spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) analyses demonstrated that the 'dry' surfaces contained much more fluorine with respect to the theoretical composition.[88] This was reduced in the 'wet' surfaces after water immersion due to the increased presence of hydrophilic PEG side chains at the polymer–water interface (Figure 5). Moreover, the hydrophobic phenyl rings migrated away from the surface after water immersion.

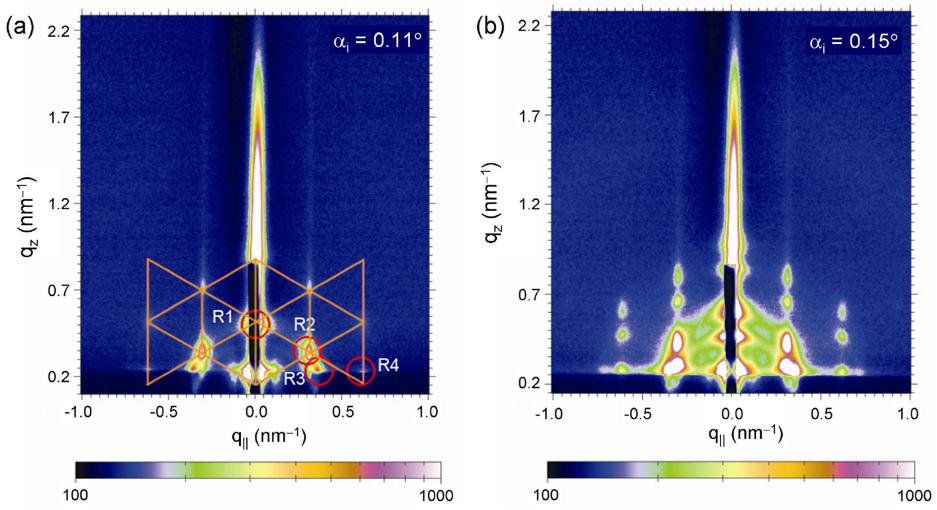

Figure 4. 2-Dimensional grazing-incidence small-angle X-ray scattering (GISAXS) maps of a block copolymer SmSzn (m=51, n=17) acquired at an X-ray angle of (a) 0.11° and (b) 0.15°. The hexagonal cylinder lattice is indicated in (a). At higher incident angles diffraction spots are split up due to reflection from the substrate. Reproduced from Ref.[86] with permission of John Wiley and Sons.

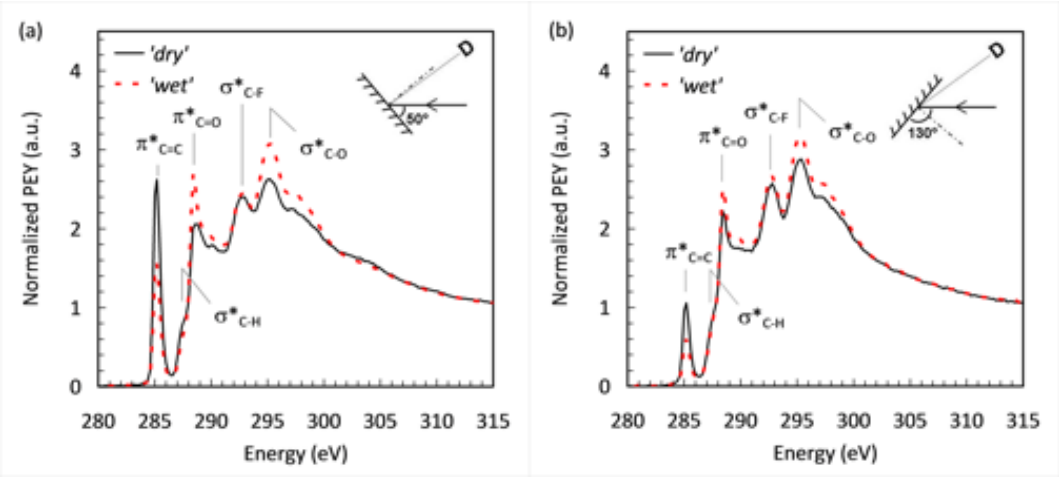

Figure 5. C(1s) NEXAFS spectra of 'dry' and 'wet' thin films of a block copolymer SmSzn (m=51, n=17), acquired at X-ray incidence angles of (a) 50° and (b) 130°. Note, e.g. the σ^*_{C-O} resonance for the PEG chains and the $\pi^*_{C=C}$ resonance for the phenyl rings. Reproduced with permission from Ref.[88]. Copyright (2010) American Chemical Society.

The SmSzn surface-active block copolymers were included in the top layer of SEBS-based two-layer coatings either alone or blended with SEBS. The coatings exhibited surface morphologies which depended on the chemical composition of the block copolymer in the top layer.[89] A transformation from well-defined surface morphologies to mixed morphologies occurred upon immersion in water. Nonetheless, the initially hydrophobic surfaces retained the time-dependent water responsiveness typical of the pristine amphiphilic copolymer.[90] Biological assays against *U. linza* revealed that all the amphiphilic coatings promoted the removal of sporelings with respect to the SEBS control. The best performer (removal >80%) was a film with an intermediate, not maximal, content of amphiphilic counits in the top layer, which exhibited the more regular surface pattern when immersed in artificial seawater (ASW) with swollen nanodomains (50–100 nm by atomic force microscopy analysis (AFM)) (Figure 6).

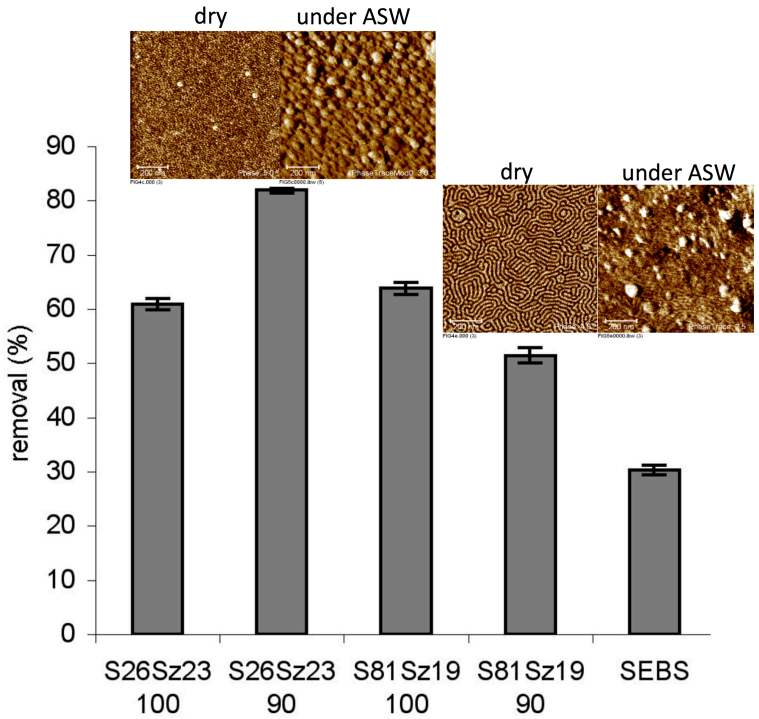

Figure 6. Removal percentage of *U. linza* sporelings from SEBS-based films with block copolymers SmSzn of different block lengths (m = 26 and 81; n = 23 and 19) and contents in the top layer (100 and 90 wt% copolymer with respect to SEBS). Insets show the AFM phase images (1 × 1 μm^2) of dry films and under ASW of S26Sz23_90 (left) and S81Sz19_90 (right). Adapted with permission from Ref.[89]. Copyright (2008) American Chemical Society.

