Efficient Formation of Difluoramino Functionalities by Direct Fluorination of Polyamides

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ABSTRACT: Efficient formation of difluoramino (NF_2) groups within the polymer matrix upon exposure of polyamides (PA6 and PA12) to elemental fluorine is reported. The reaction was assessed on bulk and thin-film samples by means of RA-FTIR (reflection−absorption FTIR), XPS (X-ray photoelectron spectroscopy), and NMR (nuclear magnetic resonance) techniques. Direct fluorination causes cleavage of the amide C−N bond and concomitant formation of the NF_2 chain-end functionalities as evident from an exceptionally large shift (+5 eV) of the N 1s binding energy and an increase of the ν(CO) frequency by about 80 cm^{-1}. The structural model is supported by the ^{19}F NMR spectra of volatile reaction products that clearly reveal the presence of the NF_2 group.

1. Introduction

The physical properties of fluorine substituents are characterized by a very low polarizability, the highest electronegativity in the periodic table, and the presence of three pairs of tightly bound nonbonding electrons.[1,2] They confer a unique behavior on fluoro-organic compounds, and as a consequence, fluorine substitution is a powerful tool in a variety of fields such as biochemistry and medicinal technology,[3] analytical chemistry,[4] material processing,[5] and others. In particular, fluorine-rich materials are important compounds in the emerging area of energetic materials.[6] Composite fluorine- and oxygen-rich polymers are expected to provide a new approach to increase the energy release rates of propellants. In the design of a new generation of advanced energetic materials, calculations indicate that it is advantageous to include oxygen oxidizers.[7] One possible component in energetic compounds is the difluoramino (NF_2) group.[6] Despite this technological interest, there has been very little published work on the structural chemistry and properties as well as synthesis of this unusual group. Here we demonstrate that it possible to produce large concentrations of terminal NF_2 groups embedded in a polyamide matrix by a brief exposure of the polymer to elemental fluorine. To the best of our knowledge, there is no report in the literature on direct fluorination of such an important class of polymers as polyamides.

2. Experimental Part

Well-defined polyamide-6 (PA6) samples [polycaprolactam, $M_w = 41\,000$, $M_w/M_n = 2.11$] were obtained from PSS (Germany). Polyamide-12 (PA12) [polylauryllactam] was supplied by EMS-Chemie (Germany). Polyamide-6 was used in the form of thin films deposited on silicon wafers and polyamide-12 as bulk samples. Polished silicon wafers (20 × 20 × 0.5 mm) were cleaned by a brief dip into hot concentrated nitric acid, followed by rinsing with copious amounts of triple distilled water, drying with nitrogen, and finally a 15 min plasma treatment. To increase the reflectivity of the substrate and adhesion of the polymer films, aluminum (99.99 grade) was first deposited onto silicon wafers by thermal evaporation in a vacuum chamber at a base pressure of about 1×10^{-6} mbar. The thickness of the Al coating (≈200 nm) was controlled by a quartz microbalance. Atomic force microscopy (Topometrix) of the coating showed distinct, cornlike surface topography[8] with the area root-mean-square (rms) roughness of 4.6 nm. The PA6 films were prepared by spin-coating from 1 to 4 wt % PA6 solutions in formic acid (Fluka, >96%). The root-mean-square roughness of the deposited PA films was significantly lower (1.8 nm) than that of the underlying aluminum. The PA6 film thickness was determined by ellipsometry measurements.

Fluorination of the PA6 and PA12 samples was performed in a stainless steel chamber. The vessel was pumped out and then filled with an N_2/F_2 gas mixture to adjust the pressure to 1 mbar. The fluorine content in the gas mixture was varied between 1 and 10 vol %. The fluorination time was always 180 s. The nonconsumed fluorine was pumped out and chemically bound by $CaO/CaCO_3$ in special absorbers. The thermal stress on the PA6 polymer films was low because of the highly diluted fluorine and the low pressure.

