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PAPER

Surface modification of polymers by reduction of
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This paper describes the grafting of diazonium salts on polymethylmethacrylate (PMMA), a polymer of wide use. Diazonium salts have been grafted by reduction with hypophosphorous acid, or by thermal decomposition. The nanometer thick films have been characterized by IR, XPS and water contact angle and the thickness of the film estimated. With long chain perfluoroalkyl substituents on the aryldiazonium group a water contact angle of 108° can be obtained on the smooth polymer, highlighting a hydrophobic surface. This process could be useful for modifying the PMMA surface when used as a glass substitute or as a substrate for microfluidic devices.

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Introduction

The modification of surfaces by reaction with diazonium salts is now a widely used method (Scheme 1).¹ It has evolved from laboratory experiments² to real life applications³ such as inks and paints,⁴ stents in the medical field,⁵ and thin layers for micro-electronics.⁶ This functionalization is assigned to the reaction of aryl radicals with various surfaces.⁷ Unless special conditions are used,⁸ this reaction usually provides multilayer films by further attack of the radicals on the first grafted aryl groups (Scheme 1). It has been applied to carbon in its various forms: diamond, glassy carbon, highly oriented pyrolytic graphite (HOPG), carbon fibers and felts, carbon nanotubes, and graphene; to different metals (from precious to industrials): such as Au, Pt, Cu, Ni, Fe, and Zn; to semiconductors: Si, Ge, and GaAs; to oxides: ITO (Indium Tin Oxide), SnO₂, TiO₂, and Fe₃O₄ nanoparticles. The aryl radical can be obtained by electrochemical reduction on conducting substrates,^{1,2} by addition of a reducing reagent (ascorbic acid,⁹ hypophosphorous acid,¹⁰ and iron¹¹), by reduction by the substrate itself if it is reducing enough (iron and carbon)¹² and by photochemical reduction in the presence of a sensitizer.¹³ The formation of the radical can also result from thermolysis,¹⁴ solvolysis,¹⁵ microwave irradiation,¹⁶ ultrasonication¹⁷ or from the decomposition of the diazoate¹⁸ formed in basic solution. However, the reaction of the highly reactive aryl radical on polymer surfaces has been little explored. Teflon has been reduced to a carbonaceous

material that was then reacted with a diazonium salt.¹⁹ A cation exchange membrane (Selemion CMV) made of sulfonated styrene and divinylbenzene²⁰ and a polysulfone membrane²¹ have been modified by reduction of the diazonium salt by iron powder and hypophosphorous acid respectively. Polyaniline has also been modified with diazonium salts.²²

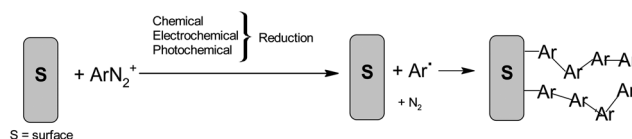
This paper presents the surface modification of PMMA, $[-CH_2-C(CH_3)-C(=O)(OCH_3)-]_n$, a polymer of wide use, by reaction with diazonium salts. This polymer is used as a transparent glass substitute for example in commercial aquariums, windows for submersibles, lenses for automobile lights; in surgery particularly as bone cement²³ and dental filling²⁴ materials, for microfluidic devices²⁵ and also for artistic uses.

Surface modification of PMMA has been achieved mainly by plasma irradiation. Atmospheric pressure air^{26,27} and oxygen^{28–31} discharge plasma increase the surface oxygen-containing polar groups such as alcohols, ketones, carboxylic acids and the hydrophilicity of the surface,²⁹ these groups permit further functionalization with, for example, streptavidin.²⁸ 2-Hydroxyethylmethacrylate (HEMA) was immobilized on PMMA intraocular lens by dielectric barrier discharge plasma; hydrophilicity of the samples was significantly and permanently improved.³² Photobioreactors using microalgae were surface treated with plasma and fluorocarbon resin to prevent the adhesion of algae.³³ Deposition of the fluorocarbon polymer onto PMMA can be accomplished *via* exposure to hexafluoropropylene