An amphiphilic triblock copolymer was prepared by post-modification of a

poly(styrene-*b*-(ethylene-*ran*-butylene)-*b*-isoprene) P(S-*b*-(E/B)-*b*-PI) precursor with the same PEGylated-perfluoroalkyl chains.[91] The effect of the Young's modulus of the SEBS matrix on *U. linza* was evaluated by using two different elastomers with modulus values of an order of magnitude in difference. The amphiphilic coatings inhibited attachment of zoospores and promoted the release of sporelings, and the attachment strength of sporelings was further reduced for the coatings with the lower modulus. Similarly, PS-*b*-P(E/B)-*b*-PI copolymers were modified by post-reaction with separated perfluoroalkyl and PEGylated side chains to establish a better control on the copolymer hydrophilic/hydrophobic character.[92] The attachment of *U. linza* zoospores was found to be higher for surfaces incorporating a large proportion of the fluoroalkyl side chains, while surfaces with a large proportion of the PEGylated segments inhibited settlement. Moreover, coatings incorporating a mixture of both PEG and fluoroalkyl side chains were excellent in promoting removal of *U. linza* sporelings. The number of cells of the diatom *N. perminuta* attached after exposure to flow decreased as the PEGylated/fluoroalkyl ratio increased.

Perfluorocarbon chains with ≥7 CF_2 groups have raised concerns associated with (bio)accumulation in the environment of possible biodegradation products such as perfluorooctanoic acid and higher homologues. This potential drawback decreases the likelihood of such polymers being adopted in commercial coatings for use in the marine environment.[93] Accordingly, shorter perfluoroalkyl chains (≤6 CF_2 groups) have also been explored for introduction into amphiphilic copolymers.[94]

Several fluorine-free surface-active copolymers were also prepared by attaching to a P(S-*b*-(E/B)-*b*-PI) triblock copolymer precursor separately PDMS and PEG pendant chains,[95] non-ionic amphiphiles, including hydrocarbon-PEGylated Brij-type side chains[96] and PEGylated-hydrocarbon side chains[87] (**3**, Figure 2). All the fluorine-free SEBS-based coatings derived therefrom shared the ability to become more hydrophilic after immersion in water, due to a reconstruction process which involved the migration to the surface of the hydrophilic PEG chains, while the non-polar segments became buried in the bulk. The films before immersion in water displayed mostly lying-down cylinders. However, this morphology changed on exposure to water, with an increase in nanodomain size (from 30–50 nm before to 40–150 nm after immersion), owing to the swelling of the hydrophilic PEG groups in water.[96] This amphiphilic and dynamic nature resulted in AF and FR attributes against the attachment of *U. linza* zoospores and the release of *U. linza* sporelings and

N. perminuta cells. In particular, surfaces coated with copolymers richer in PEG[95] or possessing longer PEG chains[87] showed higher efficacy in reducing cell attachment as well as reducing adhesion strength.

2.2. PDMS-based systems

The first published example was a one-layer system containing a diblock copolymer composed of a PDMS block and a PEGylated-fluoroalkyl modified polystyrene block (**4**, Figure 7).[97] The coating surface presented a simultaneous hydrophobic and lipophobic character, owing to the strong surface segregation of the lowest surface energy fluoroalkyl chains. However, the surfaces were able to reconstruct after relatively prolonged contact with water.

Developments in architectures composed of a surface-active amphiphilic polymer included random copolymers with PDMS and PEGylated-fluroalkyl side chains (**5**, Figure 7). The biological response of these films was found to be strictly dependent on the chemical composition of the copolymer incorporated in the PDMS.[98] Coatings containing the copolymer with the lowest amount of PEGylated-fluoroalkyl counits (10 mol%) showed the highest removal (>70%) of *U. linza* sporelings, the lowest settlement of *B. amphitrite* cyprids (<25% after 24 h-incubation) and the lowest adhesion strength (critical removal stress <0.12 MPa) of *B. amphitrite* adults. By an XPS study, it was found that all the investigated surfaces were highly enriched in fluorine even after immersion in water and the best performing coatings had the lowest concentration of fluorine at the surface.[84] Moreover, they displayed the most regular AFM surface patterns upon immersion, with worm-like nanostructures and soft globular domains (diameter <150 nm) of the swollen PEGylated portions at the surface. By contrast, the worst performers exhibited larger and irregularly distributed globular patches (diameter 0.5–1 μm). The excellent AF/FR properties of these coatings were also complemented by field immersion trials.[98] Moreover, an investigation of the frictional drag of these PDMS-based coatings revealed that the hydrodynamic behaviour was superior compared to a hydraulically smooth reference surface.[99]

Different outcomes in biological tests were noticed when amphiphilic polystyrene-based random copolymers containing polysiloxane, perfluorohexylethyl and/or PEGylated side chains were used in combination with either a SEBS or a

PDMS matrix in a two-layer geometry.[100] Firstly, the PDMS-based coatings had superior FR properties against *U. linza* compared to the SEBS-based coatings, independent of the chemistry of the surface-active copolymer in the top layer. This was attributed to the lower elastic modulus of the PDMS-based coatings (0.23 MPa) with respect to the SEBS-based ones (2.35 MPa). Secondly, the surface-active copolymer that more effectively limited the attachment or promoted the release of *U. linza* was the fluorine-free amphiphilic copolymer, containing only the polysiloxane and PEG side chains. Similar results were obtained when the FR performance against *U. linza* of two different surface-active copolymers composed of the same PDMS block and a different poly(meth)acrylate block carrying PEG or perfluorohexylethyl side chains were compared.[101] The fluorine-free amphiphilic block copolymers showed a higher removal of sporelings with respect to the fluorinated block copolymers. PDMS-based coatings containing the fluorinated copolymer totally inhibited the settlement of *B. amphitrite* (as no cyprids were found to settle on), while the PEGylated coatings performed better than the PDMS control. However, the strength of attachment of barnacle juveniles was lower for PEGylated coatings than for the PDMS control. Such differences in biological performance were correlated with the difference in surface composition of the coatings. Whereas coatings containing the fluorinated chains presented surfaces highly enriched in fluorine, those with the PEGylated component possessed surfaces more crowded by the siloxane chains, with the PEG chains present only to a minor extent.

