Introduction of Carboxylate Groups at Poly(ethylene) Surfaces by Argon Plasma Immobilization of Sodium Salts of Fatty Acids

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Received May 5, 1997. In Final Form: September 4, 1997[®]

Carboxylate groups were introduced at poly(ethylene) (PE) surfaces by immobilization of sodium 10-undecenoate (C11(:)) or sodium dodecanoate (C12) using an argon plasma treatment. The presence of carboxylate groups at the surface was confirmed by ATR-FTIR spectroscopy, contact-angle determinations, and derivatization XPS. The presence of an unsaturated bond in the alkyl chain of the surfactant enhanced the immobilization process. About 28% of the initial amount of carboxylate groups in the precoated C11(:) layer was retained at the PE surface after plasma treatment, as compared to only 6% for the C12 layer. No changes in the wettability of the modified PE surfaces were observed when they were stored at room temperature for at least 12 weeks. The use of the carboxylate groups that were introduced at polymeric surfaces with this method for further covalent coupling of other molecules is discussed.

Introduction

During the last decades, modification of polymeric surfaces has become an important subject, especially for the improvement of wetting and adhesion. Using appropriate techniques, specific functional groups can be introduced at polymeric surfaces. These functional groups can then be used for subsequent derivatizations by conventional synthetic techniques. This approach is often applied in biotechnological and biomedical research. Especially the introduction of carboxylic acid and amine groups has been of great interest.¹ For certain applications, the introduction of specific functional groups at polymeric surfaces is a goal in itself. For example, carboxylate and sulfonate groups were introduced at poly(styrene) and poly(urethane) surfaces to improve their blood compatibility.^{2,3}

With the use of plasma treatment, it is possible to introduce functional groups at the outermost surface of polymeric substrates.⁴⁻⁷ However, oxidative plasmas give multifunctional surfaces, making it difficult to control the surface chemistry. The use of carbon dioxide plasma treatment has been reported as a way to introduce carboxylic acid groups at polymeric surfaces, but the specificity of this treatment was poor, and several other groups were introduced at the surfaces as well.^{8,9}

Recently, a new method has been developed to modify polymeric surfaces in a controlled way.¹⁰ For this purpose,

a compound with a desired functional group, usually a surfactant, is coated onto the surface of a polymeric substrate. Subsequently, the substrate is treated with an argon plasma by which part of the precoated layer is covalently coupled to the surface. With this technique, it was possible to introduce sulfate groups on poly(propylene) (PP) and amine groups on poly(ethylene) (PE) by immobilizing sodium dodecane sulfate (SDS) and decylamine hydrochloride (DA·HCl), respectively.^{11,12} It was not possible to introduce carboxylic acid groups at a PE surface by the immobilization of a precoated poly(acrylic acid) (PAAc) layer. This was attributed to rapid decarboxylation of PAAc during the argon plasma treatment.^{13,14} Therefore, the requirements for the successful application of this method are that the compound that has to be immobilized can be coated onto the surface and that no severe decomposition of the functional groups takes place during plasma treatment.

The aim of this study is to selectively introduce carboxylate groups at polymeric surfaces. These groups can be used for the coupling of other molecules to the surfaces. In addition, combination of these groups with sulfonate or sulfate groups may improve the blood compatibility of the surface. The introduction of the carboxylate groups should be carried out in a selective way. Furthermore, modifications should be restricted to the outermost surface without affecting the bulk properties of the material. Finally, the method should be applicable to a wide range of polymeric surfaces. Therefore, the plasma immobilization method seems to be the most suitable approach.

Carboxylate groups are introduced at PE surfaces via the immobilization of the sodium salts of fatty acids. It may be expected that sodium carboxylate groups are less susceptible to etching during argon plasma treatment than carboxylic acid groups due to hindrance of the dehydrogenation process preceding the decarboxylation. Thus, it

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© Abstract published in *Advance ACS Abstracts*, November 15, 1997.

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may be possible to immobilize part of the coated layer without severe etching of the functional groups. By using the sodium salts of a saturated as well as an unsaturated fatty acid, the influence of a double bond in the alkyl chain of the precoated compound on the immobilization process was studied. Different techniques like ATR-FTIR spectroscopy, contact-angle determinations, contact-angle titrations, and (derivatization) XPS were applied to detect carboxylic acid groups at the modified PE surfaces.

It is also interesting to know how the composition of the surface of modified polymeric samples changes as a function of time. This process mainly determines the maximum storage time for a possible application. This issue was investigated by determining the contact angles of modified surfaces as a function of the storage time at different temperatures.

Experimental Section

Materials. PE foil without additives (LDPE, Type 2300, thickness 0.2 mm) was obtained from DSM (Geleen, The Netherlands). Argon (purity $\geq 99.999\%$) was purchased from Hoekloos (Schiedam, The Netherlands). Sodium 10-undecenoate (C11(:)) and sodium dodecanoate (C12) were purchased from Sigma Chemical Co. (St. Louis, MO). *N,N*-Di-*tert*-butylcarbodiimide and poly(acrylic acid) (PAAc) were purchased from Aldrich Chemie (Brussels, Belgium). All other chemicals were purchased from Merck (Darmstadt, Germany). All solvents were of analytical grade quality. All chemicals were used as received.

Cleaning of the Glassware. All glassware was cleaned by rinsing 3 times with toluene, 3 times with acetone, 3 times with water, and finally 3 times with acetone and then dried.

Cleaning of the PE Samples. PE samples (13 $\times$ 25 mm) were ultrasonically cleaned (10 min, 4 times in each liquid) successively in dichloromethane, acetone, and deionized water and then dried at room temperature (RT) *in vacuo*.

Preparation of the PAAc Samples. A solution of PAAc in methanol (2% (w/v)) was cast into a clean Petri dish. After evaporation of the methanol, the PAAc sample was dried at RT *in vacuo*.

Preparation of the C11(:) Pellets. C11(:) was wrapped in aluminum foil and pressed between two copper plates with the use of a hydraulic press. Subsequently, a thin layer of the upper side of the resulting pellet was scraped off with a scalpel.