The XPS data were collected on a Surface Science Instruments SSX-100 spectrometer using a monochromatized Al Kα_1 source and a hemispherical electron energy analyzer. An electron flood gun was used for charge compensation (1 V, 0.05 μA). The spectra were collected using a spot size of 250 × 1000 μm. Binding energies were referenced to the CH_2 peak in the C 1s region set at 285.0 eV. The RA-FTIR (reflection−absorption Fourier transformed infrared) spectra were recorded either with a Magna 550 (Nicolet) or a Biorad 145 instrument equipped with a MCT detector. The 256 spectra, obtained at the incident angle of 70° with respect to the surface normal and at the resolution of 4 cm^{-1}, were averaged. For the ATR-FTIR (attenuated total reflection FTIR) measurements a ZnSe crystal was used. The NMR analysis concerns the material deposited on the reaction chamber walls during repeated fluorination of PA6. The yellow deposit was soluble in DMSO and D_2O. The NMR spectra were recorded at 27 °C on JEOL Eclipse 500 (500 MHz) spectrometer (^{19}F, 470 MHz; ^{13}C, 125 MHz; ^{1}H, 500.16 MHz). The HMQC and HMBC procedures were used for the $^{1}H-^{13}C$ correlation. Chemical shifts are reported using the convention that high frequency, low field values are more positive (International Union of Pure and Applied Chemistry, IUPAC).

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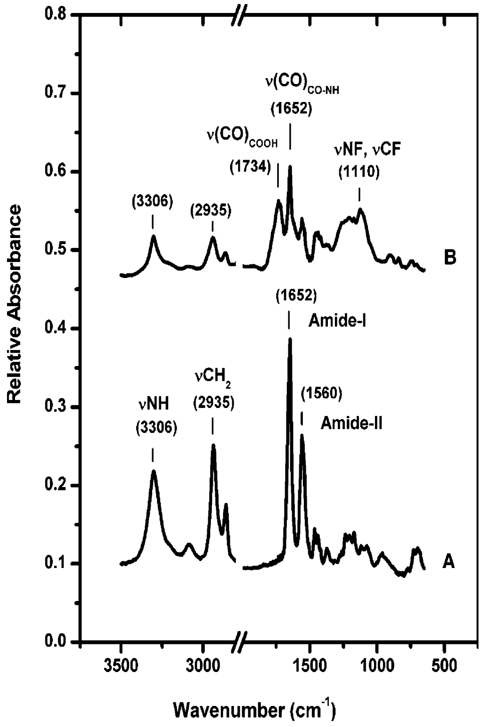

Figure 1. Reflection−absorption infrared spectra (RA-FTIRS) of a 92 nm polyamide-6 film before (A) and after (B) fluorination (4.6 vol % F_2). The spectra are normalized with respect the total ν(C═O) intensity at 1734 and 1652 cm^{-1}.

Caution: *Alkyl-NF$_2$ compounds are potentially explosive if isolated in significant amounts.*

3. Results and Discussion

This section is organized as follows. First, we consider the infrared spectra, probing the whole film thickness of the pristine and fluorinated PA6 and PA12 samples, followed by the corresponding, more surface sensitive XPS data. Finally, we briefly discuss the information obtained from an NMR analysis of volatile reaction products evolved during fluorination of PA6. Although the NMR data are only indirectly related to the surface chemical modification of polyamides, they provide valuable information on the mechanism of fluorination.

3.1. Infrared Measurements. Reflection−absorption infrared (RA-FTIR) spectra of a PA6 film before and after fluorination are shown in Figure 1. The spectrum of the pristine sample (Figure 1A) is consistent with previous results.[9] Thus, the strong band at 3306 cm^{-1} represents the N−H stretching vibration. The frequency of this band is known to be sensitive to the strength of intermolecular interactions such as hydrogen bonding. For example, for diluted solutions of methylacetamide the ν(N−H) vibration is observed at 3470 cm^{-1}.[10] The shoulder at about 3220 cm^{-1} and the band at 3085 cm^{-1} are due to a Fermi resonance of the ν(N−H) stretch and a combination band of the amide I and amide II modes, respectively. The peaks at 2935 and 2851 cm^{-1} are assigned to CH_2 asymmetric and symmetric stretching, respectively. The bands at 1649 and 1552 cm^{-1} are the so-called amide I and amide II bands. Because of their constant position and strong intensities, they are characteristic for amides. The series of weaker bands below 1500 cm^{-1} concerns the following vibrational modes: δ(CH_2) (1441 cm^{-1}), γ(CH_2) (1374 cm^{-1}), ν(CC) (1222 cm^{-1}), and ν(CN) (1096 cm^{-1}). The band at 710 cm^{-1} is the CH_2 rocking mode. Similar infrared features are also observed for PA12 (Table 1).

