring breakage is confirmed by low absorbance of infrared bands assigned to C=C groups and the disappearance of aromatic CH bands from 908 and 991 cm^{-1}. Also, the band from 1 450 cm^{-1}, which corresponds to aliphatic C—C type bonds, attests abovementioned process. Oxygen containing chemical groups was identified as shoulders at 1 716 and 1 097 cm^{-1}.

The typical XPS spectrum of plasma styrene film reveals the presence of two specific peaks, C 1s at 284.6 eV and O 1s at 531.8 eV. The atomic concentration is about 91.5% carbon and 8.5% oxygen. The C 1s peak was deconvoluted into three main components which appear at 284.6 eV corresponded to CH, C—C, and C=C groups, 286 eV related to carbon bonded to oxygen C—O type groups and 291.3 eV assigned to aromatic π–π^* transitions from aromatic ring (Figure 8a). Because of the symmetry, the O 1s core level spectrum contains a single peak (531.8 eV) corresponding to the formation of carbon–oxygen bonds (Figure 8b).[29,30] The

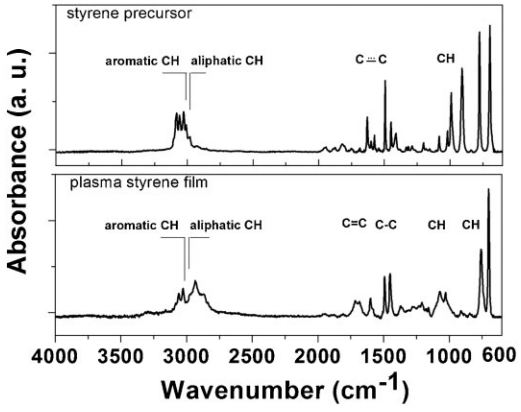


Figure 7. FT-IR spectra of styrene precursor and plasma styrene film.

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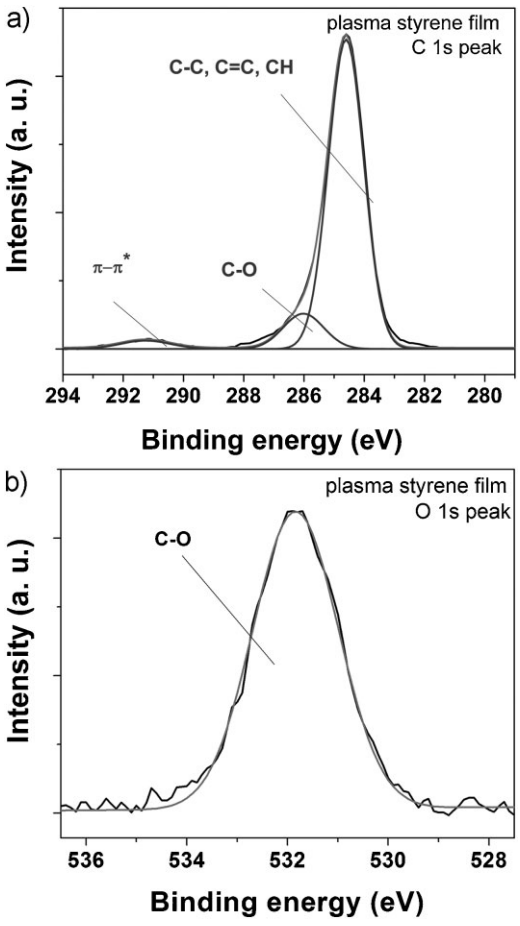


Figure 8. (a) C 1s peak deconvolution of plasma styrene film. (b) O 1s peak of plasma styrene film.

presence of oxygen containing groups in the chemical composition of polymerized film indicates that plasma styrene films are partially oxidized. Also, the aromatic π–π^* transitions from C 1s core level spectrum reveal the intact presence of aromatic ring in the polymer backbone. The results correlate well with the FT-IR spectra.

^{1}H NMR of styrene as precursor contains strong signals at 7.65–7.15 ppm assigned to aromatic protons from benzene and three distinct signals corresponding to aliphatic protons from vinyl type group at 6.7, 5.85, and 5.28 ppm, respectively (Figure 9).[22,26] Compared to precursor spectrum, ^{1}H MNR of plasma styrene film provides an enhanced broad band attributable to aromatic protons from benzene (8.2–7.0 ppm). The signal corresponding to proton bond by an unsaturated C from C=C (around 5.4 ppm) is missing from ^{1}H NMR spectrum of plasma styrene. We suppose that one carbon–carbon double bond (in the vinyl group) is replaced by a carbon–carbon single bond. The peaks around 4.1 ppm corresponds to aliphatic CH type groups. The new peaks from 1.24 and 0.85 ppm are specific to methylene CH_2 protons and methyl CH_3 protons that could be organized into aliphatic chains.