Coating of C11(:) and C12 onto PE. Clean PE samples were placed in test tubes, and aqueous solutions of C11(:) or C12 containing 1 vol % hexanol were added. The concentration of C11(:) was 0.30 M, and the concentration of C12 was 0.10 M. After 15 min, the solutions were removed from the test tubes and the polymeric samples were dried at RT *in vacuo*. The resulting samples are coded PE/C11(:) and PE/C12, respectively.

Plasma Treatment of the Polymeric Samples. Plasma treatments were performed in a tubular reactor (length 80 cm, internal diameter 6.5 cm) using three capacitively coupled externally placed electrodes. The hot electrode was placed at the center of the reactor, and the cold electrodes were placed at 10-cm distances at both sides of the hot electrode. The electrodes were connected to a rf (13.56-MHz) generator through a matching network. The vacuum side of the reactor was connected to a two-stage rotary pump and a turbomolecular pump. The gas flow to the reactor was controlled by mass flow controllers. The PE and precoated PE samples were placed on glass plates that were put in the center of the reactor between the electrodes. The reactor was evacuated to a pressure of 1×10^{-5} mbar and flushed 4 times with argon, after which an argon flow of 10 cm³/min (STP) was established through the reactor. After 15 min, the samples were treated with a static argon plasma, *i.e.*, with no flow through the reactor during the plasma treatment (45 W, 0.07 mbar). After the plasma treatment, the argon flow was established through the reactor again for 2 min. Subsequently, the reactor was brought to atmospheric pressure with argon. The samples were removed from the reactor and turned, and the other side of the samples was plasma treated according to the same procedure.

Washing of the Polymeric Samples. Polymeric samples were immersed in an aqueous solution of 0.1 mM HCl for 1 h at RT, rinsed twice with an aqueous solution of 0.1 mM HCl, and dried at RT *in vacuo*.

Reaction of the Surface Carboxylic Acid Groups with Trifluoroethanol (TFE). The surface carboxylic acid groups were reacted with TFE using a method that was described by Chilkoti et al.¹⁵ and modified for our purposes.¹³ A polymeric sample was placed on glass beads in a glass vial. Subsequently, TFE (0.45 mL), pyridine (0.20 mL), and *N,N*-di-*tert*-butylcarbodiimide (0.15 mL) were consecutively injected under the sample between the glass beads at 15 min-intervals. The vial was closed, and the reaction was allowed to proceed for 24 h at RT. The sample was then loaded for XPS analysis.

X-ray Photoelectron Spectroscopy (XPS). A Kratos XSAM-800 apparatus equipped with a Mg K α X-ray source (15 kV, 10 mA) was used to analyze the surface composition of the polymeric samples and C11(:) pellets. The analyzer was placed perpendicular to the sample surface. Survey scans (0–1100 eV) and detail scans were recorded at an analyzer pass energy of 40 eV (FWHM Ag 3d^{5/2}: 1.2 eV) and an X-ray spot size with a diameter of 3 mm. Survey scans were used to qualitatively determine the elemental composition of the samples. No charge neutralization was applied, and the reported values of the binding energies were referenced to the C 1s peak for aliphatic carbon, which was assigned a value of 284.8 eV.¹⁶ The relative peak areas for the different elements were calculated by numerical integration of the detail scans, considering empirically derived sensitivity factors. After normalization, an elemental composition in atomic percentages was obtained. All calculations were performed using the multiuser DS 800 software system (Kratos, Manchester, England).

Contact-Angle Determinations. The advancing and receding contact angles were determined using the Wilhelmy plate technique with the aid of an Electrobalance, Model RM-2, Cahn/Ventron (Paramount, CA).¹⁷ The interfacial velocity was 4 mm/min.

Contact-Angle Titrations. The contact angles of the PE and PE/C11(:) samples that were plasma treated with an argon plasma for 5 s and washed with an aqueous solution of 0.1 mM HCl were determined using aqueous solutions of different pH values. The concentration of the buffers that were used was 0.05 M: pH 3, tartaric acid ($\gamma = 71.86 \pm 0.05$ mN/m); pH 5, acetic acid ($\gamma = 71.95 \pm 0.10$ mN/m); pH 7, *N*-(2-hydroxyethyl)-piperazine-*N*-(2-ethanesulfonic acid) (HEPES) ($\gamma = 71.75 \pm 0.16$ mN/m); pH 9, 2-(*N*-cyclohexylamino)ethanesulfonic acid (CHES) ($\gamma = 69.80 \pm 0.24$ mN/m); pH 11, γ -aminobutyric acid ($\gamma = 71.75 \pm 0.04$ mN/m). For solutions of pH 1 and pH 13, 0.1 N HCl ($\gamma = 71.97 \pm 0.14$ mN/m) and 0.1 N NaOH ($\gamma = 71.69 \pm 0.02$ mN/m) were used, respectively. The surface tension of the solutions were determined with the Wilhelmy plate technique using a platinum plate and a processor tensiometer K12, Krüss GmbH (Hamburg, Germany). All measurements were performed at RT.

Attenuated Total Reflectance-Fourier Transformed Infrared (ATR-FTIR) Spectroscopy. Polymeric samples were pressed firmly to one side of a KRS-5 crystal and put in a steel sample holder. Absorption spectra were measured with a Biorad FTS-60 spectrometer (angle 45°, 256 scans, resolution 16 cm⁻¹).

Ion Exchange with Plasma-Treated and Washed PE and PE/C11(:) Samples. PE/C11(:) samples that were treated with an argon plasma for 5 s and washed with an aqueous solution of 0.1 mM HCl were immersed in an aqueous 1.0 M NaOH solution for 60 min at RT. The NaOH solution was removed, and the samples were rinsed twice with methanol in order to remove the residual NaOH.¹³ Finally, the samples were dried at RT *in vacuo*.