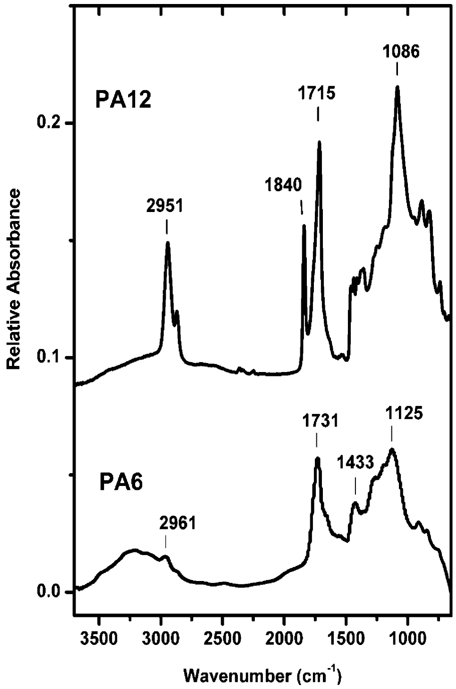

Figure 2. RA-FTIR spectrum of a 200 nm polyamide-6 film on silicon and ATR-FTIR spectrum of bulk polyamide-12. Both samples were fluorinated at 10 vol % F_2.

A number of important changes are observed in the spectra upon the fluorination. First of all, the decomposition of the amide group is obvious from the decrease of the intensities of the ν(NH), amide I, and amide II bands (Figure 1). Also, there is no indication of the appearance of an NH_2 group (which would result in two ν(NH) bands in the 3050−3200 cm^{-1} region). However, a new band appears at 1734 cm^{-1} due to ν(C═O) stretching.[11] Electron-withdrawing substituents cause an electrostatic stabilization of the C═O group and a shift of the C═O frequency to higher values, while electron-donating substituents destabilize the C═O group.[12] For perfluoroalkylcarboxylic acids the ν(C═O) frequency was observed in the range of 1730−1710 cm^{-1}.[13,14] The band at 1734 cm^{-1} for fluorinated PA6 is therefore consistent with a carboxyl group having a fluorinated carbon attached to it. This structural model is consistent with the XPS data (see below).

Partial fluorination of the CH_2 chain also takes place. As evident in Figure 1B, the intensities of the CH_2 bands at 2935 and 2851 cm^{-1} strongly decrease, while a new broad feature centered around 1150 cm^{-1} appears. In this range the ν(NF) and ν(CF) stretching modes are expected.[15,16] For example, in a study of fluorocarbon films[15] grown by chemical vapor deposition, symmetric and asymmetric ν(CF_2) stretches were observed at 1155 and 1215 cm^{-1}. For bulk poly(tetrafluoroethylene) the ν(CF) stretches appear at 1152 and 1207 cm^{-1}.[16] Thus, the spectrum in Figure 1B is consistent with partial fluorination of the CH_2 chain.

The infrared features due to fluorination are more pronounced at higher fluorine dosages. In Figure 2 the spectra for PA6 and PA12 samples at the maximum fluorine concentration in nitrogen gas possible in this study (10 vol % F_2 in N_2) are shown. From the ATR-FTIR spectrum of PA12 (upper spectrum) it is clear that the characteristic amide modes (the ν(NH), amide I, and

Table 1. Infrared Peak Assignment (cm^{-1}) for Polyamide-6 and Polyamide-12 from RA-FTIR and ATR-FTIR Measurements, Respectively

PA6 film	PA12	fluorinated PA6 film	fluorinated PA12	assignment
3307	3290	3306		ν(NH)
2935	2920	2935	2951	ν_a(CH) in $-CH_2-$
2851	2853	2851	2869	ν_s(CH) in $-CH_2-$
			1840	ν(CO) in $-C(O)F$
		1731	1715	ν(CO) in $-C(O)OH$
1649	1637	1652		amide I band
1552	1555	1555		amide II band
1441	1469	1446	1469	$\delta(CH_2)$
1374		1370	1370	$\gamma(CH_2)$
1222		1222		ν(CC), ν(CF)
		1110		$\nu(NF_2)$
1096		1092	1086	ν(CN)
710	722		735	CH_2 rock

amide II) are barely observed. The formation of N−F and C−F bonds is evident from the prominent broad feature centered at 1086 cm^{-1}. Also, the ν(C=O) band at 1715 cm^{-1}, corresponding to that at 1731 cm^{-1} for PA6, is present. For PA12, in contrast to PA6, an additional band at 1840 cm^{-1} is also present in the spectrum. It is due to the ν(C=O) stretching of the −C(O)F species,[16] and its appearance might concern inherent lower water content in PA12 as compared to PA6 and consequently a slower hydrolyses of the initially formed −C(O)F group. This aspect will be discussed below.

