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Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

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ABSTRACT

Plasma-polymerized thin films prepared from amine-containing saturated (propylamine) and unsaturated (allylamine and propargylamine) precursors were investigated in terms of the deposition rate, polymerization kinetics and thin film morphology as function of the applied power. Moreover, a mathematical model was established to correlate the physicochemical properties to the deposition kinetics under plasma polymerizations. It was found that the thin film deposition rate was primarily dictated by the amine bond dissociation energy (NH_2 BDE) of precursors. On the other hand, surface chemistry (N/C ratio, surface imine and amine contents) guided the growth of L-929 fibroblast cells on the prepared amine-functionalized surfaces. A close relationship among the deposition kinetics, the physicochemical and biological properties of the deposited amine-containing plasma polymers was presented.

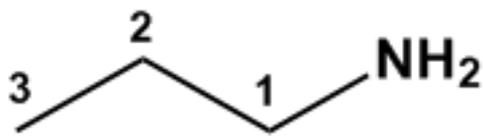
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Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

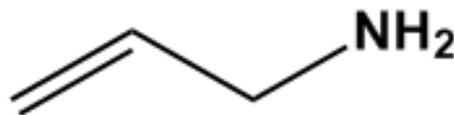
Introduction:

Allylamine was widely applied as a coating layer on biomaterials such as polyethyleneterephthalate [26], polystyrene and polyethylene powder [27], stainless steel stents or on aluminum [28], also in the fields of sensor technology [29], as well as for DNA immobilization [30].

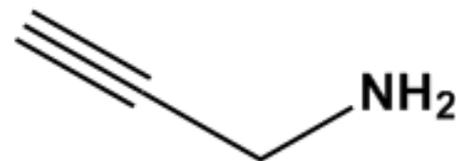
The mechanism of allylamine plasma polymerization has been reported and reviewed by different research groups [25,31]. However, the **comparisons among plasma polymerizations with other C3 amine molecules, i.e. propylamine [32,33] and propargylamine [32], were less reported.**



propan-1-amine
propylamine



prop-2-en-1-amine
allylamine



prop-2-yn-1-amine
propargylamine

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Introduction:

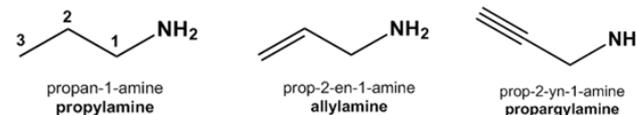
Plasma polymers differ from the conventionally synthesized polymers with **their highly complex structure, with branched or crosslinked chains** [15].

The course of plasma polymerization involves the generation and dissociation of complicated reactive species such as electrons, ions, radicals, atoms and molecules. Therefore, **only limited supporting literature detailed the relationships between the deposition kinetics with the physical–chemical properties of plasma polymers** [34–36].

Although **the potential applications of plasma polymers rely considerably on their stability, only a few works focusing on the stability of plasma polymers were found.**

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Introduction:



In this study,

- we prepared amine-containing **plasma polymers from three C3 amine precursors** with different conjugation degree.
- The triple and double bonded propargylamine and allylamine presented more than 5.6 and 1.8 folds deposition rate than that of the saturated propylamine, respectively.
- **The amine functionalities** of the three plasma polymers, on the other hand, **revealed a different correlation to the saturation degree.**
- It was observed that **the overall deposition rate** of the three plasma polymers **were controlled mainly by the plasma applied power.**
- Moreover, **the slight change in the chemistry of precursor resulted in significant difference in deposition kinetics.**
- The principal molecular structure of precursor that resulted in the **difference in deposition kinetics was presumably the amine bond dissociation energy (NH₂ BDE).**
- Furthermore, we found that the created amine plasma polymers showed direct effects on **the growth of L-929 fibroblast cells** where **the higher N/C ratio and imine/amine contents promoted higher cell density on plasma polymers.**
- **The results**, integrating experimental data and mathematical calculations, **have detailed how greatly the chemical structure of precursors influenced the physical–chemical properties of the prepared plasma polymers** and their direct applications.

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

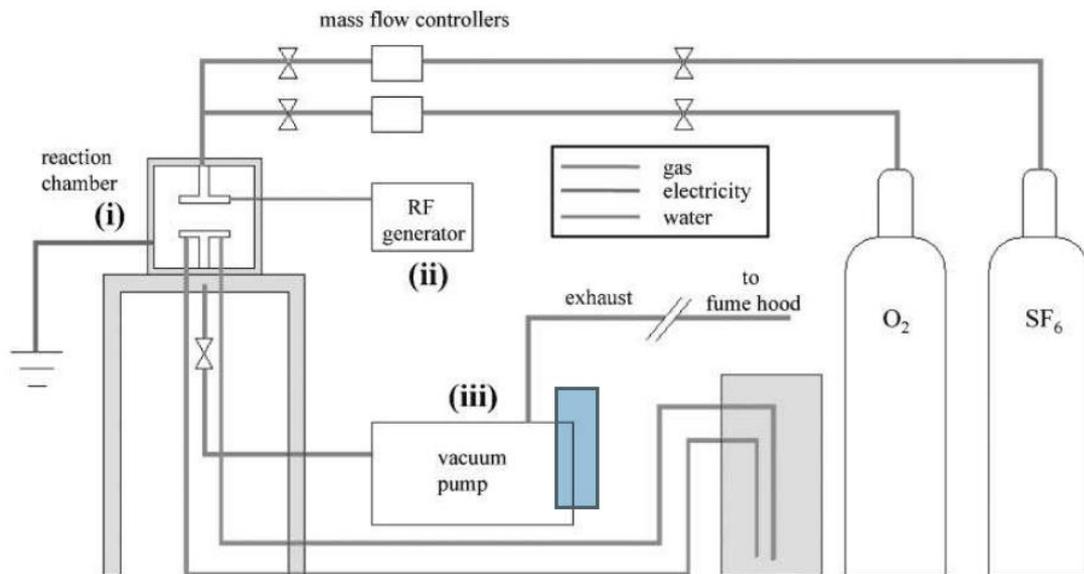
Experimental section:

2.2. Plasma polymerization

The polymerization of C3 amines was conducted in a plasma system which was modified from the previous work [42].

