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HYDROPHOBIC AND HYDROPHILIC FLUOROPOLYMERS AS NON-ADHESIVE INTERFACES IN MARINE BIOFOULING

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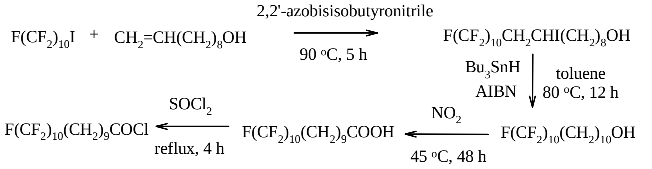
Introduction

Bioadhesion at polymer interfaces is an important issue in the biocompatibility of implants, drug delivery, tissue engineering or marine biofouling. Our work is focused on developing polymer surfaces to study and overcome the marine biofouling problem. When a surface is immersed in a marine environment, it rapidly adsorbs organic matter present in the water. This is followed by the formation of a microbial biofilm by settlement and growth of bacterial cells, diatoms, algal spores or protozoa. These organisms bind to the surface using what are referred to as extracellular polymeric substances (EPS), which include biomacromolecules such as proteins and polysaccharides. Biofilm formation promotes the settlement of larger invertebrates such as barnacles. Biofouling of ships is undesirable because of increased fuel and maintenance costs.

One way to prevent the formation of a biofilm is to develop surfaces that are resistant to adsorption of EPS of the biological cells.[1] Binding forces are stronger in the case of high-energy surfaces such as glass or metals, compared to low-energy surfaces such as poly(dimethylsiloxane). Fluoropolymers are another important class of low energy surfaces, with the surface energy of poly(tetrafluoroethylene) (18.5 mJ/m^2) comparable to that of PDMS (22 mJ/m^2). This paper will discuss liquid crystalline polymers with semifluorinated side chains that have surface energy values as low as 8 mJ/m^2, and strategies to overcome the problems normally encountered with fluoropolymers, namely, poor solubility in common solvents, poor adhesion to substrate, etc. Liquid crystallinity of the side-chains prevents molecular reconstruction under water, a phenomenon commonly observed when a hydrophobic surface is in contact with a polar medium.[2] The distinct property of segregation of fluoropolymers to an air-polymer interface will also be discussed.

Experimental

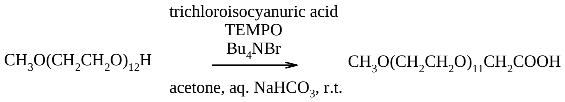
Block copolymers with fluorinated side chains were prepared by polymer analogous reactions on block copolymer precursors, or direct polymerization of fluorinated monomers by controlled free-radical polymerization. Polystyrene-block-poly(isoprene) (PS/PI) copolymers with predominantly 1,2- or 3,4-addition in the isoprene block were prepared by anionic polymerization in tetrahydrofuran at -78 °C using sec-butyllithium initiator. PS/PI block copolymers with block molecular weights of 10 kDa/12 kDa and 27 kDa/13 kDa and polydispersity indices (PDI), determined by gel permeation chromatography, of ca. 1.1 were used. Hydroxylation of the isoprene block was achieved by hydroboration/oxidation using 9-borabicyclononane and hydrogen peroxide.[3,4]



Scheme 1. Synthesis of ω-10-perfluorodecyl-decanoyl chloride

Semifluorinated acid chloride, prepared as shown in **Scheme 1**, [3,5] was then attached to hydroxylated block by reaction in pyridine and tetrahydrofuran. Quantitative esterification was confirmed by the disappearance of the O-H stretching vibrations at 3334 cm^{-1} of the PS/PI-OH precursor, and appearance of ester C=O stretching vibrations at 1737 cm^{-1} and C-F band between 1000 cm^{-1} and 1400 cm^{-1}.

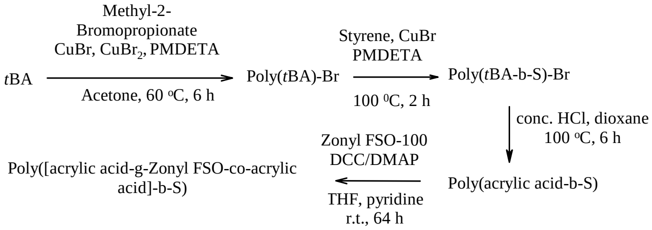
Poly(ethylene glycol) side chains. Monomethyl PEG with a molecular weight of 550 g/mol (PEG550) was oxidized to carboxy PEG using the procedure reported by Luca et al.[6] for oxidation of alcohols, as shown in **Scheme 2**. The carboxy PEG, after reaction with thionyl chloride, was attached to the hydroxylated PS/PI(27/13) block copolymer.



$$CH_3O(CH_2CH_2O)_{12}H \xrightarrow[\text{acetone, aq. NaHCO}_3\text{, r.t.}]{\text{trichloroisocyanuric acid, TEMPO, Bu}_4\text{NBr}} CH_3O(CH_2CH_2O)_{11}CH_2COOH$$