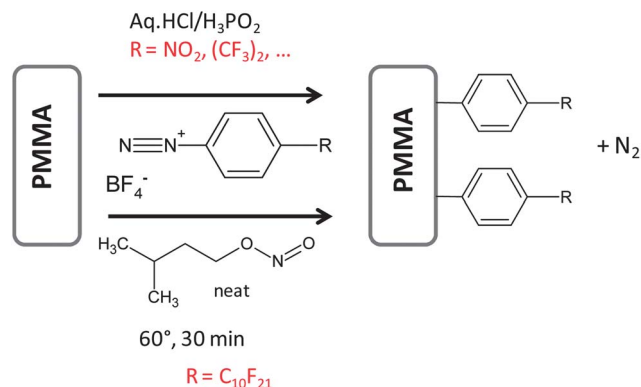
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Scheme 1 Principle of surface grafting by diazonium salts.



Scheme 2 Schematic grafting of PMMA by reaction with 4-perfluorodecylbenzene diazonium.

(HFP) plasma, resulting in an increased water contact angle of PMMA from 70 to 110 degrees.³⁴ Corona discharge has also been used to modify the surface of PMMA and permits its reaction with 3-(trimethyloxysilyl)propylmethacrylate.³⁵ Chemical methods can also be used for the surface modification of PMMA. Basic hydrolysis of a PMMA copolymer (poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate)) provides a high surface concentration of carboxylic groups.³⁶ Surface modification of PMMA microchips has been achieved with amino-poly(ethyleneglycol) or polyethyleneimine by a nucleophilic addition–elimination reaction. The esters of PMMA undergo this reaction at their acyl carbon atoms when treated with primary or secondary amines in the presence of electron donors in a basic aqueous solution.³⁷ Direct fluorination with F₂ gas is also possible.³⁸

Modification of polymer surfaces by “grafting onto”³⁹ can also be performed by insertion of carbenes in the C–H bonds of the polymer,⁴⁰ for example a dual-functional copolymer, poly(4-styrenesulfonylazide-*co-tert*-butyl-methacrylate), has been photografted on polycarbonate.⁴¹ This reaction has been applied to a number of polymers such as polyethylene,⁴² poly(etheretherketone).⁴³ Polyphenylene films have been electrografted on carbon by reduction of diazonium salts, and on top of these films, a second layer was attached by photopatterning arylazides.⁴⁴ Photografting through benzophenone groups is also possible; a film of benzoyl-phenyl groups bonded by reduction of the corresponding diazonium salt can be bonded to polystyrene⁴⁵ or methacrylic acid⁴⁶ through an H-abstraction by the biradical of benzophenone.⁴⁷

In this paper, we show that the surface of PMMA can be modified with a number of diazonium salts including 4-perfluoroalkyldiazonium salts that lead to very hydrophobic films on smooth PMMA surfaces. The thickness of the film has been estimated. After modification the surfaces remain transparent, and we also provide a test of environment durability of the modified surface. The modified surfaces will be designated as **PMMA-C₁₀F₂₁** for a surface grafted with perfluorodecyl groups as presented schematically in Scheme 2.

Experimental section

PMMA was an industrial sample from Weber Metaux, Paris; it was obtained as large 2 mm thick sheets that were cut into 1 × 1

or 5 × 5 cm plates (the largest ones being used for an environment durability test). The samples were rinsed with ethanol, ultrapure water and dried before use. Hypophosphorous acid and isopentyl nitrite were obtained from Sigma Aldrich.

