XPS investigation on the reactivity of surface imine groups with TFAA

Matthias Kehrer¹,² | Jiri Duchoslav¹ | Andreas Hinterreiter¹ | Munise Cobet¹ | Alen Mehic² | Thomas Stehrer² | David Stifter¹

¹ Johannes Kepler Universität, Center of Surface and Nanoanalytics, Altenbergstraße 69, 4040 Linz, Austria
² Fronius International GmbH, Günter-Fronius-Straße 1, 4600 Thalheim bei Wels, Austria

Correspondence
Matthias Kehrer, Johannes Kepler Universität, Center of Surface and Nanoanalytics, Altenbergstraße 69, 4040 Linz, Austria.
Email: kehrer.matthias@fronius.com; matthias.kehrer@jku.at

Funding information
Austrian Research Promotion Agency FFG (Program “Production of the Future” (Project SPOK) and Program COMET, promoted by the federal ministries BMWFW and BMVIT) and by the Governments of Lower and Upper Austria

The chemical reaction of imine groups with vapors of trifluoroacetic anhydride (TFAA) was investigated in detail with X-ray photoelectron spectroscopy (XPS) for the potential application in chemical derivatization (CD) studies of plasma treated surfaces. Imine groups were at first prepared by converting surface amine groups of a polymer precursor using a common vapor phase derivatization reaction with fluorine tagged aldehydes and ketones. The originally low yield for the imine forming reaction of approx. 50%, performed under standard conditions was dramatically enhanced up to 100% by an own developed procedure using a catalyst. This step allowed to obtain a consistent quantification and interpretation of the complex surface reaction products from different types of imine groups derivatized by TFAA.

KEYWORDS
chemical derivatization, imine groups, trifluoroacetic anhydride (TFAA), trifluorobenzaldehyde (TFBA), X-ray photoelectron spectroscopy (XPS)

1 | INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is known as one of the most powerful analytical methods for determining the surface chemistry. Nevertheless, highly complex surfaces, which contain a number of various functional groups, as it is generally the case after plasma treatment, are very difficult to be analyzed. The limited energy resolution of the XPS method makes many chemically different functional groups difficult or even impossible to distinguish as, for example, in the case of hydroxyl and ether groups.¹¹ In order to overcome the stated problem, chemical derivatization (CD) has been developed as a technique, which selectively marks specific functional groups.¹¹ Over the last decades, several different CD routines, selective for different moieties, have been developed and applied to such surfaces.¹²,¹³,¹⁴,¹⁵,¹⁶ For example trifluoroethanol can be used for labeling carboxyl groups,¹⁰,¹¹,¹²,¹³,¹⁴ trifluoroethyl hydrazine for marking carbonyl groups,¹¹,¹³,¹⁵,¹⁶ 3,5-bis(trifluoromethyl)phenyl isothiocyanate, pentafluorobenzaldehyde (PFBA) or 4-(trifluormetyl)benzaldehyde (TFBA) (Figure 1).
for labeling amine groups.\cite{2,9,17–22} Bromine may be used for highlighting unsaturated carbon bonds.\cite{13,15} Probably the most common derivatization agent is trifluoroacetic anhydride (TFAA), which is used for labeling hydroxyl groups.\cite{1–6,11,14–18,20,22,23} It is also known that TFAA exhibits a low selectivity, i.e., it reacts with several other functional groups like primary or secondary amines.\cite{1–6,11,14–18,20,22,23} Epoxy groups,\cite{3} or imines.\cite{9,23,24} Nevertheless, TFAA is used as labeling agent also for, e.g., plasma treated N-rich surfaces with coexisting hydroxyl and amine groups.\cite{17} In addition, the appearance of imine groups after nitrogen plasma treatment or on plasma treated N-rich films is known.\cite{9,17,23,25–31} However, there are either only theoretical remarks on CD of imine groups with TFAA, qualitative studies with infrared spectroscopy,\cite{9,23} or TFAA was used in the context of labeling plasma polymerized N-rich thin films.\cite{31} In a more general study standard liquid phase reactions of imines with anhydrides were also addressed, although not in the context of CD.\cite{24} Moreover, in CD XPS gas phase reactions are usually preferable over the liquid phase ones, because the latter can cause reorganization of the polymer surface.\cite{8}

When dealing with, for example, nitrogen plasma treated surfaces, usually special attention is dedicated to the determination of the amine moieties, but also the formation of imine groups is very likely.\cite{9,17,28–35} Moreover, recent publications reported even a preferred imine group formation.\cite{9,31} Unfortunately, imine groups are indistinguishable from amine groups for standard XPS.\cite{19} In this context, the understanding and knowledge of the gas phase reaction of imine groups with TFAA together with detailed spectroscopic XPS data becomes evidently more and more important.