3.2. XPS Measurements. The overview XPS spectra of pristine PA6 films on silicon (not shown) revealed only the signals expected for the polymer. This indicates that the deposited thin films were continuous. After a correction for atomic relative sensitivities the ratios C/N/O 7.3/1/0.9 were obtained, close to the values expected from the stoichiometric composition of the compound (6/1/1). The fluorinated polyamides showed an additional strong and broad fluorine signal (2.22 eV fwhm as compared to, e.g., 1.3 eV for N 1s). Also, the fluorine peak binding energy of 687.0 eV is quite low. Thus, the values around 689−688 eV are typical of simple fluorocarbon compounds,[18] indicating contributions of different fluorine species to the fluorine spectrum. Detailed spectra of a fluorinated and untreated PA6 film in the N 1s and C 1s regions are presented in Figures 3 and 4.

The N 1s binding energy for the pristine PA6 film is observed at 399.8 eV as expected for amides.[19,20] After fluorination a new nitrogen species appears with an exceptionally large N 1s chemical shift (+5 eV) (Figure 3b). The shift implies a large depletion of the electron density at nitrogen. Only strong electron-withdrawing substituents such as fluorine or oxygen directly attached to nitrogen can cause such a shift. Oxidized nitrogen groups exhibit such N 1s values (NO, 403 eV;[21] NO_2, 405.6 eV;[22] ONO, 404−405 eV[21]). We are not aware of any reports on N 1s binding energies of fluorinated nitrogen compounds. However, on the basis of the electronegativity arguments (and in conjunction with further data presented below), we assign the peak at 404.5 eV to the N 1s binding energy of the NF_2 group.

For the discussion of the C 1s spectra (Figure 4) it is important to note that the short-range nature of substituent effects leads to additive rules for the C 1s shifts.[23] Thus, the characteristic C 1s shift for carbon atom, single bonded to oxygen (alcohols, ethers, esters), is about 1.6 eV.[23] For carbon single bonded to two oxygen atoms the shift is about 2.8 eV, approximately twice the effect of a single substituent. For carbon double bonded to oxygen in simple carbonyl compounds it is about 2.6 eV.[24] On going from a carbonyl to a carboxyl group, the change in binding energy associated with the additional oxygen, single bonded to carbon, is about 1.4 eV, giving a total shift of about 4 eV.[24] In the C 1s region of a nonfluorinated film (Figure 4a) one can resolve three peaks. The lowest binding energy peak at 285.0 eV concerns the CH_2 species and serves as an internal energy standard. The peak at 288.0 eV is due to the carbonyl carbon atom. The remaining C 1s peak at about 286.0 eV is likely to arise from the carbon atom attached to the nitrogen atom. For the fluorinated film in Figure 4b one observes a decrease in the intensity of the CH_2 peak at 285.0 eV and a broad feature extending up to about 292 eV on the higher energy side. Clearly, a number of peaks contribute to this region, and their exact positions are difficult to determine. Nevertheless, important information can be extracted from the spectrum. In the CF_x compounds the following C 1s binding energies were observed: CF_3 (294.3 eV), CF_2 (292.0 eV), and CHF (290.4 eV).[25−27] Thus, the formation of CF_3 can be excluded. Also, the contribution from CF_2 is restricted to only a few percent. CHF appears to be the major fluorocarbon species formed during fluorination.