Scheme 2. Oxidation of monomethyl PEG

Ethoxylated fluoroalkyl side chains. Block copolymers with ethoxylated fluoroalkyl side chains were prepared using polystyrene-*block*-poly(*tert*-butylacrylate) precursor. The latter was synthesized by atom-transfer radical polymerization of styrene using poly(*tert*-butyl acrylate) macroinitiator/copper bromide/pentamethyl diethylenetriamine (PMDETA) system.[7] The molecular weights of the styrene (S) and *tert*-butyl acrylate (*t*BA) blocks were 8 kDA and 3 kDa, respectively. After deprotection with conc. hydrochloric acid, the acrylic acid block was reacted with Zonyl® FSO-100 [DuPont, $F(CF_2CF_2)_yCH_2CH_2O(CH_2CH_2O)_xH$ (x = 0 to 15 and y = 1 to 7)] in the presence of dicyclohexylcarbodiimide and dimethylaminopyridine.



Scheme 3. Synthesis of block copolymer with amphiphilic side chains; PS/P*t*BA(8/3)FSO-100.

Results and Discussion

Role of PS block. The PS block improves solubility of the fluorinated polymers in solvents such as chloroform and α,α,α-trifluorotoluene (TFT). It also makes the PEGylated polymer insoluble in water, preventing removal of the coating in a marine environment. To improve the adhesion of the polymers to glass or metal substrates, and to independently control the modulus and surface chemistry of the coatings for marine antifouling applications, a bilayer approach has been used where the lower layer was a polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) thermoplastic elastomer, and the top layer was the surface-active block copolymer. The PS blocks in the bottom and top layers will mix at the interface, welding the two layers.

Block copolymers with semifluorinated side chains. The liquid-crystalline nature of the block copolymers with $F(CF_2)_{10}(CH_2)_9COO$- side chains (abbreviated to F10H9) was confirmed using differential scanning calorimetry. Two distinct first-order transitions were observed at 98 °C and 113 °C, and based on previous studies,[8,9] attributed to smectic-B to smectic-A, and smectic-A to isotropic transitions, respectively. Polymer surfaces were prepared by spin-coating solutions of the block-copolymers in suitable solvents. The chemical composition and properties of the block copolymer surfaces were found to strongly depend on the method of preparation of surfaces (solvent, coating method and annealing). **Table 1** gives the water contact angles on a PS/PI(10/12)F10H9 polymer surface prepared by spin-coating a 3 % (w/v) solution of the polymer in chloroform on silicon wafers.

Table 1. PS/PI(10/12)F10H9 Surfaces Annealed at Different Temperatures for 12 h

	50 °C	50 °C & 120 °C	50 °C & 150 °C
Water contact angles (deg)			
Advancing	130 ± 3	129 ± 1	124 ± 1
Receding	65 ± 3	100 ± 1	109 ± 1
Surface order parameter and chemical composition			
$S_{\text{F-helix}}$	0	0.18	0.36
% PS	26.3	11.4	4.3

The spin-coated surfaces were dried at 50 °C for 12 hours, and two such surfaces were further annealed for 12 h at 120 °C and 150 °C. It is seen that the contact angle hysteresis decreases with annealing. Contact angle hysteresis is an indication of any or all of the following three effects: chemical heterogeneity, roughness and molecular reconstruction of surface. Analysis of the surface by atomic force microscopy showed that the root-mean-square surface roughness decreased from 18 nm to 5 nm upon annealing at 150 °C. The higher advancing angle on the 50 °C surface can be attributed to pinning of the contact line by surface roughness.

Two other important reasons for decrease in the contact angle hysteresis with annealing are (1) the enrichment of the surface with the fluorinated block, and (2) increase in order of the smectic-B phase of the semifluorinated side chains at the surface. These effects were clearly evident from the NEXAFS spectra of these surfaces shown in **Figure 2**. The decreasing intensity of the phenyl π^* transition at 285 eV and the increasing intensity of the C-F σ^* transition at 292 eV indicates segregation of the low-energy fluorinated block, displacing the higher-energy polystyrene block from the surface. In addition, the fluorinated helix order parameter, $S_{\text{F-helix}}$, calculated from the variation of the intensity of $\sigma^*_{\text{C-F}}$ peak with the angle of incidence of X-ray, increased with annealing. A value of 1 indicates an average normal orientation of the fluorinated helices of the side chains, while a value of -0.5 indicates an average orientation parallel to the surface. A perfectly normal orientation is expected to result in the lowest surface energy, as the surface would be completely covered by CF_3 groups. The 50 °C surface did not show any specific orientation of the fluorinated helix ($S_{\text{F-helix}} \sim 0$).