Aging of Plasma-Treated and Washed PE and PE/C11(:) Samples. PE and PE/C11(:) samples that were treated with an argon plasma for 5 s and washed with an aqueous solution of 0.1 mM HCl were stored in clean glass vials for different time

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Table 1. XPS Analysis of PE, PE/C11(:), and PE/C12 Samples ($n \geq 4$, $\pm$ sd)

sample	atomic % O	atomic % Na
PE	0.2 ± 0.3	<i>a</i>
PE/C11(:)	10.9 ± 1.3	6.2 ± 0.4
PE/C11(:), washed	0.1 ± 0.2	<i>a</i>
PE/C12	8.3 ± 2.3	5.0 ± 0.9
PE/C12, washed	0.1 ± 0.1	<i>a</i>

^a No peaks were observed in the detail scans of the Na 1s (1060–1080-eV) region.

intervals at -20 , 25 , and 50 °C. The extent of aging of the samples was evaluated by determining the contact angles of the samples using aqueous 0.1 M NaOH and 0.1 M HCl solutions.

Results and Discussion

Coating of C11(:) and C12 onto PE. XPS analysis of PE samples that had been immersed in an aqueous solution of C11(:) or C12 containing 1 vol % hexanol showed the presence of substantial amounts of oxygen and sodium at the surface (Table 1). This clearly indicates the presence of surfactant at the PE surface. The presence of hexanol in the surfactant solution was essential to coat surfactant onto the PE samples.¹⁸ From the XPS data, the thicknesses of the coated C11(:) and C12 layers could be calculated. In these calculations, it was assumed that C11(:) and C12 were present in an homogeneous layer on the surface without specific orientation of the surfactant molecules.¹⁸ The calculated thicknesses were 4.7 ± 1.2 and 3.1 ± 1.5 nm for the PE/C11(:) and PE/C12 samples, respectively. When the PE/C11(:) and PE/C12 samples were washed and analyzed with XPS, no sodium or oxygen could be detected at the surface anymore. Thus, all the coated material was removed upon washing.

The PE/C11(:) and PE/C12 samples were subsequently treated with an argon plasma for different time intervals to immobilize the surfactants covalently to the surface, after which the samples were washed to remove any unbound material. Surface analyses of these samples were performed and are discussed in the following sections.

ATR-FTIR Spectroscopy of (Modified) PE and PE/C11(:) Samples. ATR-FTIR spectroscopy was performed to gain information about the chemical compositions of modified polymeric samples (Figure 1). Differences between the spectra of the modified samples were only observed in the region between 1000 and 2000 cm^{-1} . The predominant peaks for PE, which are characteristic for alkanes, were observed in all spectra: $\nu_{\text{as}}(\text{CH}_2)$ at 2919 cm^{-1} , $\nu_{\text{sy}}(\text{CH}_2)$ at 2844 cm^{-1} , $\delta_{\text{s}}(\text{CH}_2)$ at 1471 cm^{-1} , and $\delta_{\text{t}}(\text{CH}_2)$ at 720 cm^{-1} . The small peak at 1371 cm^{-1} can be ascribed to $\delta_{\text{s}}(\text{CH}_3)$. Plasma treatment induced small differences in the spectrum. Some additional peaks were detected in the region of 1500 – 1800 cm^{-1} and, although very broad, in the region between 1000 and 1300 cm^{-1} . The peaks between 1500 and 1800 cm^{-1} can be ascribed to oxygen-containing groups like ketones, aldehydes, esters, and carboxylic acid groups ($\nu(\text{C}=\text{O})$ at 1680 – 1720 cm^{-1}). The peaks in the region of 1000 – 1300 cm^{-1} can be ascribed to alcohols, peroxides, or ethers ($\nu(\text{C}-\text{O})$ at 1260 – 1350 and 1000 – 1250 cm^{-1}). These findings indicate that oxygen-containing groups are introduced on PE during or after the plasma treatment. After washing the plasma-treated PE samples with an aqueous solution of 0.1 mM HCl, no significant changes in the ATR-FTIR spectrum could be observed.

The spectrum of PE/C11(:) is almost identical to the spectrum of PE. Additional to the characteristic peaks

Figure 1. ATR-FTIR spectra of PE and PE/C11(:) samples (a) The samples were treated with an argon plasma for 5 s (b) and subsequently washed with an aqueous solution of 0.1 mM HCl (c). Finally, the samples were washed with an aqueous NaOH solution and methanol (d).

for alkanes, a peak at 1557 cm^{-1} ($\nu_{\text{as}}(\text{COO}^-)$) was detected. This peak arises from the presence of a coated layer of C11(:) on the PE sample. After plasma treatment, the peak arising from the carboxylate group at 1557 cm^{-1} remains present. After washing with an aqueous solution of 0.1 mM HCl, the carboxylate peak is completely vanished. This may indicate that the coated C11(:) layer was not immobilized during argon plasma treatment and was washed from the surface. On the other hand, it is also possible that immobilization of C11(:) did take place and that ion exchange had occurred during the wash step. In this case, the sodium ions are exchanged for protons and carboxylate groups are transformed to carboxylic acid groups. However, no increased absorption at 1700 – 1720 cm^{-1} resulting from $\text{C}=\text{O}$ stretching vibrations of the carboxylic acid groups can be observed. Probably, the intensity of these vibrations is too low. To elucidate this uncertainty, spectra of plasma-treated and washed PE and PE/C11(:) samples that were immersed in an aqueous NaOH solution to exchange acidic protons for sodium ions were recorded. The samples were rinsed with methanol to remove residual NaOH. For the plasma-treated, washed, and ion-exchanged PE/C11(:) samples, the peak at 1557 cm^{-1} was present again, whereas this peak remained absent for the plasma-treated, washed, and ion-exchanged PE samples, indicating the presence of carboxylate groups at the former surfaces. Thus, the immobilization of C11(:) molecules on PE was successful, and the resulting carboxylate groups are available for ion exchange.

However, from this ATR-FTIR study, only limited information was obtained about the characteristics of the outermost surface of the plasma-treated PE and PE/C11(:) samples. This is caused by the large penetration depth

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Figure 2. Wilhelmy plate contact-angles of PE and PE/C11(:) samples that were treated with an argon plasma and subsequently washed with an aqueous solution of 0.1 mM HCl. The advancing and receding contact angles are determined using aqueous solutions of 0.1 M HCl and 0.1 M NaOH and are given as a function of the plasma treatment time ($n \geq 6$, $\pm$ sd).