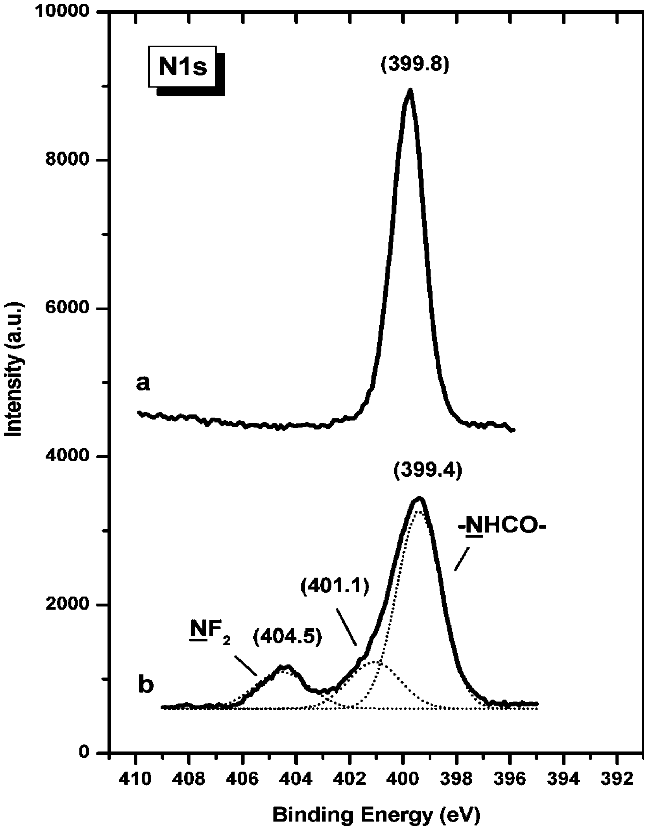

Figure 3. N 1s XPS spectra of a 92 nm thick polyamide-6 film on silicon before (a) and after (b) fluorination (4.6 vol % F_2).

We now consider the degree of fluorination of the aliphatic chain and shell obtain an estimate as follows. Before fluorination, the four CH_2 carbon atoms at a binding energy of 285.0 eV contribute to about 70% to the total C 1s intensity (Figure 4a), in reasonable agreement with the value of 67% expected from stoichiometry. After fluorination the relative intensity of the 285.0 eV peak decreases to about 48%. This roughly

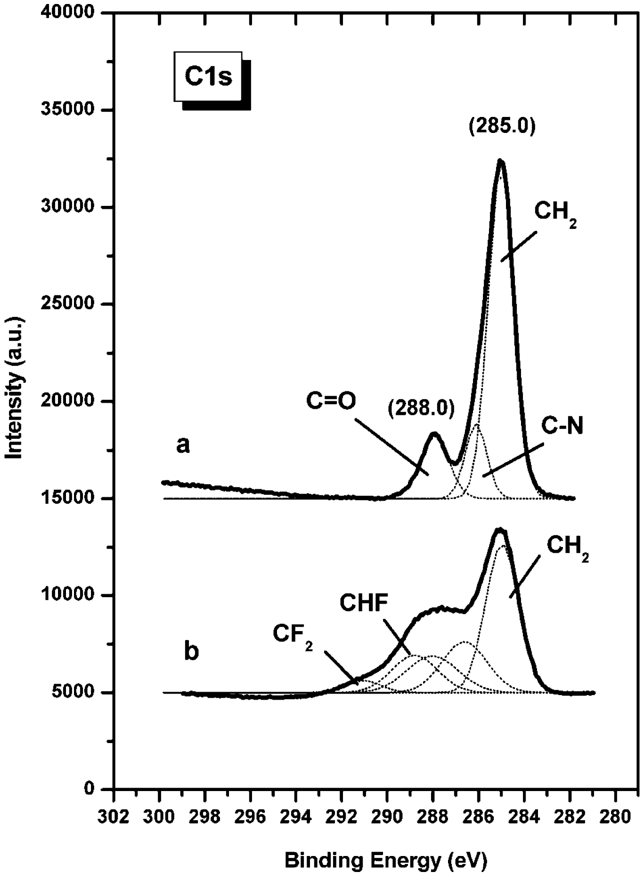

Figure 4. C 1s XPS spectra of a 92 nm thick polyamide-6 film on silicon before (a) and after (b) fluorination (4.6 vol % F_2).

