

# METHOD OF OBTAINING POROUS POLYMER STRUCTURE USING ATMOSPHERIC PRESSURE PLASMA

B.-G. RUSU<sup>2</sup>, V. POHOATA<sup>1</sup>, C. IONITA<sup>3</sup>, R. SCHRITTWIESER<sup>3</sup>, N. DUMITRASCU<sup>1</sup>

<sup>1</sup>Iasi Plasma Advanced Research Center (IPARC), Faculty of Physics, Alexandru Ioan Cuza University of Iasi, Blvd. Carol I No. 11, Iasi, 700506, Romania, E-mail: bogdan.rusu@uaic.ro

<sup>2</sup>Department of Pedotechnics, Faculty of Agriculture, University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad" of Iasi, 3 Sadoveanu Alley, Iasi, 700490, Romania

<sup>3</sup>University of Innsbruck, Institute for Ion Physics and Applied Physics, 6020 Innsbruck, Austria

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This study focuses on producing porous polymer under plasma conditions using two different monomers: ethylene glycol and styrene. A plasma discharge at atmospheric pressure was used to induce polymerisation reactions in order to obtain copolymer films based on the two monomers. The plasma source consists of a dielectric barrier discharge which operates in an argon gas flow with glass as dielectric. The porous polymer was obtained by dissolution and sonication of the hydrophilic groups from the material. The new porous material was tested in terms of protein adsorption. The films were characterized by Fourier Transform infrared spectroscopy, X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy techniques.

*Key words:* Porous polymers, plasma polymerization at atmospheric pressure, protein absorption.

## 1. INTRODUCTION

Protein adsorption is a very important phenomenon and highly dependent on the surface morphology and also on the chemistry [1–5]. Because of their highly active surface, porous materials are often used in drug adsorption and controlled drug release, chromatography, biological separation of molecules etc. [6–10]. The most common porous materials are porous silicates and zeolites. In recent years a very high importance has been given to synthesizing porous polymeric materials by various methods: direct templating methodology, block copolymer self-assembly methodology and direct synthesis methodology [11]. However, the synthesis of such materials is difficult to control due to their repetitive chemical and topographic structure. One of the most convenient method, which can be used for obtaining such material, is plasma polymerization at atmospheric pressure which present very much applications: thin layer deposition, treatment, welding and cutting, etc. [12–16].

In this way, the present study is focused on the synthesis of new polymeric porous materials using the technique of plasma polymerization at atmospheric pressure of two monomers with different wettability: ethylene glycol with a high hydrophilic character and styrene with high hydrophobic character. After synthesizing, the new polymer (Co PS-EG) film was maintained in a water bath and exposed to ultrasonication process for 30 min at room temperature in order to obtain a porous structure.

These new materials were tested for the adsorption of biomolecules. For this analysis we used bovine serum albumin (BSA). The adsorption process of biological molecules on the surfaces were analysed by Scanning Electron Microscopy (SEM) technique, X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform InfraRed Spectroscopy (FTIR).

## 2. EXPERIMENTAL SET-UP

The plasma chemical reactor consists of a discharge at atmospheric pressure, working in a plane parallel geometry with glass as dielectric barrier (Fig. 1). The electrodes were circular with 30 mm diameter and the gap distance between them were 5 mm. Experiments were made in argon with a flow rate of 2 l/min for the plasma working gas (Flowmeter 1) and 0.9 l/min for ethylene glycol monomer bubbling (Flowmeter 2) and 0.1 l/min for styrene (Flowmeter 3), respectively. The spectral purity of argon was 99.999%.

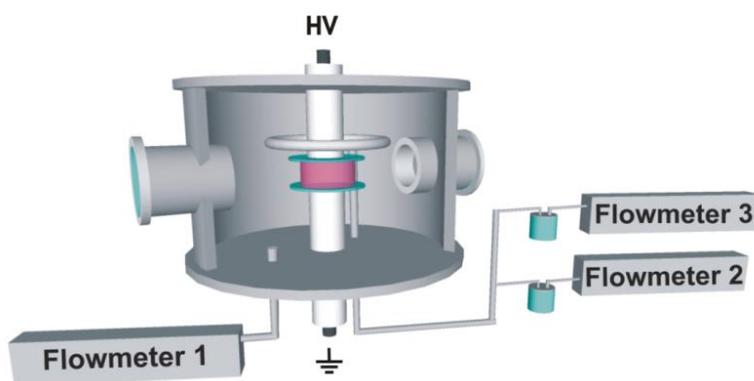


Fig. 1 – Plane parallel geometry of plasma reactor at atmospheric pressure.