In general imine groups formed on, for example, N2/H2 or NH3 plasma treated polymers usually coexist with other functional groups. However, to study the reaction mechanism of imine groups and TFAA in detail, a highly monofunctional surface chemistry and well known concentration is mandatory. Therefore, two model surfaces were created with either imine groups derived from an aldehyde or ketone. These surface imine groups were synthetized from amine groups of a model precursor polymer. In order to precisely control and evaluate the obtained reaction products fluorinated aldehydes and ketones were used. The subsequent surface reactions with TFAA in the context of CD were equally investigated in detail by means of XPS. Moreover, all the reactions were performed in gas phase, that is, the solid sample surfaces were solely exposed to the vapors of the (derivatization) agents. This approach enables a direct application of the gained results for future CD XPS. Besides a comprehensive description and valuable XPS data related to the complicated reaction products derived from the different imine groups, the obtained results also revealed a large weakness of the conventional gas phase imine preparation method, namely a very low conversion yield of only 50%. Despite this problem, which is, moreover, generally known in the CD XPS community,\cite{30} the reaction is still commonly used for labeling NH2 groups. In contrast, in the current work we newly implement a catalyst into the vapor phase derivatization reaction, which results in a significantly improved reaction yield of up to 100%.

2 | EXPERIMENTAL SECTION

2.1 | Materials

As a precursor of imine groups, a polymer containing amine NH2 groups, poly(allylamine) (PAAm, 20 wt% solution in H2O, MW 17000 g mol−1, Sigmaaldrich), was chosen. The polymer solution was diluted to 3 wt% using deionized water and coated onto cut glass pieces (5×25×2 mm3) in order to obtain smooth and accessible surfaces for the following chemical reaction experiments. 4-(Trifluormethyl)benzaldehyde (TFBA, 98%, Sigmaaldrich), 1,1,1-Trifluoraceton (TFA, 97%, Sigmaaldrich), and 1,1,1-Trifluoro-2-butane (TFB, 95%, Sigmaaldrich) were used to produce different imine groups on the PAAm surfaces. Trifluoroacetic anhydride (TFAA, >99%, Sigmaaldrich) was used to study the reactions with different surface imine groups. Tetrahydrofurane (THF, stabilized 250 ppm BHT, Sigmaaldrich), pyridine (anhydrous, Sigmaaldrich) and acetic acid (AA, ACS reagent, 99.7%, Sigmaaldrich) were used as solvent and catalysts during the performed reactions.

2.2 | Preparation of surface imine groups

Regarding the potential application of the current work in CD XPS, all chemical reactions were performed in gas phase, that is, the solid surface of the model polymer was exposed only to vapors of the used reagents. Moreover, fluorine tagged aldehyde and ketone were used as reagents, which helped with the evaluation of the achieved reaction yield by XPS. All experiments were carried out in a poly(ethylene) glove bag (VWR, DE) filled with dry nitrogen to provide an inert atmosphere. The use of an inert atmosphere was necessary mainly for experiments with TFBA, which otherwise oxidizes very fast in air. In that case a solid white product, 4-trifluoromethylenzoic acid, was found to cover the surface of the studied materials, which leads to misleading results.

Similarly as reported in our previous publication\cite{36} the polymer samples were first placed into a small glass vial (3 ml, VWR, DE) in order to guarantee no direct contact with the reagent liquid. Then 0.2 ml of TFBA was injected into a second glass vial of the same type. Both vials were finally put into a poly(propylene) PP (100 ml, VWR, DE) container, which was closed with a screw cap. The polymer sample was left to react with the TFBA vapor for 90 min at room
temperature. Afterwards the treated polymer sample was removed from the container and glove bag and immediately put into the XPS system for analysis. The same procedure was also used for creating imine groups from TFA and TFB as reactants.

