Styrene and methyl methacrylate copolymer synthesized by RF inductively coupled plasma

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Abstract. A series of random copolymers of styrene and methyl methacrylate was prepared on a silicon substrate by RF pulsed inductively coupled plasma. The plasma gas phase was investigated by optical emission spectroscopy (OES). The physico-chemical characteristics of the deposited copolymer films were analyzed by several surface techniques: X-ray photoelectron spectroscopy (XPS), Fourier-Transform infrared absorption (FT-IR), Time-of-flight secondary ion mass spectrometry (ToF-SIMS), etc. OES of the plasma and FT-IR spectra of the films are predictive: plasma emitting a higher relative benzyl radical signal results in the deposition of a more aromatic plasma polymer. The functional thin films can be deposited by selection of the co-monomers.

1. Introduction
Plasma copolymerization is a relatively new method for the synthesis of polymer materials, which have diverse applications in medicine and engineering. It was proved that by combining the properties of different monomers, plasma copolymerization have the ability to design functional thin films [1]. For decades, many studies have been focused on the polymerization and characterization of films formed by the plasma from a single precursor or a monomer and different noble gases [1-2]. Fewer reports discussed the process of copolymerization by plasma [3-5], still fewer works aimed to diagnose the plasma copolymerization process.

Compared to conventional chemistry, the reactions in the plasma are much more complex. In plasma copolymerization, the initiation reactions are based on the collision probabilities between different species (monomer molecule, electron, ion, excited species, free radicals, etc.). The injection of a second monomer adds to the complexity of the reactions among these species. These reactions can be instantaneous, or proceed stepwise; they depend on the selected co-monomers and of the parameters of the plasma process. [2-6]

We studied the effect of power, pressure, deposition time and duty cycle of radiofrequency (RF) pulsed plasma on the polymerization of styrene and methyl methacrylate (MMA). In this paper, we study that for different ratios of monomers in the plasma copolymerization process, we investigated the content of species in the plasma itself and the composition of the deposited thin films.
Polymethylmethacrylate (PMMA) is widely used as a sheet glazing material, optical lens and fluorescent solar collectors, because of its optical clarity and UV resistance. Polystyrene has reasonably good mechanical and thermal prosperities with its high refractive index, but its stability to outside weathering is poor: it becomes yellow easily on exposure. The optical properties of a cyclic olefin copolymer are attractive on account of their high use temperature, excellent optical transmission, low birefringence and low moisture uptake. The copolymerization by plasma could overcome the defects of homopolymers. [7]

In the literature, most of the optical emission spectroscopy (OES) reports cover a very limited spectral range and only the strongest lines are identified; to our knowledge, very few detailed OES analyses of co-monomer plasma have been performed. We expect, and indeed show, that much more information can be extracted from the detailed analysis of full emission spectra recorded from the UV-visible to the near infrared spectral range.

To complement this information, the copolymer films prepared by RF plasma were characterized by multiple techniques: X-Ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and Fourier-Transform Infrared spectroscopy (FT-IR). From a correlation of the information gained from the composition of the plasma phase, and the analyses of the deposited copolymer films, we will infer some mechanisms of the plasma copolymerization.

2. Experimental

The samples were prepared in a stainless steel chamber which was pumped at 0.1Pa. Plasma was generated in an inductively coupled planar radio frequency (RF) discharge (13.56MHz, ICP-P 200, JE PlasmaConsult GmbH, Germany). The reactor design is reported elsewhere [8].

The distance between the quartz window of the plasma source and the sample support is 12cm. Deposition time is 8min in each case. Styrene and MMA monomers were obtained from Acros Organics (Geel, Belgium). Copolymers of styrene and MMA were prepared onto a clean silicon substrate at a fixed plasma power of 120W, duty cycle 50\% (T_{on}=0.5ms, T_{off}=0.5ms), for a total reactor pressure of 25Pa.