The system consists of three main parts:

- (i) a reaction chamber;**
- (ii) a radio-frequency generator** (Huttinger, model PFG 300 RF, Germany);
- (iii) a vacuum system.**



In the plasma reactor, a stainless steel anode with 2 cm thickness was placed at the central part of the vacuum chamber, and its upper part was located by 10 cm above the pumping outlet. The anode was separated by 7 cm air gap from the shower-type cathode. Both electrodes were circular with a diameter of 15 cm. The deposition of all monomers was set at 100 mTorr, 20 sccm, heating temperature at 40 °C, for 60 min.

The vaporized monomer was introduced into the chamber and was polymerized with different applied power (5, 10, 30, and 50 W) on quartz, KBr pellet, and Si wafer.

Due to overheating occurred for the applied power higher than 50 W in this plasma apparatus, the experimental parameter was controlled at the applied power up to 50 W

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Experimental section:

2.4. Surface characterizations

The chemical functionality of the fabricated amine-containing plasma polymers was characterized by **Fourier-transformed infrared spectrometry (FTIR)**, model FTS-3500, Bio-Rad Digilab.

The amount of the deposited polymers on quartz substrate was quantified by **quartz crystal microbalance** (ANT Technologies Co., model ANTQ3000, Taiwan). (deposition rate)

The wettability of the surface was evaluated by measuring the **static contact angles** (Sindatek) with deionized water. At least five droplets were measured for each position, with droplet volume of 3 μL .

The surface morphology of C3 amine plasma polymers was observed by using **tapping-mode atomic force microscope** (Digital Instruments, Nanoscope III, 125 μm AFM scanning head) with scan resolution of $2 \times 2 \text{ nm}^2$.

The cell morphology of L-929 fibroblasts on different surfaces was observed by using **scanning electron microscope (SEM)**, JEOL JSM- 6300).

The chemical composition of the plasma polymerized thin films was determined **by electron spectroscopy for chemical analysis (ESCA)**. Thermo VG Scientific Theta Probe Instrument with monochromatic source of Al-K α (1,486.6 eV) as excitation source was operated, with pass energy of 50 eV. Ar ion gun was employed with 3 kV voltage and 1 mA current. The characterizations of samples were taken under takeoff angle of 53 $^\circ$, with under X-ray spot size of 400 μm .

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

3.1. The deposition of the C3 amine plasma polymers

In this study,

the experiments were conducted in a precursor-sufficient (energydeficient) region which generally demonstrated a linear trend for the deposition rate as function of the applied power

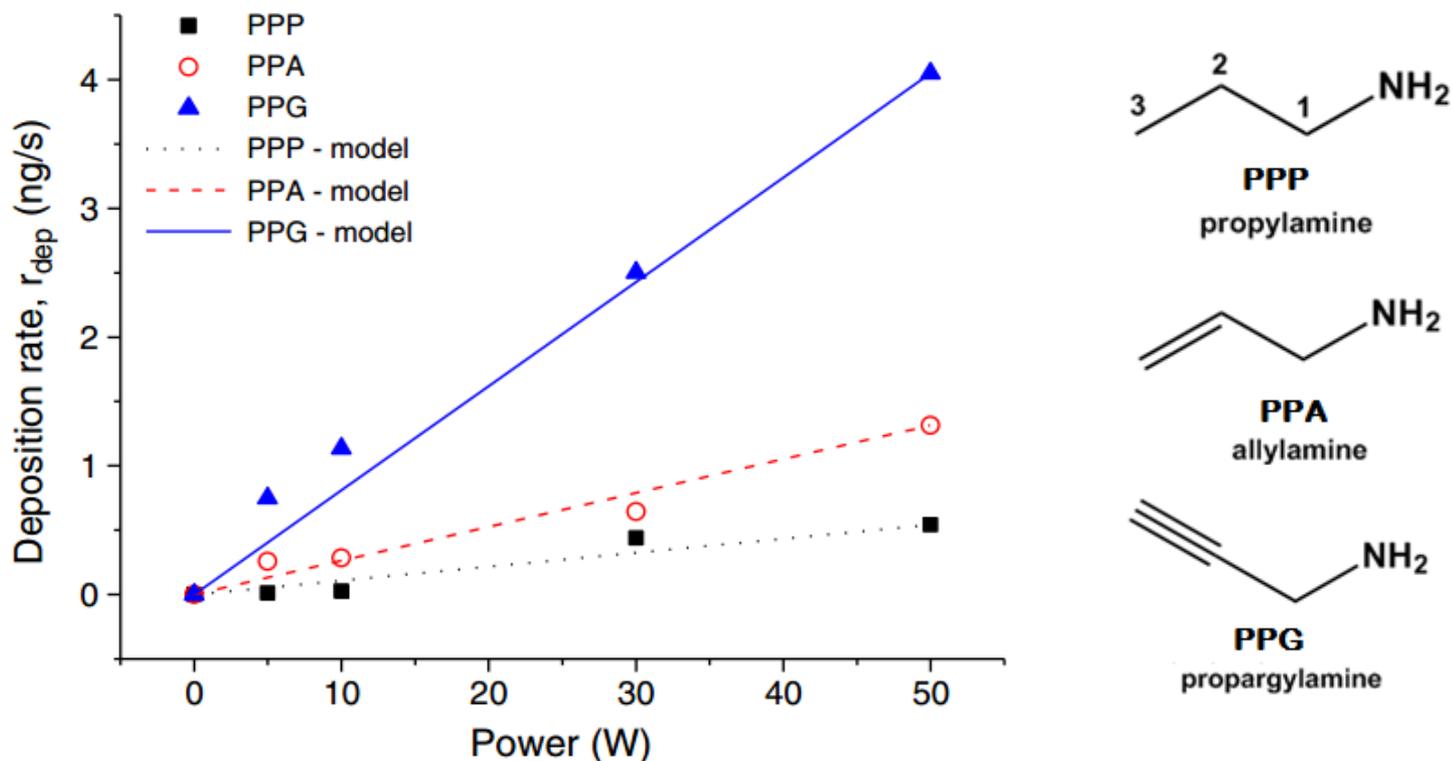
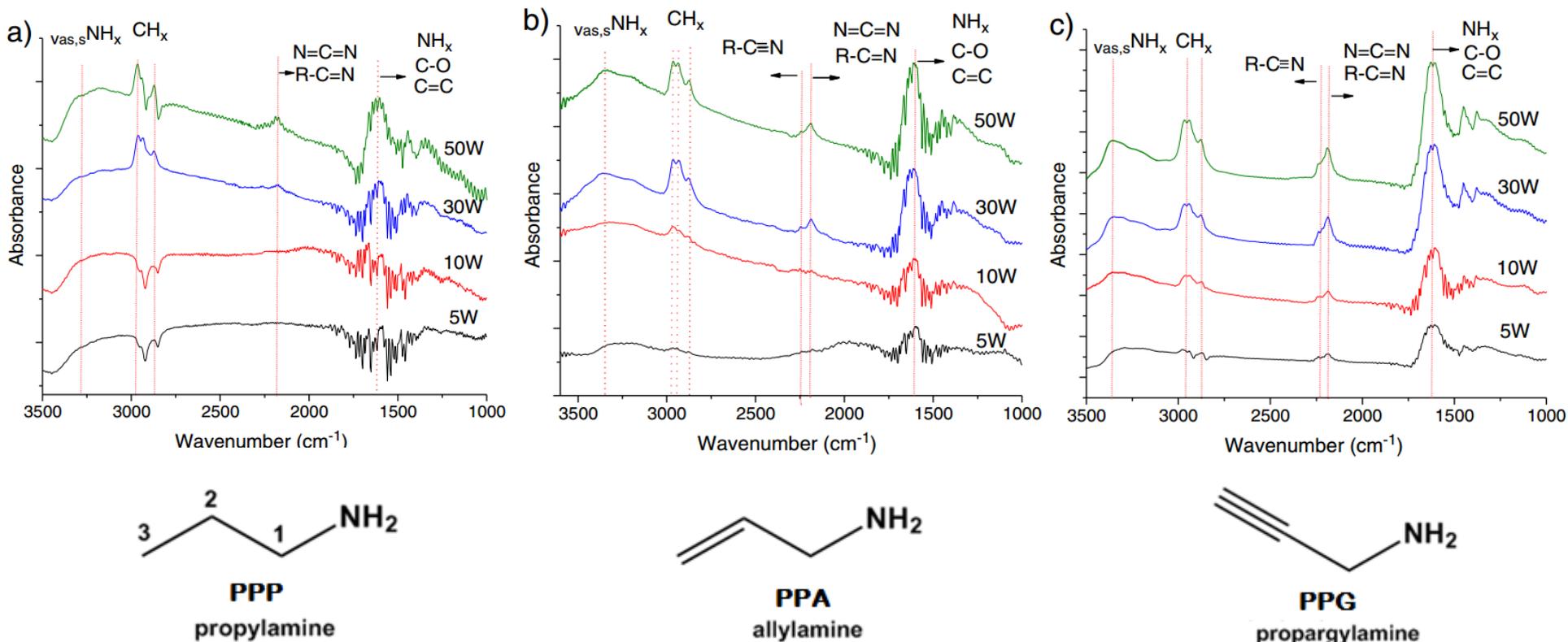