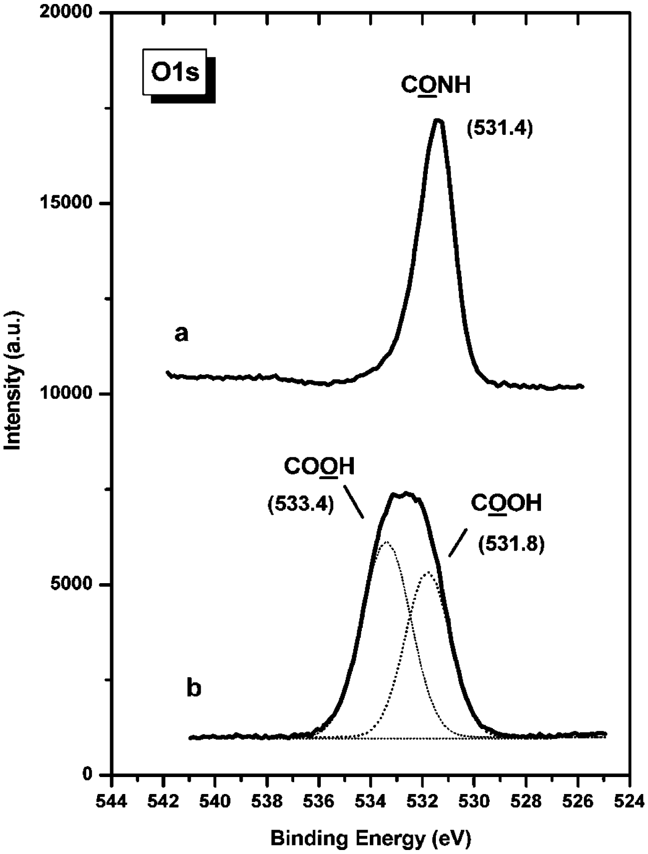

Figure 5. O 1s XPS spectra of a 92 nm thick polyamide-6 film on silicon before (a) and after (b) fluorination (4.6 vol % F_2).

corresponds to three CH_2 carbon atoms per monomer unit that are not affected by fluorination. Implicit here is that only one CH_2 carbon atom is fluorinated, with one additional, neighboring carbon atom being affected indirectly[25] through the substituent effects. The remaining carbon concerns the carbonyl group. It is interesting to note that in an XPS study on the fluorination of polyethylene only a low fluorination degree (25%) of the CH_2 chain could be achieved.[5]

Turning now to the O 1s range, we first mention that for the pristine PA6 a single peak at a binding energy of 531.4 eV was observed (Figure 5), in good agreement with previous XPS studies of compounds containing the C=O group.[28–30] Upon fluorination, however, a second peak appears at 1.6 eV higher binding energy that is assigned to the hydroxyl group. This conclusion is based on the observation that single- and double-bonded oxygen atoms exhibit a substantial shift (about 1.5 eV). Experimental[28,30] and theoretical data[29] unambiguously assign the lower binding energy compound to arise from the double bonded oxygen. On this basis we assign the two oxygen peaks of nearly equal intensity (Figure 5) observed for fluorinated PA6 to a carboxyl group formed upon fluorination as discussed below.

In conclusion, the IR and XPS data demonstrate that major chemical reactions take place between elemental gaseous fluorine and the amide group of the polymers. This leads to the formation of difluoramino and carboxyl end groups. The formation of the NF_2 group is supported by the N 1s data (showing a rather large +5 eV shift of the binding energy) and also by the NMR data presented below. The intensity of the N 1s peak (at 405 eV) correlates with the fluorine doses (Figure 6): Increasing the fluorine doses by about a factor of 2 leads to almost a doubling of the peak intensity. The formation of the COOH group is supported by the shift of the ν(CO) frequency to 1734 cm^{-1} as well as by appearance of additional (hydroxyl) oxygen in the XPS spectra.

3.3. NMR Measurements. The formation of the difluoramino groups and a partial fluorination of the CH_2 chain are further corroborated by NMR analysis of the volatile reaction products (Figure 7). We do not want to overemphasize those NMR results since they are only indirectly related to the chemical modifications of solid polyamides. However, these data are expected to provide important clues to the reaction mechanism. Briefly, the analysis revealed two major compounds of similar structure composed of a chain of six carbon atoms terminated by electronegative groups. This fact already points to a cleavage of the amide N−C bond. Only one of the compounds contains fluorine. The fluorine signals at about +31 and +16 ppm (Figure 7, lower spectrum) show a large shift toward lower fields with respect to the fluorocarbon signal (Figure 7, upper spectrum). The large and same splitting of the two doublets (581.6 Hz) means that the two fluorine atoms are geminal. The shift also implies a strong reduction in the electron density at the fluorine atoms with respect fluorine attached to carbon. These species were identified as NF_2 on the basis of literature data. Thus, the ^{19}F shifts for $(CH_3)_2CHCH_2-NF_2$ and $CH_3(CH_2)_3-NF_2$ compounds were reported as 33.0 and 54.8 ppm, respectively.[31,32] On the other hand, the ^{19}F shifts for the corresponding single fluorinated nitrogen compounds are significantly different [−140.9 ppm for $(CH_3)_2$-

