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Controlling surface-segregation of a polymer to display carboxy groups on an outermost surface using perfluoroacyl groups

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KEYWORDS. carboxy group, surface functionalization, perfluoroalkyl group, polymer coating, surface segregation.

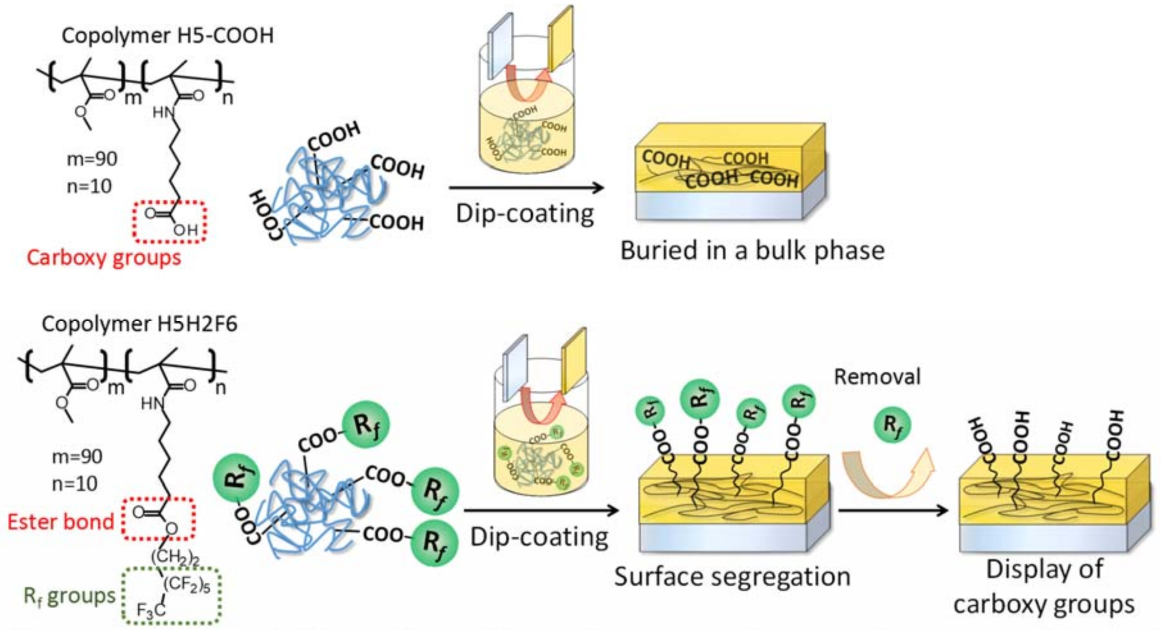
ABSTRACT. Controlling the surface properties of solid polymers is important for practical applications. We here succeeded in controlling the surface segregation of polymers to display carboxy groups on an outermost surface, which allowed the covalent immobilization of functional molecules via the carboxy groups on a substrate surface. Random methacrylate-based copolymers containing carboxy groups, in which carboxy groups were protected with perfluoroacyl (R_f) groups, were dip-coated on acrylic substrate surfaces. X-ray photoelectron spectroscopy and contact-angle measurements revealed that the R_f groups were segregated to the outermost surface of the dip-coated substrates. The R_f groups were removed by hydrolysis of the R_f esters in the copolymers, resulting in the display of carboxy groups on the surface. The quantification of carboxy groups on a surface revealed that the carboxy groups were reactive to a water-soluble solute in aqueous solution. The surface segregation was affected by the molecular structure of the copolymer used for dip-coating.

INTRODUCTION

The surface properties of solid materials play an important role in adhesion, adsorption, fouling, immobilization of functional molecules, and cell culture. A number of methods have been reported for chemically altering the surface properties of materials, and for functionalizing their surfaces. These include plasma treatment,[1] self-assembled monolayer formation,[2] vapor deposition,[3, 4] layer-by-layer assembly,[5, 6] Langmuir-Blodgett deposition,[7] solution coating (painting),[8-11] mussel-inspired adhesion,[12, 13] and physical adsorption to material surfaces.[14-16] Coating with a functional polymer solution is a versatile approach for functionalizing an inert material surface.[17, 18] The major advantages of coating are that (i) it is a simple process often requiring no special apparatus, (ii) a wide variety of functional polymers are available, which can be chemically designed and tuned to demands, (iii) various substrates including organic and inorganic materials can be coated with a functional polymer, if the polymer is adhesive to the material surface, (iv) various coating techniques including dip-coating, brush coating, spray coating, spin-coating, and electrocoating are available according to practical demands, and (v) it minimizes the amount of coating material that is required, and does not impair the substrate.

Obtaining reactive functional groups on a solid surface is an attractive and useful approach for the chemical functionalization of material surfaces.[19-23] Carboxy groups are useful surface functional groups, because they can readily react with nucleophiles to form covalent bonds.[24-26] Some of these reactions proceed in an aqueous environment, which allows the immobilization of water-soluble functional polymers, biomolecules, and ligands on solid surfaces under mild conditions. However, our preliminary investigation indicates that it is difficult to display carboxy groups on solid surfaces by coating with a polymer containing carboxy groups. Carboxy groups are relatively hydrophilic (comparing to a polymer backbone) and are likely to be buried in the bulk phase of the coating polymer (Scheme 1). This is because hydrophobic moieties in a the polymer are preferentially segregated at the air/polymer interface to minimize its surface energy.[9, 27]

We previously reported the surface segregation of amino groups by dip-coating a polymer containing amino groups with hydrophobic protecting groups.[28] There are many reports describing the segregation of perfluoroacyl (or perfluoroalkyl) groups (R_f groups) at the air/polymer interface.[9, 11, 29-34] In the current study, we report the effective display of carboxy groups on the surface of a substrate dip-coated with a functional polymer. Specifically, we synthesized several methacrylate-based random copolymers containing carboxy groups in side chains, in which carboxy groups were conjugated with R_f groups to form R_f esters. The presence of the R_f groups induced the segregation of carboxy groups at the air/polymer interface during dip-coating of the copolymer (Scheme 1). After dip-coating, the R_f groups were readily removed from the carboxy groups by hydrolysis of the R_f ester. The carboxy groups displayed on a surface were accessible and reactive for water-soluble solutes in aqueous solution.



Scheme 1 Schematic illustration of the surface segregation of carboxy groups in copolymer H5H2F6 via dip-coating.

EXPERIMENTAL

Descriptions of materials and the syntheses of a methacrylate monomer containing NH–(CH2)3–CO–methyl ester, a methacrylate monomer containing NH–CH2–CO–methyl ester, copolymers H1H2F6, H3H2F6, H5H4, H5H8, H5H3F2, H5H2F4, H5H2F6$_{5:5}$ and H5H2F6$_{7:3}$ (Scheme 2), and poly(methyl methacrylate) (PMMA) are given in the supporting information.

Synthesis of a methacrylate monomer containing NH–(CH$_2$)$_5$–CO–methyl ester

Methyl-6-aminohexanoate hydrochloride (15 mmol) and pyridine (45 mmol) were dissolved in 15 ml of chloroform. Methacryloyl chloride (18 mmol) was added dropwise to the chloroform solution. The solution was stirred at room temperature overnight. Water was added to the solution, which was then vigorously mixed. The chloroform phase was collected and then washed with water (10 ml) and 10 mM HCl aqueous solution (10 ml) three times each. The chloroform phase was collected and then evaporated. The dry residue was vacuum-dried overnight. The yield was 92.3%. The synthesized monomer was identified by ^{1}H-NMR and direct analysis in real time-mass spectrometry (DART-MS). ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 5.97 (s, H, −NH), 5.65 (s, H, −C*H*=CH), 5.29 (s, H, −CH=C*H*), 3.64 (s, 3H, $-COOCH_3$), 3.30 (q, 2H, $-NHC\mathit{H_2}-$), 2.29 (t, 2H, $-CH_2COO-$), 1.93 (s, 3H, $-CCH_3$), 1.63 (quin, 2H, $-C\mathit{H_2}CH_2COO-$), 1.55 (quin, 2H, $-NH\ CH_2C\mathit{H_2}-$), 1.35 (quin, 2H, $-C\mathit{H_2}CH_2CH_2COO-$) ppm. DART-MS: $[MH]^+$ calcd for $C_{11}H_{20}N_1O_3$, 214.28; found, 214.12.

Synthesis of a methacrylate copolymer containing NH-$(CH_2)_5$–CO–methyl ester (copolymer H5H1, Scheme 2)

A random copolymer composed of methyl methacrylate (MMA, 90 mol%) and methacrylate monomer containing NH–$(CH_2)_5$–CO–methyl ester (termed a functional monomer, 10 mol%) was synthesized via free radical polymerization. MMA (21.1 mmol), the functional monomer (2.3 mmol), and azobisisobutyronitrile (AIBN, 50 μmol) were dissolved in 10 ml of toluene in a glass vial, followed by purging with nitrogen gas. Polymerization was performed under a nitrogen atmosphere at 60 °C overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane. The precipitate was then vacuum-dried. The yield was 85.4%. The molecular weight of copolymer H5H1 was determined by size-exclusion chromatography (SEC) (GPC8020, Tosoh Corporation, Tokyo, Japan) equipped with an 80 × 300 mm column (Showa Denko K. K., Tokyo, Japan) and a RI detector (RI-8020) at 40 °C. Tetrahydrofuran was used as an elution solvent, and PMMA molecular weight standards were used to obtain a standard curve. The synthesized copolymer was identified by ^{1}H-NMR. Copolymer H5H1 had a number average molecular weight (M_n) of 2.7×10^4 g/mol and a weight average molecular weight (M_w)/M_n of 1.9. ^{1}H-NMR (500

MHz, $CDCl_3$, δ): 5.83 (s, H, −NH), 3.67 (s, 3H, $-CH_2COOCH_3$), 3.60 (s, 28H, $-COOCH_3$), 3.31 (q, 2H, $-NHCH_2-$), 2.32 (t, 2H, $-CH_2COO-$), 1.96–1.81 (m, 22H, $-CCH_2-$), 1.72–1.21 (m, 9H, $-CH_2CH_2COO-$, $-NHCH_2CH_2-$, $-CH_2CH_2CH_2COO-$), 1.01–0.83 (m, 33H, $-CCH_3$) ppm.