2.3 | Catalyzed imine forming reaction

In order to increase the usually poor yield of the imine preparation reaction under standard conditions for the gas phase CD method, AA was taken as a catalyst. During the modified, catalyzed reaction the vial with the sample to be treated was enclosed in the container with the second vial containing a mixture of 0.2 ml TFBA (or TFA or TFB) and 2 droplets (approx. 0.1 ml) of concentrated AA. The optimum reaction time was 90 min as derived by XPS. Afterwards the treated sample was removed from the container and nitrogen filled glove bag and directly placed into the XPS system.

2.4 | Reaction of imine groups with TFAA

In order to study the reactivity of imine groups with TFAA a protocol described in one of our previous works was used. The reaction was performed also as described above in a closed PP container under inert atmosphere with a mixture of 1.5 ml of THF, 0.2 ml of TFAA and 2 droplets of pyridine in the reagent glass vial. The reaction was left to take place during 30 min at laboratory temperature. Also in this case the treated polymer sample was afterwards immediately put into the XPS system and analyzed.

2.5 | Analytical method

XPS measurements were performed on a Theta Probe XPS system (Thermofisher, GBR), which features a monochromated Al-Kα X-ray source with an energy of 1486.6 eV. The spot size on the sample surface was 400 μm in diameter. The hemispherical analyzer was set to a pass energy of 20 eV for recording high resolution (HR) scans at an energy step size of 0.05 eV. For charge neutralization on the sample surface the system is equipped with a dual flood gun which simultaneously provides electrons and Ar+ ions with low kinetic energy (0.05 eV). For the calculation of sensitivity factors, the Scofield cross sections library was used, with \( \sigma_{\text{Sc}}(\text{C1s}) = 1 \), \( \sigma_{\text{Sc}}(\text{N1s}) = 1.8 \), \( \sigma_{\text{Sc}}(\text{O1s}) = 2.93 \), and \( \sigma_{\text{Sc}}(\text{F1s}) = 4.43 \). The transmission function (TF) ranged from 0.74 to 0.75 in the case of C1s, while TF(N1s) = 0.76, TF(O1s) = 0.8, and TF(F1s) = 0.86. The energy compensation factor was calculated using the kinetic approximation \( E_{\text{kin}}^{0} \). For the peak fitting procedure of the core level spectra, the product of a symmetric Lorentzian and a Gaussian shaped peak (2:3, respectively) was used.

3 | RESULTS AND DISCUSSION

For a reliable interpretation of the data, a careful study of the precursor polymer poly(allylamine) (PAAm) was performed at first. The spectra of the pristine PAAm surface are depicted in Figure 1a–d, while concentrations and binding energies of the identified functional groups are listed in Table 1. Figure 1 also includes the structure of suggested functional groups on the surface. The C1s spectrum in Figure 1a clearly shows three peaks. The peak found at 285.0 eV was addressed to C–C like carbon atoms and constitutes the backbone of the polymer. The peak shifted by 1.1 eV to higher energy side (at 286.1 eV) was related to C–N carbon atoms of the amine group. The third peak found at 288.1 eV could represent the carbons as a part of the carbonyl (C=O) or amide (CON) groups as an impurity, which is known to commonly appear on the surface of this polymer.

The interpretation of the N1s peak of the polymer (Figure 1b) revealed two peaks. The peak at 399.2 eV represents C–N like nitrogen atoms and as can be seen in Table 1 very well corresponds (also quantitatively) with the C–N peak in the C1s spectrum and thus confirms the presence of NH2 groups in the investigated polymer. The second and minor nitrogen peak, which appears at 400.8 eV probably represents a protonated amine group (i.e., –NH3+) or nitrogen atoms of amide group (which would match with the impurity like carbon peak at 288.1 eV).

The O1s spectrum in Figure 1c shows two types of oxygen, which could be interpreted as double bonded oxygen (peak at 531 eV, which corresponds also with its concentration to the carbonyl peak in the C1s spectrum), and single bonded oxygen (peak at 532.5 eV). The presence of both oxygen impurity peaks with an overall concentration of about 8 at% indicates a moderate surface contamination of the polymer.

In a subsequent step, the surface amine groups of the precursor polymer of PAAm were converted into imine moieties. The first experiments carried out with PAAm and TFB using standard reaction conditions showed unsatisfactory results. Considering the reaction yield calculated via Equation (1), where \( [F] \) is the fluorine concentration,
the concentration of nitrogen atoms and the numbers of fluorine atoms per nitrogen atom of the functional marker group (here CF₃ with a value of only approx. 50% could be achieved.

\[
Yield = \frac{F}{n \cdot [N]}
\]  

FIGURE 1 Evaluated HR XPS spectra of the C1s, N1s and O1s of pristine PAAm surface as well as the chemical structure (a-d), after conversion of amine to imine groups (e-h) and after subsequent treatment with TFAA (i-l), where 1A is the complex reaction product and 1B an amide, which coexists on the surface after hydrolysis of product 1A.