Fig. 1. Deposition rate of C₃ amine monomers by plasma polymerization as function of applied power. The data points were obtained by experiments and the lines were fitted by the developed modeling.

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

3.2. Identification of amine functionalities by FTIR



It is noted that the intensity of the characteristic peaks increased proportionally with the modulated power. In comparison with the FTIR spectra of PPP, one special signal was detected especially at high power (30 W and 50 W) at 2240 cm^{-1} , corresponding to the non-conjugated triple-bond structures of $\text{N}\backslash(\text{R}\text{C}\text{N})$ and $(\text{R}\text{C}\text{C}\text{R})$ for PPA and PPG. The results revealed that more unsaturated C, N bindings were deposited from allylamine and propargylamine under the higher applied powers.

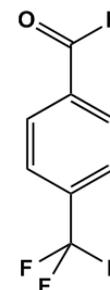
Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Experimental section:

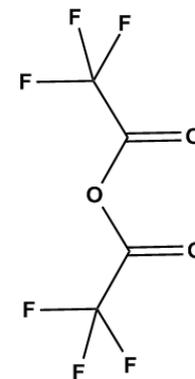
The surface concentration of primary (NH₂) and secondary (NH) amines was determined by the derivatization technique employing trifluoromethyl benzaldehyde (TFBA) and trifluoroacetic anhydride (TFAA), with the derivatization mechanism reported elsewhere [25]. The derivatization was performed by exposing the plasma polymers **30 and 10 min with TFBA and TFAA vapor, respectively**, in a sealed container at an ambient condition [43]. The amine concentrations were then calculated by applying Eqs. (1a) and (1b).

$$[NH_2] = \left[\frac{\left[\frac{F}{3} \right]}{\left[C \right] - \frac{8[F]}{3}} \right] \times 100\% \quad (1a)$$

$$[NH_2 + NH + OH] = \left[\frac{\left[\frac{F'}{3} \right]}{\left[C' \right] - \frac{2[F']}{3}} \right] \times 100\% \quad (1b)$$