Figure 3. Wilhelmy plate contact-angles of PE and PE/C11(:) samples that were treated with an argon plasma for 5 s and subsequently washed with an aqueous solution of 0.1 mM HCl. The advancing and receding contact angles are given as a function of the pH of the used solution ($n = 5$, $\pm$ sd).

of this technique relative to the modified region of the polymeric samples. For the system used, the penetration depth is calculated to be between 500 and 5000 nm,¹⁹ whereas the modification depth is expected to be only about 5 nm. Therefore, more surface-sensitive techniques have been used to study the surfaces in more detail.

Contact-Angle Determinations of (Modified) PE and PE/C11(:) Samples. The wettability of plasma-treated and washed PE and PE/C11(:) samples was investigated by determining the dynamic contact angles using aqueous solutions of 0.1 M HCl and 0.1 M NaOH (Figure 2). The advancing and the receding contact angles of plasma-treated and washed PE samples decreased as a function of the plasma treatment time. The advancing contact angle reached a plateau value of 80° and the receding contact angle reached a constant value of 0° after a plasma treatment time of 10 s. The decrease in the contact angle is probably due to oxidation of the PE samples during or after the plasma treatment.

The difference between the advancing and receding contact angles is defined as the contact-angle hysteresis. It is indicative of a rough or chemically heterogeneous surface comprising regions of varying wettability^{20,21} but can also be caused by rotational movement of hydrophilic groups away from the polymer/air interface.²² The relatively low contact-angle hysteresis of unmodified PE is due to the surface roughness. Since scanning electron microscopy did not show significant differences between the surface roughness of plasma-treated PE samples and untreated samples, an increased surface roughness is not the reason for the large increase in the contact-angle hysteresis. Most likely, the increase is caused by a combination of the presence of polar groups at the surface,

hydration of the surface, and their reorientation after contact with the liquid phase.

The results of the contact-angle determinations of plasma-treated and washed PE/C11(:) samples differed from that of the PE samples. Again the contact angles decreased as a function of the plasma treatment time. A small difference was observed between the advancing contact angles determined using 0.1 M HCl and 0.1 M NaOH. After a plasma treatment time of 10 s, the advancing contact angle of plasma-treated and washed PE/C11(:) samples reached a plateau value of 90°. The receding contact angles using 0.1 M HCl and 0.1 M NaOH differed strongly from each other, especially for plasma treatment times between 5 and 30 s. This difference was most pronounced at a plasma treatment time of 5 s. These observations can be ascribed to the presence of carboxylic acid groups at the surface of the plasma-treated and washed PE/C11(:) samples.^{23–27}

The dynamic contact angles of the PE and PE/C11(:) samples, which were plasma treated for 5 s and washed,

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Figure 4. XPS analysis of PE and PE/C11(·) samples that were treated with an argon plasma. The samples were not washed prior to XPS analysis. The atomic percentages of oxygen, sodium, and fluorine are given as a function of the plasma treatment time (when error bars are shown, $n \geq 3$).

were also determined using buffer solutions with varying pH values (Figure 3). It was assumed that, except for proton exchange, possible interactions of buffer constituents with the polymeric surfaces did not influence the contact-angle determinations. For the plasma-treated and washed PE samples, no significant differences in the advancing contact angle were observed over the measured pH range. The receding contact angles determined using buffer solutions with a high pH were lower than the contact angles determined at a low pH. The transition was observed at a pH of about 7. The same trend was observed for both the advancing and the receding contact angles of plasma-treated and washed PE/C11(·) samples. Although this effect is more pronounced for the receding contact angles than for the advancing contact angles, the advancing contact angles were significantly lower at pH = 11 and 13 than at pH = 1, 3, and 5 ($p < 0.05$).

The observed dependence of the wettability of polymeric samples on the pH is due to the presence of ionizable carboxylic acid groups at the surface. At a low pH, carboxylic acid groups present at the surface are protonated. Upon increasing the pH of the buffer solution, the carboxylic acid groups become more ionized. Due to the presence of the more hydrophilic anions at the surface, the wettability of the polymeric samples increases, resulting in a lower contact angle. At a certain pH, all carboxylic acid groups will be ionized and the contact angle becomes independent of the pH. The pK_{surface} , defined as the pH at which the transition between the higher and lower plateau values of the contact angles is observed, is approximately 7. This value is shifted about 2–3 units relative to the pK_a values of aliphatic carboxylic acids in aqueous solutions. This was also reported for other surfaces containing carboxylic acid groups and was attributed to the difficulty of forming charged groups at the interface.^{23–28} Analogous trends have also been reported for surfaces that contain basic moieties.^{24,29,30}

For the plasma-treated and washed PE samples, the effects of varying the pH of the buffer solution were less pronounced than for the plasma-treated and washed PE/C11(·) samples. This is probably due to the low amount of carboxylic acid groups on the plasma-treated and washed PE samples compared to the amount on the plasma-treated and washed PE/C11(·) samples.

XPS Analysis of (Modified) PE, PE/C11(·), and PE/C12 Samples. Although the presence of carboxylic acid groups at plasma-treated and washed PE/C11(·) samples was demonstrated with the use of ATR-FTIR spectroscopy and contact-angle determinations, these methods yield only qualitative information. Therefore, the modified surfaces were analyzed with XPS. This technique provides (semi)quantitative information on the chemical composition of the upper 100 Å of the surface. The oxygen level of plasma-treated PE samples increased with increasing plasma treatment time and reached a plateau value of about 11 atom % at a plasma treatment time of 10 s (Figure 4). This confirms the assumptions made in the previous sections that oxygen-containing groups were introduced at the plasma-treated PE surfaces.