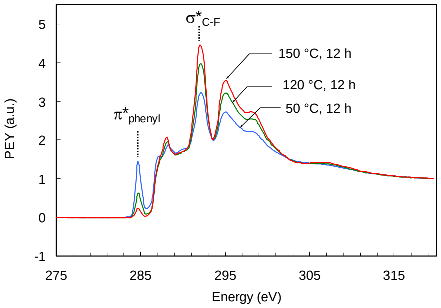


Figure 2. C-edge NEXAFS spectra of surfaces annealed at different temperatures for 12 h, obtained at 55° angle between the X-ray beam and surface.

Block copolymer with PEG side chains. Hydrated poly(ethylene oxide) surfaces are known to inhibit adsorption of proteins, possibly by a mechanism similar to the cilia found on the mucosal epithelia of living tissues.[10] We, therefore, synthesized block copolymers with hydrophilic PEG side chains to study the adhesion strength of marine organisms on protein repellant surfaces. PEGylated block copolymer surfaces were prepared by spin-coating a 3 % (w/v) chloroform solution on an SEBS layer, and dried at room temperature under vacuum for 12 h. This surface showed ca. 82 % reduction in adsorption of BSA protein compared to a hydrophobic SEBS surface (advancing water contact angle of 95°). The advancing water contact angle on the PS/PI(27/13)PEG550 surface was (44 ± 3)°, and the receding angle was less than 5°. However, annealing the surface at 60 °C in vacuum for 12 h resulted in an increase in the contact angles to (74 ± 2)° and (8 ± 2)° because of the segregation of the lower energy (39.3 mJ/m^2) PS block to the surface, partially displacing the higher energy[11] PEGylated block. NEXAFS showed that the PS content of a PS/PI(27/13)F10H9 surface subjected to solvent annealing using TFT followed by thermal annealing at 120 °C for 12 h was negligible (no π^* peak), while that of the PS/PI(27/13)PEG550 surface was ca. 38 %. Both these polymers have the same length of PS block (27 kDa).

Block copolymer with amphiphilic side chains. To ensure that the relatively higher energy PEG side chains were present at the air-polymer interface at equilibrium, block copolymers with $F(CF_2CF_2)_yCH_2CH_2O(CH_2CH_2O)_x$- side chains (x = 0 to 15 and y = 1 to 7) were synthesized. It was expected that the surface will be fluorinated in air, but will reconstruct under water, presenting the hydrophilic PEG groups. Thus, the advancing and receding water contact angles on a surface prepared by spray-coating 1.5 % (w/v) solution of PS/P*t*BA(8/3)FSO-100 copolymer in chloroform, followed by drying at 60 °C for 24 h was found to be (97 ± 2)° and (32 ± 3)°. **Figure 3** shows the NEXAFS spectra of this surface. The prominent C-F σ^* transition peak at 292 eV indicates the presence of fluoroalkyl groups at the surface. The fluorinated helix order parameter was found to be ca. 0.2. The large number of PS mers at the surface, indicated by the relatively high π^* peak, will also contribute the contact angle hysteresis.

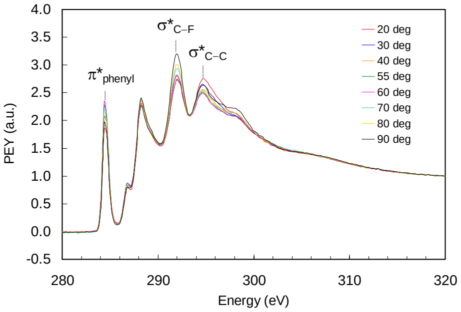


Figure 3. C-edge NEXAFS spectra of the amphiphilic block copolymer surface at different angles of incidence of X-ray beam.

Marine Antifouling Properties. Adhesion of marine algae *Ulva* and *Navicula* were studied on the block copolymer surfaces using a turbulent flow channel. While the release of *Ulva* was high on the hydrophobic (10/12)F10H9 surfaces (70 ± 10 % removal of sporelings at a wall-shear stress of 53 Pa) indicating poor adhesion, removal of *Navicula* was lower (50 ± 10 %). On the contrary, removal of *Navicula* was much higher on the hydrophilic (27/13)PEG550 surface (78 ± 4 %) compared to a hydrophobic PDMS surface (11 ± 4 %) used as a control. Interestingly, it was found that the amphiphilic surface that showed hydrophobic character in air (advancing water contact angle > 90°) resulted in (81 ± 5) % removal of settled *Navicula* cells.

Conclusions

New block copolymers with hydrophilic and amphiphilic side groups were synthesized by polymer analogous reactions on block copolymer precursors using reaction schemes that allowed high attachment of side groups to the polymer backbone. Block copolymers with liquid crystalline semifluorinated side chains were prepared using previously established techniques. The surface properties of hydrophobic, hydrophilic and amphiphilic block copolymers were studied using water-contact angle measurements, NEXAFS spectroscopy and atomic force microscopy. All the block copolymers showed promising fouling release behavior when tested with marine algal cells.

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(11) Surface energy of poly(ethylene oxide) is ca. 43 mJ/m^2.