4-(trifluoromethyl)benzaldehyde
TFBA

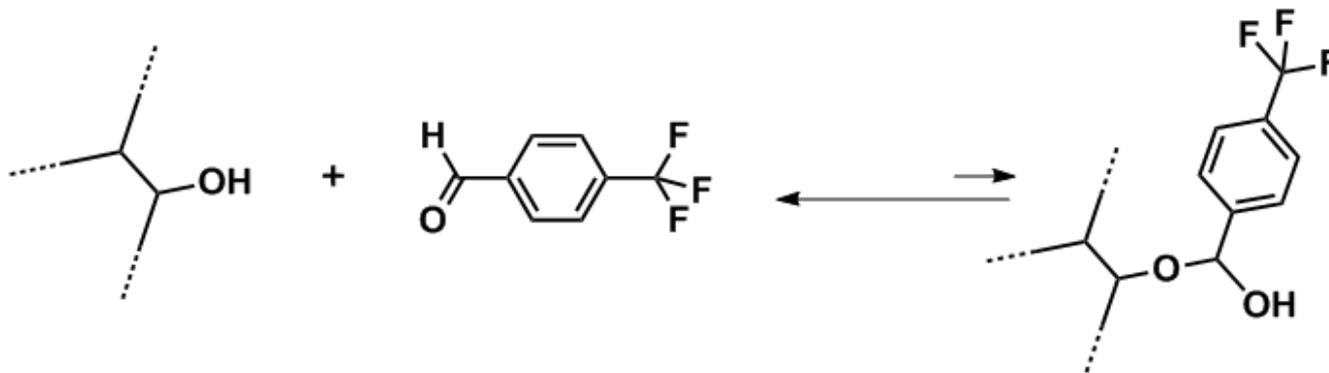
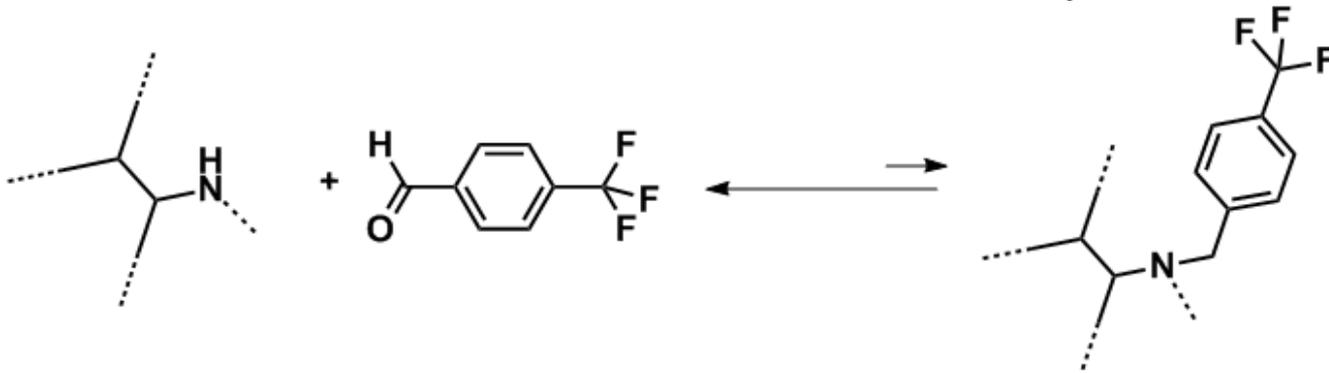
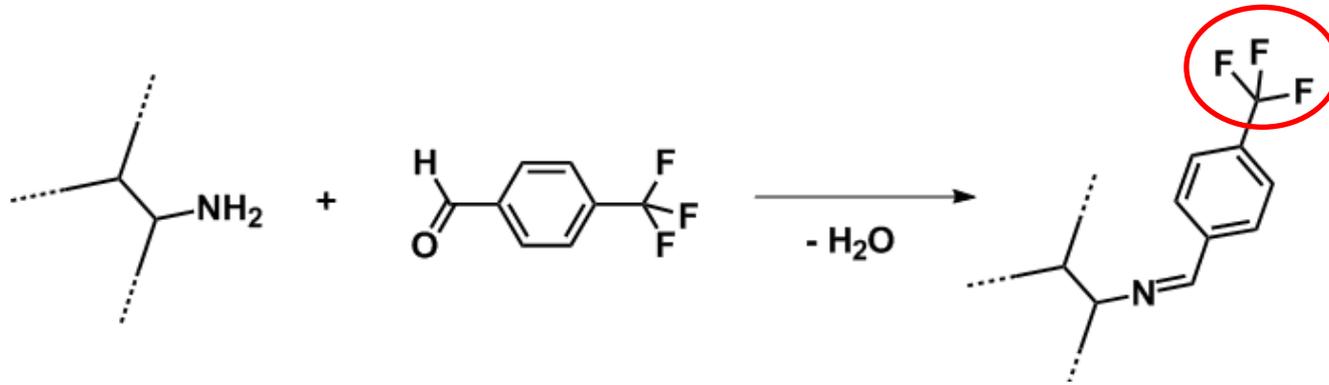


Trifluoroacetic anhydride
TFAA

[F] and [C] are the fluorine and carbon concentrations determined by ESCA after the reactions with TFBA. [F'] and [C'] are the fluorine and carbon concentrations determined by ESCA after the reactions with TFAA.

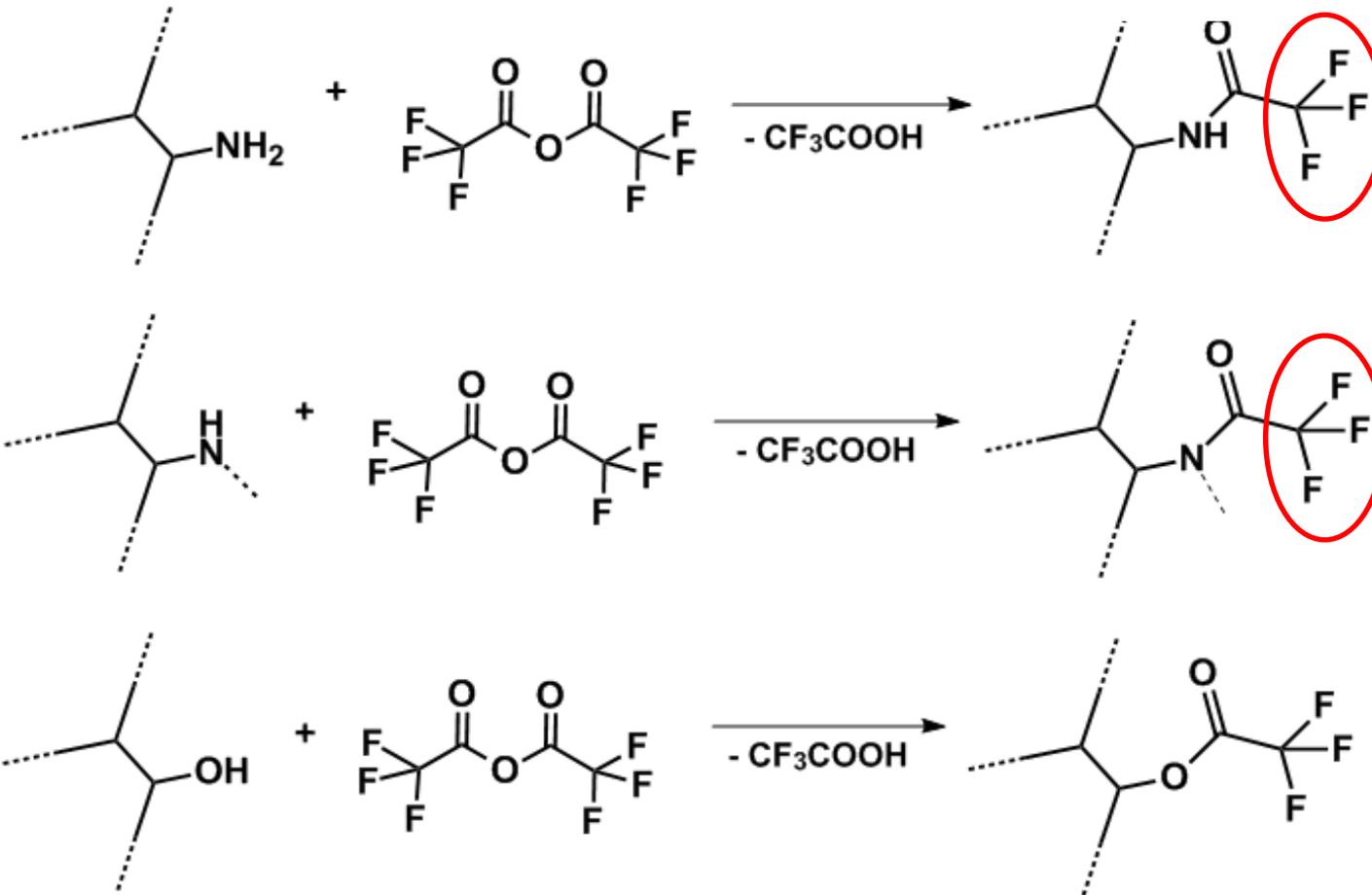
TFBA derivatization + XPS (ESCA)