Each monomer gas is injected by a transport tube terminated by a “shower ring” output, allowing a homogeneous gas distribution in the discharge region of the chamber. A pressure meter (MKS-Baratron) measures the actual pressure in the chamber. After the pressure of the reactor went down to 0.1Pa, the first monomer was injected to reach the desired pressure, then, the second monomer vapor was injected. When the total pressure reached the set value of 25Pa, it took 15min to wait until the pressure was stable. A summary of the experimental conditions used in the plasma copolymerization is given in Table 1.

| P_{st}/(P_{st}+P_{MMA}) | MMA Pa | Styrene Pa |
|-------------------------|---------|------------|
| 0 | 0 | 25 |
| 20 | 5 | 20 |
| 40 | 10 | 15 |
| 50 | 12.5 | 12.5 |
| 60 | 15 | 10 |
| 80 | 20 | 5 |
| 100 | 25 | 0 |

It is worth noting that if an ideal gas behaviour is assumed, the \( P_{st}/(P_{st}+P_{MMA}) \) ratio, where \( P_{st} \) and \( P_{MMA} \) are the monomer pressure of styrene and MMA, respectively, is also the mole fraction of styrene in the gas feed.

OES measurements were performed with a spectrometer equipped with a 3-grating monochromator (Princeton Instruments SP2756A, f/9.7). The light emitted by the plasma was collected through a
quartz window, by an optical fibre, and analyzed onto a cooled CCD camera. The spectral response of the CCD detector has been calibrated using a reference Halogen lamp (LSK114, LOT Oriel). The calibration of lines is executed by the Hg (Argon) lamp (LSP035, LOT Oriel).

The chemical composition of the deposited polymer surfaces was investigated by XPS (Surface Science SSX-100), by FT-IR spectroscopy (FT-IR, BIO-RAD 60A), and by ToF-SIMS (ToSIMS IV, ION-TOF GmbH). The deposition rate is obtained from the measurement of the polymer film thickness using a Dektak profilometer.

3. Optical emission spectroscopy of the plasma phase

Optical emission spectra measured in the 200 and 1000 nm wavelength range. The spectra are dominated by all kinds of atomic lines and molecular bands of the plasma gas which are related to the monomers used in the plasma (styrene, MMA, and mixture of both monomers).

The three spectra in Figure 1 correspond to plasma gas of pure styrene, of the 80% MMA-20% styrene mixture, and of the pure MMA, respectively. The OES spectra recorded in pure MMA and pure styrene plasma differs completely. The spectrum of MMA plasma is composed of more lines, and they are more intense compared with that of styrene plasma. Most of the atomic lines and molecular structures have been identified by using literature references [9-12], and the excited species in the plasma show as being very different of that of styrene plasma. All the experimental spectra related to the styrene show a strong blue continuum between 260nm and 350nm with a maximum intensity around 300nm, while the spectrum from the MMA plasma shows a continuum between 250nm and 800nm with a maximum intensity around 400nm.

In the OES of the pure styrene plasma (Figure 1(a)), these excited species are clearly seen: C₆H₆, CH, C₂, C, H, and H₂. Among them, the most intense molecular band observed is the ro-vibration transition (0-0) at 431 nm in the A²Δ-X²Π of the CH signature, and its higher vibrational level (2, 2) at 432nm. The continuum (260 to 350nm) corresponds to the transitions from the lowest stable triplet state (a³Σ⁺g) of the H₂ molecule to the repulsive state (b³Σ⁺u). 266.7nm, 273.9nm and 260.2nm are the vibrational band heads of the benzene molecular emission which superimpose onto the H₂ emission continuum. The molecular bands at 509nm, 512nm, and 516.2nm could be associated with the band heads of the 3 different C₂ vibrational levels of d¹Πᵣ-a¹Πₑ electronic transition, known as the “swan system” [10][13]. Moreover, a weak continuum between 420 and 600nm is attributed to the hot incandescent carbon particles produced in the discharge [14]. The Fulcher-α band around 600nm corresponds to transition between the d¹Πₑ-a³Σ⁺g electronic states. The H₂ atomic line (656.2nm) formed in the styrene plasma is very intense. The other hydrogen atomic lines (434nm and 486nm) can be observed in higher plasma power and at lower pressure. No optical emission bands or atomic lines from oxygen were detected in the wavelength range of the optical emission system, so the representation of the H₂ molecules can directly be explained from the combination of hydrogen atom in the plasma gas. The carbon atomic line at 887.3nm and 889.9nm observed are weak.
In the MMA plasma (Figure 1.c), at least ten systems of carbon monoxide dominate the emission spectrum (Table 1) on the whole range of wavelengths including the Angstrom system $B^3\Sigma_{2u}^+ \rightarrow A^1\Pi_u$, the third positive system $b^3\Sigma_{2u}^+ \rightarrow a^3\Pi_{1g}$ and the Asundi system $a^1\Sigma_{2u}^+ \rightarrow a^3\Pi_{1g}$ [15] which is superimposed onto a continuum emission due to the chemiluminescence accompanying the recombination of CO and O [16]. In the 800-1000nm range, the O$_2$ and H$_2$O molecules can also be identified, but with a weaker intensity. The complex secondary spectrum of H$_2$ Fulcher-α appears too, while the emission of CH at 431.4nm (established using a higher resolution) is very weak: it is quite difficult to observe.