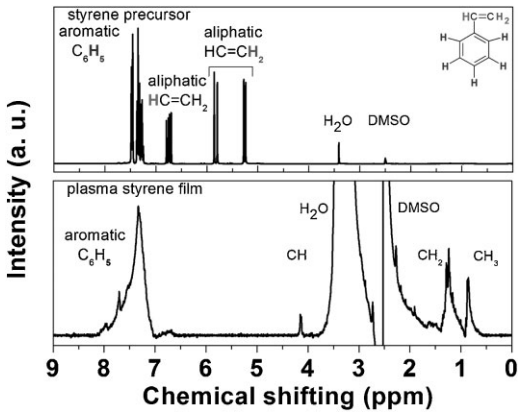
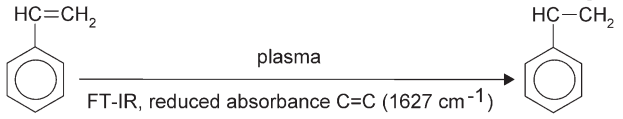


Figure 9. ^{1}H NMR spectra of styrene and plasma styrene film.

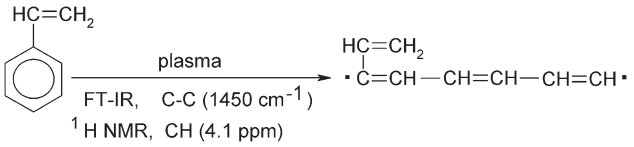
From the spectroscopic analysis we could emphasize the intermediary reactions during plasma polymerization of styrene. FTIR absorption spectrum of plasma styrene films contains small signals of aromatic C=C stretching in the spectral region 1 630–1 600 cm^{-1} that indicates the polymerization reactions could be started by π bond breakage from vinyl group (Scheme 13). The small signals of aromatic CH stretching from "fingerprint" region and the reduced aromatic/aliphatic CH ratio suggests that styrene molecules exposed to plasma environment are broken at the aromatic ring level. The ^{1}H NMR spectrum confirms the benzene breakage (Scheme 14) and the reorganization of resulting fragments into aliphatic chains like alkanes (Scheme 15).

Different recombination reactions of radicals are possible. Scheme 16 shows a plausible recombination reaction between styrene radicals and aliphatic chains.

Working at atmospheric pressure, the helium plasma contains atomic helium and oxygen, or molecular species based on nitrogen, oxygen, and hydrogen.[3] The radicals obtained by plasma activation and fragmentation of initial monomer are highly chemically reactive and could react with the plasma species. XPS spectrum reveals the presence of oxygen containing groups in the plasma styrene film that



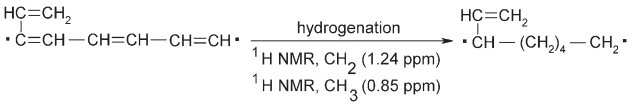
Scheme 13. Styrene radical generation by breaking the π bond from vinyl group.



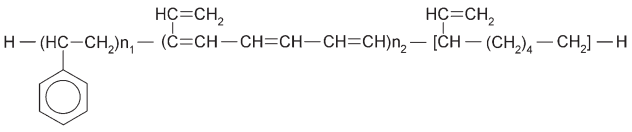
Scheme 14. Aliphatic chains production by aromatic ring breakage.

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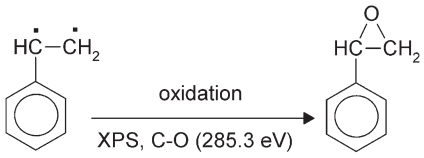
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Scheme 15. Hydrogenation of the aliphatic chain.



Scheme 16. The recombination process between styrene radicals and aliphatic chains (n_1 and n_2 are the number of styrene radicals and aliphatic chains, respectively).



Scheme 17. Styrene radical oxidation.

are obtained by oxidation of reactive species during film growth (Scheme 17).