$$[NH_2] = \left[\frac{\left[\frac{F}{3} \right]}{\left[C \right] - \frac{8[F]}{3}} \right] \times 100\%$$



TFAA derivatization + XPS (ESCA)

$$[NH_2 + NH + OH] = \left[\frac{\left[\frac{F'}{3} \right]}{\left[C' \right] - \frac{2[F']}{3}} \right] \times 100\%$$



The authors did not consider the contribution of OH groups in the derivatization results and correlated the fluorine concentration after the reaction only with amines. While OH groups could have contributed to those results, we have found here that hydroxyls do not play an important role in aging of pp-allylamine.

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

3.3. ESCA surface characterizations

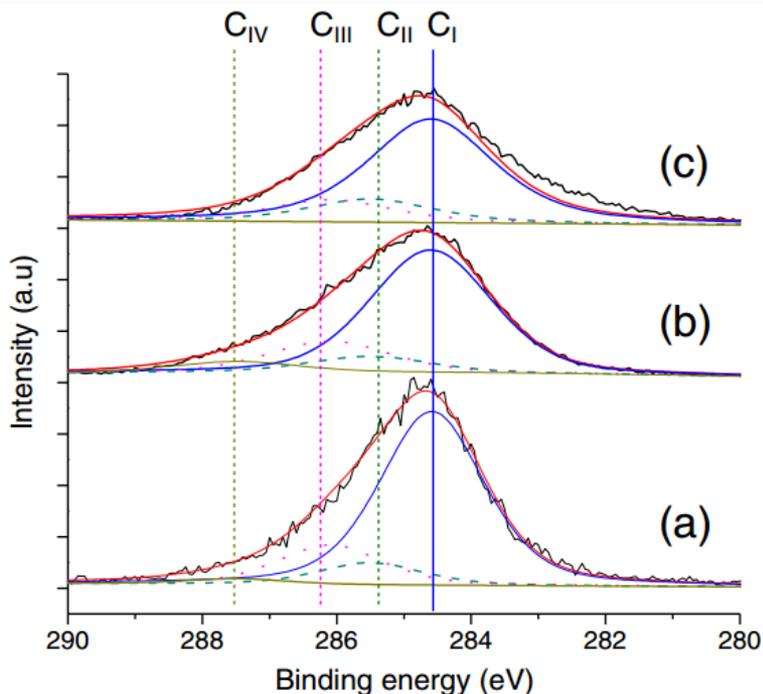


Fig. 3. ESCA high-resolution C1s spectra of PPP (a), PPA (b), and PPG (c), deposited at 20 sccm flowrate, 100 mTorr pressure, 50 W for 60 min.

Table 1

The chemical composition and the ESCA high-resolution C1s peak deconvolution of plasma polymerized C₃ amines.

Plasma polymer	PPP	PPA	PPG	
Covalent bonds	1	2	3	
C (%)	78.7	74.7	80.8	
O (%)	5.7	8.9	4.2	
N (%)	15.6	16.4	15	
N/C (%)	19.82	21.95	18.95	
C _I (284.6 eV)	C-C (%)	72	68.5	64.8
C _{II} (285.5 eV)	C-N (%)	9.2	8.7	13.9
C _{III} (286.1 eV)	C=N, C-O, C-C≡N (%)	16.5	17.1	14.2
C _{IV} (287.6 eV)	CO-NH, C=O (%)	2.3	5.7	7.1
R ²	0.99	0.99	0.99	

PPA possessed the highest nitrogen content, in particular CIII (17.1%), than that of PPP and PPG (16.5 and 14.2%, respectively).

It was reported that nitrile (C\C`N) and alcohol (C\O) component were the minor constituents in the CIII peak [47], while **imine (\C=N) was the major functional groups** (more than 50%) [32].

The N/C ratio from the wide scan corresponded proportionally to the CIII content, suggesting that the **deposition of PPA introduced significantly higher imine functionalities** than that of PPP and PPG

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

3.3. ESCA surface characterizations

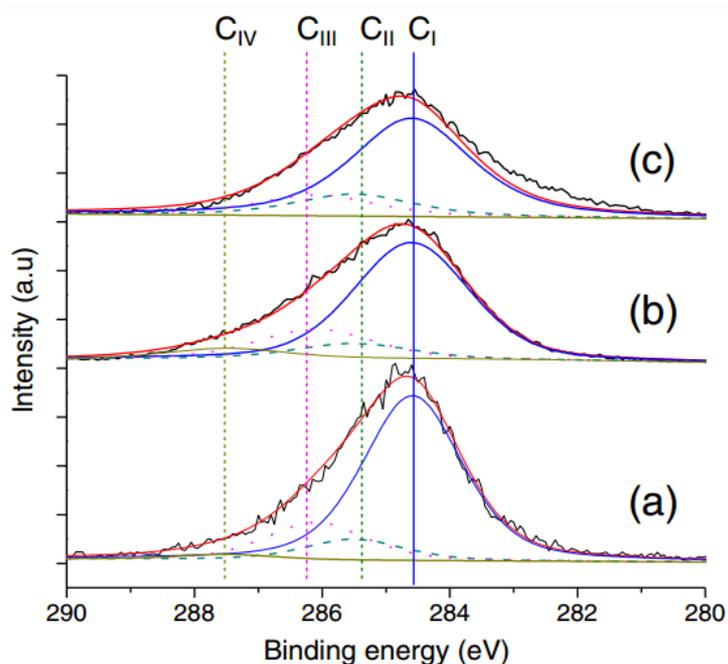


Fig. 3. ESCA high-resolution C1s spectra of PPP (a), PPA (b), and PPG (c), deposited at 20 sccm flowrate, 100 mTorr pressure, 50 W for 60 min.