The introduction of oxygen onto a PE surface by means of an argon plasma treatment is due to the effects of ultraviolet (UV) radiation and chemically active species produced by the plasma. UV radiation as well as the collision of metastables, and possibly ions, with the surface can produce free radicals.³¹ Some of these radicals remain entrapped in the sample and can react with oxygen when the plasma-treated surfaces are exposed to air.³² Besides radical formation, direct surface oxidation is possible if an oxygen source is present during plasma treatment.³³ Despite the fact that precautions are taken, oxygen sources such as small air leakages or water adsorbed onto the inside of the reactor walls and possibly onto the polymeric samples are present. Because the surface is also bombarded with argon ions, sputtering (etching) of the polymeric surface takes place.³⁴ At prolonged plasma treatment times, the processes of the formation of radicals and oxygen-containing groups at the surface and etching of the surface are in equilibrium. This leads to a constant oxygen level at plasma treatment times of more than 10 s.

The oxygen level of plasma-treated PE/C11(·) samples did not significantly change as a function of the plasma treatment time. Although oxygen is incorporated at the surface of these samples by the same mechanisms as described for the PE samples, carboxylate groups of the coated C11(·) molecules are simultaneously etched off from

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Table 2. XPS Analysis of Sodium 10-Undecenoate (C11(:)) before and after Treatment with an Argon Plasma for 150 s

compd	atomic %				
	C	O	Na	F	Si
C11(:)	76.7 (78.6)	14.3 (14.3)	9.0 (7.1)	<i>b</i>	<i>b</i>
C11(:), stored in plasma reactor	76.3	13.1	9.7	0.9	<i>b</i>
C11(:), Ar 150 s, Ar reactor	61.4	17.1	16.7	4.8	<i>b</i>
C11(:), Ar 150 s, CF ₄ reactor	48.3	18.9	14.8	16.6	1.4

^a The theoretical values for the untreated materials are given in parentheses. The C11(:) pellets were either stored in the plasma reactor for 14 h, treated with an argon plasma, or treated with an argon plasma in a reactor that is normally used for CF₄ plasma treatments. ^b No peaks were observed in the detail scans of the F 1s (680–700-eV) or Si 2p (95–115-eV) region.

the surface (decarboxylation). Incorporation of oxygen at the surface and decarboxylation result in a constant oxygen level of the plasma-treated PE/C11(:) samples at plasma treatment times longer than 2 s.

Besides the expected elements such as oxygen and sodium, also fluorine was detected at the surface of the plasma-treated PE/C11(:) samples. This fluorine level increased with increasing plasma treatment time. The binding energy of the F 1s electrons was 684.5 ± 0.3 eV, suggesting the presence of fluorine as fluoride ions.³⁵ Since no elements other than carbon, oxygen, and sodium were detected at the surface, it seems likely that the fluorine is present in NaF. The reported binding energy of F 1s electrons in NaF is 684.5 eV.³⁶ With conventional titration techniques, no fluoride ions could be detected in C11(:). Therefore, it can be concluded that the fluorine contamination was not present in the surfactant but was introduced during the argon plasma treatment.

To study the effects of an argon plasma treatment on C11(:) pellets of this surfactant were prepared and treated with an argon plasma for 150 s. Both untreated and plasma-treated pellets were analyzed with XPS (Table 2). The theoretical and measured elemental compositions of the untreated material agreed well. A small amount of fluorine was detected on the untreated pellet which was stored in the gas plasma reactor at a pressure of 10^{-6} mbar for 14 h. After argon plasma treatment, the atomic percentage of oxygen and sodium detected on the pellet was increased. The shoulder at the higher binding energy side of the C 1s spectra of the original pellets was largely reduced for the plasma-treated materials, indicating a strong decarboxylation of the materials (spectra not shown). Furthermore, an increase in the atomic percentage of fluorine was detected. The binding energy of the F 1s peak for all pellets was 684.7 ± 0.7 eV. This also indicates that the fluorine introduced during the argon plasma treatment was probably present in the form of NaF.

The introduction of fluorine onto the PE/C11(:) samples and the surfactant pellets during argon plasma treatment can be explained by the fact that the plasma apparatus is also used for tetrafluoromethane (CF₄) plasma treatment of polymers. Although the CF₄ and argon treatments are performed in different glass reactors, it is possible that fluorine-containing species remain at the walls of parts of the equipment that are not exchanged. During

evacuation and argon plasma treatment, fluoride-containing species can be released from these parts and form NaF with the positively charged sodium ions on the PE/C11(:) samples or C11(:) pellets. To verify this assumption, a C11(:) pellet was treated with an argon plasma for 150 s in the glass reactor normally used for the CF₄ treatments. XPS analysis of this pellet showed a very high atomic percentage of fluorine (Table 2). The F 1s spectrum consisted of two peaks with binding energies of 685.4 and 687.1 eV. Additional silicon was detected at the surface (103.8 eV). In this respect, it is worth mentioning that during plasma treatment of NaCl with fluorine-containing plasmas, Na₂SiF₆ was formed through the reaction of sodium ions with a fluorsilicon compound such as SiF₄. The binding energies of the F 1s and Si 2p electrons in Na₂SiF₆ are 686.4 and 104.2 eV, respectively. The formation of Na₂SiF₆ was considered to be a consequence of ablation of silicon from the glass tube.^{37,38} It is very well possible that the formation of NaF during argon plasma treatment of the PE/C11(:) samples and the introduction of fluorine and silicon at the surfactant pellets in this study is caused by analogous mechanisms.

In Figure 5, the results of the XPS analysis of plasma-treated samples which were subsequently washed with an aqueous solution of 0.1 mM HCl are presented. The oxygen levels of the plasma-treated and washed PE samples were comparable to the oxygen levels of the nonwashed PE samples. The atomic percentage of oxygen on the plasma-treated and washed PE/C11(:) samples was smaller than the atomic percentage detected on the plasma-treated PE/C11(:) samples before washing and also smaller than on the plasma-treated PE samples. Apparently, part of the oxygen-containing material is washed off from the plasma-treated PE/C11(:) samples. Oxygen of two different origins is probably removed from the plasma-treated PE/C11(:) samples during the washing procedure: carboxylate groups of surfactant molecules that are not immobilized on the surface and oxygen-containing groups introduced during or after plasma treatment on these surfactant molecules. No sodium could be detected on the plasma-treated and washed PE/C11(:) samples. So if C11(:) molecules were immobilized on the surface, the carboxylate groups were protonated during washing with an aqueous solution of 0.1 mM HCl. The possibility of this ion exchange was already demonstrated in the previous sections on ATR-FTIR spectroscopy and contact-angle determinations. After washing of the plasma-treated PE/C11(:) samples, also no fluorine could be detected at these surfaces anymore, indicating that the fluorine-containing contamination could easily be removed.

