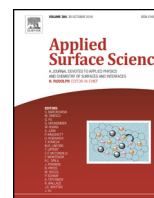




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Photografting of perfluoroalkanes onto polyethylene surfaces via azide/nitrene chemistry

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ABSTRACT

Water, oil and dirt repellent surfaces of plastic materials are desirable for many applications. Polyethylene is a common plastic and, because of its inertness, difficult to graft. We chose polyethylene as example because of its ubiquity and model character. As graft chains perfluoroalkanes were chosen, and photografting was selected as grafting method.

Photolytically generated nitrenes can insert into carbon-hydrogen bonds and are therefore suited for binding to polyethylene. Hydrophobic photo reactive surface modifiers based on azide/nitrene chemistry are designed, synthesized in high yield and characterized. Four new molecules are described.

One problem is to demonstrate that the photografted surface modifiers are bound covalently to the polyethylene. Abrasion tests show that all new molecules, when photografted to polyethylene, have a higher abrasion resistance than a polyethylene surface coated with a long-chain perfluoroalkane. An abrasion model using ice is developed. Also, other issues are addressed, such as differences in the UV-spectra of the new compounds in solution and in the neat state. Exitonic coupling of the chromophores of the surface modifiers is observed for specific molecules. A linear correlation of water contact angle with fluorine surface content, as measured by photoelectron spectroscopy, in grafted polyethylene surfaces is established.

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1. Introduction

Highly hydrophobic surfaces are desirable for many purposes, such as water, oil and dirt repellent outfit of polymeric materials. Polyethylene finds widespread uses as commodity plastic in a wealth of consumer goods. We therefore set ourselves to modify polyethylene surfaces in such a way that they become strongly hydrophobic. Further, this hydrophobicity should be resistant against abrasion and wear. From the point of view of a chemist, polyethylene is interesting as an example polymer, because it consists of carbon-carbon and carbon-hydrogen bonds only, which make it very inert and difficult to modify. If polyethylene surfaces can be rendered strongly and permanently hydrophobic, then other plastics could presumably be treated in the same way. Perfluorinated alky chains are known to possess a high water- and

oil repellency which makes them apt to be used as hydrophobic surface modifiers. The task therefore is to graft polyethylene with perfluorinated alky chains.

The modification of polymer surfaces has become an important theme for many applications [1]. From the methods developed, surface grafting has emerged as simple, useful and versatile approach. One of the major techniques is ultra violet (UV) light induced grafting, in all of its variations [2]. Yet unreactive surfaces, such as the surfaces of polyolefines, can be grafted using UV-light [3]. However, drastic conditions have to be used which were originally developed for photoaffinity labeling in bio-chemistry [4]. This method relies on photochemically generated singlet nitrenes. A singlet nitrene is a nitrogen species having only six valence electrons (a sextet), that is highly reactive and therefore capable of inserting even into carbon-hydrogen bonds of the substrate [5,6]. This approach has been applied to surfaces, too. Two publications describe the surface modification of polysulfon with polyethylene glycol using photochemically generated nitrenes for the prevention of cell adhesion [7,8].

The precursor molecule for the generation of a nitrene species usually is an azide [9,10]. Organic azides intermediately form

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nitrenes by the uptake of energy, such as temperature or light, followed by the elimination of dinitrogen. However, because nitrenes are highly reactive, rearrangements of the parent molecule are frequent [11]. In order to convert azides into nitrenes by UV-radiation, the azide has to be bound to a chromophore (a light absorbing part), that is, an aromatic moiety. Since aromatic systems are stabilized by resonance, rearrangements of the intermediate nitrene are somewhat suppressed. However, one of the main reactions of phenyl nitrenes is their ring expansion to azacycloheptatetraenes which react further and do not yield the insertion product [12]. Hence, perfluorinated phenyl nitrenes were investigated and it was found that by their use rearrangements can be hindered in such a way that the desired carbon-hydrogen insertion reaction becomes dominant [12,13]. Adhesion promoters on the basis of photoreactive perfluorophenyl azide derivatives have been developed [14].

The desired hydrophobic and oleophobic effect is caused by the highly water repellent perfluorinated carbon chain. Such a chain has to be attached to the perfluorophenyl azide in order to obtain a photo reactive surface modifier. As fluorotelomer alcohols are readily available (they are extensively employed as water and dirt repellent substituents in the textile industry) it immediately suggests itself to use those alcohols as the hydrophobic part in the new molecules. Linking the fluorotelomer alcohol to the perfluorophenyl azide moiety is conveniently achieved by an ester functionality. The target molecule is therefore composed of four segments: The azide as the reactive group, the perfluorinated aromatic ring as chromophore and stabilizer, the ester functionality as linker and the fluorotelomer alcohol as the hydrophobic part. In the following sections synthesis, photochemistry and stability studies of the new molecules and surfaces are described.

2. Materials and methods

2.1. Materials

All Chemicals were used without further purification. Fluoro-carbon chemicals were purchased from Apollo Scientific Ltd, UK. Anhydrous dichloromethane was purchased from TCI Deutschland GmbH. Sodium azide (purum, p. a., $\geq 99.0\%$) and triethylamine (puriss, p. a., $\geq 99.5\%$) were from Sigma-Aldrich Chemie GmbH, Switzerland. Other chemicals were purchased from Sigma-Aldrich Chemie GmbH, Switzerland. Polyethylene was a high-density Borstar ME3440 type from Borealis, and the polyethylene plates had a thickness of 2 mm.