Table 2

Primary and secondary amine contents of plasma polymers.

Amines type	Amines per 100 C atoms		
	PPP	PPA	PPG
Primary [NH ₂]	0.61	0.71	0.44
Secondary [NH]	4.07	6.73	2.39
Total amines	4.68	7.44	2.83

It was demonstrated that the **PPA incorporates the highest amount of primary and secondary amines** into the corresponding thin films compared to those synthesized from PPP and PPG.

Moreover, **the density of the secondary amine was more than five folds higher than the primary amine.**

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

3.4. Surface morphology and stability of plasma polymerized C3 amine thin films

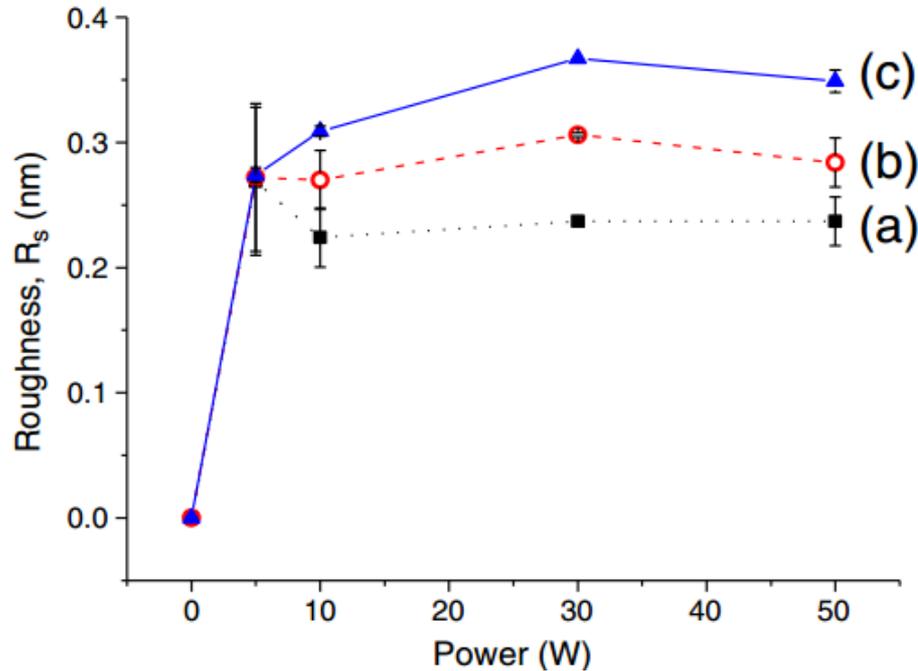


Fig. 4. Surface roughness of PPP (a), PPA (b), and PPG (c), deposited as function of the applied power (lines are drawn only to guide eye).

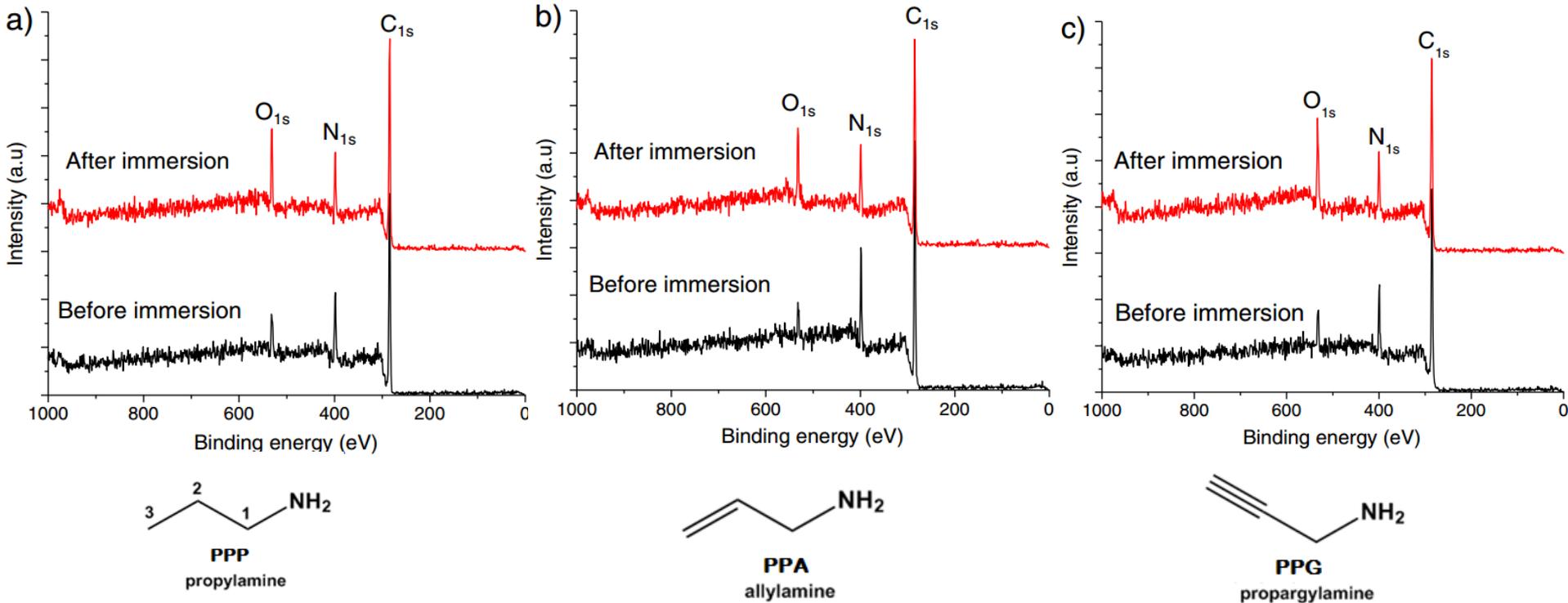
The surface morphology of the plasma polymerized polymers prepared from three C3 amine precursors under various applied power was analyzed by AFM.