Synthesis of a methacrylate-based copolymer containing carboxy groups (copolymer H5-COOH, Scheme 2)

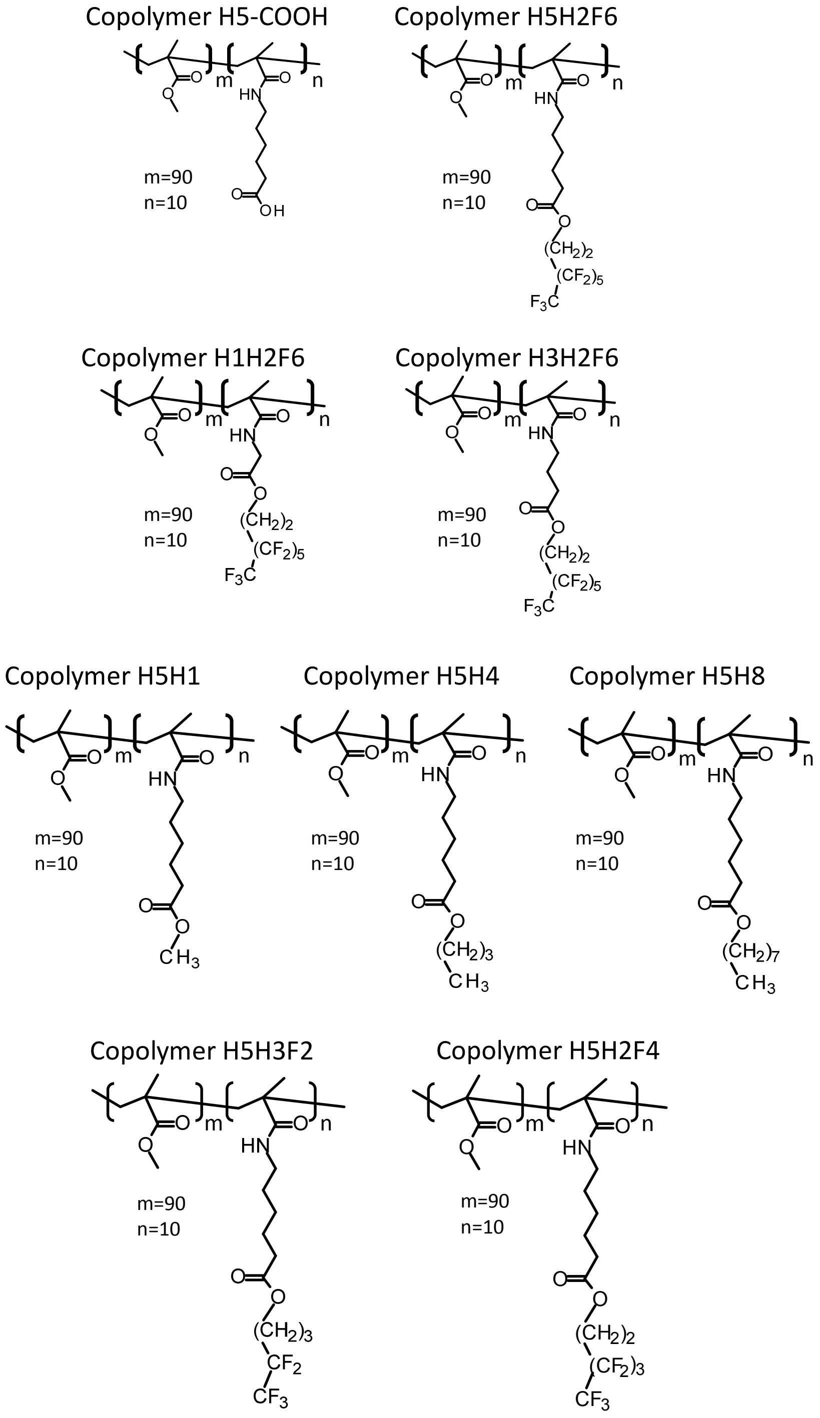
Copolymer H5H1 (1.0 g) was dissolved in a mixture (10 ml) of DMF/water (9:1 v/v) containing 0.5 M sodium hydroxide. The solution was stirred at room temperature for 4 h. The copolymer was precipitated by adding an excess amount of water, and the precipitate was freeze-dried overnight. The yield was 89.2%. Copolymer H5-COOH had a M_n of 2.7×10^4 g/mol and a M_w/M_n of 1.9. ^1H-NMR (500 MHz, $CDCl_3$, δ): 5.95 (s, H, −NH), 3.69 (s, 30H, $-COOCH_3$), 3.41 (q, 2H, $-NHCH_2-$), 2.43 (t, 2H, $-CH_2COO-$), 2.01–1.75 (m, 24H, $-CCH_2-$), 1.72–1.21 (m, 7H, $-CH_2CH_2COO-$, $-NHCH_2CH_2-$, $-CH_2CH_2CH_2COO-$), 1.01–0.83 (m, 31H, $-CCH_3$) ppm.

Synthesis of a methacrylate-based copolymer containing R_f groups (copolymer H5H2F6, Scheme 2)

Copolymer H5-COOH (0.5 g) was dissolved in 20 ml of dichloromethane (CH_2Cl_2). *N*-Dimethyl-4-aminopyridine (DMAP) (0.05 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (0.5 mmol), pyridine (1.36 mmol), and 1H,1H,2H,2H-tridecafluoro-1-*n*-octanol (2.27 mmol) were added to the solution. The solution was stirred at room temperature overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane. The precipitate was washed with excess *n*-hexane and then excess water. The precipitate was freeze-dried overnight. The yield was 91.6%. Copolymer H5H2F6 had a M_n of 2.6×10^4 g/mol and a M_w/M_n of 2.0. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 6.00 (s, H, −NH), 4.44 (t, 2H, $-COOCH_2CH_2$), 3.65 (s, 29H, $-COOCH_3$), 3.28 (q, 2H, $-NHCH_2-$), 2.45 (t, 2H, $-CH_2COO-$), 2.21–1.81 (m, 20H, $-CCH_2-$), 1.75–1.19 (m, 12H, $-COOCH_2CH_2-$, $-CH_2CH_2COO-$, $-NHCH_2CH_2-$, $-CH_2CH_2CH_2COO-$), 1.14–0.75 (m, 33H, $-CCH_3$) ppm. The elemental analysis indicated that R_f groups were introduced to 90% of the carboxy groups in copolymer H5H2F6.

Synthesis of cleavable fluorescent compound[34]

Cystamine (1.2 mmol) and triethylamine (40 µL) were dissolved in 7 ml of methanol/water (5:2 v/v). A fluorescein isothiocyanate (FITC) (0.13 mmol) and triethylamine (5 µL) solution in methanol (5 ml) was added dropwise to the solution. The solution was stirred at room temperature overnight. The cleavable fluorescent compound was precipitated by adding the solution to 100 ml of acetonitrile/methanol (10:1 v/v). This precipitation procedure using acetonitrile/methanol was repeated three times, and the precipitate was then vacuum-dried. The cleavable fluorescent compound was characterized by ^{1}H-NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI TOF-MS) (UltrafleXtreme, Bruker, Billerica, MA, USA). ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.61–6.60 (m, 9H, fluorescence), 3.55–2.95 (m, 8H, $-CH_2$) ppm. MALDI TOF-MS (m/z): $[MH]^+$ calcd for $C_{25}H_{23}N_3O_5S_3$, 542.7; found, 542.8.


Copolymer H5-COOH

Copolymer H5H2F6

Copolymer H1H2F6

Copolymer H3H2F6

Copolymer H5H1

Copolymer H5H4

Copolymer H5H8

Copolymer H5H3F2

Copolymer H5H2F4

Scheme 2 Molecular structures of the synthesized copolymers.

Dip-coating of acrylic substrates using copolymers

The dip-coating of acrylic substrates was carried out as follows. A copolymer was dissolved in chloroform to give a copolymer concentration of 1 wt%. An acrylic substrate (1 cm × 1 cm, 0.5 mm thick) was immersed in the copolymer solution for 5 s (i.e. dip-coated), and was then withdrawn over 2 s and dried in a vacuum chamber overnight at 25 °C. The dip-coated substrate was then immersed in an aqueous solution (2 ml) of sodium hydroxide (2 M), to remove R_f groups from the surface via the hydrolysis of ester bonds. The substrate was then immersed in 5 mM HCl aqueous solution (2 ml), then rinsed with excess water, before drying in a vacuum chamber overnight at 25 °C.