TABLE 1 Summary of binding energies and concentrations of evaluated functional groups of the pristine PAAm surface and after reactions with TFBA, TFA, and TFAA

| Binding Energy [eV] (Concentration [at%]) | PAAm | PAAm+TFBA | PAAm+TFBA+TFAA | PAAm+TFA | PAAm+TFA+TFAA |
|-----------------------------------------|------|-----------|----------------|-----------|---------------|
| **C1s** | | | | | |
| C─C | 285.0 (56.2) | 285.0 (50.5) | 285.0 (28.7) | 285.0 (31.9) | 285.0 (20.9) |
| C═N/C═N/C═O | 286.1 (14.5) | 285.7 (13.7) | 286.1 (5.7) | 286.0 (13.1) | 286.0 (9.1) |
| CF₃─C═N/─N | | | | 287.2 (6.4) | 287.3 (5.0) |
| C═O/CON | 288.1 (3.8) | 288.6 (6.6) | 288.4 (1.5) | 288.6 (4.7) |
| O═C═O | 290.2 (2.7) | | 290.1 (0.8) |
| CF₃ | | 292.6 (7.4) | 292.8 (10.9) | 292.6 (7.0) | 292.8 (9.4) |
| C1s total: | (74.5) | (71.6) | (54.6) | (59.9) | (49.9) |
| **N1s** | | | | | |
| C═N/N═C | 399.2 (14.5) | 398.8 (6.4) | 399.0 (0.3) | 399.5 (10.2) | 399.4 (1.7) |
| N═C═O | 400.6 (4.6) | | | 400.4 (5.6) |
| −NH₃⁺ | 400.8 (2.9) | | | 401.4 (1.6) | 401.8 (0.6) |
| N1s total: | (17.4) | (6.4) | (4.9) | (11.8) | (7.9) |
| **O1s** | | | | | |
| O═C/O═C═N | 531.0 (4.6) | 531.5 (1.6) | 531.9 (4.1) | 531.3 (1.7) | 532.0 (6.4) |
| O═C | 532.5 (3.5) | | 534.4 (2.3) | 532.8 (3.7) | 533.9 (1.9) |
| O═C═O | | | | 533.2 (1.8) |
| O1s total: | (8.1) | (1.6) | (9.2) | (5.4) | (8.3) |
| **F1s** | | | | | |
| FṣC | 688.1 (20.0) | 688.4 (32.4) | 688.3 (22.8) | 688.4 (34.1) |
As further depicted in Figure 2, saturation was reached after a reaction time of 60 min. Moreover, this finding is in a very good agreement with the already reported results for TFBA being used for vapor phase chemical derivatization of amine groups with low yields of only 50–60%.[30] Unfortunately, this low yield represents a problem for the further derivatization steps in our work, since the unreacted amine groups of the precursor polymer can also react with TFBA, as known from literature,[4,9,36,37] significantly increasing the complexity of the analytical work and affecting the reliability of the evaluated and discussed results.

For this reason additional effort had to be invested into the problem stated above. An inspiration was found in literature related to general organic chemistry, where for this kind of reaction an acid is used as catalyst,[39] as schematically depicted in Figure 3. Within the first step, a nucleophilic attack of the amine on the TFBA takes place, where a proton is transferred from the nitrogen to the oxygen, which creates a carbinoalamic group. In a second step the acid (HA) protonates the hydroxyl group and generates a better leaving group. The final step is a deprotonation of the positively charged nitrogen by the acid anion (A−), resulting in the final product 4-(trifluoromethyl)phenyl)methanimine labeled as aldime.