In order to detect carboxylic acid groups at the surface of plasma-treated and washed PE and PE/C11(:) samples, these samples were subjected to a derivatization reaction with TFE and analyzed with XPS. The results are presented in Figure 6. The oxygen levels of the TFE-derivatized samples were the same as the oxygen levels of the samples before derivatization. The fluorine content of the PE samples increased with increasing plasma treatment time and reached a plateau value of 1 atom % at a plasma treatment time of 10 s. The fluorine level of the PE/C11(:) samples initially increased with the plasma treatment time, reached a maximum of 5.3 atom % at a plasma treatment time of 5 s, and subsequently decreased.

XPS analysis of the TFE-derivatized PAAc samples showed values of 19.5 atom % O and 29.8 atom % F at the

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Figure 5. XPS analysis of PE and PE/C11(:) samples that were treated with an argon plasma and subsequently washed with an aqueous solution of 0.1 mM HCl. The atomic percentages of oxygen are given as a function of the plasma treatment time (when error bars are shown, $n \geq 3$).

Figure 6. XPS analysis of PE and PE/C11(:) samples that were treated with an argon plasma, washed with an aqueous solution of 0.1 mM HCl, and derivatized with TFE to tag carboxylic acid groups at the surface. The atomic percentages of oxygen and fluorine are given as a function of the plasma treatment time (when error bars are shown, $n \geq 3$).

surface compared to the expected theoretical values of 20 and 30 atom % at complete conversion of all the carboxylic acid groups present in the analyzed surface layer. Thus, TFE almost quantitatively reacts with carboxylic acid groups present at the surface of PAAc samples. Since TFE shows a minor side reaction only with surface epoxides,³⁹ the atomic percentage of fluorine is representative for the atomic percentage of oxygen present in carboxylic acid groups esterified with TFE at a surface. Thus, it can be calculated that at a plasma treatment time of 5 s, 47% of the oxygen detected at the surface of the plasma-treated and washed PE/C11(:) samples is present in carboxylic acid groups esterified with TFE compared to 7% for PE. Consequently, it is possible to introduce a relatively large amount of carboxylic acid groups onto PE by immobilizing a carboxylate-group-containing surfactant on a PE surface. Compared to the CO₂ plasma treatment of PE where only 14–25% of the oxygen introduced at the surface was present in carboxylic acid groups,^{8,9} the selectivity toward the introduction of carboxylic groups at a polymeric surface is greatly enhanced.

The competition between the immobilization and the removal of the coated surfactant layer due to etching of the surface is evident (Figure 6). Immobilization of C11(:) on PE resulted in the introduction of carboxylate groups onto the surface. However, after a plasma treatment time of 10 s, etching played a predominant role, resulting in a decrease in the amount of carboxylate groups. Apparently, the decarboxylation of the C11(:) layer is not as fast

Figure 7. XPS analysis of PE/C12 samples that were treated with an argon plasma, washed with an aqueous solution of 0.1 mM HCl, and derivatized with TFE to tag carboxylic acid groups at the surface. The atomic percentages of oxygen and fluorine are given as a function of the plasma treatment time (when error bars are shown, $n \geq 3$).

as found for PAAc,¹³ supporting the hypothesis that the sodium carboxylates are more stable during argon plasma treatment than the carboxylic acid groups. Consequently, it was possible to immobilize part of the coated C11(:) on PE before the surfactant layer was completely decarboxylated.

In Figure 7, the XPS results of plasma-treated, washed, and TFE-derivatized PE/C12 samples are presented. Although the atomic percentage of fluorine measured at these surfaces was higher than on the PE samples, it was much lower than the atomic percentage of fluorine detected on the PE/C11(:) samples. Thus, it can be concluded that

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Figure 8. Immobilization efficiency of a precoated layer of C11(:) and C12 onto PE given as a function of the argon plasma treatment time. The efficiency was calculated according to eq 1 (when error bars are shown, $n \geq 3$).

also C12 can be immobilized on PE, although the immobilization is less effective than the immobilization of C11(:) on PE.

Immobilization Efficiencies of C11(:) and C12 on PE. The results of immobilization of C11(:) and C12 on PE can be compared to each other by calculating their immobilization efficiencies (Figure 8). The immobilization efficiency is defined as the atomic percentage of oxygen present in carboxylic acid groups of immobilized surfactant molecules relative to the atomic percentage of oxygen present in carboxylate groups on precoated polymeric samples. The immobilization efficiency of C11(:) on PE is calculated according to (see Appendix)

$$\text{immobilization efficiency of C11(:) on PE [\%]} = \frac{\left\{ \frac{O_{\text{PE}} F_{\text{PE/C11(:)}} - O_{\text{PE/C11(:)}} F_{\text{PE}}}{1.5 O_{\text{PE}} - F_{\text{PE}}} \right\}}{O_{\text{PE/C11(:),coated}}} 100 \quad (1)$$

where O_{PE} , F_{PE} , $O_{\text{PE/C11(:)}}$, and $F_{\text{PE/C11(:)}}$ are the atomic percentages of oxygen and fluorine on plasma-treated, washed, and TFE-derivatized PE and PE/C11(:) samples, respectively, and $O_{\text{PE/C11(:),coated}}$ is the atomic percentage of oxygen on the precoated PE/C11(:) samples. The calculation of the immobilization efficiency of C12 on PE is performed using an equation analogous to eq 1.