4-Substituted aniline ArNH₂ (Ar = –C₆H₄OH, –CH₂OH, –COOH, –SO₂NH₂, –C₆H₄–(OCH₃)₂, –C₆H₄–(CH₃)₂, –C₆H₃–(CF₃)₂, –C₆H₄–I and –C₆H₄–C₆H₄–NO₂) was obtained from Sigma Aldrich; 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide and 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorodecane were obtained from Lancaster, all of them were used without further purification. The synthesis of NH₂–C₆H₄–C₆F₁₃ has been described previously⁴⁸ and NH₂–C₆H₄–C₁₀F₂₁ was prepared as follows:⁴⁹ a mixture of 4-iodoaniline (0.3 g, 1.4 mmol), 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorodecane (1 g, 1.5 mmol) and copper (0.3 g, 4.6 mmol) in DMSO (5 mL) was heated to 140 °C under argon for 3 h. Addition of charcoal to this dark solution and stirring for 15 minutes lead to a clear mixture after filtration. The filtrate was diluted with 50 mL of ether and washed with water and brine then dried over magnesium sulfate. Removal of the solvent followed by crystallization in ether–hexane gave 0.7 g, 73% of white solid. NH₂–C₆H₄–C₁₀F₂₁. Mp 78.5 °C. IR, cm^{–1}: 1598 (C=C_{Ar}), ¹H-NMR δ: 3.95 (br s, 2H), 6.75 (d, *j* = 8.2 Hz, 2H), 7.33 (d, *j* = 8.2 Hz, 2H); ¹³C-NMR δ: 107–109 (m), 110–112 (m), 114, 118 (m), 128.3, 149.8; ¹⁹F NMR δ: –53.6, –50.2, –49.5, –49.4, –48.9, –37.1 (m), –8.4 (m).

Diazonium salts

4-Nitrobenzenediazonium tetrafluoroborate was obtained from Sigma Aldrich. ArN₂⁺BF₄[–] (Ar = C₆H₄OH, –CH₂OH, –COOH, –SO₂NH₂, –C₆H₄–(OCH₃)₂, –C₆H₄–(CH₃)₂, –C₆H₃–(CF₃)₂, –C₆H₄–C₆F₁₃, and –C₆H₄–C₆H₄–NO₂) was prepared in aqueous 25% HBF₄ in the presence of 1.1 mole equivalent of NaNO₂ from the commercial amines, filtered, rinsed with ether, dried under vacuum, and stored at –20 °C.

The diazonium salt of 4-perfluorodecylbenzenediazonium was prepared in pure isopentyl nitrite and thermally decomposed (60 °C) in the same medium.⁵⁰

Modification of PMMA surfaces

Two methods were used for the surface modification of PMMA samples. In the first, they were stirred in a solution containing HCl (0.5 M) and hypophosphorous acid H₃PO₂ as the reducing agent (50 : 50 v/v) and the diazonium tetrafluoroborate was added (final concentration, *c* = 20 mM); stirring was continued for 30 minutes (Method 1). Another solution containing HBF₄ (50%) and H₃PO₂ (50%) (50 : 50 v/v) gave similar results. In the second method (Method 2), the amine NH₂–C₆H₄–C₁₀F₂₁ (*c* = 50 mM) was prepared, transformed into the diazonium salt and at the same time grafted on PMMA by immersion in isopentyl nitrite (without solvent) and heated at 60° for 30 minutes.⁵⁰ The PMMA samples were then rinsed with alcohol followed by ultrapure water. Method 2 was used for 4-perfluorodecylbenzenediazonium that is not soluble enough in aqueous medium. To demonstrate the radical character of both Methods 1 and 2 a radical trap (4-hydroxy-TEMPO, Aldrich) was

added in equimolar amounts to the 4-nitrobenzene diazonium (Method 1) and 4-nitroaniline (Method 2).

IR spectra

IRRAS and ATR spectra were recorded using a JASCO FT/IR-6100 Fourier Transform Infra Red Spectrometer equipped with an MCT detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm^{-1} . The background recorded before each spectrum was that of a clean PMMA substrate.

Thickness of the film

It was estimated by two methods: in the first one the IRATR absorbance of a SAM of 4-nitrobenzenethiol was compared with that of a **PMMA-NO₂** film. The sum of the s- and as-NO₂ stretching bands was compared as their ratio depends on the orientation and the organization of the groups on the surface due to the IR selection rules on surfaces.^{51,52} In the second

method the visible spectrum (Jasco V630) of **NH₂-C₆H₄-C₆H₄-NO₂** was recorded ($\lambda_{\text{max}} = 433\text{ nm}$) and **⁺N₂-C₆H₄-C₆H₄-NO₂**, prepared in aqueous solution as above, was grafted on PMMA by Method 1. The visible spectrum of **PMMA-C₆H₄-C₆H₄-NO₂** was recorded ($\lambda_{\text{max}} \sim 450\text{ nm}$); the absorbances of two visible spectra were compared assuming the same molar absorptivity: $\text{Abs}(\text{NH}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NO}_2)/\text{Abs}(\text{PMMA-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NO}_2) = cl/l$ where c is the concentration in mol cm^{-3} of an ACN solution of **NH₂-C₆H₄-C₆H₄-NO₂**, l is the pathlength in cm and l is the surface concentration in mol cm^{-2} .