High voltage monopolar pulses were delivered using a voltage amplifier (Trek Inc.) connected with a waveform generator (Tabor Electronics Inc.). During the polymerisation process, the electrical parameters were maintained constant, respectively high voltage  $V = 6$  kV, repetition rate  $f = 2$  kHz and duration of polymerization was 10 minutes. The discharge mode is glow characterized by two current peaks at each applied voltage pulse, where the first current peak is called the primary discharge, and the second peak the secondary discharge [17, 18].

The discharge used in order to obtain polymeric surfaces by plasma polymerization at atmospheric pressure conditions is characterized by well-defined current pulses, with pulse duration of a few microseconds, contrary to the filamentary regime which is characterized by the presence of current peaks corresponding to a micro-discharge or streamers regime with a lifetime in the order of nanosec-

onds. The typical discharge current signals (Fig. 2) shows the homogeneous (diffuse) mode in which the discharge operates.

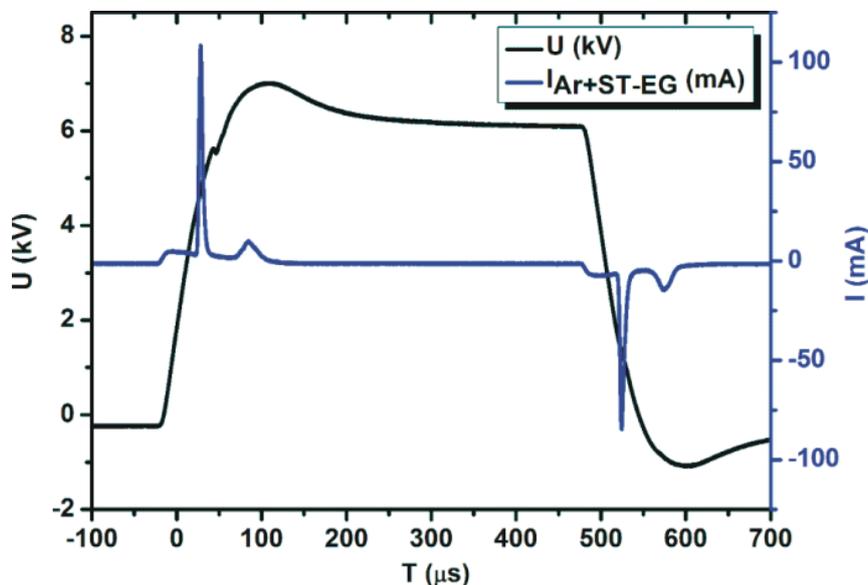


Fig. 2 – Current-voltage waveform of DBD discharge at atmospheric pressure in Ar and Ar+monomer vapours.

Complementary information on the barrier-discharge parameters was obtained by emission spectroscopy. In order to characterize the discharge, the global emission spectrum of the DBD plasma in Ar and mixture of Ar and monomers was recorded. The light emitted by the plasma was analysed with a high resolution spectrometer (Jobin Triax rumor) equipped with a CCD as a detector (Symphony Horiba Jobin Yvon).

A typical emission spectrum of DBD plasma produced in Ar and Ar-monomer mixture is shown in Figure 3. In addition to other excited argon species, the spectrum revealed the line corresponding to air impurities (oxygen, nitrogen) who are supplementary involved in the discharge.

After additions of the monomers, all emission lines decrease. This can be explained by the consumption of plasma particle energy (excited atoms and molecules) due to fragmentation of the monomers who are introduced into the discharge chamber.

The chemical structure of the films was investigated with FTIR spectroscopy. The spectra were registered by a Bomem MB-Series 104 spectrometer in the range of  $4000\text{--}400\text{ cm}^{-1}$ ,  $4\text{ cm}^{-1}$  resolution and also by XPS (5000 VersaProbe spectrometer, equipped with a monochromatic Al  $K\alpha$  X-ray source ( $h\nu = 1486.7\text{ eV}$ )).