Table 2 Species identified in MMA and Styrene plasmas.

| Species in styrene plasma | Species in MMA plasma |
|---------------------------|-----------------------|
| Species                  | Configuration         | Wavelength (nm) | Species                  | Configuration         | Wavelength (nm) |
| C$_6$H$_6$                | A$^1\Pi$-X$^1\Sigma$  | 266.7, 273.9, 260.2 | CO                      | b$^3\Sigma_{2u}^+ \rightarrow a^3\Pi_{1g}$ | (0→0) 283.3 |
| CH                       | A$^2\Delta-X^2\Pi$    | 431               | (0→1)                   | 297.3                   |
|                          | (2→2)                 | 432               | (0→2)                   | 312.7                   |
| C$_2$                    | d$^3\Pi_{a} \rightarrow a^3\Pi_u$ | 516.5 | (0→3)                   | 329.7                   |
|                          | (1→1)                 | 512.5             | (0→4)                   | 348.5                   |
|                          | (2→2)                 | 509.7             | (0→5)                   | 369.4                   |
| H$_2$ Fulcher $\alpha$   | d$^3\Pi_{a} \rightarrow a^3\Sigma^+$ | 570-650 | B$^3\Sigma_{2u}^+ \rightarrow a^3\Pi_{1g}$ (0→0) | 451.0                   |
|                          |                       |                   | (0→1)                   | 483.5                   |
|                          |                       |                   | (0→2)                   | 519.8                   |
|                          |                       |                   | (0→3)                   | 561                     |
|                          |                       |                   | (0→4)                   | 607.99                  |
|                          |                       |                   | (0→5)                   | 662.03                  |
|                          | Atomic line           |                   |                         |                         |
| C                        | 5s1P-p3D              | 887.3             | H                       | 4d-2p                   | 434                     |
|                          | 8s1D-3d1D             | 889.9             | H                       | 5d-2p                   | 486.1                   |
| H                        | H$_\beta$             | 434               | H                       | 3d-2p                   | 656.2                   |
|                          | 4d-2p                 |                   | H$_\gamma$              | 5d-2p                   | 486.1                   |
|                          |                       |                   | H$_\alpha$              | 3d-2p                   | 656.2                   |
|                          |                       |                   | O                       | 3p5P-3s5S               | 777.2                   |

Adding the styrene monomer into the MMA plasma, the OES changes drastically, but this emission spectrum has superimposed both the characteristic peaks of styrene and MMA plasma (Figure 1 (b)), including the CO systems, the molecular bands CH, C$_6$H$_6$, H, and O$_2$, the two strong continuums and the atomic lines H, O. The several systems do overlap each other, so high resolution OES is required to confirm the identification of these species. At least ten systems of CO from the composition of MMA are identified; the emission from H, H$_2$, CH and C$_2$, in the 350-850nm part of the OES, superimpose onto the different systems of CO. A continuum of 400-700nm observed in the OES of MMA plasma is less intense than that in the pure MMA plasma and the hydrogen continuum of 200-350nm are also visible. Only when the styrene content added into the co-monomer plasma is enough high, it is possible to observe the C$_2$ band.