X-ray photoelectron spectroscopy (XPS) analysis

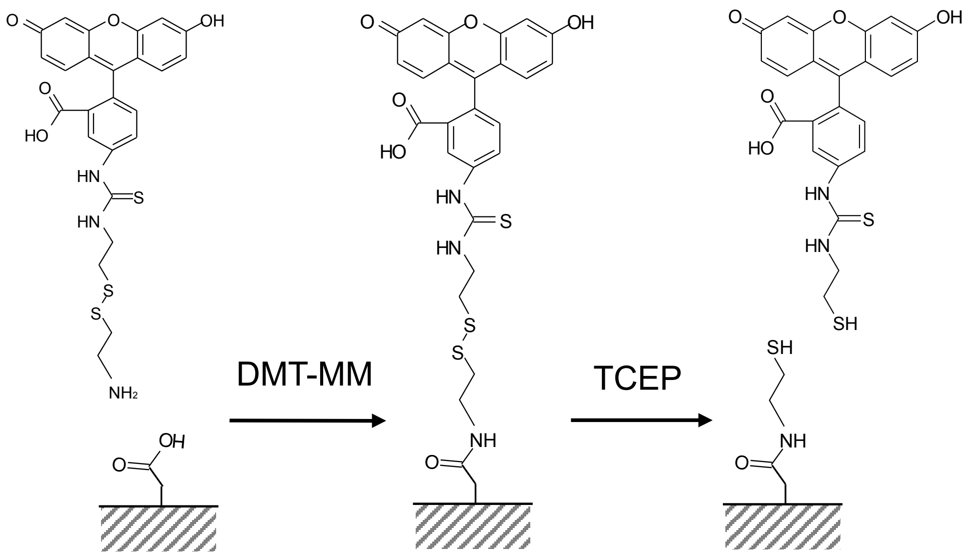
XPS measurements were performed with a PHI X-tool X-ray photon spectroscopic instrument (ULVAC, Chigasaki, Japan) using an Al Kα source (15kV, 4W). The photoelectron take-off angle was 45° and a spot size was 24 μm × 24 μm. Survey scans were performed with pass energy of 280 and step size of 0.5 eV.

Contact angle measurements

Static contact angles of water droplets (1 mM NaOH aqueous solution, 4.5 μl) were measured using a digital automated contact angle goniometer (Kyowa Interface Science Co., Ltd., Japan) at 25 °C. A NaOH aqueous solution was used for a water droplet to obtain reproducible data. One second after placing a droplet (4.5 μl), images of the droplet were captured, from which the contact angle was determined. The measurement was performed at five different locations on each substrate, and reported values are averages of these five measurements. Error bars represent standard deviations.

Quantification of carboxy groups on a surface using a fluorescent compound (Scheme 3)[34]

The dip-coated substrates were immersed in 2 ml of phosphate buffer (0.1 M, pH 8.0) containing 5 vol% dimethyl sulfoxide, 0.2 mM cleavable fluorescent compound, and 1 mM 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) for 2 h at 25 °C. The substrates were washed with phosphate buffer three times, and then immersed in 5 mM HCl aqueous solution (10 ml) for 1 h at 40 °C. The HCl aqueous solution was then replaced with fresh NaOH aqueous solution (5 mM, 10 ml), and the solution containing the substrates was agitated for 1 h at 40 °C to wash out non-reacted and physically absorbed fluorescent compound. The substrates were finally rinsed with phosphate buffer three times, and then immersed in 2 ml of phosphate buffer containing 2 mM tris(2-carboxyethyl)phosphine hydrochloride (TCEP-HCl) for 1 h at 40 °C to cleave the disulfide bond in the cleavable fluorescent compound. The fluorescence intensity of the solution was measured using a fluorescence spectrophotometer (FP-8200, Jasco, Tokyo, Japan). The excitation and emission wavelengths were 490 nm and 513 nm, respectively. The excitation and emission band widths were 5 nm. The lower detection limit was 0.8 pmol/cm^2. Dip-coating and the subsequent quantification were carried out five times unless otherwise stated, to ensure reproducible results. Reported values are averages of these five measurements.



Scheme 3 Quantification of carboxy groups on a surface using a cleavable fluorescent compound.

RESULTS AND DISCUSSION

XPS measurements of the dip-coated surfaces.

When the copolymers were dip-coated on a substrate, no peeling or detachment of the coated copolymers from the substrate was observed in acidic, basic, or neutral aqueous solutions even after soaking in the solutions for 1 day at 25 °C. This indicated that the coatings were stable (no peeling). The adhesion of the coated copolymer to the substrates was supposed to be entanglement of copolymer with the bulk PMMA, dipole−dipole interaction and van der Waals force. Since synthesized copolymers are compatible with PMMA, the dip-coated copolymers would penetrate into a bulk of a PMMA substrate to form a boundary-less coating. The thickness of the dip-coated film prepared with 1 wt% copolymer H5H2F6 solution was typically 1.1 μm. This was determined by the weight change of the substrate (more than 10 pieces), on the assumption that the copolymer density was similar to that of PMMA (1.18 g/cm^3). The field-emission scanning electron microscopic observation revealed that the dip-coated surface was not damaged by the solvent (Figure S1).

XPS measurements revealed that the bare substrate and substrate dip-coated with copolymer H5-COOH exhibited O1s and C1s peaks, but no F1s peaks (Figure 1a and b). The surface of the substrate dip-coated with copolymer H5H2F6 showed F1s and F_{kll} peaks at 689 eV and 835 eV, respectively, in addition to the O1s and C1s peaks (Figure 1c). This indicated the presence of R_f groups on the dip-coated surface. Following hydrolysis of the ester bond in the side chain of copolymer H5H2F6, the XPS spectrum of the dip-coated substrate showed no detectable F1s peak at 689 eV (Figure 1d). The calculated F/C elemental ratio of the hydrolyzed substrate was 0, whereas that of the non-hydrolyzed substrate was 0.28. These results demonstrated the display of R_f groups on the surface coated with copolymer H5H2F6 before hydrolysis, and then the removal of R_f groups from the surface by hydrolysis. XPS spectra of the N1s region are shown in Figure S2. The bare substrate and substrate dip-coated with copolymer H5-COOH did not exhibit any N1s peaks (Figure 1a and b), despite that copolymer H5-COOH contained –CONH– groups. The absence of N1s peaks for the substrate dip-coated with copolymer H5-COOH indicated that the –CONH– groups were buried in the bulk phase along with the carboxy groups. Figure S2c shows a small peak at 400 eV that was derived from the –CONH– groups in the functional monomer. After hydrolysis, this peak was still present (Figure S2d). These results demonstrated the presence of copolymer H5H2F6 on the coated surfaces after hydrolysis, and implied the surface segregation of the functional monomer.

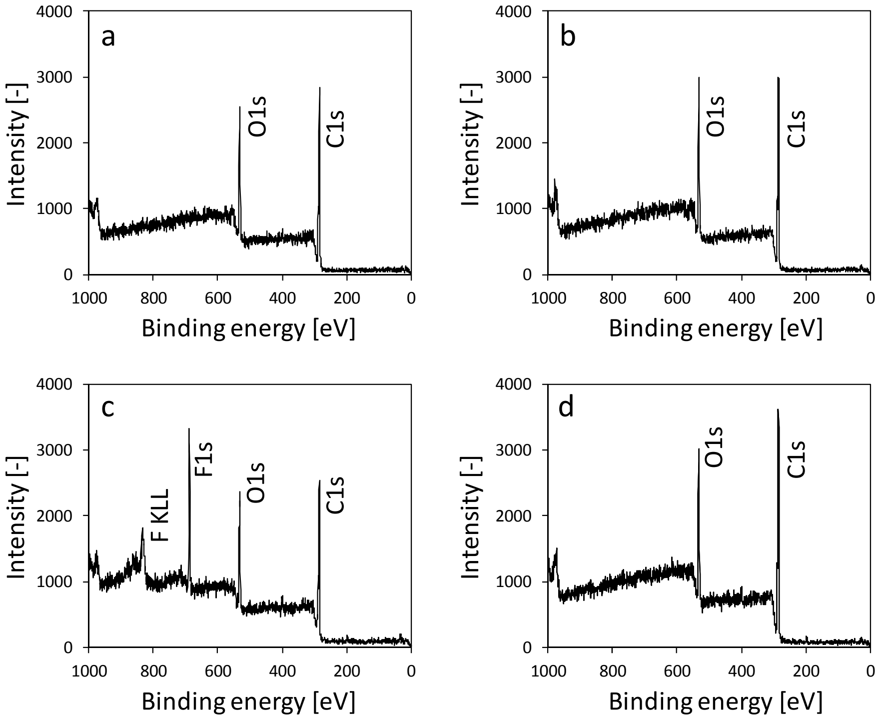


Figure 1. XPS spectra of the surfaces of acrylic substrates. a) Bare substrate, and substrates dip-coated with b) copolymer H5-COOH, c) copolymer H5H2F6 before hydrolysis, and d) copolymer H5H2F6 after hydrolysis.

Water contact angle measurements of the dip-coated surfaces.