The immobilization efficiency of C11(:) and C12 on PE showed a maximum at a plasma treatment time of 5 s, but the absolute value was much higher for C11(:) than for C12. At a plasma treatment time of 5 s, 28% of the initial amount of carboxylate groups in the precoated C11(:) layer was retained at the PE surfaces, whereas this was only 6% in the case of C12. These differences are caused by the presence of the terminal double bond of C11(:). Immobilization of surfactants on polymeric surfaces probably proceeds through a radical mechanism. Radicals are generated at the polymeric surface and the aliphatic chains of the surfactant molecules during plasma treatment. Recombination of a surface radical and a surfactant radical leads to the formation of a covalent bond. In addition, a surface radical may open the C=C bond of unsaturated surfactants. Apparently, this process has a higher probability than the recombination of a surface radical and a surfactant radical. Thus, unsaturation in the alkyl chain promotes the covalent coupling of C11(:) to the PE surface.

Based upon the thickness of the initially coated surfactant layers and the maximum values of the immobilization efficiency, an estimation can be made of the minimum surface area per carboxylic acid group for the immobilization of C11(:) ($\rho = 0.99 \text{ g/cm}^3$; $M = 206.3 \text{ g/mol}$)

and C12 ($\rho = 0.99 \text{ g/cm}^3$; $M = 224.3 \text{ g/mol}$). This results in values of 27 and $190 \text{ \AA}^2$ for the immobilization of C11(:) and C12 on PE, respectively. Taking into account the geometry of the C11(:) molecules, this would mean that on an average base about a monolayer of C11(:) is immobilized on the PE surface. However, such a monolayer is not an accurate picture of the actual situation because no ordered structure of the immobilized surfactant molecules is expected after plasma treatment.

The values of the immobilization efficiency obtained in this study are somewhat in contrast with previous studies on the immobilization of surfactants on polymeric surfaces by means of an argon plasma treatment. Immobilization efficiencies of 25% and 50% were reported when immobilizing SDS and DA·HCl, both saturated surfactants, on PP and PE, respectively.^{11,12} These differences may be explained by the fact that not only is the aliphatic chain of the surfactant of importance but the chemical structure of the surface also plays a predominant role (as for SDS on PP). In the case of the immobilization of DA·HCl, other aspects like immobilization through the functional group seem to play a role. A detailed study on the mechanism of immobilization of surfactants onto polymeric surfaces, in which the influence of the double bond in the surfactant chain and different polymeric substrates is discussed, is presented elsewhere.^{40,41}

Aging of the Modified PE Samples. Polymeric surfaces modified by gas plasma treatments may be susceptible to aging.^{9,42,43} This process depends on a number of factors such as temperature and storage environment and is responsible for changes in the surface composition of modified polymeric samples upon storage. Functional groups, initially present at the surface, can migrate away from the interface between the polymer and its environment in order to minimize the surface free energy. These rearrangements are initially limited to the upper layer of the surface and are presumably reversible. At prolonged storage times, segments containing functional groups can migrate further into the bulk of the polymer. This process is diffusion controlled and is claimed to be irreversible.^{9,43,44}

The stability of the plasma-treated and washed PE and PE/C11(:) samples was investigated by storing them in

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Figure 9. Wilhelmy plate contact-angles of PE and PE/C11(·) samples that were treated with an argon plasma for 5 s and subsequently washed with an aqueous solution of 0.1 mM HCl. The advancing and receding contact angles are determined using aqueous solutions of 0.1 M HCl and 0.1 M NaOH and are given as a function of the storage time at -20, 25, and 50 °C in air ($n = 3$, $\pm$ sd).

air at -20, 25, and 50 °C and by determining their wettability. Therefore, contact-angle determinations using aqueous solutions of 0.1 M HCl and 0.1 M NaOH were performed at different time intervals (Figure 9). At storage temperatures of -20 and 25 °C, no significant changes in the contact angles were observed up to an aging time of 2000 h (12 weeks). At 50 °C, both the plasma-treated and washed PE and PE/C11(·) samples showed a rapid increase in the advancing and receding contact angles within the first 2 days, after which they remained constant. The difference between the contact angles determined using 0.1 M HCl and 0.1 M NaOH remained also largely unaffected for the plasma-treated and washed PE and PE/C11(·) samples stored at -20 and 25 °C. Upon storage at 50 °C, the difference between the values of the advancing contact angles of the plasma-treated and washed PE/C11(·) samples disappeared. The difference between the values of the receding contact angles of the plasma-treated and washed PE samples seemed to become smaller, whereas for the values of the receding contact angles of the plasma-treated and washed PE/C11(·) samples, this difference remained the same.

The contact angles remained unchanged upon storage at -20 °C because at this temperature the mobility of functional-group-containing polymer chains is low. Upon increasing the temperature, the mobility increases and the contact angles will increase upon storage. At 25 °C, no significant changes could be observed, which indicates that the mobility is still limited. These observations are in contrast to the results of studies on the aging of CO₂ plasma-treated PE surfaces.^{9,43} In these studies, a rapid reorganization of the surface was observed when the CO₂ plasma-treated polymeric samples were stored in air at room temperature. An explanation for the observed stability of the plasma-treated and washed PE and PE/C11(·) samples is that argon and other noble gas plasma treatments of polymers result in a highly cross-linked surface matrix.⁴⁵⁻⁴⁷ Therefore, the chain segments at the

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surface may have a very restricted mobility, preventing large-scale rearrangements.

The rapid increase in the values of the contact angles in the first 2 days of storage at 50 °C may be caused by the movements of the polymer segments near the surface. It is possible that carboxylic acid groups at the surfaces of the plasma-treated and washed PE/C11(:) samples migrate away from the polymer–air interface at higher temperatures. The occurrence of this process is indicated by the convergence of the values of the advancing contact angles determined using 0.1 M HCl and 0.1 M NaOH. Because the difference between the values of the receding contact angles using these media remained unaltered, it is concluded that the rearrangements are only restricted to the uppermost surface and that the carboxylic acid groups already reappear at the polymer–liquid interface within the time interval necessary to perform the contact-angle determinations, which is of the order of a few minutes.

Applicability of the Current Modification Method.

