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RESEARCH ARTICLE

Spectroscopy on photografted polyethylene surfaces using a perfluorophenyl azide: Evidence for covalent attachment

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The present study was conducted in order to confirm C—H insertion of a perfluorophenyl nitrene, produced by UV-irradiation of a perfluorophenyl azide, to polyethylene surfaces.

It was shown previously that water-repelling, oil-repelling, and dirt-repelling polyethylene surfaces can be created by "grafting to" of perfluoroalkanes using a photoreactive surface modifier based on azide/nitrene chemistry. The abrasion resistance of the new surfaces was enhanced compared with a coating using a simple, long-chain perfluoroalkane. However, covalent binding of the surface modifier was not unequivocally demonstrated.

Here, spectroscopic information is presented suggesting that, indeed, a monomolecular, covalently bound grafted layer is formed from the photodecomposition of a perfluorophenyl azide on polyethylene surfaces.

Infrared spectroscopy showed that the peak from the azide moiety disappeared upon UV-irradiation, and the light dose for completion of the photo decomposition was determined to be approximately 322 mJ/cm^2.

A model compound mimicking the grafted nitrene species was synthesized, having a λ_{max} of 281 nm in hexane. The photografted and washed layer had a λ_{max} of 286 nm, indicating a good conformity with the model compound.

X-ray photoelectron spectroscopy of the nitrogen species from the photografted layer showed a peak at 400.0 eV. The model compound had a N 1s binding energy of 399.7 eV, thus being comparable.

KEYWORDS

insertion, nitrene, perfluorophenyl azide, photografting, polyethylene, spectroscopy

1 | INTRODUCTION

Refining of polymer surfaces can be achieved by grafting.[1] Hydrophilic, biocompatible, conducting, anti-fouling, or anti-fogging surface properties can, for example, be created.[2] A major technique employed is UV light-induced grafting in all of its variations.[3]

In a previous publication, photografting of polyethylene surfaces with perfluoroalkanes using azide/nitrene chemistry for hydrophobicity was described.[4] Although the new surfaces had an increased resistance to wear compared with a coating with a simple perfluoroalkane, covalent bonding of the surface modifiers was not unequivocally demonstrated. Herein, spectroscopic studies on grafted polyethylene surfaces that consolidate the formation of a covalently bound, monomolecular grafted layer are presented.

Actually developed for photoaffinity labeling in biochemistry,[5] perfluorophenyl azides have become an important tool for surface functionalization.[6-8] For example, covalent immobilization of antibacterial molecules via photochemical activation of perfluorophenyl azide on silicon oxide surfaces has been demonstrated.[9] This work is an example of "grafting from" in which the perfluorophenyl azide containing linker molecule is used as an adhesion promotor.

Another example of "grafting from" relevant to this work is described by Yan and Ren.[10] Polypropylene ultrathin films are covalently immobilized on silicon wafers using a perfluorphenyl azide-silane adhesion promoter.

However, there are fewer examples of "grafting to" using perfluorophenyl azides. One such publication reported an easy and patternable method for the surface modification of carbon nanotube forests using perfluoroarylazides.[11] Superhydrophilic and superhydrophobic surfaces, depending on the perfluorophenyl azide employed, were thus obtained. The perfluorophenyl azide used for obtaining the superhydrophobic characteristics of the carbon nanotubes forests is analogous to the molecule described herein:[4] A fluorotelomer chain is attached via an amide linker to the perfluorophenyl azide moiety, which, upon UV irradiation, intermediately decomposes into a perfluorophenyl nitrene. The nitrene then covalently links the hydrophobic fluorotelomer moiety to the carbon nanotube.

Another publication describing an analogous perfluorophenyl azide dealt with the derivatization of pristine graphene with well-defined chemical functionalities.[12] In one of the compounds described, a fluorotelomer chain is attached via an ester to the perfluorophenyl azide. This molecule is thermally or photochemically activated, forming the intermediate nitrene that can subsequently undergo C=C addition reactions with the sp^2 carbon network in graphene forming the aziridine adduct, thus linking the fluorotelomer moiety covalently to the graphene sheet.[12] The graphene thus treated became soluble in organic solvents.

X-ray photoelectron spectroscopy has been used to corroborate the binding of graphene to surfaces using photoactivated perfluorophenyl azides.[13] The nitrogen species was investigated, and there was strong evidence for the formation of covalent bonds during the perfluorophenyl azide photocoupling process.