When the relative fraction of the two monomers is varied (for a fixed total pressure: p=25Pa), the characteristic peaks corresponding to the different monomer plasma evolve differently, particularly in the CO system. A high resolution spectrum is shown as a function of the MMA content in Figure 2. The emission intensity of excited species (CO, C$_6$H$_6$ benzyl radical, etc.) correlates with the concentration of the monomer in the plasma. The CO emission peak is very intense even after the small amount of quantitative MMA was added to the plasma. In the other hand, the H$_2$ continuum around 300nm became increasingly weak and the H atomic line at 656.2nm compared with the CO peaks is also weak. As for the CO and C$_6$H$_6$ band intensities, one notes (Figure 3) that the CO
emission peak intensity increased and the C₆H₆ benzyl radical decreased as the MMA monomer increased.

![Figure 2](image2.png)  
**Figure 2** Spectral evolution of the C₆H₆ benzene and CO molecular bands as a function of MMA fraction.

![Figure 3](image3.png)  
**Figure 3** Intensity of the CO and C₆H₆ benzene bands as a function of the MMA fraction.

### 4. Physico-chemical characteristics of the deposited copolymer films

Figure 4 (a) presents the curve-fitted high resolution XPS spectrum in the C1s region for the plasma deposited MMA (PMMA) surface. Three different carbon environments are found, as expected: carbon bonds at 284.5eV, C-O bonds at 285.5eV, C=O bonds at 288.5eV. With a small fraction of styrene, the plasma copolymer surface immediately shows the characteristics of a plasma-polystyrene surface, with the fingerprinting π−π* transition peak at 291eV (Figure 4 (b)); the intensity of this shake-up transition increases with the styrene fraction in the plasma discharge. The styrene XPS signals dominate the XPS spectrum for each deposited copolymer. Similar behaviour can be observed in the evolution of the copolymer deposition rate (Figure 5). One notes that, although the addition of styrene is very small, the deposition rate dramatically increases, while the XPS spectrum of the deposited material becomes dominated by the styrene component. The styrene monomer has the function of an accelerator for the deposition rate.

![Figure 4](image4.png)  
**Figure 4** XPS C1s spectra for ‘pure’ polyMMA (a) and (b) for a MMA/styrene 80-20% copolymer system.

Figure 4 suggests that the surface aromaticity of MMA and styrene copolymer films increases with the addition of styrene in plasma. This behavior is consistent with infrared spectra (Figure 6). The C-H stretch band at 3100-3000cm⁻¹ is characteristic of films which contain aromatic moieties. Figure 6 shows that the peak height of the aromatic C-H stretching vibration at 3027cm⁻¹ increases by comparison to that of the asymmetric methylene C-H stretching vibration, with addition of styrene. The corresponding aromatic to aliphatic absorption intensity ratios obtained from the IR spectra are shown Figure 7. More aromaticity was observed in the deposited copolymer films, in agreement with
the OES of co-monomer plasma. On the contrary, the CO\textsubscript{2} asymmetric and the C=O carbonyl bands decrease.

**Figure 5** Deposition rate as a function of MMA fraction.

Surfaces of several styrene−MMA copolymer films have been analyzed by ToF-SIMS in order to detect any possible surface segregation of one of the two components. From the XPS data, one has indeed noticed that a small fraction of styrene content in the plasma gas resulted in a material with a surface showing essentially a styrene-like content (Figure 4 (b)). SIMS spectra of styrene based polymers are mainly composed of hydrocarbon clusters with unsaturated and/or aromatic fragments ($\text{C}_2\text{H}_2^{+}$, $\text{C}_2\text{H}_3^{+}$, $\text{C}_3\text{H}_4^{+}$, $\text{C}_4\text{H}_5^{+}$, $\text{C}_5\text{H}_6^{+}$, $\text{C}_6\text{H}_7^{+}$, $\text{C}_7\text{H}_8^{+}$, $\text{C}_8\text{H}_9^{+}$, and $\text{C}_{13}\text{H}_{14}^{+}$ at $m/z$ 26, 27, 39, 51, 63, 77, 91, 103, 105, 115, 165, and 193, respectively). Figure 8(a) shows these polystyrene characteristic peaks, which have been discussed in the literature [17].