The hydrophilicity of bare and dip-coated substrates was evaluated by contact angle measurements of water droplets (1 mM NaOH aqueous solution) (Figure 2). Prior to the measurements, a substrate coated with copolymer H5H2F6 was hydrolyzed with 2 M NaOH aqueous solution to remove R_f groups from the surface. The bare substrate exhibited a contact angle of 60 ± 1°. Even though copolymer H5-COOH contained carboxy groups, the substrate coated with copolymer H5-COOH exhibited a contact angle of 64 ± 3°, which was very close to that of the bare substrate. The substrate coated with copolymer H5H2F6 (before hydrolysis) exhibited a contact angle of 91 ± 3°. The remarkably high contact angle of the substrate with copolymer H5H2F6 was derived from the R_f groups on the outermost surface, which was consistent with the XPS measurements. The R_f groups of copolymer H5H2F6 were preferentially segregated on the outermost surface through dip-coating and drying. After hydrolysis, the substrate coated with copolymer H5H2F6 exhibited a contact angle of 32 ± 2°, which was 60° lower than that of the substrate before hydrolysis, and 30° lower than that of the substrate dip-coated with copolymer H5-COOH. These results suggested that the hydrolytic removal of R_f groups significantly decreased the hydrophobicity of the dip-coated surface, producing a relatively hydrophilic surface which differed from the surface coated with copolymer H5-COOH. This was despite copolymer H5-COOH having the same chemical structure as hydrolyzed copolymer H5H2F6.

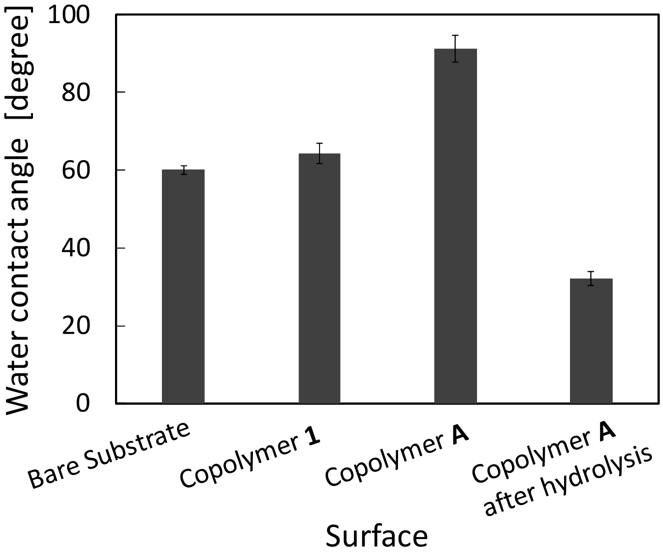


Figure 2. Water contact angles of the surfaces of bare and dip-coated substrates.

Quantification of carboxy groups on the surfaces

To identify carboxy groups on the dip-coated surfaces, we synthesized a cleavable fluorescent compound that could covalently bind to carboxy groups, and liberate a fluorophore via reduction (Scheme 3).[34, 35] The fluorophore liberated in solution could be quantified using a conventional fluorophotometer, and give quantitative information on the carboxy groups on the solid surface which were accessible and reactive to solutes in aqueous solution.[28] The bare substrate and dip-coated substrates were treated with the cleavable fluorescent compound and a condensation agent (DMT-MM). This was followed by reduction to cleave the disulfide bond in the fluorescent compound. Figure 3a shows the concentrations of fluorophore liberated from the substrate surfaces. The bare substrate and substrates coated with copolymer H5-COOH and copolymer H5H2F6 (before hydrolysis) exhibited virtually no liberated fluorophore, which suggested that no carboxy groups were present on their surfaces. The surface coated with copolymer H5H2F6 (after hydrolysis) exhibited 22 pmol/cm^2 of fluorophore, indicating the equivalent amount of carboxy groups on its surface. These results provided three conclusions: i) dip-coating of a copolymer containing carboxy groups without R_f groups did not provide carboxy groups on the coated surface, because the carboxy groups were buried in the bulk phase; ii) R_f groups induced the surface-segregation of the carboxy groups; iii) after the removal of R_f groups, the carboxy groups, which were surface-segregated, were accessible and reactive to solutes in the aqueous phase. This was the reason for the surface coated with copolymer H5H2F6 (after hydrolysis) exhibiting remarkable hydrophilicity compared to that coated with copolymer H5-COOH.

Many of polymer matrices in a solid state are labile at room temperature owing to flexible backbones and side chains of polymers (migration). We investigated the stability of the surface segregation of the dip-coated surface (copolymer H5H2F6) after the removal of R_f groups. When the dip-coated substrate was kept in water at room temperature for 1 week, there was only negligible change in the carboxy groups displayed on the surface. When the dip-coated substrate was kept in air at room temperature for 1 week, the amount of carboxy groups displayed decreased by 30%. When kept for 1 month, it decreased to a half. These results indicate that the surface-displayed carboxy groups can exist on a surface in water but not in air probably due to the mobility of the side chains in the copolymer.

In our previous study, amino groups (~70 pmol/cm^2) were displayed on a dip-coated surface using p-toluenesulfonate and tert-butoxycarbonyl groups as segregation-inducing protection groups for amino groups. The present amount of carboxy group displayed on a surface was lower than that of amino group in our previous study. The amino group-containing polymer was previously synthesized in a 2-propanol/water mixture, which might affect the polymer structure (e.g. the monomer sequence). That would be a possible reason for the difference in the amounts of functional groups displayed on surfaces.

We then investigated the effect of the copolymer H5H2F6 concentration on the display of carboxy groups on the surface. Copolymer H5H2F6 solutions of varying concentrations were dip-coated onto substrates. The substrates were then dried and subjected to hydrolysis to remove the R_f groups. Figure 3b shows that the concentration of liberated fluorophore increased with increasing copolymer concentration, which indicated that a higher amount of carboxy groups were displayed on the surface.

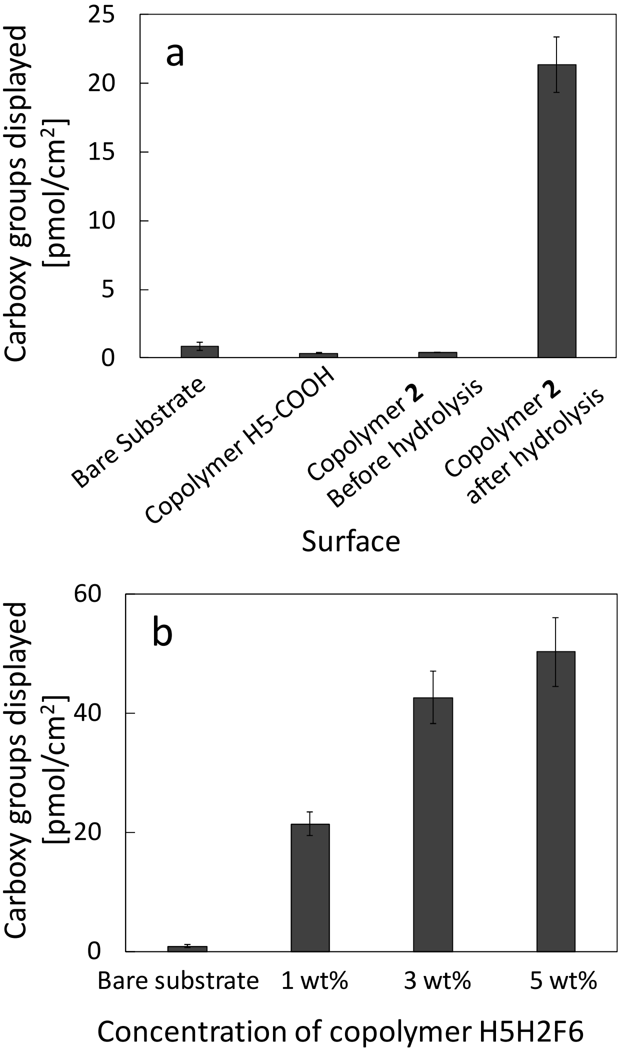


Figure 3. Carboxy groups displayed on bare and dip-coated surfaces. a) Effect of dip-coating with various copolymers. b) Effect of the concentration of copolymer H5H2F6. The amounts of carboxy groups on the surfaces were determined using a cleavable fluorescent compound.

Effect of the length of R_f groups on the surface-segregation of carboxy groups

The above investigations demonstrated that the surface segregation of carboxy groups was achieved by dip-coating a copolymer containing carboxy groups and R_f groups. We then investigated the effect of the length of the R_f group on the surface-segregation of carboxy groups. We synthesized three copolymers containing carboxy groups, in which the carboxy groups were protected with three different R_f groups having different perfluoroacyl-chain lengths (Scheme 2). Substrates were dip-coated with copolymer H5-COOH, copolymer H5H3F2, copolymer H5H2F4, and copolymer H5H2F6. The hydrophilicity of the bare and dip-coated substrates was evaluated by contact angle measurements of water droplets (1 mM NaOH aqueous solution) (Figure 4a). The substrates coated with copolymer H5H3F2, copolymer H5H2F4, and copolymer H5H2F6 exhibited contact angles of 70 ± 3°, 87 ± 3°, and 91 ± 3°, respectively. Increasing the length of the perfluoroacyl chain (R_f group) led to an increase in the hydrophobicity of the dip-coated surface. This observation implied the surface segregation of the R_f groups of copolymers H5H3F2 and H5H2F4on their outermost surfaces. After hydrolysis, the surfaces coated with copolymers containing R_f groups all exhibited drastically decreased contact angles. The contact angles of the surfaces coated with copolymers H5H3F2, H5H2F4, and H5H2F6 were 40 ± 2°, 35 ± 4°, and 32 ± 2°, respectively, which were 40–60° lower than those before hydrolysis. The contact angle after hydrolysis decreased with increasing length of the R_f group. This indicated differences in the amount of carboxy groups displayed on the outermost surfaces. We quantified the carboxy groups on the surfaces coated with these copolymers. Figure 4b shows that carboxy groups were also displayed on the surfaces coated with copolymers H5H3F2 and H5H2F4, and that the amount of carboxy groups displayed on a dip-coated surface increased with increasing length of the R_f group. These results indicated that long R_f groups effectively induced the surface-segregation of carboxy groups.