Although acid catalysts are commonly used within organic synthesis, this approach seems never to have been applied under gas phase reaction conditions or for CD XPS. For these conditions a proper acid has to be chosen, which exhibits a sufficiently high vapor pressure. Therefore, AA was selected as a proper catalyst. As can be seen in Figure 2, when a mixture of TFBA with AA was used, the reaction yield dramatically increased to almost 100%. The evaluated HR XPS spectra, concentrations and binding energies of the found elemental components (functional groups) for such a treated PAAm surface are shown in Figure 1e–g and given in Table 1, respectively. The C1s spectrum (Figure 1e) could be fitted with four peaks. Starting from lowest binding energy, the peak at 285.0 eV is related to aliphatic carbon (C–C/C–H). Due to the very small energy shift between the C–N (286.1 eV) and C≡N related carbon peaks (285.7 eV[19]), only a single “mixed” peak labeled C=N/C≡N was fitted with an energy of 285.7 eV. A weak shake-up satellite peak was found at 290.9 eV and confirmed the presence of the conjugated system in the TFBA molecule. The trifluoromethyl group is fitted with a peak at 292.6 eV.[37] The N1s spectrum in Figure 1f shows only one peak (398.8 eV). Together with the corresponding C1s peak at 285.7 eV this indicates the presence of the imine functional group.[19] Furthermore, the single nitrogen peak also hints at the high selectivity and yield of the performed reaction. Similarly, the peak of very low intensity in the oxygen spectrum of Figure 1g (probably originating from the impurities of the pristine PAAm polymer) also confirms that the proceeded reaction led to 4-(trifluoromethyl)phenyl)methanimine being the predicted and desired product.

Subsequently, the prepared aldime (labeled as PAAm-TFBA) sample was exposed to TFBA vapor as described in the experimental section by using a new protocol for CD XPS.[36] The recorded C1s, N1s, and O1s spectra are shown in Figure 1i–l, whereas the peak binding energies and concentrations are listed in Table 1. In contrast to aldime (Figure 1e), two more peaks were found in the C1s spectrum after the reaction with TFBA (Figure 1l). These peaks are linked to C–C (285.0 eV), C=N/C≡N (286.1 eV), O=C=N/amid (288.6 eV), O≡C–O (290.2 eV) and CF3 groups (292.8 eV). The corresponding N1s spectrum in Figure 1j indicates two different types of nitrogen: an amide (peak at 400.6 eV) as the major one and an amine/imine (399.0 eV) in a very minor form. The O1s spectrum presented in Figure k shows three different kinds of oxygen species, the one with a peak at 531.9 eV may refer to an amide group, while the other two at 533.2 eV and 534.4 eV in form of C=O and C–O are both part of the trifluoroacetate group.[36] Considering the known mechanism of a reaction between an imine with acetic anhydride, which was performed in liquid phase, a (2,2,2-trifluoroacetoamido)(4-trifluoromethyl)phenyl)methyl 2,2,2-trifluoroacetate group (Figure 1l, labeled as 1A) can be expected to be produced.[24] In general such a moiety is claimed to be of rather low stability,[9] however, due to the presence of the aromatic ring originating from the used aldehyde (TFBA) in our case, the stated structure might stable.[24] Nevertheless, when the peak concentrations are taken into the account, the structure labeled as 1A cannot be the only reaction product. For instance, the relative concentration of amide like carbon is higher than for the carboxyl one. Similarly, the oxygen concentration related to the amide group exceeds the concentration of both oxygen types from the carboxyl group. A potential explanation might

![Figure 2](image-url)
be found in a partial hydrolysis of the discussed structure.\[24\] The hydrolysis leads to a simple trifluoroacetamide group (Figure 1, labeled as 1B) with a simultaneous loss of volatile species of trifluoroacetic acid and TFBA, occurring, for example, during transfer/pumping prior the XPS measurement. Using Equation (2), the percentages \( w \) of the two products A and B can be calculated from the amide concentration determined from the N1s spectrum and the carboxyl concentration determined from the C1s peak:

\[
w_A = \frac{C_{1s}(\text{Carboxyl})}{C_{1s}(\text{amid})}; \quad w_B = 1 - w_A \quad (2)
\]

The final chemistry on the surface of TFAA treated aldimine was accordingly determined to contain approx. 60% of product 1A and 40% of product 1B.