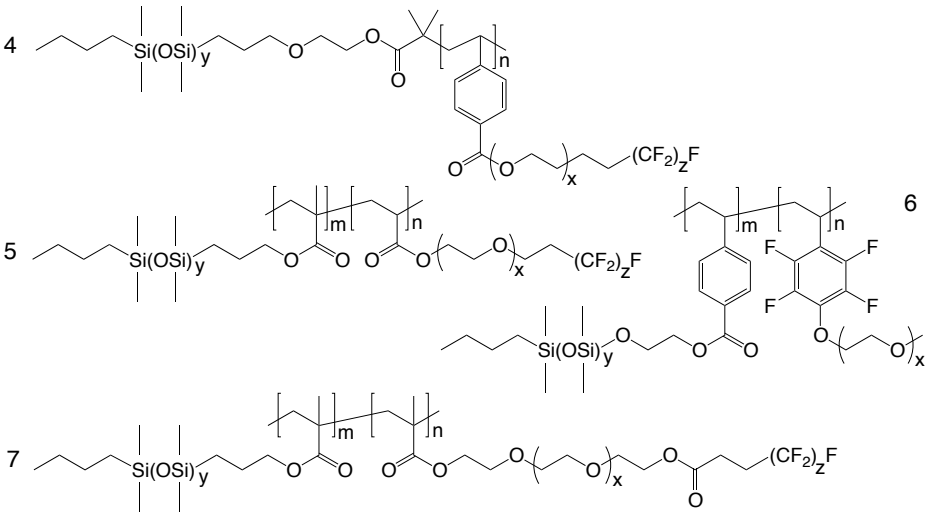

Figure 7. Illustrations of surface-active (co)polymers containing hydrophilic PEG units, hydrophobic PDMS units and hydrophobic/lipophobic fluorinated units of

varying length (x, y and z, respectively) for introduction into PDMS-based systems.[97,98,102,103]

3. Amphiphilic layer-by-layer polymer films

The layer-by-layer (LbL) technique has been used to deposit thin polymer films to prevent protein adsorption, bacterial and marine fouling by covalent or electrostatic LbL approaches.[104–108] In one example of amphiphilic LbL polymer film, a polyanion was synthesised through partial alcoholysis of poly(isobutylene-*alt*-maleic anhydride) (PIAMA) with an amphiphilic perfluoroalkyl-PEG and subsequently combined with a polyethyleneimine (PEI) polycation (Figure 8).[109] The LbL films were also cross-linked by formation of interchain amide bonds.

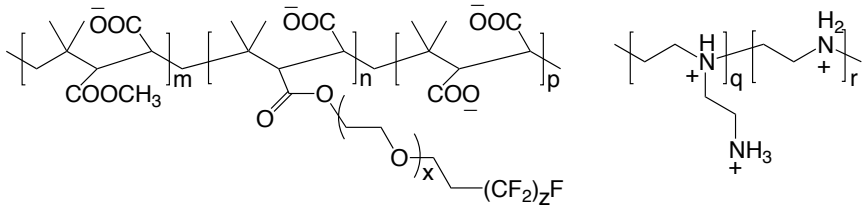

Figure 8. PIAMA polyanion-PEI polycation system for deposition of an amphiphilic LbL film.[109]

Low water receding contact angle and large water contact angle hysteresis were detected, suggesting the presence of a dynamic surface with ability for environmentally dependent surface reconstruction. Such films showed a relatively low resistance to attachment of the benthic diatom *Amphora coffeaeformis* with respect to the uncoated silicon wafer control, while they were able to significantly inhibit the adhesion of the marine bacterium *Pseudomonas* (NCIMB 2021).

4. Amphiphilic hyperbranched polymer networks

The fabrication of hyperbranched networks via the chemical reaction of precursors with different philicity/phobicity is another means to alter and modulate the surface properties of a film. Supramolecular assembly and dynamic reorganisation upon water immersion are both regarded as potential contributors to the biological properties. Specifically, the antifouling activity is believed to depend on a combination of

complex surface compositions, morphologies and topographies generated after immersion in water at the nano-to-micro length scale. Early work on this type of AF/FR polymer network consisted of a PEG-cross-linked hyperbranched fluoropolymer (HBFP) deposited on amine-functionalised glass (Figure 9).[110,111] The films displayed complex surface morphology and topography resulting from the phase separation of the incompatible HBFP and PEG components. Moreover, the surface was capable of dynamically and reversibly responding to the outer environment. Films enriched in PEG (45–55 wt%) were highly effective in inhibiting the adsorption of proteins and lipopolysaccharides and reducing the settlement of *U. linza* zoospores. The coatings containing 45% PEG, that is an intermediate, not highest hydrophile content, showed maximal removal (40%) of zoospores and sporelings (almost 100%), thus outperforming the PDMS control (50% removal).[111]

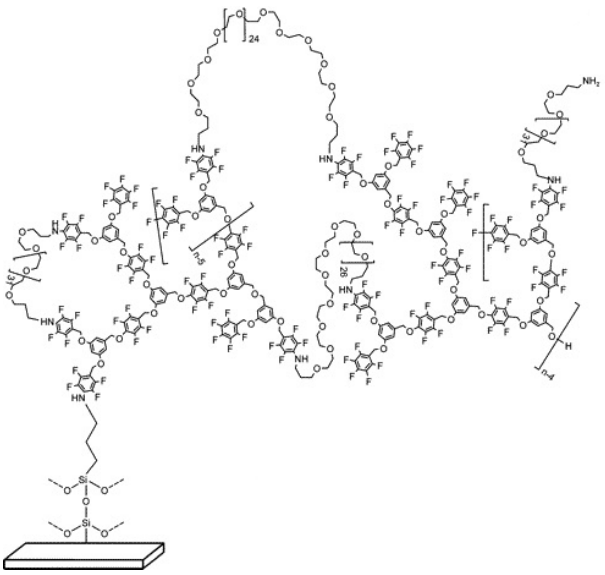

Figure 9. Schematic of a HBFP-PEG polymer network deposited on amine-functionalised glass substrate. Adapted with permission from Ref.[111]. Copyright (2005) American Chemical Society.