XPS spectra

X-ray photoelectron spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a micro-focused, monochromatic Al K α X-ray source (1486.6 eV) and a magnetic lens, which increases the electron acceptance angle and hence the sensitivity. An X-ray beam of 650 μm size was used (15 kV \times

Table 1 Modification of PMMA samples by different diazonium salts

	Water contact angle, degrees	Characteristic IR bands (wavenumbers, cm^{-1})		
PMMA	72.7 ± 3.6	Unmodified CH stretch 2993, 2949 C=O 1726 C-O-C 1141		
Benzenediazonium salt^{a,b} (⁺N₂-C₆H₄R)		Modified surfaces	PMMA-Ar	C₆H₅R^c or ⁺N₂C₆H₄R^d
4-Hydroxy ^a (-C ₆ H ₄ -OH)	60.5 ± 7.3	-OH stretch	3548, 3271	3229 ^c
		Ring vibration	1622, 1563, 1517	1606, 1598, 1569, 1532, 1501
4-Hydroxymethyl ^a (-C ₆ H ₄ CH ₂ OH)	65.2 ± 1.3	Out-of-plane CH	732	754, 691
		-OH stretching	3264	3226 ^c
		as CH ₂ stretching	2928	2932
		s CH ₂ stretching	2851	2875
4-Carboxy ^a (-C ₆ H ₄ -COOH)	67.6 ± 4.7 76.0 ± 4.7^f	Ring vibration	1622, 1559	1607-1454
		-COOH	3646-3012	3073-2554 ^c
		-C=O	^g	1689
		Ring vibration	1615, 1559, 1503	1603, 1585, 1464
4-Sulfonamido ^a (-C ₆ H ₄ -SO ₂ -NH ₂)	76.1 ± 4.7	Out-of-plane CH	833	709
		NH ₂ stretching	3215, 3133	3346, 3248 ^c
		Ring vibration	1485	1453
4-Nitro ^a (-C ₆ H ₄ -NO ₂)	85.1 ± 2.2	Sulfone	1386	1377, 1366
		Ring vibration	1598	1607 ^c
		as NO ₂ stretching	1520	1521
3,5-Dimethoxy ^a (-C ₆ H ₄ -(OCH ₃) ₂)	89.4 ± 2.9	s NO ₂ stretching	1347	1347
		Ring vibration	1459	1685, 1616, 1483 ^c
		as O-CH ₃ stretch	1216	1221
3,5-Dimethyl ^a (-C ₆ H ₃ -(CH ₃) ₂)	85.9 ± 2.3	s O-CH ₃ stretch	1177	1164
		as C-H stretching	2968, 2916	2946, 2921 ^c
		s C-H stretching	2848	2864
3,5-Bis-trifluoromethyl ^a (-C ₆ H ₃ -(CF ₃) ₂)	94.8 ± 2.9	Ring vibration	1469	1592-1462
		Ring vibration	1620	1596 ^d
4-Perfluorohexyl ^a (-C ₆ H ₄ -C ₆ F ₁₃)	108.1 ± 3.3	CF ₃	1280, 1132	1275, 1139
4-Perfluorodecyl ^b (-C ₆ H ₄ -C ₁₀ F ₂₁)	107.6 ± 5.8	CF ₂ , CF ₃	1213, 1182	1205, 1150 ^{c,e}
		CF ₂ , CF ₃	1209, 1150	1205, 1150 ^e



^a Reduction by hypophosphorous acid (Method 1). ^b By heating in the presence of isopentyl nitrite (Method 2). ^c C₆H₅-R from ref. 54. ^d Diazonium salt. ^e Perfluorodecylamine. ^f After dipping in NaOH 5%. ^g Hidden by the residual PMMA bands.