The surface of the PPG thin film revealed a roughness of 0.34 nm which is higher than that of PPA (0.28 nm) and PPP (0.23 nm), suggesting that the higher surface roughness of the deposited films was resulted from the higher unsaturation degree in precursor.

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

3.4. Surface morphology and stability of plasma polymerized C3 amine thin films



The **stability tests** were performed by preparing two sets of plasma polymers from the **three precursors independently under the experimental conditions of 20 sccm, 10 W, and 60 min.** **After immersing** the deposited amine-containing specimens in PBS for 48 h, dissolution and swelling were not observed.

ESCA characterizations confirmed that there was **no significant change in chemical composition** for the films **after the immersion.**

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

3.4. Surface morphology and stability of plasma polymerized C3 amine thin films

Table 3

Atomic composition of amine-containing plasma polymers before and after immersion in PBS for 48 h.

Plasma polymer	Condition	C (%)	N (%)	O (%)
PPP	Before	77.9 ± 0.7	17.1 ± 1.8	5.1 ± 1.1
	After	75.0 ± 2.3	14.2 ± 0.5	10.9 ± 2.8
PPA	Before	78.8 ± 0.9	17.2 ± 1.3	4.2 ± 0.5
	After	75.6 ± 2.3	13.5 ± 0.1	11.0 ± 2.3
PPG	Before	79.5 ± 0.8	15.5 ± 0.1	5.1 ± 0.6
	After	75.4 ± 0.2	12.0 ± 0.4	12.7 ± 0.1

For all the three plasma polymers, more than 95% of carbon and nitrogen content were preserved and only slight oxidation was detected by about 5% for PPP, and 7% for PPA and PPG which is presumably due to the sample immersion in oxidative condition.

It is therefore reasonable to conclude that all of the **prepared amine-containing plasma polymers were exceptionally stable** that the superior properties can assist further applications in surface coatings and surface functionalization of biomedical devices.

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

4.2. Cell response related to surface chemistry of C3 amines plasma polymers

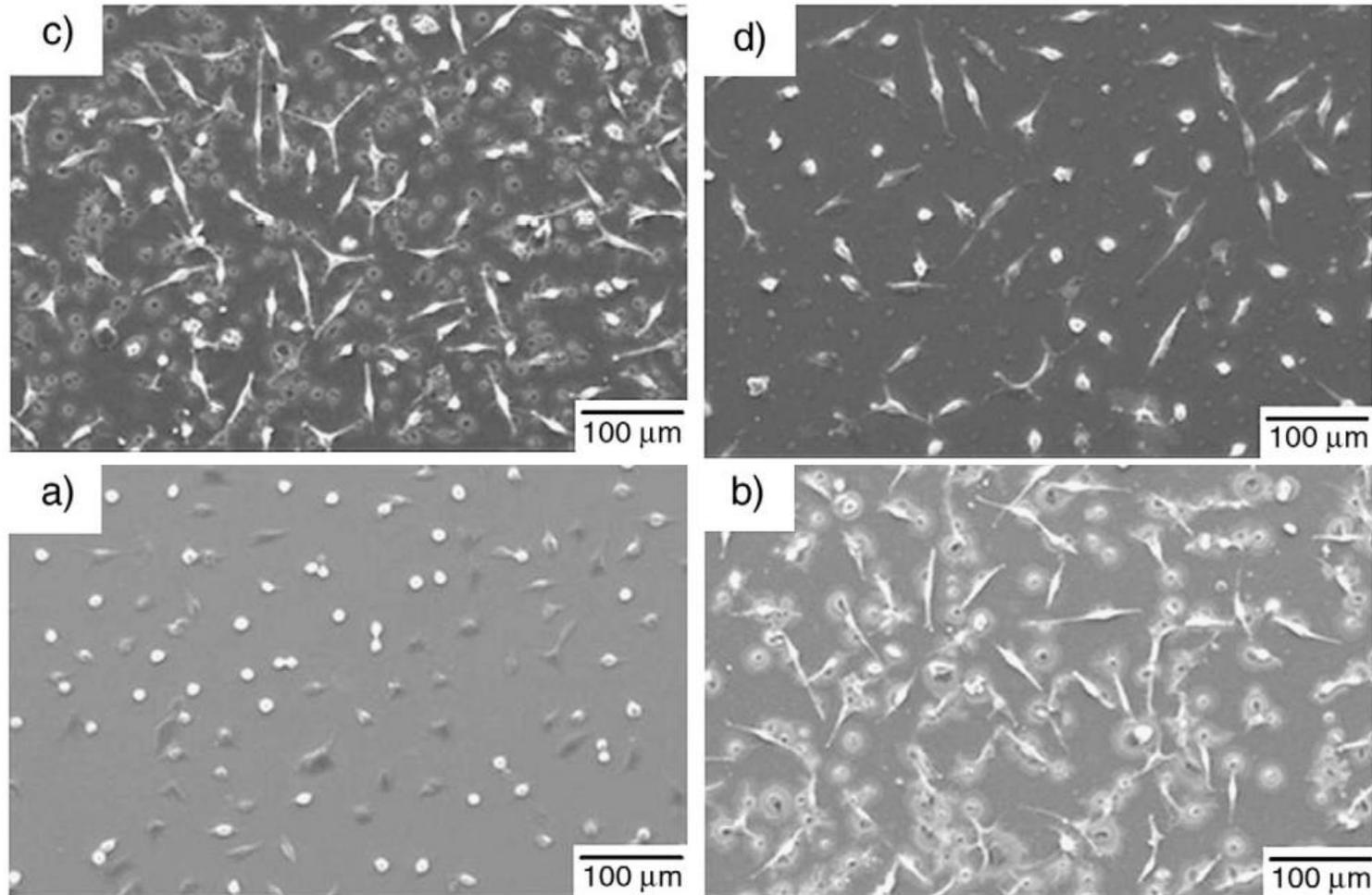


Fig. 6. Cell behavior of L-929 fibroblasts on surfaces of bare Si wafer (a), PPP (b), PPA (c), and PPG (d).