However, although the modification of sp^2 carbon networks using perfluorophenyl nitrenes has been studied, no other report on grafting of polyethylene surfaces using UV light-activated perfluorophenyl azides was found. Thus, the proof of covalent attachment of photochemically generated perfluorophenyl nitrenes to sp^3 carbon surfaces, as in polyethylene, remains an open task. In the present study, infrared, visible, ultra-violet, and X-ray photoelectron spectroscopy are used to corroborate covalent binding of a photolytically generated nitrene species via C—H insertion to a polyethylene surface.

2 | EXPERIMENTAL PROCEDURES

2.1 | Substrates and solvents

For the IR and UV-Vis investigations, a transparent polyethylene foil 7 μm thick (Tangan N° 11, Migros, Switzerland) was used. The additive-less foil consists of 52% LDPE and 48% LLDPE. For the XPS analyses, 2-mm-thick polyethylene plates (high-density Borstar ME3440 type from Borealis) were employed. The substrates were thoroughly washed with the corresponding solvent (acetone or acetonitrile) prior to use.

Solvents of spectroscopic quality were acetone for spectroscopy (Uvasol) from Merck KGaA, Acetonitrile Multisolvent for HPLC (ACS ISO UV-VIS) from Scharlab S.L., Spain, and hexane for HPLC ≥95% from Sigma-Aldrich, Switzerland. Other solvents for spectroscopy were of the highest available purity.

2.2 | Spray-coating

Spray-coating was performed using a 0.1% (w/w) solution of 1H, 1H, 2H, 2H-heptadecafluoro-1-decyl 4-azidotetraflurobenzoate (**1**) (synthesized as described elsewhere)[4] in perfluorinated polyether (Galden HT80). The samples were air-dried after spray-coating for at least 1 minute.

2.3 | Photografting

For photografting, the probes were standardly irradiated for 2 minutes with light from an ozone-free, middle-pressure mercury vapor lamp from Uviterno AG, Berneck, Switzerland. Ozone-free means that radiation below 240 nm was filtered out by the quartz light bulb, and thus ozone formation was suppressed. The arc length was 100 mm, and the diameter of the bulb was 13 mm. The light bulb was mounted in a hand-held box. The distance from the sample to the light bulb was approximately 30 mm. The electrical power ranged from approximately 200 to 350 W. At approximately 300-W electrical power, a total light intensity of 453 mW/cm^2 was measured using an UVpad spectral radiometer from Opsytec Dr. Gröbel GmbH, Germany. Dose determinations were performed using the same type of radiometer.

2.4 | ATR-IR measurements

Infrared spectra were recorded using an attenuated total reflection-infrared (ATR-IR) spectrometer (Alpha FT-IR from Bruker with a Platinum-ATR unit) equipped with a diamond ATR-crystal. The signal to noise ratio was better than 50′000:1, and the spectral resolution was better than 2 cm^{-1}. The wavenumber accuracy was better than 0.05 cm^{-1} at 2′000 cm^{-1}. The photometric accuracy was better than 0.1% transmission. The resolution of the spectra measured was 4 cm^{-1}. Sixteen individual scans each were summed to obtain both the background and the spectrum of the sample. The size of the spectra measured ranged from 4000 to 400 cm^{-1}.

2.5 | UV-Vis spectra measurements

UV–Vis spectra were taken on a UV/VIS/NIR-spectrometer (Lambda 950 from Perkin Elmer). The data interval was 1 nm, and the PMT response time was 2 seconds. The shares of reflection and scattering were not considered.

2.6 | XPS analysis

X-ray photoelectron spectroscopic measurements were performed on a SPECS™ spectrometer from SPECS GmbH, Berlin, Germany, equipped with a PCU 300 detection unit. Spectra were acquired with a non-monochromated Mg Kα X-ray source and a 0° takeoff angle. The takeoff angle was defined as the angle between the sample surface normal and the axis of the XPS analyzer lens. The pressure in the analytical chamber during spectral acquisition was less than 5×10^{-8} hPa. The step width was 0.1 eV, and the spectra displayed were the sum over 15 scans each. The aperture of the lens used was 7 × 20 mm, and the analyzer pass energy was 10 eV.

2.7 | Synthesis

1H, 1H, 2H, 2H-heptadecafluoro-1-decyl 2, 3, 5, 6-tetrafluoro-4-(isopropylamino)benzoate (**2**) was synthesized from 1H, 1H, 2H, 2H-heptadecafluoro-1-decyl pentafluorobenzoate[4] and isopropylamine in a nucleophilic aromatic substitution reaction (see Supporting Information) and recrystallized from ethanol.