In later HBFP-PEG coatings, the HBFP was synthesised by atom transfer radical self-condensing vinyl copolymerisation (ATR-SCVCP) of 4-chloro- or 4-bromomethylstyrene with 2,3,4,5,6-pentafluorostyrene (PFS).[112] Because of the brittleness of the films derived therefrom, a third-generation amphiphilic HBFP was prepared by ATR-SCVCP of 4-[oxy(triethylene glycol)bromoisobutyryl]-2,3,5,6-tetrafluorostyrene and PFS in an attempt to advance the mechanical properties along with adding amphiphilicity within the HBFP framework.[113] Dual-mode, i.e. active

and passive, films were then obtained by decorating the HBFP-PEG network surface with noradrenaline (NA), a bioactive fouling-deterrent molecule. On the one hand, the combination of PEG and HBFP generated passive AF surfaces with topographic features at the nanoscale and amphiphilicity. On the other hand, the incorporation of NA units actively enhanced the ability of the entire system of inhibiting the settlement of barnacle larvae with respect to unmodified HBFP-PEG surfaces.[114] The investigation was extended to an array of HBFP-PEG compositions in order to optimise the physical-chemical properties and the antifouling performances.[115] In both the dry and water-swollen states, the water contact angle decreased as the amount of PEG cross-linker increased in the formulations, indicating a higher surface hydrophilicity. However, a 'contraphilic' behaviour of higher hydrophobicity was observed in passing from the dry to the water-swollen state, as evidenced by a larger water contact angle (Figure 10). This peculiar behaviour was accounted for by the varied chemical composition of the immersed surfaces, which became richer in fluorine. Tested films were shown to completely deter the settlement of barnacle cyprids of *B. amphitrite*. The removal percentage of the diatom *Navicula incerta* was 2–3 folds higher than that of the PDMS control. However, spores of *U. linza* settled on the surfaces and were more difficult to remove with respect to the PDMS.

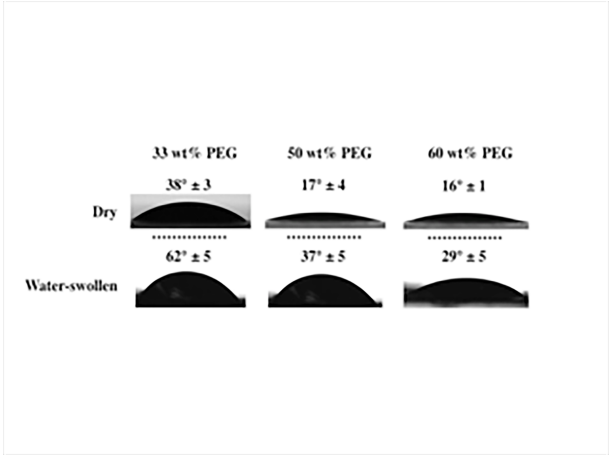

Figure 10. Static water contact angles of coatings from an HBFP-PEG with 67 mol% PFS, cross-linked with 33, 50 and 60 wt% PEG in the dry and water-swollen states. Reproduced from Ref.[115] with permission of The Royal Society of Chemistry.

More recently linear PDMS was additionally introduced in the hyperbranched structure, thus leading to HBFP-PEG-PDMS terpolymer networks.[116] A PEG-dependent surface reconstruction was observed, which had opposite effects on the

wettability of immersed coatings. Formulations containing 0–25 wt% PEG exhibited an increase in water contact angle post-immersion, consistent with a contraphilic effect. By contrast, formulations containing more than 50 wt% PEG showed a general decrease in contact angle upon immersion in water, suggesting that the PEG-rich domains were discrete enough for isolated regions of water uptake to occur. The terpolymer networks showed a high resistance to the adsorption of bovine serum albumin with respect to a commercial PDMS, but the AF/FR performance against marine organisms was not tested. Highly branched and dendritic networks were also developed by thiol-ene click chemistry of alkene-functionalised Boltorn polyesters with PEG tetrathiol and pentaerythrityl tetra(3-mercaptopropionate) (PETMP) in the presence of a UV photoinitiator.[117] It was observed that the thermal, mechanical and surface properties (wettability and topography) depended on the PEG and PETMP contents. In particular, the nanoscopic surface features changed with PEG concentration, the surface becoming increasingly rough with increasing PEG content. Biological performance against *U. linza* was tested on coatings having a constant PETMP concentration (16 wt%) at varying PEG content (0–35 wt%). Spore settlement was low on all the amphiphilic networks compared to that on PDMS control and increased with PEG content. On the other hand, the adhesion of sporelings was stronger on all of the coatings than on PDMS and decreased with PEG concentration.

5. UV-cured amphiphilic polymer networks

UV-photopolymerisation can offer advantages on designing elastomeric networks with tailored surface amphiphilicity. For example, dimethacryloxy-functionalised perfluoropolyethers (PFPE-DMA) (**8**, Figure 11) were photocross-linked into networks with monomethacryloxy-functionalised PEG (PEG-MA) or dimethacryloxy-functionalised PEG (PEG-DMA) with a photoinitiator.[118] Amphiphilicity was modulated by varying the PFPE/PEG ratio over a compositional range (from 95/5 to 70/30 wt/wt), while keeping a low surface energy of the films (~14 mN m^{-1}). Even though none of the formulations displayed better FR of *U. linza* sporelings and *B. amphitrite* juveniles in comparison to the PDMS control, it was noted that PFPE/PEG-MA better promoted the release of both sporelings and juveniles than

PFPE/PEG-DMA. These findings were attributed to a greater flexibility of the PEG-MA chains, which could migrate to polymer–water interface in a hydrophilic environment. Conversely, the tightly cross-linked PEG chains in the PFPE/PEG-DMA films were more restricted and impeded to effectively migrate to the surface. The environmental humidity at the time of curing played a role in determining the surface properties of the network and its AF/FR performance.[118] Photocuring at higher humidity (57%) in fact enhanced phase separation between PFPE and PEG, the PEG segments being more segregated at the polymer–air interface. The surface enrichment in PEG resulted in more promising AF properties, as few spores germinated or grew into sporelings on coatings cured in 57% humidity, with respect to those prepared in 24% humidity.

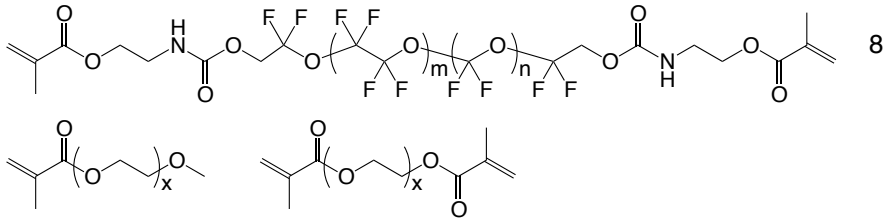

Figure 11. Chemical structures of building blocks for UV-photocured amphiphilic PFPE-based networks with hydrophilic PEG-MA and PEG-DMA.[118,119]

More recently, novel two- and three-polymer component films were prepared by photopolymerisation of (meth)acrylic (macro)monomers carrying PDMS, PEG and perfluorohexylethyl side chains.[120] All the polymer networks retained an elastomeric behaviour (storage modulus <5 MPa) due to the high content (>90 wt%) of the PDMS macromonomer in the formulation. In addition, the amphiphilic nature was modulated by varying the PEG/fluoroalkyl ratio. The films were tested against the serpulid *Ficopomatus enigmaticus* and the diatom *Navicula salinicola*. The FR properties were markedly influenced by the film formulation. Both *F. enigmaticus* and *N. salinicola* were easily released from films richer in PEG chains, with highest removal being detected for films with a PEG content as low as 5 wt%.