The topography of the polymer films was investigated by Scanning Electron Microscopy (SEM) technique, using a Hitachi S-3400N microscope working at an acceleration voltage of 20 kV. The polymer sample was metalized with gold in a magnetron discharge for good conductivity.

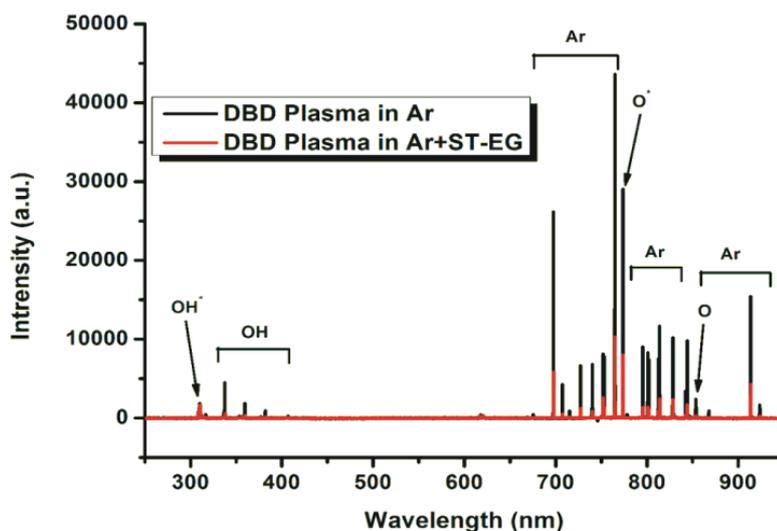


Fig. 3 – Optical emission spectrum of the DBD discharge at atmospheric pressure in Ar and Ar+monomer vapours.

### 3. RESULTS AND DISCUSSION

Atomic Force Microscopy-AFM examinations revealed a value of the root mean square roughness ( $R_{\text{RMS}}$ ) of 1.6 nm for the Co PS-EG films showing that simultaneous styrene-PEG plasma polymerization leads to low roughness polymer films. The topography image shows well defined peaks with maximum height of 18 nm. They are randomly positioned on the film surface with a density of  $\sim 10$  peaks/ $\mu\text{m}^2$  (Fig. 4(a)).

This randomly distributed peaks can be attributed to the hydrophilic structure and can appear by phase separation phenomena which are occurring during the plasma deposition process.

After the dissolution and sonication process, the hydrophilic structure is removed, the surface topography becomes porous, with a pore diameter around 50 nm (calculated with ImageJ program) (Fig. 4(b, c)). The SEM images prove that the adsorbed BSA proteins cover the entire surface of the polymer, the pores are not visible (Fig. 4(d)).