Anal. Calcd for $C_{20}H_{12}NO_2F_{21}$: C, 34.45; H, 1.73; N, 2.01. Found: C, 34.63; H, 1.77; N, 2.03.

(Analysis from Lab. f. Organic Chemistry, ETH Zurich, Switzerland).

The specific density of compound **2** was 1.787 ± 0.004 g/cm^3 (determined by helium pyknometry at EMPA, Dübendorf, Switzerland).

3 | RESULTS AND DISCUSSION

Azide **1** was photografted onto a polyethylene substrate. Figure 1 schematically illustrates the process. Three molecules of azide **1** and one polyethylene chain are exemplarily displayed. Presumably, azide **1** becomes excited upon the absorption of a photon. One relaxation process may then be splitting off dinitrogen, forming a short-lived nitrene intermediate. Having only 6 valence electrons, this nitrene is highly reactive and can insert into a C—H bond of the polyethylene substrate. The whole molecule thus becomes covalently attached to the polyethylene surface.

In the following sections, results corroborating the formation of a monomolecular grafted layer on polyethylene as depicted in Figure 1 are presented. The spectroscopic investigations are organized in ascending photon energy (ie, infrared [Section 3.1], visible and ultraviolet [Section 3.2], X-ray photoelectron [Section 3.3] spectroscopy).

3.1 | Infrared spectroscopy (IR) of the surfaces

ATR-IR spectroscopy was used for surface analysis. The penetration depth of the infrared light—and thus information depth—into the sample is typically between 0.5 and 2 μm, with the exact value being determined by the wavelength, the angle of incidence, and the indices of refraction for the ATR crystal and the medium being probed.[14] Figure 2 shows a section of the ATR-IR spectrum of the polyethylene foil after spray-coating with azide **1** and subsequent drying (solid line). In this section of the spectrum, the N N=N stretching absorption is observed. No interfering absorptions from the polyethylene substrate are present in this region. The stretching vibration of the —N$_3$ substituent is observed at a wavenumber of 2138 cm^{-1}.[4] The fact that this peak was observed leads to the conclusion that the thickness of the sprayed layer of azide **1** was significantly above monolayer coverage. A monolayer of approximately 1 nm thickness should not be noticeable using ATR-IR.

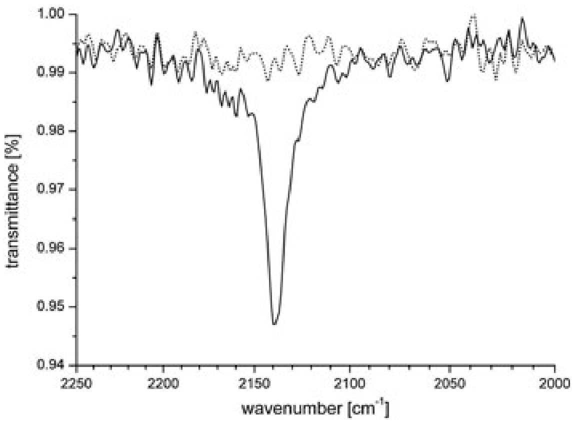


FIGURE 2 A section of the ATR-IR spectrum of polyethylene spray-coated with azide **1** before (solid line) and after (dotted line) UV irradiation

Figure 2 also shows the same section of the spectrum after irradiation of the same sample with light from the ozone-free, middle-pressure mercury vapor lamp (dotted line). It can be seen that the peak at 2138 cm^{-1} has disappeared, and it was thus concluded that the azide moiety had reacted, presumably by splitting off dinitrogen (the nitrene