3.4. Analysis of Benzyl Chloride-Based Plasma Polymer Film

Infrared spectrum of benzyl chloride precursor shows absorbance bands ascribed to aromatic CH stretching between 3 150 and 3 000 cm^{-1}, CH from methylene chloride H_2C-Cl stretching from 3 000 to 2 830 cm^{-1} spectral region, aromatic C=C vibrations into benzene ring at 1 494 and 1 453 cm^{-1}, the methylene chloride vibration modes at 1 265 cm^{-1}, aromatic CH in-plane deformation bending at 1 207, 1 073, and 1 027 cm^{-1} and aromatic CH out-of-plane deformation bending at 817, 766, 699, and 679 cm^{-1} (Figure 10).[22,31]

Infrared spectrum of plasma benzyl chloride films contains new absorption bands associated to hydroxil OH groups between 3 670 and 2 730 cm^{-1} and carbonyl C=O groups at 1 720 cm^{-1}, respectively. The new bands from 1 607 cm^{-1}, 1 030 cm^{-1} are specific to aliphatic C−C and CH groups, respectively. The presence of new oxygen containing groups in the polymer backbone is a result of oxidation processes.

XPS spectrum of plasma benzyl chloride films indicate the presence of C 1s peak at 284.6 eV, O 1s at 532 eV, Cl 2p at 199.5 eV, and Cl 2s at 270.6 eV. Quantitative analysis shows the presence of 82.3% carbon, 14.6% oxygen, and 3.1% chlorine.[23,32–34]

C 1s cover could be divided into five components (Figure 11a) assigned to CH, C−C and C^{-1}C at 284.5 eV,

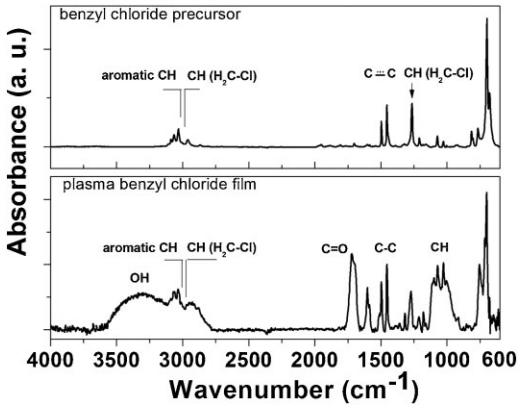


Figure 10. FT-IR spectra of benzyl chloride precursor and plasma benzyl chloride films.

ether C−O−C, chlorine based groups C−Cl and alcohol C−OH at 286 eV, carbonyl C=O bonds at 287.3 eV, ester −O−C=O type groups at 288.6 eV, and aromatic transitions π–π^* from aromatic ring at 291.4 eV. The assimetric peak Cl 2p consists on Cl 2p1/2 and Cl 2p3/2 peak components of relative area 1:2, separated by 1.7 eV. The Cl 2p1/2 components are located at about 201.2 eV related to covalently bonded chlorine species in C−Cl type groups and 198.8 eV is assignable to ionic chlorine (Cl^-). The same components can be observed in Cl 2p3/2 component but at different binding energy values, respectively, 199.5 and 197.2 eV (Figure 11b). O 1s peak contains two components attributable to −O− (532.4 eV) and =O (531.6 eV) type bonds (Figure 11c).

^{1}H NMR spectrum of monomer benzyl chloride contains two distinct signals attributable to aromatic protons from benzene ring at 7.6 to 7.3 ppm and protons from methylene CH_2 group at 4.74 ppm (Figure 12).[22,26,35] Compared to the monomer spectrum, the ^{1}H NMR spectrum of plasma benzyl chloride films shows chemical shifting of the aromatic protons into a larger range, between 8.3 and 6.7 ppm domain, while new chemical shifting belonging to aliphatic protons can be detected in the 1.26–0.85 ppm spectral region. The chemical shifting from the aromatic region indicates the presence of the intact aromatic ring into the final product. The signals around 4.1 ppm corresponds to CH groups from aliphatic type. The signals from 1.24 to 0.89 ppm are specific to methylene CH_2 and methyl CH_3 protons that suggest the presence of aliphatic chains into final compound. However, part of aromatic rings could be fragmented into aliphatic type groups and reorganized into alkane like hydrocarbons.