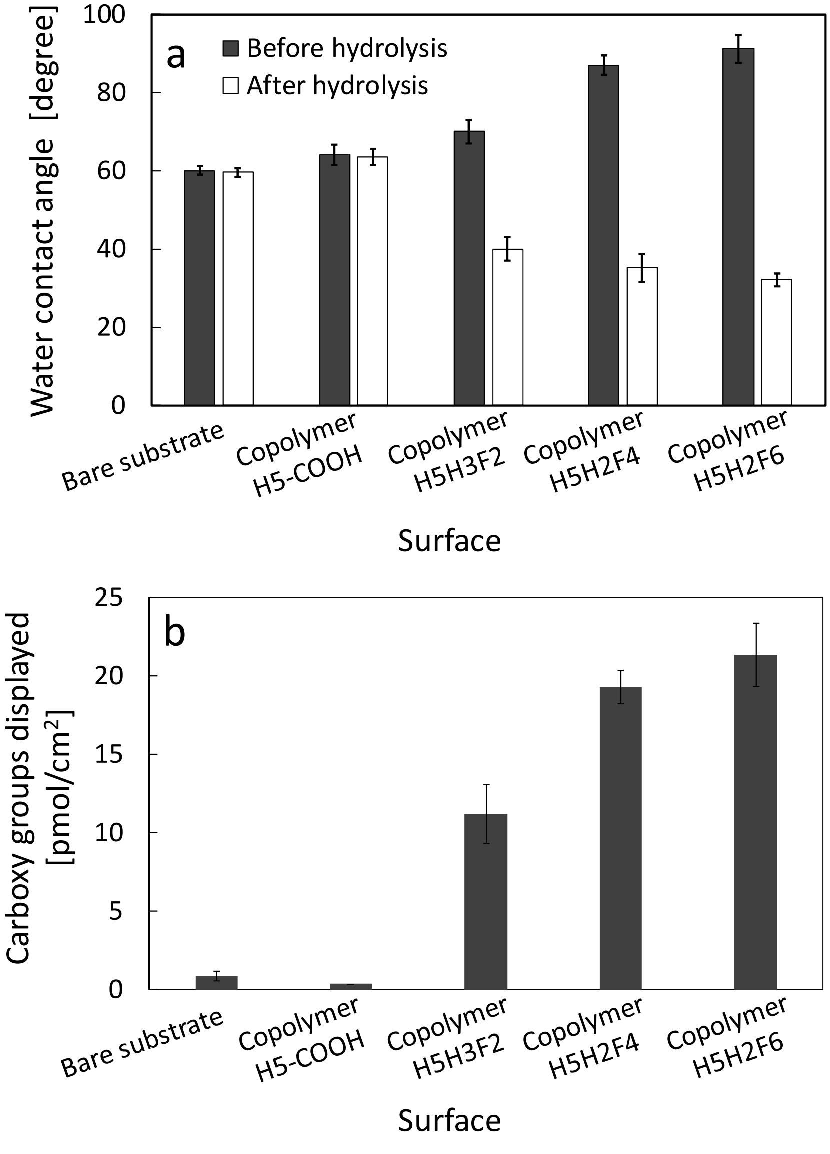


Figure 4. Effect of the length of the perfluoroacyl chains (Rf groups) on the surface-segregation of carboxy groups in the copolymers. a) Water contact angles of the surfaces of the bare and dip-coated substrates. Black and gray bars indicate before and after hydrolysis, respectively. b) Amounts of carboxy groups displayed on the bare and dip-coated surfaces.

Effect of the copolymer structure on the surface-segregation of carboxy groups

There are many reports describing the surface segregation of R_f groups and fluorine-containing groups. However, hydrophobic groups without fluorine also exhibit surface segregation.[28, 34] We synthesized several copolymers containing carboxy groups, in which the carboxy groups were protected with hydrophobic acyl groups (i.e. not containing fluorine). After dip-coating and drying, the protecting groups were removed from the surfaces via hydrolysis using 2 M NaOH aqueous solution. Methyl and *n*-butyl groups did not induce the surface segregation of carboxy groups (Figure 5a). *n*-Octyl groups produced a surface displaying 3.5 pmol/cm^2 of carboxy groups, which was only one-sixth of that of the surface displaying R_f groups. These results demonstrated that the R_f group imparted very strong surface segregation properties.

In the present study, carboxy groups were present in the side chains of the copolymers. The length of the copolymer side chain is an important factor for surface segregation, because the side chain length affects its mobility and thus the crystallinity of the overall polymer.[36-38] We synthesized copolymers having C2, C4, and C6 length side chains with R_f groups. The dip-coated surfaces were prepared as described above. Figure 5b shows that the amount of carboxy groups displayed on the dip-coated surface increased with increasing side-chain length. A longer side chain was more mobile, which aided the surface segregation of the R_f-protected carboxy groups.

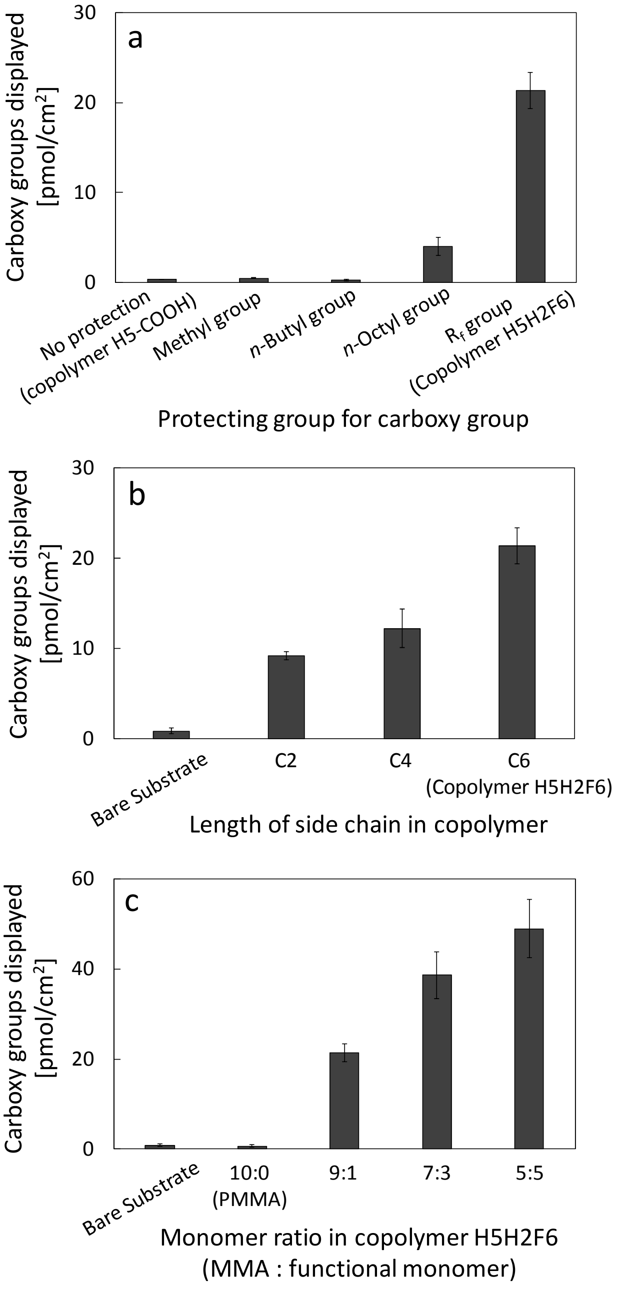


Figure 5. Amounts of carboxy groups displayed on bare and dip-coated surfaces. a) Effect of different carboxy protecting groups in the copolymer. b) Effect of the copolymer side chain length. c) Effect of the monomer ratio (MMA: functional monomer) in the copolymer. The copolymer concentrations were 1 wt%.

Since copolymer H5H2F6 was composed of two different monomers (MMA and the functional monomer), we varied the monomer composition to prepare copolymer H5H2F6 derivatives with R_f groups (Figure 5c). Increasing the amount of functional monomer in the monomer ratio led to an increase in the amount of carboxy groups displayed on the surface. A monomer ratio of 5:5 resulted in 51 pmol/cm^2 of carboxy groups displayed on the dip-coated surface.

The above investigation demonstrated that the amount of functional monomer in the monomer ratio could control the amount of carboxy groups displayed on the dip-coated surface. However, it is more practical and useful to be able to control the amount of carboxy groups displayed by changing the mixing of copolymer H5H2F6 and PMMA during dip-coating.[28, 34] We prepared solutions of copolymer H5H2F6 and PMMA with various mixing ratios, and dip-coated substrates with these polymer mixtures. The total polymer concentration was held constant at 1 wt%. Figure 6 shows that the amount of carboxy groups displayed on the surface was proportional to the content of copolymer H5H2F6. This indicates that the amount of carboxy groups on the surface could be controlled by the mixing of copolymer H5H2F6 and PMMA.