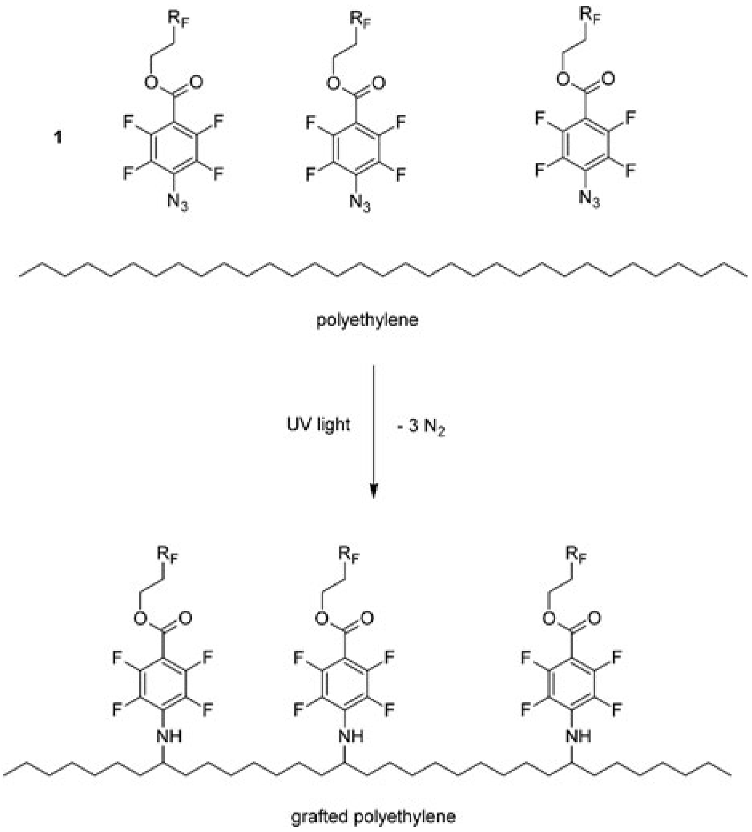


FIGURE 1 Photografting of a polyethylene surface using azide **1** for hydrophobicity (R$_F$ = −C$_8$F$_{17}$)

species thus produced will react further). The dose of light at which the azide decomposition reaction occurs could be determined by varying the irradiation time and intensity. It was found that a minimal light dose from the ozone-free, middle-pressure mercury vapor lamp of approximately 322 mJ/cm^2 was necessary for the total disappearance of the azide peak and thus completion of the reaction. The spectral composition of this dose was as follows: 200 to 280 nm: 1 mJ/cm^2; 280 to 315 nm: 101 mJ/cm^2; 315 to 380 nm: 112 mJ/cm^2; 380 to 440 nm: 108 mJ/cm^2.

3.2 | Ultra violet and visible light spectroscopy (UV-Vis) on coated polyethylene foil

Thin, transparent polyethylene foil was used as the substrate for UV-Vis experiments. From the spectra measured, the absorbance of pristine foil was always subtracted as background. The foil was spray-coated with a solution of azide **1** and dried. It was then mounted in a UV-Vis spectrometer, and a spectrum from 200 to 800 nm was recorded. Figure 3 shows the absorption spectrum. A peak at 275 nm having a shoulder at approximately 291 nm is observed. Thus, azide **1** crystallized on the foil forming excitons as discussed earlier.[4] The foil was removed and irradiated with light from the ozone-free, middle-pressure mercury vapor lamp for 2 minutes. Thereafter, a second spectrum was recorded and is displayed in Figure 3. The new spectrum differs significantly from the first one. The peak at 275 nm disappeared, indicating that the majority of the chromophores were destroyed. When the experiment was conducted on a quartz plate instead of the polyethylene foil, comparable spectra were obtained.

Because the sprayed layer was significantly thicker than monolayer coverage, most of azide **1** did not react with the surface but formed other, unidentified photodecomposition products upon illumination. These photodecomposition products could be washed away with acetone or acetonitrile.

To corroborate the binding as depicted in Figure 1, photolysis of azide **1** was carried out on a quartz plate and compared with the same reaction on the polyethylene foil. After illumination, the quartz plate and the polyethylene foil were thoroughly washed with acetonitrile to remove non-bound material.

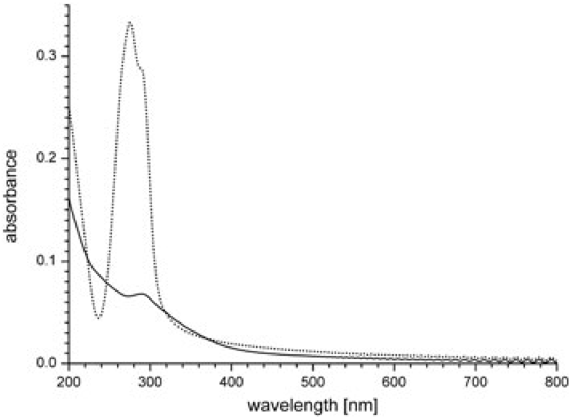


FIGURE 3 UV-Vis absorption spectrum of azide **1** on polyethylene before (dotted line) and after (solid line) irradiation with light from an ozone-free, middle-pressure mercury vapor lamp