6. Condensation-cured amphiphilic polysiloxane networks

Cross-linked PDMS-polyurethane films were found to have potential against a number of marine organisms.[121,122] These coatings were designed to possess

improved durability and toughness over other PDMS-based coatings owing to the reinforcement of the polyurethane combined with the low surface energy of the polysiloxane. Libraries of polysiloxane-polyurethane coatings were also formulated with selected, independent polymer variables and used for a combinatorial and high-throughput screening of the effect of siloxane composition, on e.g. algal adhesion.[123] Moreover, the PDMS component could self-stratify at the surface of the film while the polyurethane constituted the bulk. Following the same approach, amphiphilic coatings were prepared by incorporating a PDMS functionalised with pendant hydrophilic carboxylic acid groups into a polyurethane or polyurethane-urea matrix (Figure 12).[124] The functional PDMS self-stratified at the film surface and the carboxylic acid moieties were also dragged to the surface. Amphiphilic coatings displayed improved FR of the diatom *N. incerta* with respect to the hydrophobic PDMS-polyurethane controls, while no significant differences were detected for the removal of the bacterial biofilms of *Halomonas pacifica* and *Cellulophaga lytica*. On the other hand, removal of barnacles and *U. linza* sporelings from the amphiphilic coatings was generally lower than from the corresponding PDMS-polyurethane not containing the hydrophilic carboxylic acid groups.

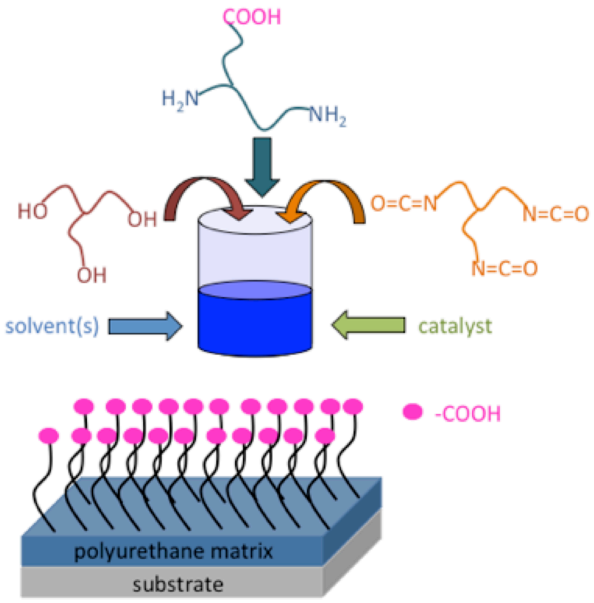

Figure 12. Schematic of preparation of a self-stratified polyurethane matrix film with pendant carboxylic acid groups. Drawn after Ref.[124]

A combinatorial and high-throughput method was also applied to a range of amphiphilic silicone networks by condensation curing disilanol-terminated PDMS,

disilanol-terminated polytrifluoropropylmethylsiloxane (CF_3-PDMS) and 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (TMS-PEG) macromonomers.[125] Amphiphilicity was tuned by systematically varying the CF_3-PDMS/TMS-PEG ratio (**9** and **10**, Figure 13). Hexamethyldisilazane-treated fumed silica was also incorporated in order to improve the mechanical resistance of the films. The presence of CF_3-PDMS facilitated the migration of TMS-PEG to the polymer–air interface during the curing process, thus favouring a more massive surface reconstruction after immersion in water. It was found that the films with the highest amounts of both TMS-PEG and CF_3-PDMS displayed almost 100% removal of marine bacteria *C. lytica* and *H. pacifica*, much higher than that of the films containing only one of either surface-active component (<50%). A strong synergy between TMS-PEG and CF_3-PDMS was also observed in the reattachment test of adult barnacle *B. amphitrite*. In fact, films with the highest concentration of TMS-PEG and CF_3-PDMS showed the lowest adhesion strength of adult barnacles.

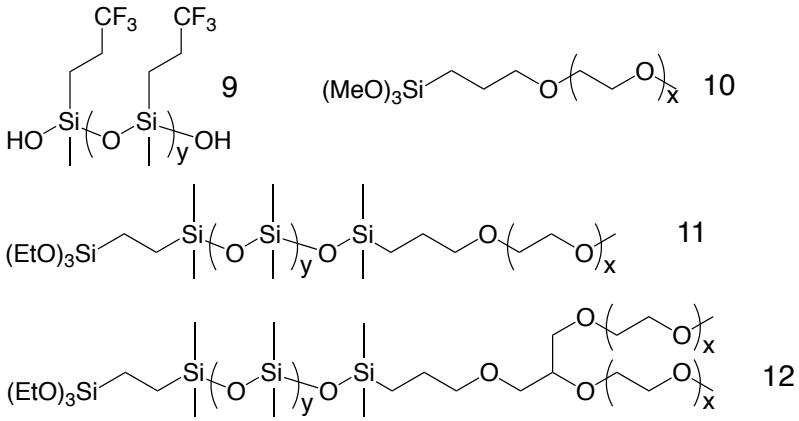

Figure 13. Chemical structures of modifying agents for construction of amphiphilic PDMS-based networks.[125–129]

In a different approach to PEG-engineering the surface of silicone networks a sol–gel reaction was exploited for condensing a disilanol-terminated PDMS with a series of linear or branched triethoxysilane PDMS-PEG tethers (**11** and **12**, Figure 13).[126,127] Quantitative nanomechanical mapping of the coating surface was performed via surface force spectroscopy (SFS) before and after exposure to phosphate buffer solution (PBS) during 140 min. This enabled to capture changes in topography, modulus, adhesion force and dissipation force caused by the temporal restructuring at the nanoscale (Figure 14).[128] Overall, it was found that films with

longer tethers became more hydrophilic after immersion in PBS, as PEG segments were more readily driven to the surface. The entire reorganisation process and kinetics were rationalised in several steps which started with the migration of PEG-rich regions towards the surface and evolved by digression of PEG-poor regions from the surface, extension of PEG-rich regions from the matrix, swelling of PEG-rich nodes and ended with a final solvation of PEG tails (Figure 15). In this state great water–PEG interaction volumes were generated, resulting in increased surface roughness, elastic modulus, adhesion force and dissipation. The capability of the amphiphilic PDMS to resist protein adsorption increased with extended incubation periods, in agreement with the observed temporal changes in the reorganised surface. The AF performance was tested against the bacterium *Bacillus* sp. 416, the diatom *Nitzschia closterium* and a mix of both species. Moreover, in situ microfouling was assessed in field trials on raft panels. In any case, films containing the PEG-siloxane tether with the longest siloxane segment displayed the best ability to reduce biofouling formation.[129]