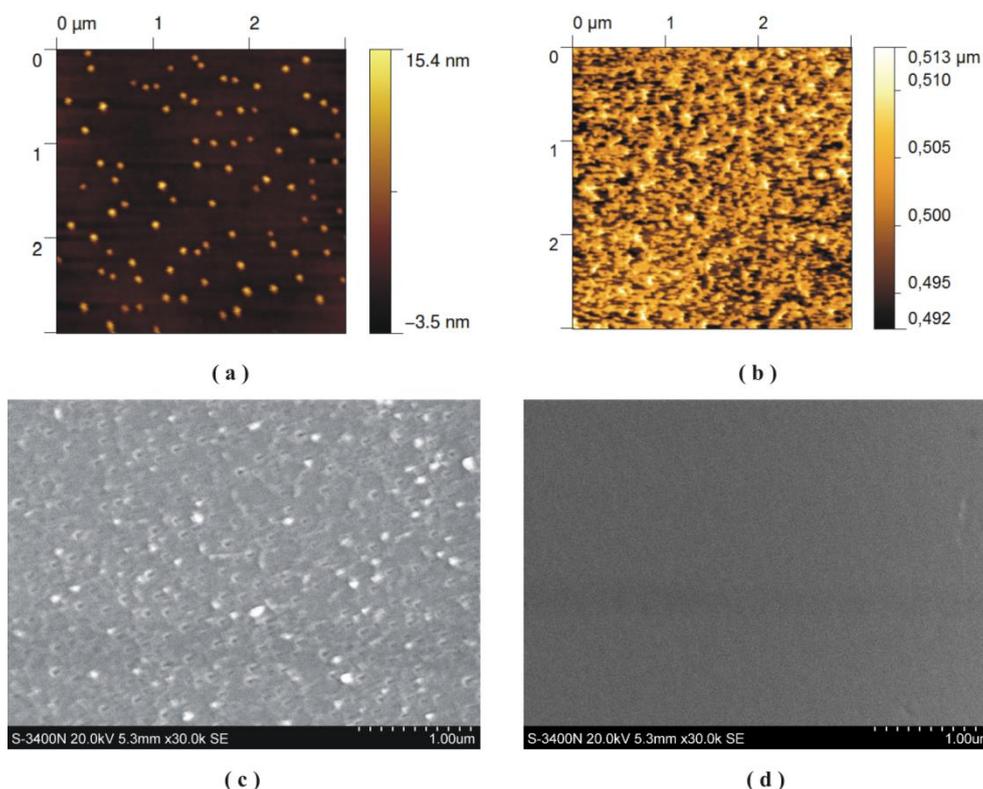


Fig. 4 – AFM images of Co PS-EG films (a) and Co PS-EG films sonicated for 30 min (b), SEM images of Co PS-EG films sonicated for 30 min (c), Co PS-EG films sonicated for 30 min and immersed in BSA (0.1 mg/ml) solution for 24 hours (d).

FTIR spectra of Co PS-EG film show sharp peaks corresponding to the specific following groups of the polystyrene (ppPS) and polyethylene glycol (ppEG). We identified the aromatic C-H group bending at 700, 757 and 909  $\text{cm}^{-1}$ , C-H in-plane deformation bending at 1073 and 1029  $\text{cm}^{-1}$ , aromatic C-H stretching at 3025  $\text{cm}^{-1}$  and 3061  $\text{cm}^{-1}$  and aromatic C=C stretching at 1683, 1600, and 1493  $\text{cm}^{-1}$ .

Also, methylene C-H stretching bands at 2930 and 2866  $\text{cm}^{-1}$  and C-H bending at 1450  $\text{cm}^{-1}$ , specific for both polystyrene and polyethylene glycol were identified. Evidence for carboxyl, COOH groups is confirmed by the broad band between 3600–3200  $\text{cm}^{-1}$ , corresponding to OH stretching. These broad bands are decreasing after the sonication process, which means that the hydrophilic structures are removed from the polymeric surface (Fig. 5).

After the removal of ppEG structure from the copolymer matrix, the new material was immersed in a solution of BSA at 0.1 mg/ml concentration for 24 hours.

The protein adsorption process is identified by the presence of C-N peaks between 1500–1650  $\text{cm}^{-1}$ . Moreover, in the case of large wavenumbers, the FTIR spectrum shows a peak at 3300  $\text{cm}^{-1}$  which is characteristic for type NH bonds. All these peaks, which appear after BSA immobilisation on the polymeric surface, are in good correlations with BSA powder FTIR spectrum.

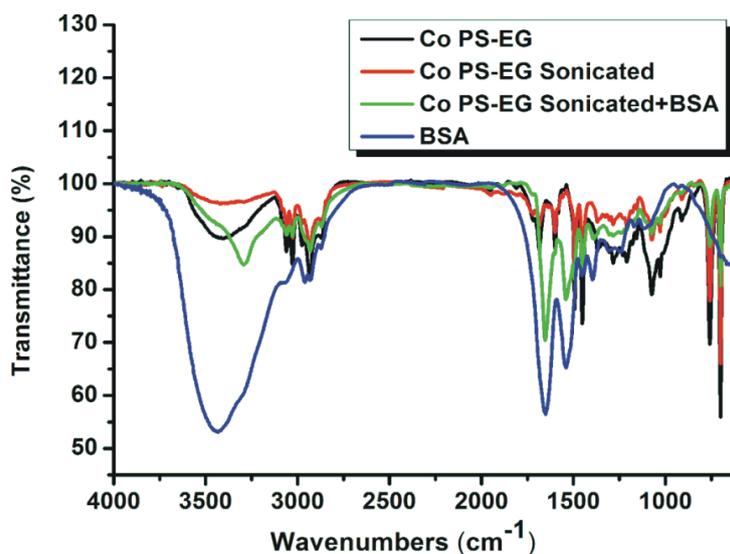
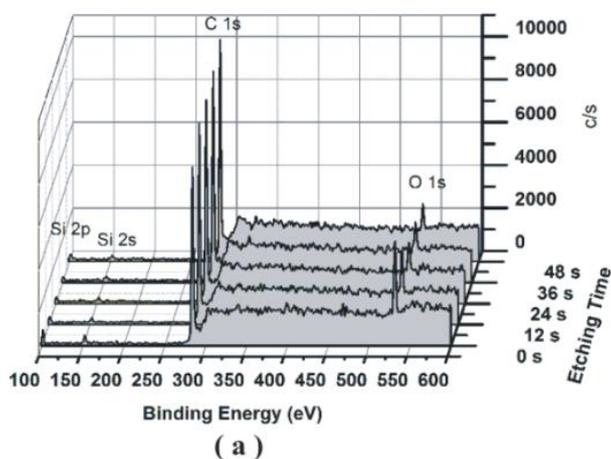