In order to identify the intermediary reactions of benzyl chloride, the following discussions can be made. FTIR absorption spectrum of plasma benzyl chloride films provides a small signal assigned to methylene chloride groups, indicating that radical formation is possible by

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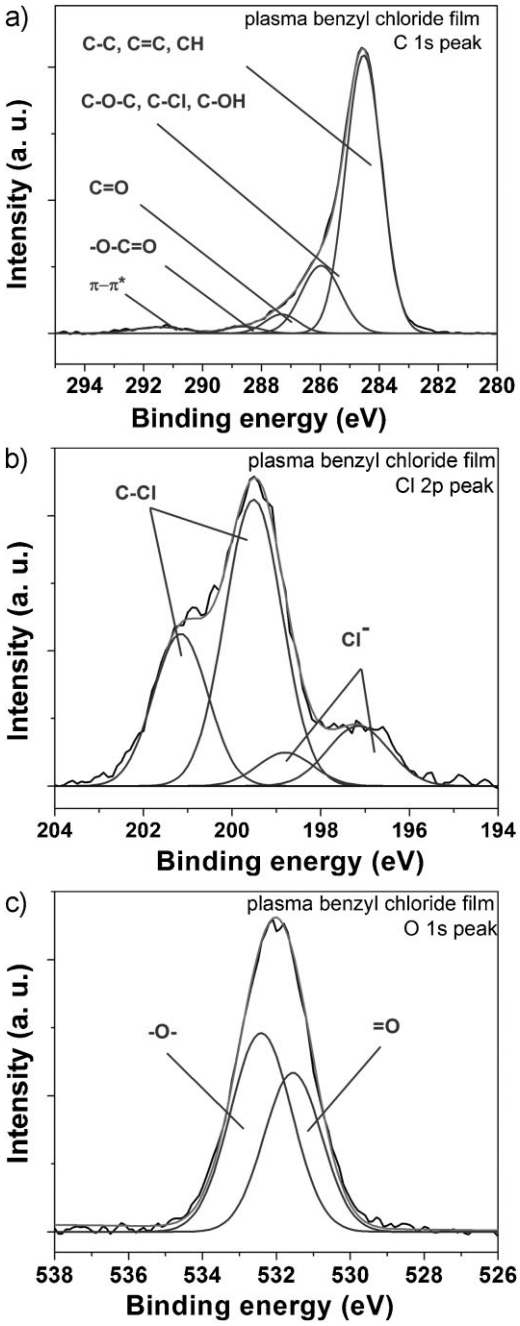


Figure 11. (a) C 1s peak deconvolution of plasma benzyl chloride films. (b) Cl 2p peak deconvolution of plasma benzyl chloride films. (c) O 1s peak deconvolution of plasma benzyl chloride films.

chlorine detachments from benzyl chloride molecule (Scheme 18). The ^{1}H NMR spectrum reveals the presence of two signals attributable to methylene CH_2 protons and methyl CH_3 protons as results of aromatic ring breakage (Scheme 19) by the plasma exposure and hydrogenation of aliphatic chain (Scheme 20). XPS spectrum indicates the formation of oxygen containing chemical groups that could

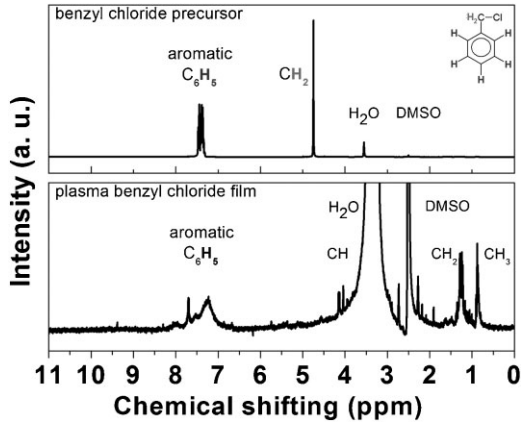
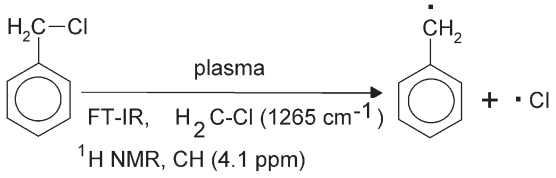
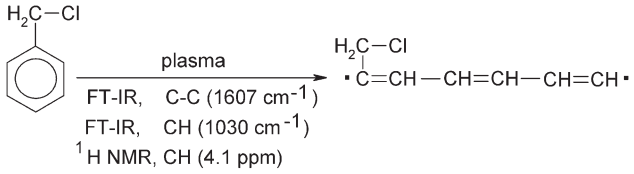


Figure 12. ^{1}H NMR spectra of benzyl chloride and plasma benzyl chloride film.