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Results:

4.2. Cell response related to surface chemistry of C3 amines plasma polymers

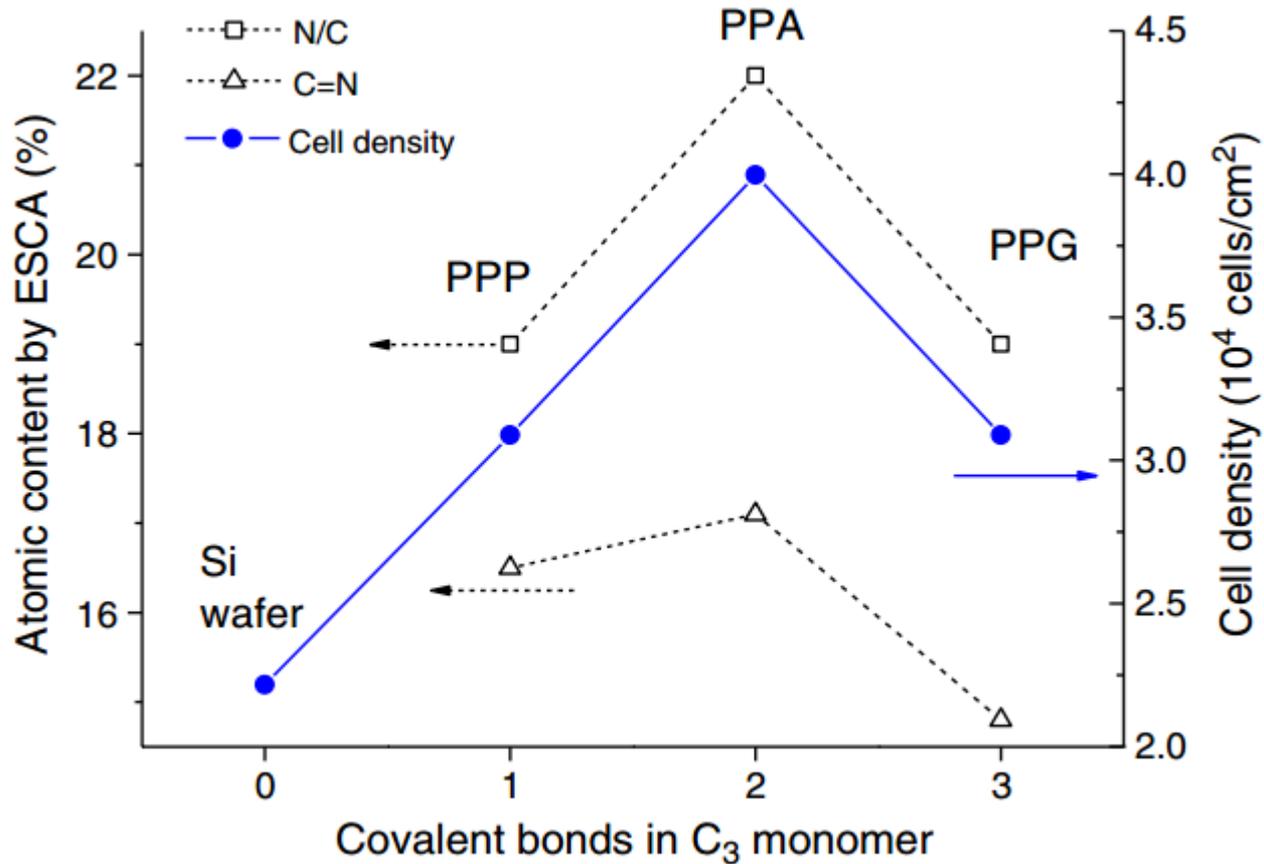


Fig. 7. Relationship between surface chemistry of C₃ amines plasma polymers towards L-929 fibroblast cell density

Plasma polymerization of amine-containing thin films and the studies on the deposition kinetics

Conclusions:

Amine-containing plasma polymer thin films were successfully prepared from three types of C3 amine precursors with different saturation degree.

Notable difference in deposition rates of more than two and six folds was observed from allylamine and propargylamine comparing with propylamine precursors.

FTIR and ESCA characterizations identified the increase of the intensity of amine functionalities as function of the applied power for the three C3 amine precursors.

Further analyses on the three C3 amine precursors revealed that the amine bond dissociation energy of precursor governed the polymerization kinetics by showing a linear relationship with the deposition constant K_{dep} .

Moreover, the cell responses on the C3 amine polymerized thin films demonstrated that the **imine content and amine contents as well as the N/C ratio play a pivotal role in promoting cell adhesion.**

With the exceptional stability, controllability, and biocompatibility, the amine-containing plasma polymers possess vast potential for the application in surface coating and the surface modifications for biomaterials.

Thank you

with the derivatization mechanism reported elsewhere [25]:

23086

J. Phys. Chem. B **2005**, *109*, 23086–23095

Mechanistic Studies of Plasma Polymerization of Allylamine

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Primary and secondary amine surface concentrations were obtained by performing derivatization reactions with gaseous reagents at their vapor pressure. For the detection of primary and secondary amine groups, two reagents were used:^{6,68} (a) trifluoromethyl benzaldehyde (TFBA), which reacts only with NH_2 , and (b) trifluoroacetic anhydride (TFAA), which reacts with NH_2 , NH , and OH . TFBA and TFAA underwent several freeze–thaw cycles to remove dissolved gases prior to use. XPS was applied afterward to determine the element composition of the films. Primary and secondary amine concentrations were derived as previously described.⁶⁹

Results

The FTIR spectra of pp-allylamine deposited at different powers are given in Figure 1. The assignment of IR bands is made according to ref 16 and summarized in Table 1.

The spectrum in the absorption region from 3700 to 2700 cm^{-1} is a very broad superposition of different contributions. Primary and secondary amines (R-NH_2 , $\text{R-NH-R}'$) give rise to asymmetric ($\nu_{\text{as}} \sim 3350 \text{ cm}^{-1}$), symmetric ($\nu_{\text{s}} \sim 3270 \text{ cm}^{-1}$) N-H stretching, and symmetric ($\delta_{\text{s}} \sim 1590 \text{ cm}^{-1}$) N-H deformation vibrations, which overlap with C-H stretches and other vibrational modes. Stretching vibrations of hydroxyl groups ($-\text{OH}$) are also observed. The elemental analysis of plasma polymer films (see below) reveals several percent of oxygen, which is less than half that of nitrogen. Previous research¹⁶ showed that hydroxyls are unlikely in amine-containing plasma polymers with a high nitrogen content, as the oxygen is bound mainly in amide species.