PMMA also has characteristic SIMS spectra (Figure 8(c)), similar to those described in the literature [18]: fragments ($\text{C}_5\text{H}_7\text{O}^2^{+}$ and $\text{C}_5\text{H}_9\text{O}^2^{+}$ at $m/z=99$ and 101, respectively) associated with the MMA repeat unit ($\text{C}_5\text{H}_8\text{O}^2$) appear protonated or result from the loss or addition of one hydrogen atom. Other oxygen-containing peaks (as $\text{C}_4\text{H}_5^{+}$, $\text{C}_7\text{H}_9^{+}$ at $m/z=69$ and 109) are characteristic of the main chain with the pendant group. The methyl ester pendant group has also characteristic peaks at $m/z$ 15 ($\text{CH}_3^{+}$) and 59 ($\text{C}_5\text{H}_7\text{O}^2^{+}$). Branched hydrocarbon ions observed in the PMMA SIMS spectrum ($\text{C}_6\text{H}_7^{+}$, $\text{C}_7\text{H}_7^{+}$, $\text{C}_8\text{H}_7^{+}$, $\text{C}_9\text{H}_7^{+}$, $\text{C}_{10}\text{H}_7^{+}$, and $\text{C}_{11}\text{H}_{11}^{+}$ at $m/z$ 53, 55, 67, 69, 79, 81, 93, 95, and 107, respectively) can be directly related to the PMMA backbone fragmentation [18-19].

**Figure 6** IR spectra of deposited films for different MMA fraction.

**Figure 7** FTIR aromatic vs. aliphatic C-H stretching absorbance ratio at variable MMA fraction.

**Figure 8** Positive SIMS spectra of (a) polyStyrene, (b) a copolymer, and (c) PMMA.

The SIMS spectrum of a copolymer containing 20% styrene is shown in Figure 8(b). Even with only an addition of 20% styrene in the copolymer, the polystyrene characteristic peaks dominated the
SIMS spectra, compared with most peaks of the MMA. The absolute intensity of peaks from styrene or MMA units was monitored as a function of the MMA content: hydrocarbon fragments such as CH$_3^+$, C$_2$H$_3^+$, C$_3$H$_5^+$, and C$_7$H$_9^+$ at $m/z = 15, 27, 29, 41$, and $93$, respectively, decreased with increasing styrene content. By contrast, some characteristic styrene peaks (such as C$_5$H$_3^+$, C$_7$H$_7^+$, C$_8$H$_7^+$, and C$_8$H$_9^+$ at $m/z = 63, 91, 103$, and $105$, respectively) showed an absolute intensity higher than those observed for polystyrene. In the SIMS spectra of copolymer and homopolymer films (Figure 8), the intensity of the fragments containing oxygen became very weak. The C$_7$H$_7^+$ trypropyl ion is characteristic of the styrene unit, but we found its intensity does not quickly increase with the addition of styrene monomer in the plasma gas.

Figure 9 shows the intensity of fragments from the PMMA, such as CH$_3^+$, C$_3$H$_5^+$, and C$_3$H$_3$O$^+$: a large increase in intensity with the MMA content is observed. Several aromatic fragments from the copolymers, related to the styrene unit, like C$_6$H$_5^+$, C$_7$H$_7^+$, and C$_8$H$_9^+$, are evolving too (Figure 10). All these characteristic fragments exhibit higher peak intensities for the copolymer films, and are even higher than those observed for homopolymer films.

5. Conclusion
By controlling the monomer content in the gas phase, plasma copolymerization can be used to deposit polymer thin films with different composition. This is due to reactions in the gas phase that depend strongly on the bond dissociation of each monomer and the reaction among the species in plasma gas. Some typical functional groups from styrene and MMA, which were identified in the OES, can be directly found in the copolymer films. Both FT-IR and XPS show that the contribution from the styrene monomer is very strong in the deposited films. The OES spectra also showed that the characteristics from styrene dominated the OES spectra of the co-monomer plasma. The $\pi$-$\pi^*$ C1s peak (characteristic of aromatic rings) in the films increases quickly while the amount of C$_6$H$_6$ benzene excited species in the OES increases. This is confirmed from SIMS spectra.

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