Based on our chemical understanding, nitrenes should not react with quartz. Thus, a quartz plate was spray-coated with azide **1**, dried, exposed to light from the ozone-free, middle-pressure mercury vapor lamp for 2 minutes, and washed with acetonitrile for approximately 4 minutes. A UV spectrum was then recorded and is displayed in Figure 4 (the absorption of the clean quartz plate is subtracted). Only traces of UV-absorbing material remained at the surface of the treated quartz plate. Hence, it was concluded that most of the products from the photodecomposition of azide **1** were washed away.

When the polyethylene foil was treated in the same manner as the quartz plate, the spectrum also displayed in Figure 4 was obtained after washing. It is important to note that the UV irradiation procedure will induce radiation damage in the polyethylene that is visible in the spectra.[15] Thus, as background for the spectrum shown in Figure 4, a pristine polyethylene foil was used that was irradiated with light from the ozone-free, middle-pressure mercury vapor lamp. Additionally, the use of ultrasound for cleaning will blur the polyethylene surfaces and was therefore avoided in UV-Vis spectroscopy.

After washing the photografted sample, a peak at approximately 286 nm with 0.005 absorbance was observed (Figure 4).

Repetition of the experiment on a second spray-coated and illuminated polyethylene sample yielded a peak at 285 nm after washing with acetonitrile. The absorbance of that peak was 0.007. Considering the very small absorbances of the peaks obtained, the repeatability of the experiment was fairly good.

Prolonged washing with acetonitrile gradually reduced the intensity of this peak, but after 47 minutes of washing, its absorbance remained at approximately 80% of the absorbance shown in Figure 4. It is conceivable that photografted azide **1** was eventually washed away from the surface, together with its anchoring hydrocarbon chain.[4] The observation that fluorotelomer-grafted polyethylene chains became soluble in organic solvents such as acetonitrile is in line with the reported solubilization of graphene sheets grafted with an analogous perflurophenyl azide.[12]

To model the UV spectrum of the photografted polyethylene surface seen in Figure 4, compound **2** was synthesized (see Figure 5) (for synthetic procedure and analytical data see Supporting Information).

Amine **2** possesses the same chromophore as the presumed C—H insertion product from photografting azide **1** to polyethylene (Figure 1). The polyethylene chain is modeled by an isopropyl residue.

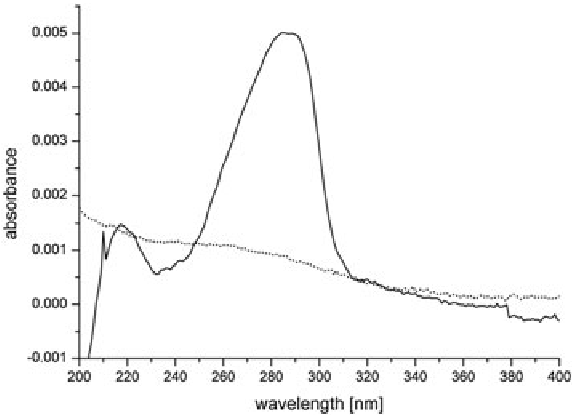
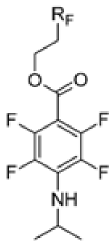


FIGURE 4 UV spectra of spray-coated, UV-exposed, and washed quartz (dotted line) and polyethylene (solid line)



2

FIGURE 5 Amine **2**, a model compound for photograft **1** ($R_F = -C_8F_{17}$)

Thus, all substituents on the benzene nucleus are comparable to photografted azide **1**, and it is expected that nearly identical UV-Vis absorption characteristics will be obtained. The optical properties of amine **2** in different solvents are summarized in Table 1.

It can be seen from Table 1 that a more polar solvent resulted in a redshift of the absorption maximum of compound **2**. The extinction coefficients for amine **2** were determined in hexane and acetonitrile and are comparable. For this reason, it was assumed that the photografted layer also possessed a similar extinction coefficient.

Figure 6 compares the normalized absorption spectra of **2** in acetonitrile and hexane with the normalized absorption spectrum of the photografted surface from Figure 4.