Scheme 18. The possibility of benzyl radical formation from benzyl chloride.



Scheme 19. Aliphatic chains production by aromatic ring breakage.

be obtained from oxidation reactions. FTIR spectrum confirms their presence. Taking into consideration the chemical structure of plasma benzyl chloride films it is possible to estimate the existence of following processes:

The reactive species can recombine as Scheme 21.

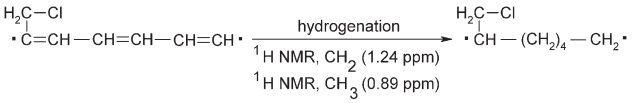
The radical created during plasma polymerization reactions could be oxidized; for example, the attachment of hydroxyl group to benzyl radical (Scheme 22).

3.5. Plasma Polymerization Mechanism of Aromatic Compounds

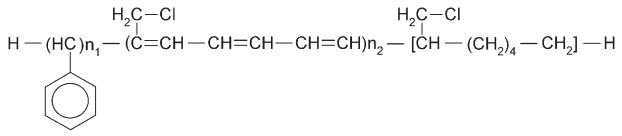
Taking into account the most probable reactions during plasma polymerization of benzaldehyde, benzyl alcohol, styrene, and benzyl chloride, respectively, a plasma polymerization mechanism can be drawn. First, we

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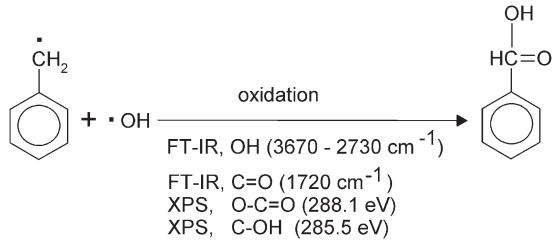
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Scheme 20. Hydrogenation of the aliphatic chain.



Scheme 21. Schematically draw of plasma benzyl chloride films (n_1 is the number of benzyl radicals, n_2 is the number of aliphatic chains).

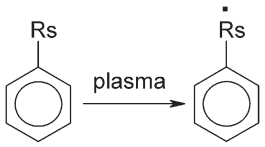


Scheme 22. Benzyl radical oxidation.

consider that the aromatic monomers used in this paper are composed by an alkyl radical attached to a phenyl group (Scheme 1).

When organic vapors are exposed to plasma environment, different processes of radical production are possible. FT-IR, XPS, and ^{1}H NMR data reveal that plasma polymerization reactions are initiated by breaking the π bond of aldehyde group from benzaldehyde (FT-IR, C–O, 1 068 cm^{-1}; XPS, C–O, 288 eV) and of vinyl group from styrene (FT-IR, reduced C=C, 1 627 cm^{-1}) or by hydroxyl group detachment from benzyl alcohol (FT-IR, aliphatic CH, 3 000–2 830 cm^{-1}; ^{1}H NMR, CH 4.2 ppm) and chlorine detachment from benzyl chloride (FT-IR, CH_2-Cl, 1 265 cm^{-1}). The overall activation reaction of aromatic molecules is schematically drawn as Scheme 23.

FT-IR and ^{1}H NMR spectra contain informations about the fragmentation processes of benzene under plasma conditions. Compared to monomers spectra, FT-IR spectra of all plasma-polymerized films show that the aromatic/aliphatic CH ratio is drastically reduced (FT-IR spectral region 3 150–3 000 cm^{-1} and 3 000–2 850 cm^{-1}, respectively). Also, the reduced absorption bands from FT-IR "fingerprint" region attests the fragmentation processes at aromatic ring level. In accord with ^{1}H NMR spectra of final compounds (multiplet around 1.23 ppm and triplet around 0.85 ppm, respectively), part of aromatic rings, in plasma environment, are fragmented into aliphatic methyl and methylene units and reorganized into hydrocarbons like

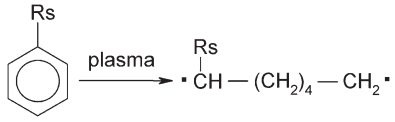


Scheme 23. Activation reaction of aromatic molecules; $\dot{R}s$ is the radical obtained in the plasma environment that could be of $\dot{H}C-\dot{O}$ type (from aldehyde group), $\dot{C}H_2$ type (from alcohol and methylene choride group) or $\dot{H}C-\dot{C}H_2$ type (from vinyl group).

alkanes. Taking into consideration the aromatic ring breakage from benzaldehyde, benzyl alcohol, styrene, and benzyl chloride precursors, a general fragmentation reaction can be drawn as Scheme 24.