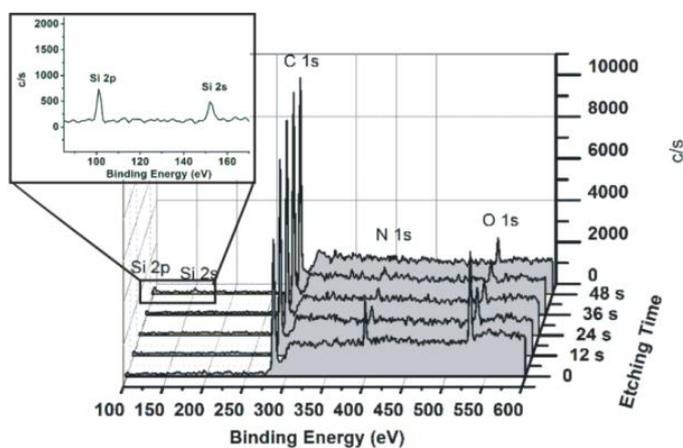
Fig. 5 – Comparative infrared spectra of Co PS-EG films, Co PS-EG films sonicated for 30 min, Co PS-EG films sonicated for 30 min and immersed in BSA (0,1 mg/ml) solution for 24 hours and BSA powder.

The protein adsorption process was demonstrated also by X-ray Photoelectron Spectroscopy (XPS) technique. In addition to the C1s peak at 284 eV and O1s peak presented at 534 eV, appears another peak at 399 eV, which can be attributed to N1s. Moreover, as can be observed in Fig. 6 (a), for large XPS spectra of porous polymers Co PS-EG, peaks of Si 2p and Si 2s appear corresponding to the substrate of polymer films. This proves that the new polymer presents a porous structure by its thickness (Fig. 6 (a)).

Depth profiling by XPS is one of the most useful techniques for the observation of the cross-sectional elemental distribution. The depth profiles are obtained by alternately recording the intensity of specific peaks and removing material from the sample surface by the Ar ion beam etching [19]. By this method we demonstrate a tridimensional adsorption of the BSA molecules inside of the Co PS-EG porous polymers (Fig. 6 (b)).



(a)



(b)

Fig. 6 – XPS global spectra of the Co PS-EG porous surfaces before the absorption of BSA molecules (a) and after the absorption of BSA molecules (b).

All above data prove a good affinity of the BSA onto the surface of porous polymeric material (Co PS-EG) synthesized by plasma polymerization process at atmospheric pressure.

#### 4. CONCLUSION

Plasma polymerization in a mixture of styrene and ethylene glycol vapours is an efficient method to obtain co-polymeric structures from two monomers having different wettability properties. These structures were modified by two processes

(dissolution and sonication) providing a porous structure with a pore diameter around 50 nm.

These structures have been studied with respect to the BSA adsorption and present a good affinity of these proteins onto the polymeric surface. Thus, we demonstrate that bioactive porous structure may be easily prepared by plasma polymerization at atmospheric pressure and can be useful in biomedical applications.