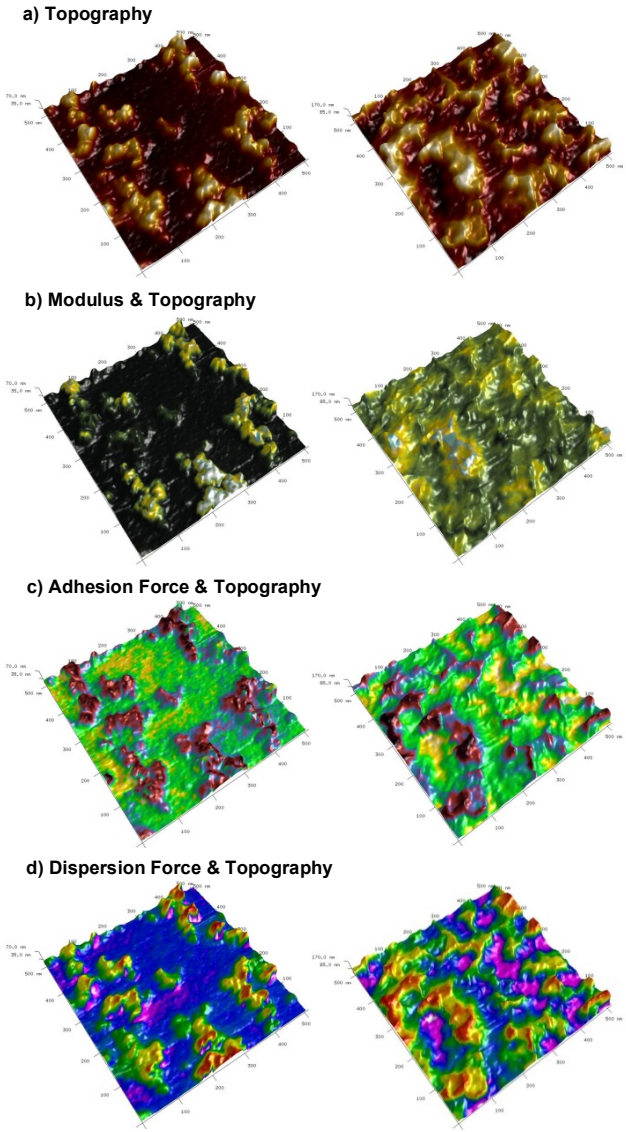

Figure 14. SFS images of a 0.25 μm^2 area before (left) and after (right) exposure to PBS of a PDMS network with PEG tethers; 500 × 500 nm^2 field of view. Displayed ranges are 0–60 nm, 0.1–2.5 MPa, 10–20 pN and 0–20 eV for the pre-incubation (left) and 0–140 nm, 4–11 MPa, 2.5–7.5 nN and 1–8 keV for the post-incubation (right) samples. Reproduced from Ref.[128] with permission of The Royal Society of Chemistry.

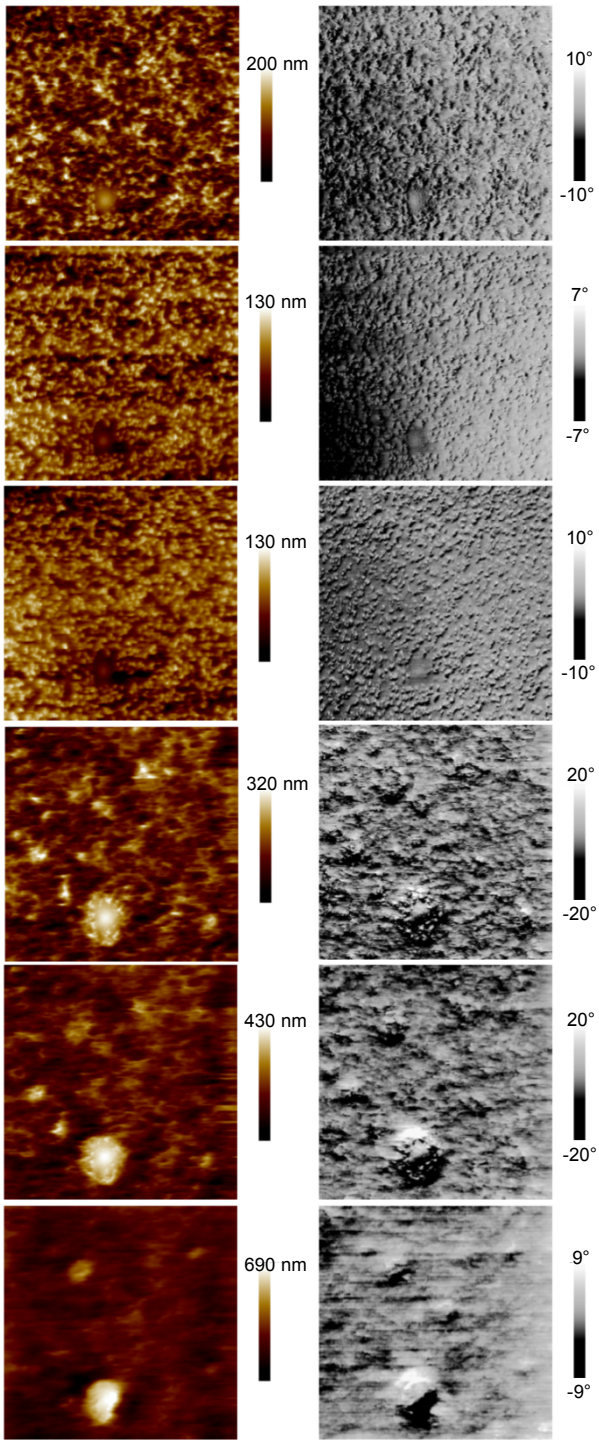

Figure 15. AFM height (left) and phase (right) images showing dynamic surface reorganisation over 140 min. Top to bottom: initial state, PEG expression towards surface at 10 min, PDMS recession into matrix at 15 min, PEG expression over surface at 30 min, PEG swelling at 60 min and solvation of tethered PEG tails at 120 min. Reproduced from Ref.[128] with permission of The Royal Society of Chemistry.

7. Amphiphilic zwitterionic polymers

Zwitterions, such as phosphobetaines, sulfobetaines and carboxybetaines, are charge-

neutral hydrophilic compounds known for their ability to resist the adsorption of proteins and cells[130] as well as the settlement of micro- and macro-foulers.[131,132] The AF properties are generally attributed to the presence of a strong hydration layer which prevents the formation of a stable bond between the organism's adhesive and the substrate, given the inability to exclude a large volume of water molecules from the interface.[133] Although zwitterionic polymers have been reported to be non-toxic,[134] a few amphiphilic systems have been developed which consist of a zwitterionic polymer as the hydrophilic component. Methacrylic copolymers containing both hydrophilic phosphorylcholine pendant groups and hydrophobic lauryl side chains were investigated as AF/FR surfaces against the diatom *N. closterium* (Figure 16).[135] In addition to the two base components, trimethoxysilylpropyl methacrylate was used as a cross-linker and 2-hydroxypropyl methacrylate was included to adjust the extent of water uptake into the network.