In order to provide comprehensive information about the general reactivity of imine groups with TFAA, the second type of imine groups – ketimine – was investigated. The ketamine sample was prepared from poly(allylamine) by reaction with trifluoroacetonitrile (TFA), as indicated in Figures 4 and 5. The prepared samples were also analyzed by XPS and the corresponding C1s, N1s, and O1s spectra as well as suggested functional groups on the surface are shown in Figure 4a–h, while concentrations and binding energies of the found groups are summarized in Table 1. The C1s spectrum revealed newly five peaks related to C–C/C–H (285.0 eV) and C–N (286.0 eV) like carbon, F3C–C–N (287.3 eV), carbonyl or amide (288.6 eV), carboxyl (290.1 eV), and CF3 groups (292.8 eV). The analysis of the N1s spectrum showed three peaks representing amine or imine groups (399.4 eV), amid groups (400.4 eV) and finally ammonium like nitrogen (401.8 eV). The O1s spectrum again revealed C=O and C–O based groups (peaks at 532.0 eV and 533.9 eV). Considering the binding energies and concentrations summarized in Table 1 a reaction scheme with different reaction products is suggested, as presented and summarized in Figure 5. Neglecting ammonium as well as unreacted amine and imine species, three different types of the surface moieties can be deduced:

- 2,2,2-trifluoro-N-(3,3,3-trifluoroprop-1-en-2-yl)acetamide labeled as 2A (Figures 4h and 5).
- 1,1,1-trifluoro-2-(2,2,2-trifluoroacetamido)propan-2-yl 2,2,2-trifluoroacetate labeled as 2B.
- (1,1,1-trifluoromethyl)amide labeled as 2C.

As can be seen, 2,2,2-trifluoro-N-(3,3,3-trifluoroprop-1-en-2-yl)acetamide (2A) was found to be a minor reaction product when compared to the previous case of TFAA treated aldimine (i.e., the analogous structure 1A was there the dominant reaction product).

### CONCLUSIONS

The vapor phase reaction between TFAA and two different types of surface imine groups (aldimine and ketimine) was
investigated in detail. For this purpose the surface imine groups were prepared from amine groups of a precursor polymer (PAAm) via a gas phase reaction with fluorine tagged aldehyde or ketone. Nevertheless, a very low yield of only 50% was obtained for the imine forming reaction, which was performed under the standard conditions as used for CD XPS. As one of the major results of this work, a dramatic increase of the reaction yield to almost 100% for aldimine (using TFBA) and 60% for ketimine (derived from TFA) was achieved by implementing acetic acid as a catalyst to the vapor phase reaction. Furthermore, both successfully prepared imine types were subjected to treatment with TFAA vapors. Due to the equally high yields of this reaction only minor amounts of remaining C≡N were subsequently found on the surface. However, a detailed evaluation of the XPS data newly revealed a very complex character of the obtained products, which were, moreover, significantly dependent on the type of the imine group. The presented results in this work give a comprehensive and consistent quantification of the surface chemistry including all binding energies after each experimental step. Therefore, the newly gained knowledge, including the catalyzed preparation of surface imine from amine groups resulting in a significantly enhanced yield as well as the reactivity of different imine groups with TFAA, can be directly applied for chemical derivatization techniques.

ACKNOWLEDGMENTS

Financial support by the Austrian Research Promotion Agency FFG (Program “Production of the Future“ (Project SPOK) and Program COMET, promoted by the federal ministries BMWFW and BMVIT) and by the Governments of Lower and Upper Austria is gratefully acknowledged. Part of this work was also carried out within the IWV/EFRE program, co-financed by the European Regional Development Fund and the State of Upper Austria (Project BIOCARB-K).
REFERENCES