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#### REFERENCES

1. A. L. Othman, Z.A. A Review: *Fundamental Aspects of Silicate Mesoporous Materials*, *Materials*, **5**, 2874–2902 (2012).
2. M.S. Lord, M. Foss, F. Besenbacher, *Influence of nanoscale surface topography on protein adsorption and cellular response*, *Nano Today*, **5**, 66–78 (2010).
3. E.A. Vogler, *Protein adsorption in three dimensions*, *Biomaterials* **33** (2012).
4. M. Rabe, D. Verdes, S. Seeger, *Understanding protein adsorption phenomena at solid surfaces*, *Advances in Colloid and Interface Science*, **162**, 1–2, 87–106 (2011).
5. H. Muguruma, H. Takahashi, *Protein patterning on functionalized surface prepared by selective plasma polymerization*, *Surface & Coatings Technology* **205**, 2490–2494 (2010).
6. B.-G. Rusu, F. Cunin, M. Barboiu, *Real-Time Optical Detection of Stabilized Artificial G-Quadruplexes Under Confined Conditions*, *Angew. Chem. Int. Ed.*, **52**, 12597–12601 (2013).
7. V. S.-Y. Lin, K. Motesharei, K.-P. S. Dancil, M. J. Sailor, M. R. Ghadiri, *A porous silicon-based optical interferometric biosensor*, *Science*, **278**, 840–843 (1997).
8. E.J. Anglin, L. Cheng, W.R. Freeman, M.J. Sailor, *Porous silicon in drug delivery devices and materials*, *Advanced drug delivery reviews* **60** (11), 1266–1277 (2008).
9. F. Hoffmann, M. Cornelius, J. Morell, M. Froba, *Silica-Based Mesoporous Organic–Inorganic Hybrid Materials*, *Angew. Chem. Int. Ed.*, **45**, 3216–3251 (2006).
10. A. Cazacu, Y.M. Legrand, A. Pasc, G. Nasr, A. van der Lee, M. Barboiu, *Dynamic hybrid materials for constitutional selective membranes*, *Proc. Natl. Acad. Sci.*, **106**, 8117–8122 (2009).
11. Dingcai Wu, Fei Xu, Bin Sun, Ruowen Fu, Hongkun He, and Krzysztof Matyjaszewski, *Design and Preparation of Porous Polymers*, *Chem. Rev.*, **112**, 3959–4015 (2012).
12. X. Deng, A. Yu Nikiforov, P. Vanraes, C. Leys, *Deposition of nanosilvr-organosilicon composite films using an atmospheric pressure DC plasma JET*, *Romanian Reports in Physics*, **66**, 4, 1088–1098 (2014).
13. L. I. Kravets, S. N. Dmitriev, V. Satulu, B. Mitu, G. Dinescu, *Formation of composite polymer ‘DIODE-LIKE’ membranes*, *Romanian Reports in Physics*, **66**, 4, 1165–1179 (2014).
14. A. Tamošiūnas, P. Valatkevičius, V. Grigaitienė, V. Valinčius, *Operational parameters of thermal water vaporplasma torch and diagnostics of generated plasma jet*, *Romanian Reports in Physics*, **66**, 4, 1125–1136 (2014).
15. D. Zaharie-Butucel, S. D. Anghel, *Optical characterization and application of an atmospheric pressure Ar plasma in contact with liquids for organic dyes degradation*, *Rom. Journ. Phys.*, **59**, 7–8, 757–766 (2014).
16. A. Kaminska, A. Bialek, M. Dudeck, *Performances of an argon ARC-JET thruster for satellites*, *Rom. Journ. Phys.*, **60**, 3-4, 549–559 (2015).

17. A.S. Chiper, A.V. Nastuta, G.B. Rusu, G. Popa, *On surface elementary processes and polymer surface modifications induced by double pulsed dielectric barrier discharge*, Nuclear Instruments and Methods in Physics Research B **267**, 313–316 (2009).
18. A. S. Chiper, G. B. Rusu, C. Vitelaru, I. Mihaila, G. Popa, *A comparative study of helium and argon DBD plasmas suitable for thermosensitive materials processing*, Romanian Journal of Physics, **56 S**, 126–131 (2011).
19. Yuji Sakai, Yoshitoki Iijima, Daiki Asakawa and Kenzo Hiraoka, *XPS depth profiling of polystyrene etched by electrospray droplet impact*, Surf. Interface Anal., **42**, 658–661 (2010).