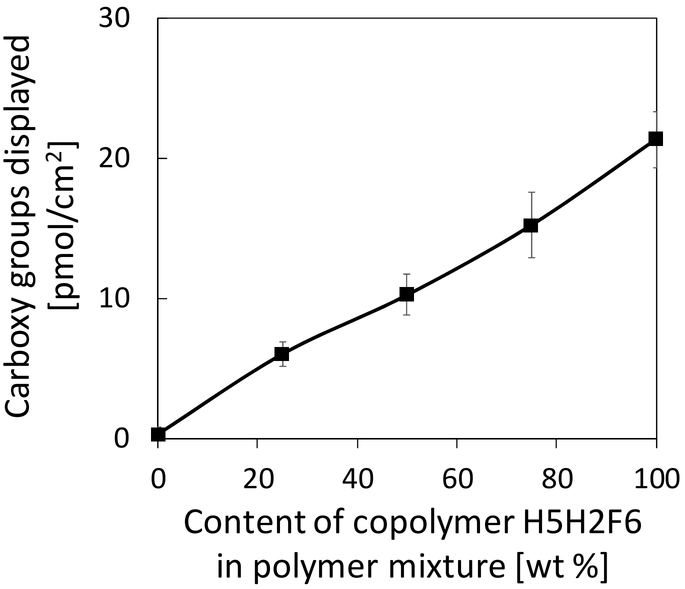


Figure 6. Effect of the content of copolymer H5H2F6 in the mixture of PMMA and copolymer H5H2F6, on the amount of carboxy groups displayed on the dip-coated surface.

An attractive feature of dip-coating is its versatility. Various materials can be used as substrates, providing that the coating polymer forms a stable layer on the substrate surface. We dip-coated three different types of polymeric substrates with copolymers (1 wt%), and then displayed the carboxy groups via hydrolysis. Copolymers H5-COOH and H5H2F6 were satisfactorily dip-coated on all tested substrates, with no peeling observed in aqueous solution. Investigations using the cleavable fluorescent compound showed that a bare nylon 6 substrate exhibited a small amount of liberated fluorophore (Figure 7), which would be due to the nonspecific adsorption of the cleavable fluorescent compound on the nylon 6 surface. The dip-coating of copolymer H5-COOH did not produce any detectable amounts of carboxy groups on any substrate surface. The dip-coating of copolymer H5H2F6 produced considerable amounts of carboxy groups (22–25 pmol/cm^2) on the surfaces. There was no significant difference in the amounts among the three different substrates. The surface segregation of the coating copolymer at the air/polymer interface occurred relatively far (0.7 μm) from the substrate surface. This meant that the substrate material did not influence the surface-segregation of the Rf-protected carboxy groups. These results demonstrated that the dip-coating of copolymer H5H2F6 produced similar functional surfaces on various substrates with ease.

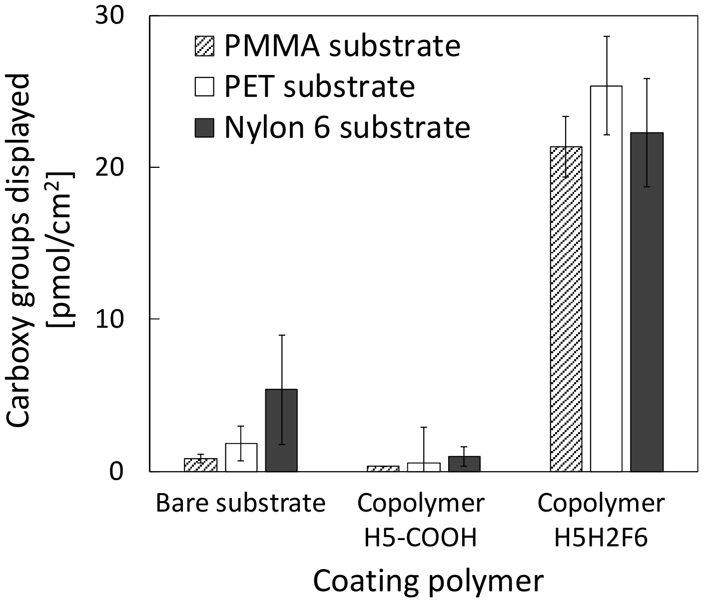


Figure 7. Carboxy groups displayed on dip-coated surfaces of three different plastic substrates.

CONCLUSION

The surface properties of solid polymeric materials play various roles in our life and in industry. Introducing reactive functional groups is a practical and rational approach for functionalizing the surface of solid polymeric materials. In the present study, we produced carboxy groups on substrate surfaces by dip-coating the substrates in functional polymer solutions. We synthesized various methacrylate-based copolymers containing carboxy groups, in which the carboxy groups were protected with perfluoroacyl (Rf) groups. The Rf groups were segregated at the outermost surface of the dip-coated substrates, when dip-coating with the copolymer. The removal of Rf groups via hydrolysis produced carboxy groups at the outermost surface. The carboxy groups displayed on the surface were accessible and reactive to a water-soluble solute in aqueous solution. The surface segregation of the carboxy groups was strongly affected by the copolymer side-chain length, the R_f-chain length, and the concentration of the functional copolymer used for dip-coating. The present study demonstrates the potential of molecular design in controlling the surface segregation of polymers. This strategy will be extended to other kinds of functional groups (e.g. hydroxy and amino groups) in polymers. The surface segregation of functional groups leads to the surface functionalization of a wide variety of solid polymeric materials, such as commodity plastics, at the molecular level, and also to controlling adhesion properties without impairing substrate surfaces.

ASSOCIATED CONTENT

Supporting Information

Descriptions of materials, syntheses of copolymer H5H2F6 derivatives and PMMA, and XPS spectra of the N1s region of dip-coated substrates (PDF).

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Notes

The authors declare no competing financial interest.

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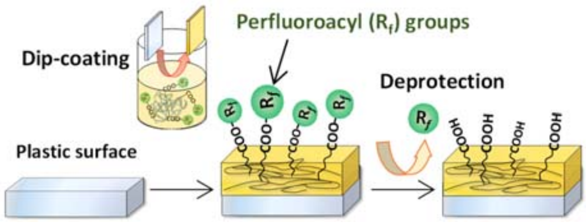

Supporting Information

Controlling surface-segregation of a polymer to display carboxy groups on an outermost surface using perfluoroacyl groups

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Experimental

Materials

Methyl methacrylate (MMA), methacryloyl chloride, 2,2’-azobisisobutyronitrile (AIBN), trimethylamine, 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM), *N,N*-dimethyl-4-aminopyridine (DMAP), pyridine, sodium hydroxide, 5 M hydrochloric acid aqueous solution, *N,N*-dimethylformamide (DMF), chloroform, ethyl acetate, toluene, dichloromethane, 1-butanol, and 1-octanol were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Methyl-6-aminohexanoate hydrochloride, methyl-4-aminobutyrate hydrochloride, and fluorescein isothiocyanate isomer I (FITC) were purchased from Sigma-Aldrich Inc. (St Louis, MO, USA). 1H,1H,2H,2H-Tridecafluoro-1-*n*-octanol, cystamine dihydrochloride, and tris(2-carboxyethyl)phosphine hydrochloride (TCEP) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Glycine methyl ester hydrochloride and *n*-hexane were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) was purchased from Dojindo Molecular Technologies Inc. (Kumamoto, Japan). A PMMA substrate was purchased from Nitto Jushi Kogyo Co., Ltd. (Tokyo, Japan). A polyethylene terephthalate (PET) film (0.1 mm thick) was obtained from Hitachi Maxell, Ltd. (Tokyo, Japan).

Nylon 6 was obtained from Toray Industries, Inc. (Tokyo, Japan) and melt-pressed to prepare nylon films (0.1 mm thick). Substrates were cleaned with a detergent solution and cut into 1 cm × 1 cm pieces prior to use.

Water used in experiments was high-quality deionized water (DI water, > 15 MΩ·cm) produced by an Elix-5 system (Millipore, Molsheim, France).

Synthesis of a methacrylate monomer containing $NH–(CH_2)_3–CO$–methyl ester

Methyl 4-aminobutyrate hydrochloride (15 mmol) and pyridine (45 mmol) were dissolved in 20 ml of *N*,*N*-dimethylformamide (DMF). Methacryloyl chloride (18 mmol) was added dropwise to the solution. The solution was stirred at room temperature overnight. After evaporation, the dry residue was dissolved in chloroform. An equivalent volume of water was added to the solution which was then vigorously mixed. The chloroform phase was collected and then washed with water (10 ml) and 10 mM HCl aqueous solution (10 ml) three times each. The chloroform phase was collected and then evaporated. The dry residue was vacuum-dried overnight. The yield was 88.6%. The synthesized monomer was identified by ^{1}H-NMR and DART-MS. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 6.11 (s, H, $-NH$), 5.69 (s, H, $-CH{=}CH$), 5.31 (s, H, $-CH{=}CH$), 3.67 (s, 3H, $-COOCH_3$), 3.36 (q, 2H, $-NHCH_2-$), 2.41 (t, 2H, $-CH_2COO-$), 1.95 (s, 3H, $-CCH_3$), 1.90 (quin, 2H, $-CH_2CH_2CH_2-$) ppm. DART-MS: $[MH]^+$ calcd for $C_9H_{15}N_1O_3$, 186.23; found, 186.10.