TABLE 1 Optical properties of amine **2** in various solvents

Solvent	λ-max[a], nm	Extinction Coefficient ε_0[b], cm^{-1} M^{-1}
Hexane	281	$2.12 \cdot 10^4 \pm 407$
Cyclohexane	284	n.d.
Tert.-butyl methyl ether	287	n.d.
Dioxane	289	n.d.
Ethyl acetate	290	n.d.
Acetonitrile	291	$2.37 \cdot 10^4 \pm 41$
Isopropyl alcohol	292	n.d.
Ethanol	293	n.d.

[a] The resolution of the method used is ±1 nm.

[b] The standard deviation was determined from the linear regression over 8 single measurements; n.d.: not determined.

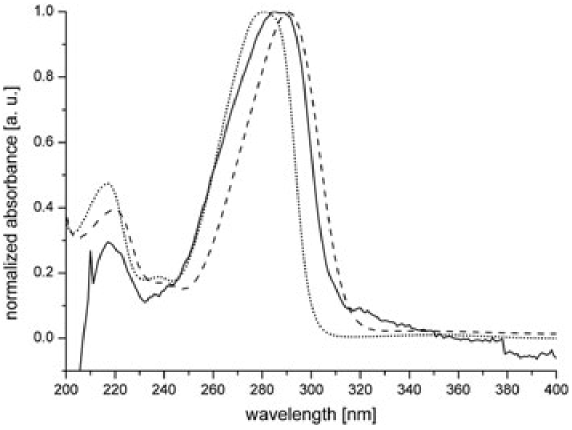


FIGURE 6 Comparison of UV spectra for amine **2** in hexane (dotted line) and acetonitrile solutions (dashed line) with the photografted polyethylene surface (solid line)

It can be seen that the absorption maximum of the photografted surface lies between the absorption maxima of amine **2** in hexane and acetonitrile. Additionally, the peak of the photografted surface is somewhat broader than the peaks in solution. This feature can be explained by assuming varying chemical environments of the grafted molecules. Some of the grafted molecules may lie on the polyethylene, others may stand upright, and still others may stack parallel to each other. In any case, the grafted molecules experience different neighborhoods and therefore exhibit slightly different UV absorption characteristics, resulting in a broadening of the absorption peak.

It was concluded that the comparison of the UV spectra of amine **2** with that of the photografted surface is consistent with binding as proposed in Figure 1.

To obtain an estimate of the photografted layer thickness, the following assumptions were made:

1. The coating is homogeneous.
2. The Beer-Lambert model is applicable.
3. A solution of amine **2** in hexane and the photografted layer have similar optical properties. In particular, the extinction coefficients are comparable.

From Table 1, it follows that a 1 molar solution of amine **2** in hexane possesses an absorbance of $A_A = 2.12 \cdot 10^4$ at an optical path length of 1 cm. One liter (1000 cm^3) of this solution at said thickness (1 cm) therefore covers an area, S = 1000 cm^2. If the solvent is evaporated, 697 g (1 mole) of amine **2** will be homogeneously spread over this area. Using the density of compound **2** (1.787 g/cm^3), this amount corresponds to a volume, V = 390 cm^3, and the layer thickness becomes $d_A = V/S = 0.390$ cm. From the Beer-Lambert model, it is known that absorbance is proportional to layer thickness. As extinction coefficients for amine **2** and photografted layer are assumed to be comparable, the thickness of the photografted layer (d_P) becomes (Equation 1):

$$d_P = d_A \frac{A_P}{A_A} \tag{1}$$

Equation 1 Thickness of the photografted layer, d_P. d_A is the thickness of the layer of amine **2**. A_P is the absorbance of the photografted layer, and A_A is the absorbance of the amine **2** layer.

The absorbance of the photografted layer at λ_{max} is $A_p = 0.005$ (see Figure 4). The thickness of the photografted layer therefore becomes $d_P = 9.2\ 10^{-8}$ cm = 0.92 nm.

This order of magnitude seemed appropriate for a monomolecular coating.