200 W) [500 μm (15 kV to 150 W) for linescans]. The pass energy was set at 150 and 40 eV for the survey and the narrow regions, respectively. The *Avantage* Software, version 4.67, was used for digital acquisition and data processing. The spectra were calibrated against C1s set at 285 eV.

Water contact angles

They were measured with a Krüss DSA3 instrument. 3 μL of Milli-Q water was automatically deposited on the top of the test sample placed in a horizontal position on the instrument stage. At least five measurements were conducted for each sample. The values of the contact angles were calculated by the tangent method using Drop Shape Analysis software.

Results and discussion

As shown in Scheme 2, two methods were used for the surface modification of PMMA samples. Either by reduction of the diazonium salt in the presence of hypophosphorous acid (Method 1) or by thermal decomposition at 60° of the diazonium salt prepared *in situ* by reaction of the amine $\text{NH}_2\text{-C}_6\text{H}_4\text{-C}_{10}\text{F}_{21}$ with neat isopentyl nitrite (Method 2) as the corresponding diazonium salt is not soluble enough in water. The samples were characterized by IRATR, XPS and through their water contact angle. The IR and water contact angle results are gathered in Table 1.

IR spectra

Fig. 1 presents the IRATR spectra of PMMA modified by reaction with 4-nitro (*PMMA-NO₂*), 3,5-bis-trifluoromethyl (*PMMA-(CF₃)₂*), and perfluorodecylbenzenediazonium tetrafluoroborate (*PMMA-C₁₀F₂₁*); the IR signature of these three groups is clearly observed (Table 1). Note that the last spectrum corresponds to disordered chains; the spectrum of Fig. 1c that corresponds to surface bonded 4-perfluorodecylphenyl groups is similar to that of liquid 4-perfluorodecylaniline, but different from the spectrum of the ordered perfluorothiol SAMs $(\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH})^{49,53}$ that present very strong bands at 1372 and 1336 cm^{-1} .

XPS spectra

The surface was also characterized by XPS, the spectrum of *PMMA-C₁₀F₂₁* is presented in Fig. 2. The survey spectrum shows the presence of carbon C1s (281–298 eV, 52.5 atom%), oxygen O1s (532.8 eV, 8.5 atom%), fluor F1s (689.4 eV, 38.9%; by comparison 689.67 eV for polytetrafluoroethylene⁵⁵) and F2s (34.5 eV) and a minute amount of nitrogen (that is nearly always observed during the grafting of diazonium salts and has been assigned to azo bonds inside the film⁵⁶). The presence of F1s and F2s, and the high percentage of fluorine indicate the presence of the perfluoro group and the baseline steps observed after the peaks F1s and F2s correspond to inelastically scattered electrons inside the perfluoro film. The deconvolution of the C1s signal permits the evidence of the peaks corresponding to CF_3 (293.6, 7% of C1s; by comparison ~ 293.9 eV for Viton A: a fluorinated polymer bearing CF_3 groups⁵⁵); CF_2 (291.5 eV, 49% of C1s; by comparison 292.48 and 291.77 eV for polytetrafluoroethylene and Viton A respectively⁵⁵) and 288.8 and