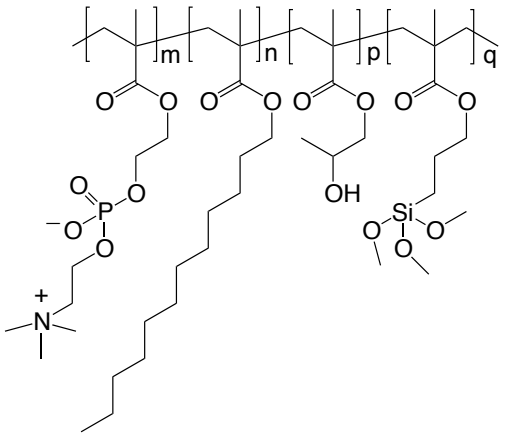

Figure 16. Chemical structure of phosphorylcholine zwitterionic copolymers.[135]

Without pre-swelling, the films favoured the attachment of the diatom owing to the preferential location of the hydrophobic lauryl chains at the outermost surface layers. However, 2 h-swollen films were able to better resist the settlement and promote the release of *N. closterium*. Beside swelling, it was found that the film thickness was important in determining the AF/FR properties. In fact, both the attachment densities and the retention densities of the attached cells markedly decreased with increasing film thickness (11–147 Å). No significant improvement was observed for films thicker than 147 Å. This was attributed to the fact that thinner films displayed rough topographies with the lauryl chains preferentially expelled to the surface as there was no sufficient space to accommodate them in the bulk. By

contrast, in thicker films the lauryl chains were more easily hidden back in the film bulk and more phosphorylcholine groups were exposed at the outer polymer surface. This built up a packed hydrophilic layer notably after immersion in water. Furthermore, thinner films produced rougher surface imperfections, generating more adhesion sites for diatoms. Surface adsorption sites made the adhesion of diatom stronger, thus resulting in a larger number of retained cells.

In a completely different approach, an amphiphilic phosphorylcholine platform was derived from the post-modification of a poly(styrene-*co*-allyl phospholane) prepolymer in which the phosphotriester moieties were reacted with tertiary amines leading to phosphorylcholine.[136] The chemistry of the tertiary amines was designed to modulate the cross-linking degree of the network and enable the anchorage of the polymer to the substrate through a trialkoxysilyl functional group. Wettability, chemical composition and topographic profiles of the surface were adjusted by modulating the cross-linking extent.

Modifications of PDMS with zwitterions were introduced to form bifunctional surfaces which could express a combination of the AF properties attributed to zwitterionic polymers and the FR capability of PDMS in one single system.[137–140] In one example, poly(sulfobetaine methacrylate) (poly(SBMA)) was grafted from poly(vinylmethylsiloxane) elastomer films by a sequence of thiol-ene click chemistry (for the immobilisation of the initiator on the surface) and activator regenerated by electron transfer for atom transfer radical polymerisation (ARGET-ATRP) (for the surface-initiated polymerisation) (Figure 17).[140] It was shown that the coatings displayed a short-term (~hours) resistance to the attachment of the bacterium *Cobetia marina* and the settlement of the barnacle *B. amphitrite*. In particular, zwitterion-modified PDMS surfaces reduced the attachment density of *C. marina* by ~95% and ~50% with respect to the unmodified surface after incubation for 2 h and 5 d, respectively. However, coverage with bacteria of the amphiphilic PDMS surfaces rose to >97% in an extended two-week assay.

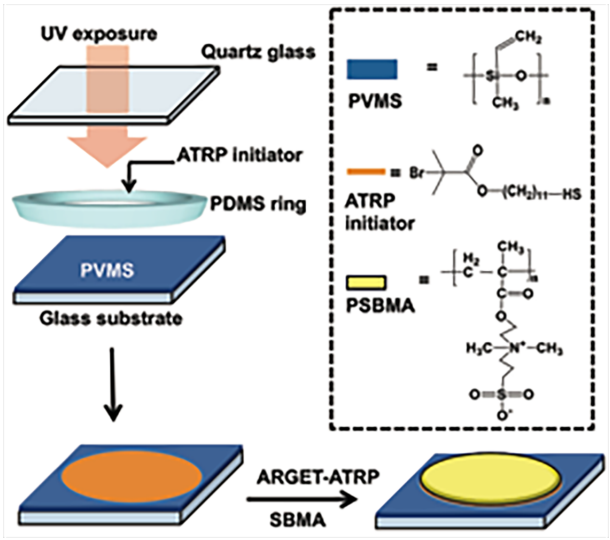

Figure 17. Procedure for grafting-from of P(SBMA): a PVMS elastomer coating cured on a glass substrate is covered with an ATRP initiator contained in a PDMS ring; the top surface is then exposed to UV light to immobilise ATRP-initiator from which the ARGET-ATRP of SBMA follows. Reproduced with permission from Ref.[140]. Copyright (2015) American Chemical Society.

8. Amphiphilic polysaccharides

Hydrophilic natural polymers from renewable resources, such as polysaccharides, may represent an alternative to PEG to store water owing to the high concentration of hydroxyl groups in the chemical structure of their repeat sugar motif.[141–143] Several studies have been reported on the resistance of different polysaccharide-coated surfaces to protein and cell adsorption as well as marine biofouling.[144–146] More recently, the AF properties of saccharide-functionalised alkanethiol self-assembled monolayers (SAMs) were also investigated against both proteins and marine fouling organisms.[147,148]

Significant examples of amphiphilic polysaccharide-based coatings consisted of fluorinated hyaluronic acid (HA) and chondroitin sulphate (CS) which were obtained by post-modification of the corresponding glycosaminoglycans with the hydrophobic trifluoroethylamine (TFEA) (Figure 18).[149] XPS analysis indicated that a small fraction of carboxylic acid groups (1–2%) was functionalised with TFEA, as most of them were involved in the anchoring to the substrate. Nonetheless, this low amount of fluorine was able to increase the water contact angle of the hydrophilic sugars by ~10%. Generally, the attachment and removal of the bacterium *C. marina*, the zoospores of *U. linza* and the cells of *N. incerta* were reduced with respect to the

uncoated glass. In particular, while TFEA end-capped HA displayed enhanced or similar AF/FR properties compared to unmodified HA, TFEA end-capped CS performed worse than the hydrophilic CS. In a more recent work,[150] the library of amphiphilic polysaccharides was expanded to using alginic acid (AA), a polymer found in the seaweed cell wall and extracellular matrix of bacteria. In these materials, the functionalisation with TFEA prevented the interaction between the two carboxylic groups of the dimer unit of AA with bivalent ions, namely Ca^{2+}, present in seawater, thus reducing a Ca-induced collapse of the coating and improving its stability. The hydrophobic capping of AA reduced the critical removal stress required to detach 50% of the adhered *C. marina* and *N. incerta*. Moreover, the settlement of both *B. amphitrite* larvae and *U. linza* zoospores was better reduced and the removal of the latter was improved with respect to the pristine AA. Short-term (24 h) field immersion trials seemed to confirm the results of the laboratory experiments, showing that settlement on TFEA-modified AA and HA was reduced by ~50%. On the other hand, an enhanced settlement by ~50% was observed on TFEA-CS.[150]