2.2. Instrumentation

Melting points were determined on a Differential Scanning Calorimeter, DSC 204 F1 Phoenix from Netzsch Gerätebau GmbH. UV-Spectra were recorded on a Perkin Elmer 950 Spectrophotometer, equipped with a 150 mm integrating sphere for the neat spectra; fluorescence spectra on a LS 55 Fluorescence Spectrometer from Perkin Elmer. ATR-IR spectra were recorded using a Perkin Elmer Spectrum 100 FT-IR Spectrometer. Most NMR Spectra were run on a Bruker Ascend™ 500 instrument. The MALDI-MS and the elemental analyses were from the Lab. for Organic Chemistry, ETH Zurich, Switzerland. Static water contact angles were measured using a Krüss DSA 100 instrument. XPS Spectra were obtained using a SPECS™ spectrometer from SPECS GmbH, Berlin, Germany. The UV radiometer was an UVpad spectral radiometer from Opsytec Dr. Gröbel GmbH, Germany. The UV belt drier was from Uviterno AG, Switzerland, equipped with a 150 mm light tube with a maximal power of 3 kW. Standard irradiation procedure was as follows: Speed of the belt: 0.026 m/s; lamp power 1.2 kW; dis-

tance lamp-sample 0.07 m. The spray-coated polyethylene samples were exposed 2 to 3 times to these conditions.

2.3. General method for the synthesis of pentafluorobenzoates (4a–d)

The reaction was kept under an inert atmosphere of dry nitrogen at all times. To a stirred solution of 1 equiv. fluorotelomer alcohol 3a–d in dry dichloromethane (about 0.3 molar for alcohols 3a–c; about 0.05 molar for alcohol 3d) at 0 °C was added 1.05 equiv. perfluorobenzoyl chloride (2) via a syringe. Then, 2.1 equiv. of triethylamine were added via a syringe. The mixture was stirred for 2 h at 0 °C, allowed to warm to room temperature and stirred overnight.

Work up: The solution was washed twice with equal amounts of 1 molar hydrochloric acid. Then, the organic phase was washed once with saturated sodium bicarbonate solution and once with water. The organic phase was dried with anhydrous sodium sulfate, filtered, and the dichloromethane was distilled off. The perfluorobenzoates were not purified but used as obtained for the next step.

2.4. 1H, 1H, 2H, 2H-Nonafluoro-1-hexyl Pentafluorobenzoate (4a)

Liquid, yield 95% ATR-IR 1746, 1653, 1499, 1331, 1216, 1132, 1007 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.70 (t, J=6.4 Hz, 2H) 2.63 (t x t, J=6.4 Hz, $^3\text{J}(^{19}\text{F}, ^1\text{H})=18.1$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.6, 146.7–136.6, 121–107, 58.3 t, $^3\text{J}(^{19}\text{F}, ^{13}\text{C})=4.6$ Hz, 30.3 (t, $^2\text{J}(^{19}\text{F}, ^{13}\text{C})=22.0$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ –81.4 (m), –114.1 (m), –124.7 (m), –126.2 (m), –138.1 (m), –148 (m), –160.5 (m).

2.5. 1H, 1H, 2H, 2H-Tridecafluoro-1-octyl Pentafluorobenzoate (4b)

Liquid, yield 96% ATR-IR 1746, 1653, 1500, 1331, 1190, 1144, 1009 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.70 (t, J=6.5 Hz, 2H) 2.63 (t x t, J=6.4 Hz, $^3\text{J}(^{19}\text{F}, ^1\text{H})=18.1$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.6, 146.7–136.6, 121–107, 58.2 (t, $^3\text{J}(^{19}\text{F}, ^{13}\text{C})=4.5$ Hz), 30.3 (t, $^2\text{J}(^{19}\text{F}, ^{13}\text{C})=21.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ –81.5 (m), –114.1 (m), –122.3 (m), –123.3 (m) –126.2 (m), –124.0 (m), –126.6 (m), –138.4 (m), –148.5 (m), –161.0 (m).

2.6. 1H, 1H, 2H, 2H-Heptadecafluoro-1-decyl Pentafluorobenzoate (4c)

Solid, yield 97% ATR-IR 1738, 1652, 1501, 1332, 1197, 1145, 987 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 4.69 (t, J=6.4 Hz, 2H) 2.61 (t x t, J=6.4 Hz, $^3\text{J}(^{19}\text{F}, ^1\text{H})=18.0$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.6, 147–136, 119–107, 58.3 (t, $^3\text{J}(^{19}\text{F}, ^{13}\text{C})=4.8$ Hz), 30.4 (t, $^2\text{J}(^{19}\text{F}, ^{13}\text{C})=22.0$ Hz); ^{19}F NMR (282 MHz, CDCl_3) δ –81.1 (m), –113.8 (m), –121.8 (m), –122.1 (m), –122.9 (m), –123.7 (m), –126.3 (m), –138.0 (m), –147.9 (m), –160.4 (m).

2.7. 1H, 1H, 2H, 2H-Henicosafuoro-1-dodecyl Pentafluorobenzoate (4d)

Solid, yield 97% ATR-IR 1738, 1653, 1529, 1497, 1199, 1147, 1006 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.68 (t, J=6.4 Hz, 2H) 2.61 (t x t, J=6.4 Hz, $^3\text{J}(^{19}\text{F}, ^1\text{H})=18.1$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.8, 147–137, 119–107, 58.5 (t, $^3\text{J}(^{19}\text{F}, ^{13}\text{C})=4.6$ Hz), 30.6 (t, $^2\text{J}(^{19}\text{F}, ^{13}\text{C})=21.9$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ –81.0 (m), –113.8 (m), –121.9 (m), –122.0 (m), –122.8 (m), –123.7 (m), –126.3 (m), –137.9 (m), –147.7 (m), –160.3 (m).

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