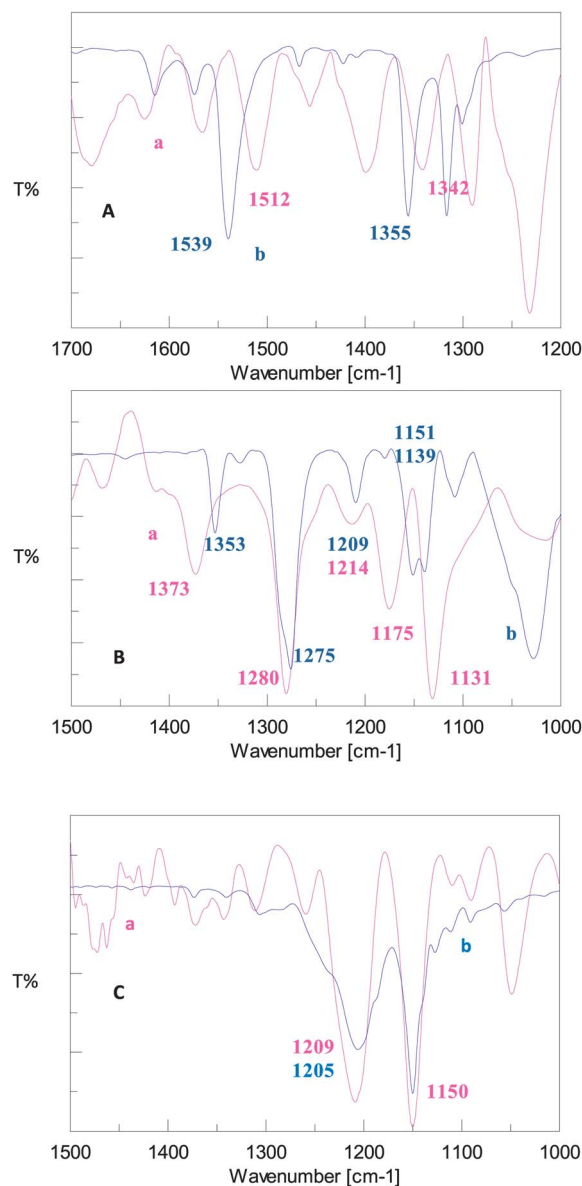


Fig. 1 IRATR spectra of (a) PMMA plates modified with (Aa) 4-nitrophenyl groups; (Ba) 5-bis-trifluoromethyl groups; (Ca) 4-perfluorodecyl groups; (Ab) 4-nitrobenzenediazonium; (Bb) 3,5-bis-trifluoromethylbenzenediazonium tetrafluoroborate and (Cb) 4-perfluorodecylaniline. Aa and Ba were obtained by Method 1 and Ca by Method 2.

286.6 eV pertaining to PMMA (O-CH_3 and O-C=O), respectively. The peak centred at 290.6 eV is assigned to the CF_2 carbon atom in the Ar-CF_2 chemical environment.⁵⁵ The ratio $\% \text{CF}_2/\% \text{CF}_3 = 49/7 = 7$ is close to but somewhat higher than the expected value ($18/3 = 6$). If the chains were upright on the surface, one would have expected the $\% \text{CF}_2/\% \text{CF}_3$ ratio to be smaller than 6; this result is in agreement with the IR spectrum and also indicates disordered films.

Water contact angles

As could be expected (Table 1), the hydroxyl groups decrease the water contact angle, while it increases with hydrophobic groups