Synthesis of a methacrylate monomer containing $NH–CH_2–CO$–methyl ester

Glycine methyl ester hydrochloride (15 mmol) and pyridine (45 mmol) were dissolved in 20 ml of DMF/water (9:1 v/v). Methacryloyl chloride (18 mmol) was added dropwise to the solution. The solution was stirred at room temperature overnight. After evaporation, the dry residue was dissolved in ethyl acetate. An equivalent volume of water was added to the solution which was then vigorously mixed. The ethyl acetate phase was collected and then washed with water (10 ml) and 10 mM HCl aqueous solution (10 ml) three times each. The ethyl acetate phase was washed with an equivalent volume of water. The ethyl acetate phase was evaporated. The yield was 64.3%. The synthesized monomer was identified by ^{1}H-NMR and DART-MS. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 6.30 (s, H, −NH), 5.77 (s, H, −C*H*=CH), 5.39 (s, H, −CH=C*H*), 4.11 (d, 2H, $-NHCH_2-$), 3.78 (s, 3H, $-COOCH_3$), 1.99 (s, 3H, $-CCH_3$) ppm. DART-MS: $[MH]^+$ calcd for $C_7H_{12}N_1O_3$, 158.18; found, 158.12.

Synthesis of copolymers H1H2F6 and H3H2F6

A random copolymer composed of methyl methacrylate (MMA, 92 mol%) and methacrylate-based monomer containing $NH–CH_2–CO$–methyl ester (8 mol%) was synthesized via free radical polymerization. MMA (32 mmol), the functional monomer (3.5 mmol), and AIBN (0.11 mmol) were dissolved in 20 ml of toluene in a glass vial, followed by purging with nitrogen gas. Polymerization was performed under a nitrogen atmosphere at 60 °C overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane, and the precipitate was then vacuum-dried. The dry residue (1.0 g) was dissolved in a mixture (10 ml) of DMF/water (9:1 v/v) containing 0.5 M sodium hydroxide. The solution was stirred at room temperature for 4 h. The copolymer was precipitated by adding excess water, and the precipitate was then freeze-dried overnight. The dry residue (0.5 g) was dissolved in 20 ml of CH_2Cl_2. DMAP (0.05 mmol), EDC (0.5 mmol), pyridine (1.36 mmol), and 1H,1H,2H,2H-tridecafluoro-1-*n*-octanol (2.27 mmol) were added to the solution. The solution was stirred at room temperature overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane. The precipitate was washed with excess *n*-hexane and then excess water. The precipitate was freeze-dried overnight. The yield of copolymer H1H2F6 was 68.9%. Copolymer H1H2F6 had a M_n of 3.1×10^4 g/mol and a M_w/M_n of 2.0. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 5.98 (s, H, −NH), 4.16 (q, 2H, $-NHCH_2-$), 4.05 (t, 2H,

−COO*CH₂*CH₂), 3.48 (s, 28H, −COO*CH₃*), 1.95 (t, 3H, −COOCH₂*CH₂*−), 1.21–0.89 (m, 31H, −CCH₃) ppm. The elemental analysis indicated that R$_f$ groups were introduced to 69% of the carboxy groups in copolymer H1H2F6.

To synthesize copolymer H3H2F6, A random copolymer composed of MMA (90 mol%) and methacrylate-based monomer containing NH–$(CH_2)_3$–CO–methyl ester (10 mol%) was synthesized similar to that of copolymer H3H2F6. The yield of copolymer H3H2F6 was 78.5%. Copolymer H3H2F6 had a M_n of 2.3× 10^4 g/mol and a M_w/M_n of 2.2. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 5.88 (s, H, −NH), 4.21 (t, 2H, $-COOCH_2CH_2$), 3.58 (s, 29H, $-COOCH_3$), 3.18 (q, 2H, $-NHCH_2-$), 2.59 (t, 2H, $-CH_2COO-$), 2.31–1.75 (m, 24H, $-CCH_2-$, $-CH_2CH_2CH_2-$, $-COOCH_2CH_2-$), 1.23–0.89 (m, 33H, $-CCH_3$) ppm. The elemental analysis indicated that R$_f$ groups were introduced to 73% of the carboxy groups in copolymer H3H2F6.

Synthesis of copolymers H5H4 and H5H8

Copolymer H5-COOH (0.5 g) was dissolved in 20 ml of CH_2Cl_2. DMAP (0.05 mmol), EDC (0.5 mmol), pyridine (1.36 mmol), and 1-butanol (2.27 mmol) were added to the solution. The solution was stirred at room temperature overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane. The precipitate was washed with excess *n*-hexane and then excess water. The precipitate was freeze-dried overnight. The yield of copolymer H5H4 was 80.6%. Copolymer H5H4 had a M_n of 2.7× 10^4 g/mol and a M_w/M_n of 1.9. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 5.96 (s, H, −NH), 4.15 (t, 2H, $-COOCH_2-$), 3.78 (s, 32H, $-COOCH_3$), 3.22 (q, 2H, $-NHCH_2-$), 2.22 (t, 2H, $-CH_2COO-$), 2.12–1.76 (m, 23H, $-CCH_2-$), 1.68–1.29 (m, 10H, $-NHCH_2CH_2CH_2CH_2CH_2COO-$, $-COOCH_2CH_2CH_2-$), 1.16–0.93 (m, 30H, $-CCH_3$), 0.83 (t, 3H, $-CH_2CH_3$) ppm. The elemental analysis indicated that *n*-butyl ester groups were introduced to 85% of the carboxy groups in copolymer H5H4.

To prepare copolymer H5H8, 1-octanol (2.27 mmol), instead of 1-butanol, was used for the ester formation. The yield of copolymer H5H8 was 82.3%. Copolymer H5H8 had a M_n of 2.7×10^4 g/mol and a $M_\mathrm{w}/M_\mathrm{n}$ of 1.9. ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$, δ): 5.88 (s, H, $-\mathrm{NH}$), 4.20 (t, 2H, $-\mathrm{COO}\mathit{CH_2}-$), 3.67 (s, 29H, $-\mathrm{COO}\mathit{CH_3}$), 3.26 (q, 2H, $-\mathrm{NHC}\mathit{H_2}-$), 2.36 (t, 2H, $-\mathrm{CH_2COO}-$), 2.09–1.83 (m, 24H, $-\mathrm{CCH_2}-$), 1.70–1.19 (m, 20H, $-\mathrm{NHCH_2}\mathit{CH_2CH_2CH_2}\mathrm{CH_2COO}-$, $-\mathrm{COOCH_2}\mathit{CH_2CH_2CH_2CH_2CH_2CH_2}-$), 1.07–0.90 (m, 31H, $-\mathrm{CCH_3}$), 0.82 (t, 3H, $-\mathrm{CH_2}\mathit{CH_3}$) ppm. The elemental analysis indicated that *n*-octyl ester groups were introduced to 85% of the carboxy groups in copolymer H5H8.

Synthesis of copolymers H5H3F2 and H5H2F4

Copolymer H5-COOH (0.3 g) was dissolved in 20 ml of $\mathrm{CH_2Cl_2}$. DMAP (0.03 mmol), EDC (0.3 mmol), pyridine (0.82 mmol), and 4,4,5,5,5-pentafluoro-1-pentanol (1.36 mmol) were added to the solution. The solution was stirred at room temperature overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane. The precipitate was washed with excess *n*-hexane and then excess water. The precipitate was freeze-dried overnight. The yield of copolymer H5H3F2 was 73.2%. Copolymer H5H3F2 had a M_n of 2.6×10^4 g/mol and a $M_\mathrm{w}/M_\mathrm{n}$ of 1.8. ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$, δ): 6.06 (s, H, $-\mathrm{NH}$), 4.30 (t, 2H, $-\mathrm{COO}\mathit{CH_2}\mathrm{CH_2}$), 3.64 (s, 30H, $-\mathrm{COO}\mathit{CH_3}$), 3.18 (q, 2H, $-\mathrm{NHC}\mathit{H_2}-$), 2.42 (t, 2H, $-\mathrm{CH_2COO}-$), 2.25–1.80 (m, 20H, $-\mathrm{CCH_2}-$), 1.71–1.13 (m, 10H, $-\mathrm{COOCH_2}\mathit{CH_2}-$, $-\mathrm{C}\mathit{H_2}\mathrm{CH_2COO}-$, $-\mathrm{NHCH_2C}\mathit{H_2}-$, $-\mathrm{C}\mathit{H_2}\mathrm{CH_2CH_2COO}-$), 1.09–0.80 (m, 29H, $-\mathrm{CCH_3}$) ppm. The elemental analysis indicated that $\mathrm{R_f}$ groups were introduced to 82% of the carboxy groups in copolymer H5H3F2.