Recombination process refers to addition between two or more radicals and deposition of reactive species at the surfaces in contact with plasma. In this paper, the spectroscopic measurements allowed us to identify the chemical composition of final products; the intermediary compounds are not detected. Precise recombination reactions between reactive species are difficult to predict. However, the ^{1}H NMR spectra of plasma-polymerized films contain signals of aliphatic protons assignable to CH_2 and CH_3 type units that could be organized into aliphatic chains like alkanes (^{1}H NMR, CH, 4.1 ppm; ^{1}H NMR, CH_2, 1.25 ppm; ^{1}H NMR, CH_3, 0.89 ppm). Scheme 25 illustrates the possible recombination reactions of radicals that are common to all types of plasma-polymerized films.

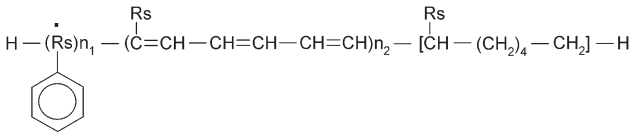
The new created radicals are highly chemically reactive species and suffer oxidation and/or recombination processes. Working at atmospheric pressure, the helium plasma incorporates impurities which influence the chemical structure of final compounds. The presence of oxygen containing groups lead to radical oxidation reactions during plasma polymerization process (oxidation in volume) and/or surface oxidation of coatings after the polymerization process ends (surface oxidation). In the present work, oxidation reactions are mainly emphasized by XPS results. It was found that plasma-polymerized films contain ether C–O–C, alcohol C–OH, carbonyl C=O, ester O–C=O, or carbonate O–CO–O type units that could be formed not only by molecules fragmentation but also by radicals oxidation. FT-IR spectra of polymerized-films confirm the presence of oxidation processes. The oxidation processes are of two types: hydroxyl attachment to benzaldehyde and benzyl radicals (FT-IR, OH at 3 300 cm^{-1}; XPS, C–OH at 285.5 eV) and oxygen attachment



Scheme 24. Aliphatic chain production by aromatic ring breakage.

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Scheme 25. Recombination reactions of radicals (n_1 is the number of alkyl radicals and n_2 is the number of and aliphatic chains).

to styrene radical (FT-IR, C—O, 1 097 cm^{-1}; XPS, C—O, 285.3 eV). The oxidation reactions are emphasized in Schemes 6, 11, 12, 17, and 22.

We should notice that recombination reactions are taking place simultaneously with oxidation processes. The reaction products recombine randomly and become re-activated or re-fragmented into small amounts, cross-cycle reactions being possible. On the other hand, under plasma energy influence, these scindations can take place further on the formed compounds leading to three-dimensional polymeric networks.

4. Conclusions

In this paper, a cold atmospheric pressure glow discharge has been used to initiate polymerization reactions of various organic compounds. Our pulsed plasma system based on barrier discharge principles, allows two ongoing distinct phases in the chemical process: species generation, during plasma on time and species recombination, during plasma off time. We have successfully obtained plasma polymer films from different aromatic precursors. For example, benzyl alcohol and benzyl chloride cannot be polymerized by using conventional wet chemistry. The polymer structure has been determined by means of FT-IR, XPS, and ^{1}H NMR spectroscopic techniques.

The polymerization mechanism of different aromatic compounds has been developed in the context of plasma chemistry. This approach derives from the chemical composition of plasma-polymerized films and reveals some reactions that could be possible during plasma polymerization process. The mechanistic aspects have been based on plasma-induced radical chain-growth concept, which considers that plasma provides energy to activate and dissociate organic compounds followed by poly-recombination of reactive species into randomly structured.

It should be noted that all techniques provide information about intermediary reactions in polymer forming. Particularly, activation and fragmentation reactions are mainly identified from FT-IR spectra of polymerized films by comparing to FT-IR spectra of initial molecules. Additionally, ^{1}H NMR spectra of plasma polymers provide important information about molecules fragmentation at the aromatic ring level. XPS measurements confirm the above mentioned reactions and provide further evidences on oxidation reactions of radicals during plasma polymerization processes.

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