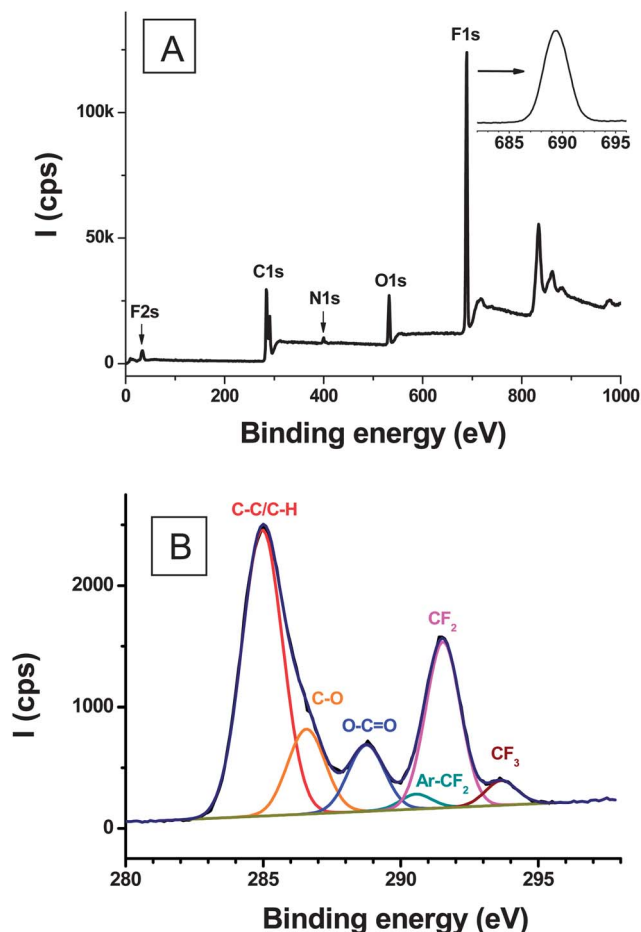


Fig. 2 XPS spectrum of $PMMA-C_{10}F_{21}$. (A) survey and F1s regions; (B) deconvolution of the C1s peak. The sample prepared by Method 2.

(dimethyl, dimethoxy, bis-trifluoromethyl, perfluorohexyl, and perfluorodecyl). Note the high contact angle obtained on a smooth surface with 4-perfluorohexyl and 4-perfluorodecyl substituents, the values (108.1 and 107.6° , respectively) are similar and very close to the maximum that can be obtained on smooth surfaces ($\sim 110^\circ$), this indicates that further lengthening of the perfluoroalkyl chains beside C_6F_{13} does not increase the water contact angle.

Thickness and surface concentration of the film

The methods that permit measurement of the thickness of thin films on carbon or metals do not apply on a PMMA surface. Ellipsometry and electrochemistry⁵⁷ necessitate a reflective and a conductive surface respectively. AFM scratching must be performed on a very flat and hard carbon surface (pyrolyzed photoresist).⁵⁸ Rutherford backscattering is a powerful method for determining surface concentrations of thin organic films, but on PMMA the sample was burnt by the ion beam. We therefore estimated the thickness of the $PMMA-NO_2$ film by comparison of the IRATR spectrum of this sample (Fig. 1Aa) with that of a SAM monolayer $Au-S-C_6H_4NO_2$.⁵⁹ By comparing the absorbances of the sum of the two NO_2 stretching vibrations

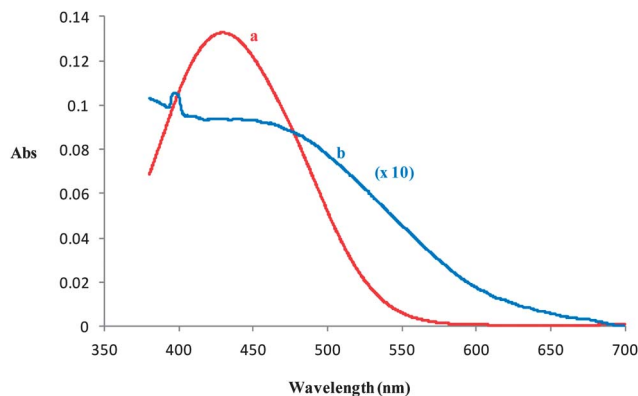


Fig. 3 Visible spectra of (a) an ACN solution of $NH_2-C_6H_4-C_6H_4-NO_2$ and (b) $PMMA-C_6H_4-C_6H_4-NO_2$.

(Table 1 and see the Experimental section) with that of the SAM, one finds that a bilayer is approximately attached to the surface of PMMA (~ 1.1 nm). We also used another method: $NH_2-C_6H_4-C_6H_4-NO_2$ in an ACN solution absorbs in the visible region at 433 nm,⁶⁰ its diazonium salt was grafted to PMMA by Method 1 and the resulting $PMMA-C_6H_4-C_6H_4-NO_2$ shows a broad absorbance at ~ 450 nm (Fig. 3). By comparing the absorbances of the two spectra (see the Experimental section), one finds $\Gamma \sim 10^{-9}$ mol cm^{-2} ; by comparing with the value measured for a monolayer⁶¹ of 4-nitrophenyl groups: 2.5×10^{-10} mol cm^{-2} , one finds that approximately 4 layers are present on the surface of PMMA.

The IR comparison with a SAM and the UV comparison with the absorption of the parent solution are in reasonable agreement indicating that a few (between 1 and 5) layers are attached to the surface of PMMA. This is also in agreement with the XPS spectrum where the PMMA substrate is observed, indicating that the film is thinner than ~ 10 nm.