3.3 | X-ray photoelectron spectroscopy (XPS) of the nitrogen species

X-ray photoelectron spectroscopy of the carbon species of photografted polyethylene was described previously.[4] There, it was found that the C 1s core level spectrum of grafted and washed polyethylene can be fit into 4 components at 284.9 (area: 30%) (C—H), 287.6 (area: 37%) (C—F), 291.6 (area: 30%) (CF_2), and 294.0 eV (area 3%) (CF_3). The intensity of the signal at 284.9 eV (C—H) was larger than expected from the composition of **1** alone. Because the C 1s signal of the polyethylene substrate added to this peak, this enhancement is logical. It was concluded that the XPS of the carbon species in photografted polyethylene was consistent with a thin layer of **1** at the surface. However, the binding of **1** via an amine to the polyethylene cannot be demonstrated by the XPS of the carbon species. A comparable C 1s spectrum was expected if compound **1** was only physically adsorbed at the surface. Thus, the XPS of the nitrogen species was investigated. If azide **1** were only adsorbed physically at the polyethylene, 3 different nitrogen species corresponding to the $-N_3$ substituent would be expected. On the other hand, only one N 1s peak was expected for photografted **1** at the surface, with the appropriate binding energy. Hence, the binding of azide **1** to the polyethylene surface was studied using XPS. To this end, azide **1** was photografted onto polyethylene, followed by washing with acetone using ultrasound. The washing procedure removed unbound material, thus ensuring monolayer coverage. High-resolution N 1s core level spectra were recorded and are displayed in Figure 7. Raw data were fitted into a single peak by the Levenberg-Marquardt algorithm yielding a binding energy of 399.98 eV.[16] This value was referenced to an internal standard, the C 1s binding energy of the polyethylene substrate at 285.00 eV.[17] In order to classify the N 1s binding energy and to compare it with known structures, amine **2** was investigated using XPS. The nitrogen species in amine **2** has comparable chemical surroundings to the nitrogen species proposed in the perfluorophenylazide-modified surface (see Figure 1). Thus, it was expected that the binding energy of the N 1s electrons in the nitrogen species from amine **2** resembled that of the photografted surface. Hence, polyethylene was spray-coated with amine **2**, dried, and measured. The result is shown in Figure 7. Fitting of the raw data yielded an N 1s binding energy of 399.70 eV, referenced to the binding energy of the C 1s peak of polyethylene. The difference in N 1s binding energy between the photografted surface and the model case is 0.28 eV. This difference is very small and could originate from the spectrometer or the referencing (for example, the step width was 0.1 eV). However, although small, this difference could also mean that the electron density around the nitrogen species is slightly lower in the grafted case.

The full widths at half maximum of the fits were 2.06 and 2.80 eV for the model case and the photografted surface, respectively. The N 1s peak of the photografted surface is thus slightly broader than that of amine **2**. This broadening could originate from the slightly different binding environments of the grafted species.

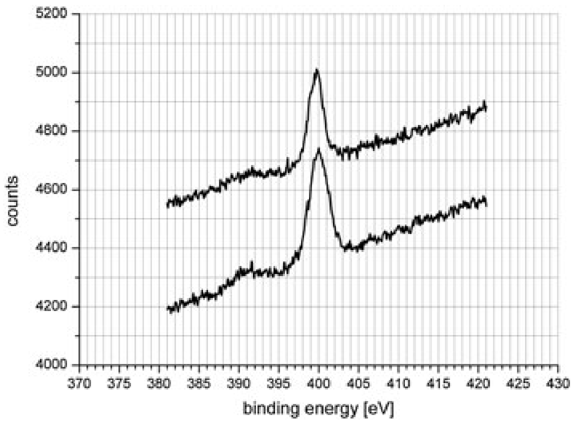


FIGURE 7 High-resolution N 1s core level XP spectra of photografted perfluorophenylazide **1** (below) and amine **2** (above) on polyethylene

In conclusion, the XPS measurements of the N 1s core level electrons supported the binding as depicted in Figure 1.

4 | SUMMARY AND CONCLUSION

Spectroscopy on a perfluorophenyl azide grafted polyethylene surface yielded the following results:

1. Infrared spectroscopy showed the disappearance of the azide peak after photografting. The minimal light dose needed for photodecomposition was determined.
2. Ultra-violet spectroscopy indicated that a monolayer of molecules with comparable absorption characteristics to a model compound (mimicking the presumed binding) was present at the polyethylene surface. This monolayer was not (or only slowly) removed by washing with acetone or acetonitrile.
3. X-ray photoelectron spectroscopy of the nitrogen species in photografted and washed polyethylene revealed a peak of comparable binding energy to that of the model compound mimicking the presumed binding.

From the previous findings, it was concluded that photografting of perfluorophenyl azide **1** to polyethylene resulted in C—H insertion of the intermediately formed nitrene species forming a monomolecular grafted layer at the surface.

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SUPPORTING INFORMATION

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