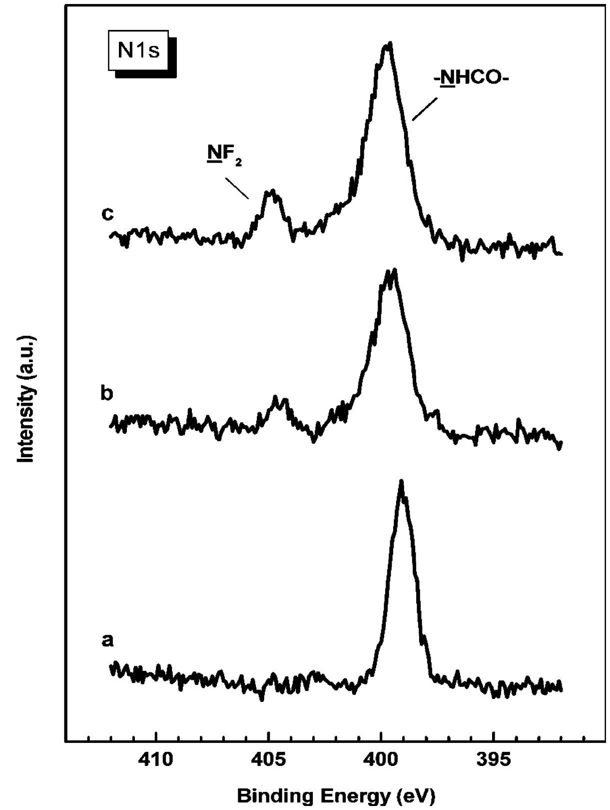

Figure 6. N 1s XPS spectra of pristine (a) and fluorinated (b; 5 vol %) and (c; 10 vol % F_2) polyamide-6.

$CHCH_2-NHF$ and −116.6 ppm for $CH_3(CH_2)_3-NHF$].[31] Consequently, we assign the lower spectrum in Figure 6 to the NF_2 group. Partial fluorination of the CH_2 chain is presented in the upper spectrum of Figure 7 obtained at high fields. Only one carbon atom is found to be fluorinated. Its position was unambiguously determined from ^{13}C correlation as the carbon atom attached directly to the carbonyl: $F_2N-(CH_2)_4-CHF-COOH$. The observed splitting of the fluorine signal in Figure 7 (upper spectrum) is due to the geminal hydrogen (48.6 Hz) and the two hydrogen atoms on the neighboring CH_2 unit (26.7 Hz). The chemical shift of −190 ppm is typical for fluorocarbons.[33]

We now consider the reaction mechanism. The nitrogen species of 404.5 eV binding energy (Figures 3 and 5) are likely to be formed by free radical reactions. Early electron spin resonance (ESR) studies[34] pointed to the free radical reactions of elemental fluorine with hydrocarbon polymers. Thereby the initial reactions, either (1a) or (1b), generate radicals

$$-CH_2-CH_2-CH_2- + F_2 \rightarrow -CH_2-CH^{\bullet}-CH_2- + HF + F^{\bullet} \quad (1a)$$

$$-CH_2-CH_2-CH_2- + F^{\bullet} \rightarrow -CH_2-CH^{\bullet}-CH_2- + HF \quad (1b)$$

followed by the reaction

$$F_2 + -CH_2-CH^{\bullet}-CH_2- \rightarrow -CH_2-CHF-CH_2- + F^{\bullet} \quad (2)$$