Transparency

After modification of the PMMA surface, all the samples remain transparent as shown in Fig. 4 for $PMMA-NO_2$. To quantify the transparency of the sample we have recorded the visible spectrum of $PMMA-NO_2$ by reference to a clean PMMA sample; the



Fig. 4 An image recorded through a 2 mm thick $PMMA-NO_2$.

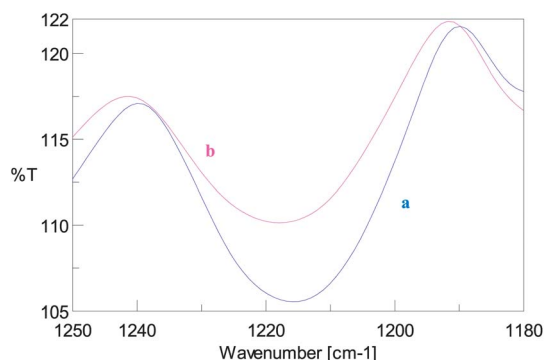
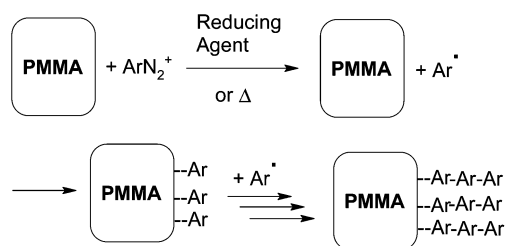


Fig. 5 IRATR spectrum of a $\text{PMMA-C}_6\text{F}_{13}$ sample (a) before and (b) after ~ 1000 km in front of a motorbike.



Scheme 3 The grafting mechanism of diazonium salts on PMMA.

absorbance varies from 0.007 a.u. at 800 nm to 0.023 a.u. at 400 nm, this very small absorption being due to nitrophenyl groups that start absorbing at this wavelength.

Environment durability

An accelerated test to weather resistance has shown that the film obtained by reaction with 4-perfluorohexylbenzenediazonium tetrafluoroborate on a 5×5 cm PMMA plate partly resists 1000 km in front of a motorbike in urban and road circulation (limited to 110 km h^{-1}). The initial and final IR spectra are presented in Fig. 5; the absorbance CF_2 band decreases by about 1/3 (Fig. 5). The water contact angle decreases from 108.1 ± 3.3 to $74.8 \pm 8.0^\circ$ (measurements on 10 different points). The decrease of the IR spectra and the large variation in the water contact angle indicate that about 1/3 of the perfluorohexyl groups have been eroded by the airflow and the contained particles and that the erosion is inhomogeneous. We also tested the stability of a $\text{PMMA-(CF}_3)_2$ sample in water on an oscillating platform for 10 hours; the IRATR spectrum before and after the test did not show significant differences.

Mechanism of the grafting reaction

We have checked that both Methods 1 and 2 involve the attack of radicals by adding a radical trap (4-hydroxy TEMPO) in the solutions (aqueous and isopentyl nitrite, respectively) used for grafting 4-nitrobenzenediazonium, in this case the IR spectrum shows the complete disappearance of the NO_2 bands. The same mechanism as on metals and carbon, involving the attack of an aryl radical on the PMMA surface is therefore operative. Once

the first layer is attached to the surface of PMMA, the growth of further layers should be independent of the substrate and follow the mechanism already described (Scheme 3).^{56a}

Conclusion

In contrast to plasma methods that necessitate complex equipment, modification of PMMA by a simple chemical reaction with diazonium salts is possible that only necessitates dipping the sample in a solution containing the diazonium salt or the parent amine. A large number of substituents can be introduced on the attached aryl group. The modified surfaces have been characterized by IR, XPS and water contact angle. The film that is attached to PMMA is in the 1–5 nm range. The mechanism involves intermediate aryl radicals that react with the surface. This surface modification permits the hydrophilicity/phobicity of the surface to be controlled which could be useful for applications where PMMA is used as a substitute of glass and also as a modifier to impart specific properties to microfluidic channels.

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