[1] C. D. Batch, Appl. Surf. Sci. 1988, 32, 57.
[2] P. Favia, M. V. Stendardo, Plasma Polym. 1996, 1, 91.
[3] A. Chilkoti, B. D. Ratner, Surf. Interface Anal. 1991, 17, 567.
[4] A. Holländer, F. Pippig, M. Dubreuil, D. Vangeneugden, Plasma Polym. 2008, 5, 345.
[5] P. L. Girard-Lauriault, I. Retzko, S. Swaraj, N. Matsubayashi, T. Gross, R. Mix, W. E. S. Unger, Plasma Process. Polym. 2010, 7, 474.
[6] A. Chilkoti, B. D. Ratner, D. Briggs, Chem. Mater. 1991, 3, 51.
[7] C. S. Fadley, Electron Spectroscopy: Theory, Experiments and Applications (Eds: C. R. Brundle, A. D. Baker), 2, 1978.
[8] J. R. Rasmussen, D. E. Bergbreiter, G. M. Whitesides, J. Am. Chem. Soc. 1976, 99, 4746.
[9] C.-P. Klages, S. Kotula, Plasma Process. Polym. 2016, 13, 1.
[10] M. Alexander, Surf. Interface Anal. 1996, 24, 217 http://onlinelibrary.wiley.com/doi/10.1002/sia.9918(199603)24-3%3C217::AID-SIA103%3E3.0.CO;2-L/abstract.
[11] H. Kondo, Y. Nishida, Bull. Chem. Soc. Jpn. 2007, 80, 1405.
[12] M. Strobel, V. Jones, C. S. Lyons, M. Ulsh, M. J. Kushner, R. Dorai, M. C. Branch, Plasma Polym. 2003, 8, 61.
[13] V. I. Povstugar, S. S. Mikhailova, J. Anal. Chem. 2000, 55, 405.
[14] D. S. Everhart, C. N. Reilley, Anal. Chem. 1981, 53, 665.
[15] Y. Xing, N. Dementev, E. Borguet, Curr. Opin. Solid State Mater. Sci. 2007, 11, 86.
[16] L. A. Langley, D. E. Villanueva, D. H. Fairbrother, Chem. Mater. 2006, 18, 169.
[17] J. C. Ruiz, S. Taheri, A. Michelmore, D. E. Robinson, R. D. Short, K. Vasilev, R. Föhr, Plasma Process. Polym. 2014, 11, 888.
[18] N. Graf, A. Lippitz, T. Gross, F. Pippig, A. Holländer, W. E. S. Unger, Anal. Bioanal. Chem. 2010, 396, 725.
[19] E. Yegen, A. Lippitz, D. Treu, W. E. S. Unger, Surf. Interface Anal. 2008, 40, 176.
[20] P. Films, U. Gas, C. Modification, J. Polym. Sci. 1988, 26, 559.
[21] M. Nitschke, G. Schmack, A. Janke, F. Simon, D. Pleul, C. Werner, Biomed. Mater. Res. 2002, 59, 632.
[22] R. Dickie, J. Hammond, Anal. Chem. 1982, 54, 2045.
[23] C. P. Klages, Z. Khasravi, A. Hinze, Plasma Process. Polym. 2013, 10, 307.
[24] H. Bredderveld, Recueil 1969, 70, 401.
[25] A. G. Shard, J. D. Whittle, A. J. Beck, P. N. Brooke, N. A. Bullet, R. A. Talib, A. Mistry, D. Barton, S. L. McArthur, J. Phys. Chem. B 2004, 108, 12472.
[26] Z. Khasravi, S. Kotula, A. Lippitz, W. E. S. Unger, C. P. Klages, Plasma Process. Polym. 2017, 15, 1.
[27] R. W. Paynter, R. W. Paynter, Surf. Interface Anal. 1998, 26, 674.
[28] U. Lommatzsch, D. Pasedag, A. Baalmann, G. Ellinghorst, H. E. Wagner, Plasma Process. Polym. 2007, 4, 1041.
[29] N. Shahizadeh-Ahmadi, F. Arefi-Khonsari, J. Amouroux, J. Mater. Chem. 1995, 5, 229.
[30] P. L. Girard-Lauriault, W. E. S. Unger, P. M. Dietrich, A. Holländer, Plasma Process. Polym. 2015, 12, 953.
[31] D. Mangindaan, W. H. Kuo, C. C. Chang, S. L. Wang, H. C. Liu, M. J. Wang, Surf. Coatings Technol. 2011, 206, 1299.
[32] P. L. Girard-Lauriault, P. M. Dietrich, T. Gross, T. Wirth, W. E. S. Unger, Plasma Process. Polym. 2013, 10, 388.
[33] E. M. Liston, L. Martiniu, M. R. Wertheimer, J. Adhes. Sci. Technol. 1993, 7, 1091.
[34] E. E. Johnston, B. D. Ratner, J. Electron Spectros. Relat. Phenomena. 1996, 81, 303.
[35] B. Finke, K. Schröder, A. Ohl, Plasma Process. Polym. 2008, 5, 386.
[36] J. Duchoslav, M. Kehrer, A. Hinterreiter, V. Duchoslav, C. Unterweger, C. Fürst, R. Steinberger, D. Stifter, Appl. Surf. Sci. 2018, 443, 244.
[37] G. Beaman, D. Briggs, The XPS of Polymers Database, Surface Spectra, UK 2000.
[38] F. Pippig, S. Sarghini, A. Holländer, S. Paulussen, H. Terrvn, Surf. Interface Anal. 2009, 41, 421.
[39] J. McMurry, Organic Chemistry, 7e ed. Brooks/Cole, Belmont, USA 2008.