to form CHF species. Such reactions are unique to fluorine and consistent with the low dissociation energy of fluorine (155 kJ/mol) and the high hydrogen−fluorine bond energy (565 kJ/mol). The occurrence of reaction 1b may be attributed to the high order of electrophilic reactivity shown by fluorine. The large exothermicity of reactions 1a ($\Delta H = -143$ kJ/mol) and 1b ($\Delta H = -286$ kJ/mol) ensures an efficient propagation. One would expect that electrophilic fluorine atoms should react with the most nucleophilic CH site, i.e., sites that are furthest away from the electron-withdrawing carbonyl group,[35] which was not observed for polyamides. A possible reason for the preferred fluorination of the α carbon atom might be a competing process involving enol forms of the acids. It is well-known that its formation is acid or base catalyzed, which in this case might involve a local increase or decrease of pH due to small amounts of water within polyamides in the presence of F_2. Enols are electron-rich and behave as nucleophiles. Within an acid- or base-catalyzed substitution enol reacts very rapidly with electrophilic species such as fluorine. Protons at other positions on the chain cannot be substituted because the enolate anion is not stabilized by an adjacent carbonyl group. After C−F bond formation, the electronegative fluorine atom makes the system less nucleophilic and, therefore, less susceptible toward attack by fluorine radicals, as is observed. On the other hand, the fluorine substitution on the α

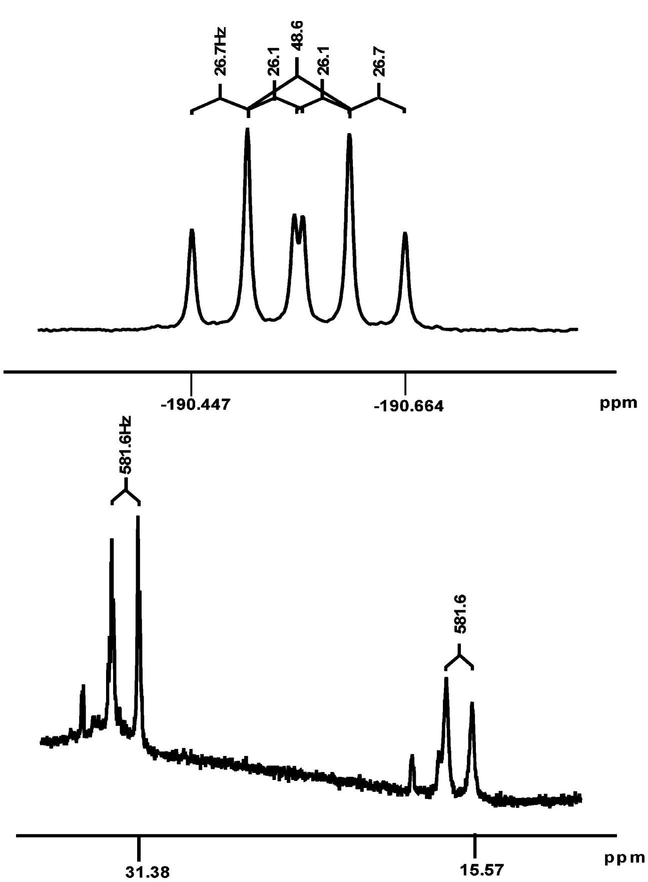

Figure 7. ^{19}F NMR spectra of volatile reaction products of the PA6 fluorination. The multiple splitting in the high field part of the spectrum (upper spectrum) concerns the single fluorinated carbon next to carbonyl with geminal hydrogen coupling of $^2J = 48.6$ Hz and two couplings to the hydrogen atoms on the neighboring carbon of $^3J = 26.7$ Hz. The large and equal splitting (581.6 Hz) in the low field part of the ^{19}F spectrum (lower spectrum) concerns two geminal fluorine atoms directly attached to nitrogen.

carbon is expected to induce a very strong effect on the properties of the adjacent functional groups.[35] Concomitantly, this might lead to destabilization the amide group, stipulating further reactions leading to the cleavage of the C−N bond and the formation of the NF_2 and C(O)F end groups. The reaction is favored by the large nitrogen−fluorine bond energy (278 kJ/mol). The hydrolysis of the C(O)F group is very favorable,[16] and intrinsic traces of water within the polymers (as high as a few vol % for polyamides) result in the formation of the COOH group. Since the water content in PA12 is known to be much lower than in the PA6, the 1840 cm^{-1} band characteristic of the C(O)F group is observed for PA12 but not for PA6 (Figure 2). Although details of the proposed reaction mechanism are still speculative and further dynamic studies are necessary to reveal details, the present XPS and IR data clearly demonstrate that the amide group of the polyamides is involved in the major chemical reactions during fluorination, leading to the formation of difluoramino functionalities.

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