The method of introducing carboxylic acid groups at PE can probably be expanded to a wide variety of polymeric surfaces, although in each particular case the method should be optimized. Furthermore, the geometries of the polymeric substrates can be varied, which makes this method widely applicable. The carboxylic acid groups introduced with this method are available for ion exchange, as was shown by ATR–FTIR spectroscopy and contact-angle determinations. Furthermore, XPS showed that small molecules like TFE can be covalently coupled to the carboxylic acid groups. The carboxylic acid groups are also suitable for reaction with larger molecules carried out in solution. In a separate study, it was demonstrated that the carboxylic acid groups can be used for the covalent immobilization of large molecules to the surface. Albumin–heparin conjugate was immobilized on PS surfaces via activation of carboxylic acid groups that were introduced at a PS surface by means of the method reported in this paper.⁴⁸

Conclusions

Carboxylate groups can be introduced at PE surfaces by immobilizing a precoated layer of the sodium salt of a fatty acid. The precoated layer was immobilized on the polymeric surface by means of an argon plasma treatment. The carboxylate groups are available for ion exchange and further covalent coupling. The presence of a carbon–carbon double bond in the alkyl chain of the sodium salt of the fatty acid enhances the immobilization efficiency. The selectivity and yield of the used modification method with respect to the introduction of carboxylic acid groups are largely improved compared to conventional gas-discharge techniques. Furthermore, the surfaces are more stable than surfaces modified with other gas-discharge techniques. No changes in the wettability are observed when the modified polymeric samples are stored at room temperature for at least 12 weeks.

Acknowledgment. This study was financed by Cordis Europa N.V., Roden, The Netherlands.

Appendix: Calculation of the Immobilization Efficiency of C11(:) on PE

When PE samples are treated with an argon plasma, the polymeric surface is oxidized. Part of the oxygen that is introduced at the surface is present in carboxylic acid groups. These carboxylic acid groups can be derivatized

Figure 10. Schematic representation of plasma-treated, washed, and TFE-derivatized PE and PE/C11(:) samples. On the PE/C11(:) samples, oxygen and fluorine originate from the immobilized and derivatized C11(:) molecules (1) and from the oxygen-containing functional groups including carboxylic acid groups introduced by the oxidation during plasma treatment (2).

with TFE (Figure 10). When PE/C11(:) samples are treated with an argon plasma, part of the coated surfactant layer is immobilized. Simultaneously, the surface is oxidized. Carboxylic acid groups of both sources are derivatized with TFE (Figure 10).

The atomic percentages of oxygen and fluorine at the surfaces of the plasma-treated, washed, and TFE-derivatized PE samples are represented by O_{PE} and F_{PE} , respectively. The atomic percentages of oxygen and fluorine at the surfaces of plasma-treated, washed, and TFE-derivatized PE/C11(:) samples present in the immobilized surfactant molecules are represented by $O_{PE/C11(:)}^1$ and $F_{PE/C11(:)}^1$, respectively. Finally, the atomic percentages of oxygen and fluorine that are present in the oxidized part of the surfaces of the plasma-treated, washed, and TFE-derivatized PE/C11(:) samples are represented by $O_{PE/C11(:)}^2$ and $F_{PE/C11(:)}^2$, respectively. The total atomic percentages of oxygen ($O_{PE/C11(:)}$) and fluorine ($F_{PE/C11(:)}$) at the surfaces of the plasma-treated, washed, and TFE-derivatized PE/C11(:) samples are given by

$$O_{PE/C11(:)} = O_{PE/C11(:)}^1 + O_{PE/C11(:)}^2 \quad (A1)$$

$$F_{PE/C11(:)} = F_{PE/C11(:)}^1 + F_{PE/C11(:)}^2 \quad (A2)$$

The immobilization efficiency of C11(:) on PE is defined as the atomic percentage of oxygen present in the carboxylic acid groups of immobilized surfactant molecules relative to the atomic percentage of oxygen present in the carboxylate groups on precoated PE/C11(:) samples ($O_{PE/C11(:),coated}$):

immobilization efficiency of C11(:) on PE [%] =

$$\frac{O_{PE/C11(:)}^1}{O_{PE/C11(:),coated}} 100 \quad (A3)$$

When it is assumed that TFE quantitatively reacts with only carboxylic acid groups at the polymeric surfaces and that the expansion of the derivatized surface layer due to the introduction of the TFE molecules is one-dimensional and perpendicular to the sample surface, the immobilization efficiency of C11(:) on PE can be calculated according

immobilization efficiency of C11(:) on PE [%] =

$$\frac{F_{PE/C11(:)}^1}{1.5 O_{PE/C11(:),coated}} 100 \quad (A4)$$

Furthermore, it is assumed that the relative amount of carboxylic acid groups at PE and PE/C11(:) surfaces that

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is introduced through oxidation during the argon plasma treatment is the same. Thus

$$\frac{F_{\text{PE/C11}(\cdot)}^2}{O_{\text{PE/C11}(\cdot)}^2} = \frac{F_{\text{PE}}}{O_{\text{PE}}} \quad (\text{A5})$$

Combination of eqs A2 and A5 yields

$$F_{\text{PE/C11}(\cdot)}^1 = F_{\text{PE/C11}(\cdot)} - \frac{O_{\text{PE/C11}(\cdot)}^2}{O_{\text{PE}}} F_{\text{PE}} \quad (\text{A6})$$

Combination of eqs A1 and A3 yields

$$O_{\text{PE/C11}(\cdot)}^2 = O_{\text{PE/C11}(\cdot)} - \frac{(\text{imm. eff. of C11}(\cdot) \text{ on PE [\%]) } O_{\text{PE/C11}(\cdot), \text{coated}}}{100} \quad (\text{A7})$$

Finally, the immobilization efficiency of C11(·) on PE can be calculated by combination of eqs A4, A6, and A7:

$$\text{immobilization efficiency of C11}(\cdot) \text{ on PE [\%]} = \frac{\left\{ \frac{O_{\text{PE}} F_{\text{PE/C11}(\cdot)} - O_{\text{PE/C11}(\cdot)} F_{\text{PE}}}{1.5 O_{\text{PE}} - F_{\text{PE}}} \right\}}{O_{\text{PE/C11}(\cdot), \text{coated}}} 100 \quad (\text{A8})$$

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