To prepare copolymer H5H2F4, 1H,1H,2H,2H-Nonafluoro-1-hexanol (1.36 mmol) were used instead of 4,4,5,5,5-pentafluoro-1-pentanol. The yield of copolymer H5H2F4 was 92.6%. Copolymer H5H2F4 had a M_n of 2.7×10^4 g/mol and a $M_\mathrm{w}/M_\mathrm{n}$ of 1.8. ^{1}H-NMR (500 MHz,

$\mathrm{CDCl_3}$, δ): 6.13 (s, H, $-\mathrm{NH}$), 4.16 (t, 2H, $-\mathrm{COO}CH_2\mathrm{CH_2}$), 3.65 (s, 28H, $-\mathrm{COO}CH_3$), 3.09 (q, 2H, $-\mathrm{NHC}H_2-$), 2.41 (t, 2H, $-\mathrm{CH_2COO}-$), 2.33–1.90 (m, 19H, $-\mathrm{CCH_2}-$), 1.78–1.24 (m, 8H, $-\mathrm{COOCH_2}CH_2-$, $-\mathrm{C}H_2\mathrm{CH_2COO}-$, $-\mathrm{NHCH_2C}H_2-$, $-\mathrm{C}H_2\mathrm{CH_2CH_2COO}-$), 1.17–0.85 (m, 29H, $-\mathrm{CCH_3}$) ppm. The elemental analysis indicated that $\mathrm{R_f}$ groups were introduced to 77% of the carboxy groups in copolymer H5H2F4.

Synthesis of copolymer H5H2F6$_{5:5}$ (monomer ratio of 5:5) and copolymer H5H2F6$_{7:3}$ (monomer ratio of 7:3)

A random copolymer composed of MMA (44 mol%) and methacrylate-based monomer containing NH–$(\mathrm{CH_2})_5$–CO–methyl ester (56 mol%) was synthesized via free radical polymerization. MMA (8.4 mmol), the functional monomer (8.4 mmol), and AIBN (0.08 mmol) were dissolved in 12 ml of toluene in a glass vial, followed by purging with nitrogen gas. Polymerization was performed under a nitrogen atmosphere at 60 °C overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane, and the precipitate was then vacuum-dried. The copolymer (1.0 g) was dissolved in a mixture (10 ml) of DMF/water (9:1 v/v) containing 0.5 M sodium hydroxide. The solution was stirred at room temperature for 4 h. The copolymer was precipitated by adding excess water, and the precipitate was freeze-dried overnight. The dry residue (0.5 g) was dissolved in 20 ml of $\mathrm{CH_2Cl_2}$. DMAP (0.17 mmol), EDC (1.84 mmol), pyridine (5.01 mmol), and 1H,1H,2H,2H-tridecafluoro-1-*n*-octanol (8.35 mmol) were added to the solution. The solution was stirred at room temperature overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane. The precipitate was washed with excess *n*-hexane and then excess water. The precipitate was freeze-dried overnight. The yield of copolymer H5H2F6$_{5:5}$ was 73%. Copolymer H5H2F6$_{5:5}$ had a M_n of 1.0×10^4 g/mol and a $M_\mathrm{w}/M_\mathrm{n}$ of 1.9. ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$, δ): 6.05 (s, 4H, $-\mathrm{NH}$), 4.50 (t, 11H, $-\mathrm{COO}CH_2\mathrm{CH_2}$), 3.60 (s, 17H, $-\mathrm{COO}CH_3$), 3.27 (q, 8H, $-\mathrm{NHC}H_2-$), 2.56 (t, 10H, $-\mathrm{CH_2COO}-$), 2.26–1.70 (m, 21H, $-\mathrm{CCH_2}-$), 1.75–1.19 (m, 42H, $-\mathrm{COOCH_2}CH_2-$,

$-\mathrm{C}\mathit{H_2}\mathrm{CH_2COO}-$, $-\mathrm{NHCH_2C}\mathit{H_2}-$, $-\mathrm{C}\mathit{H_2}\mathrm{CH_2CH_2COO}-$), 1.11–0.85 (m, 15H, $-\mathrm{CCH_3}$) ppm. The elemental analysis indicated that $\mathrm{R_f}$ groups were introduced to 93% of the carboxy groups in copolymer $\mathrm{H5H2F6}_{\mathbf{5:5}}$ (monomer ratio of 5:5).

To synthesize copolymer $\mathrm{H5H2F6}_{7:3}$ (monomer ratio of 7:3), MMA (31 mmol), the functional monomer (13 mmol), and AIBN (0.18 mmol) were used for polymerization. The yield was 76%. Copolymer $\mathrm{H5H2F6}_{7:3}$ had a M_n of 2.1×10^4 g/mol and a $M_\mathrm{w}/M_\mathrm{n}$ of 2.1. ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$, δ): 6.12 (s, 3H, $-\mathrm{NH}$), 4.22 (t, 6H, $-\mathrm{COO}\mathit{CH_2}\mathrm{CH_2}-$), 3.44 (s, 22H, $-\mathrm{COO}\mathit{CH_3}$), 3.16 (q, 7H, $-\mathrm{NHC}\mathit{H_2}-$), 2.41 (t, 6H, $-\mathrm{CH_2COO}-$), 2.21–1.79 (m, 21H, $-\mathrm{CCH_2}-$), 1.63–1.20 (m, 26H, $-\mathrm{COOCH_2}\mathit{CH_2}-$, $-\mathrm{C}\mathit{H_2}\mathrm{CH_2COO}-$, $-\mathrm{NHCH_2C}\mathit{H_2}-$, $-\mathrm{C}\mathit{H_2}\mathrm{CH_2CH_2COO}-$), 1.09–0.77 (m, 21H, $-\mathrm{CCH_3}$) ppm. The elemental analysis indicated that $\mathrm{R_f}$ groups were introduced to 79% of the carboxy groups in copolymer $\mathrm{H5H2F6}_{\mathbf{7:3}}$ (monomer ratio of 7:3).

Synthesis of poly(methyl methacrylate) (PMMA)

MMA (100 mmol) and AIBN (0.30 mmol) were dissolved in 46 ml of toluene in a glass vial, followed by purging with nitrogen gas. Polymerization was performed under a nitrogen atmosphere at 60 °C overnight. The copolymer was precipitated by adding the solution to 200 ml of *n*-hexane, and the precipitate was then vacuum-dried. The yield of PMMA was 91.2 %. PMMA had a M_n of 3.9×10^4 g/mol and a $M_\mathrm{w}/M_\mathrm{n}$ of 1.9. ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$, δ): 3.48 (s, 3H, $-\mathrm{COO}\mathit{CH_3}$), 1.03–0.78 (m, 3H, $-\mathrm{CCH_3}$) ppm.

Results

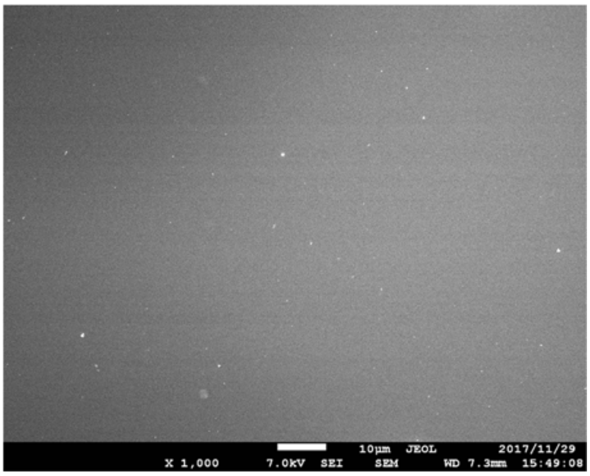

Figure S1. Field-emission scanning electron microscope image of the PMMA substrate dip-coated with copolymer H5H2F6. The surface was coated with OsO_4 using an osmium coater (Neoc, Meiwaforsis Co., Ltd. Tokyo, Japan). FE-SEM observations were carried out using a field-emission scanning electron microscope (JSM-7500F, JEOL, Tokyo, Japan) operating at an accelerating voltage of 7 kV.

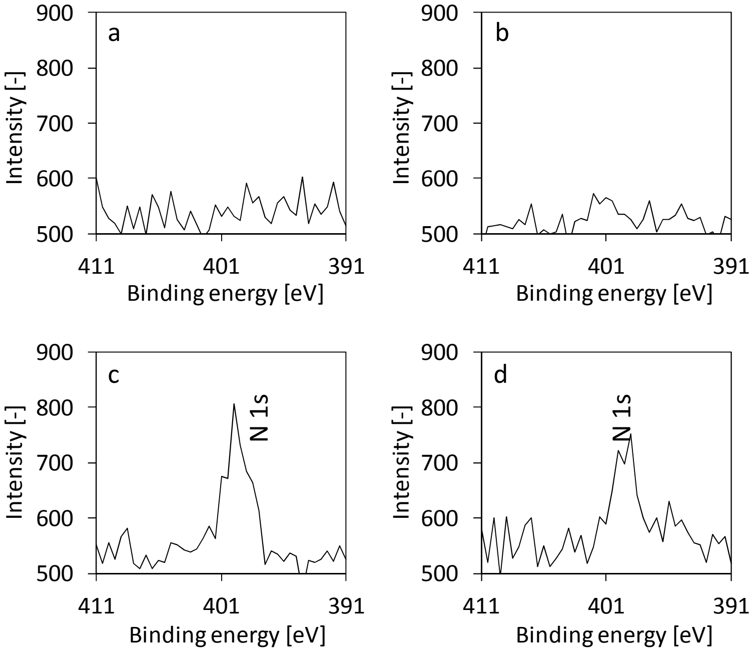

Figure S2. XPS spectra of the N1s region of the surfaces of acrylic substrates: a) Bare substrate, and substrates dip-coated with b) copolymer H5-COOH, c) copolymer H5H2F6 before hydrolysis using NaOH solution, and d) copolymer H5H2F6 after hydrolysis.