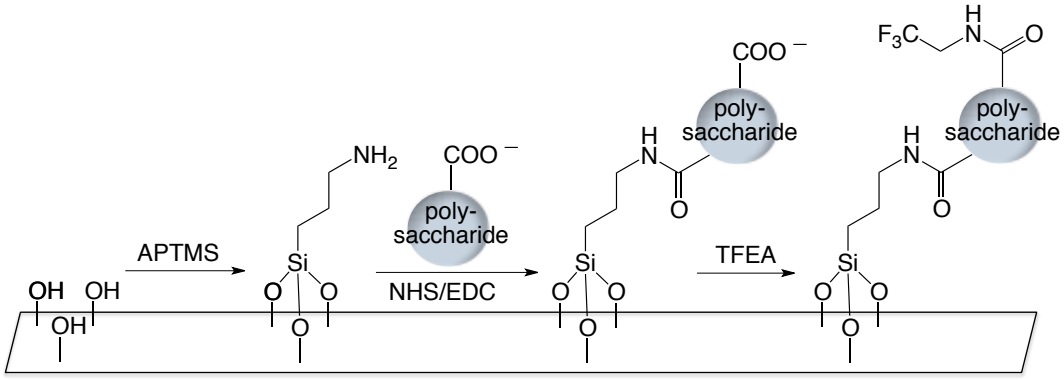

Figure 18. Scheme of polysaccharide immobilisation and modification by a sequence of reactions with (i) 3-aminopropyltrimethoxy silane (APTMS), (ii) *N*-hydroxysuccinimide (NHS) and *N*-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride (EDC) and (iii) 2,2,2-trifluoroethylamine (TFEA). Redrawn from Ref.[149].

9. Amphiphilic polypeptides and peptide-mimic polymers

The wide array of natural and non-natural aminoacids provides a polypeptide platform that can be designed to meet a broad range of physical-chemical requirements,[151,152] including inherent amphiphilicity.[153,154] Therefore, opportunely custom-tailored polypeptides can be exploited to finely and systematically tune the amphiphilic

balance of the films. This can be achieved by controlling the exact order of addition of the aminoacid building blocks and therefore the location of the hydrophilic and hydrophobic components in the peptide chain backbone. Peptide SAMs with alternating or uniformly distributed negative and positive charges, as well as amphiphilic and zwitterionic peptide SAMs were proven to be effective in limiting the adsorption of non-specific proteins.[155,156]

Novel amphiphilic oligopeptide-based systems were synthesised with a blocky or alternating distribution of the selected hydrophilic and hydrophobic aminoacids and attached to a polystyrene-*b*-poly(dimethylsiloxane-*co*-vinylmethylsiloxane) (PS-*b*-P(DMS-*co*-VMS)) diblock copolymer via thiol-ene click chemistry.[157] NEXAFS analysis evidenced the lack of oligopeptide at the surface and the almost exclusive presence of the lowest surface energy PDMS component, both before and after 3 d-immersion in water. However, a decrease by ~40°–50° in underwater bubble contact angle suggested that the surface turned to more hydrophilic after reorganisation. Interestingly, the blocky oligopeptide structure was more hydrophilic than the alternating one. Oligopeptide-modified films better inhibited the spore settlement and promoted the release of *U. linza* sporelings with respect to the unmodified PS-*b*-P(DMS-*co*-VMS) and the SEBS control. Thus, while the sequence of aminoacids in the oligopeptide segments markedly affected the wettability of the films, it appeared to have no significant effect on spore attachment or sporeling removal, or on protein adsorption.

Polypeptoids are constitutional isomers of polypeptides, being composed of *N*-substituted repeat units in which the side chain is linked to the nitrogen atom of the peptide backbone, rather than to the α-carbon as in the corresponding aminoacid. This structural difference implies the absence of intermolecular hydrogen bonds which results in an enhanced thermal and solution processability with respect to most biopolymers. SAMs of polypeptoids and glycopeptoids have been reported to significantly reduce the attachment of non-specific proteins, cells and bacteria.[158–161]

N-substituted glycine units can be used as the building blocks of sequence-specific polypeptoids for precise location and control of multiple and contrasting functionalities. Consistent with this approach, the sequence and amount of the hydrophilic *N*-(2-methoxyethyl)glycine and the hydrophobic *N*-(2,2,3,3,4,4,4-heptafluorobutyl)glycine in an amphiphilic polypeptoid drastically affected the

surface properties and the restructuring process after immersion in water of a hybrid block copolymer, poly(styrene-*b*-peptoid) (Figure 19).[162]

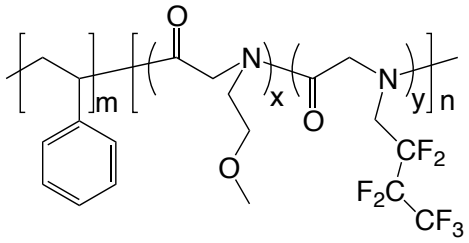

Figure 19. Chemical structure of an amphiphilic polystyrene-polypeptoid block copolymer with hydrophilic and hydrophobic *N*-glycine units.[162].

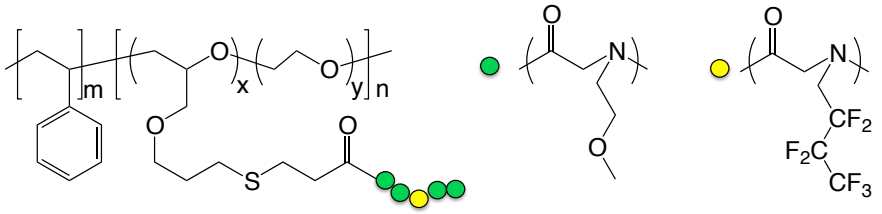

Figure 20. Schematic of the chemical structure of a block copolymer functionalised with amphiphilic polypeptoid tethers with sequences of hydrophilic (green) and hydrophobic (yellow) *N*-glycine units. Redrawn from Ref.[163].

With the aim to develop films for AF/FR of marine species, a polystyrene-*b*-poly(ethyleneoxide-*co*-allylglycidyl ether) (PS-P(EO-*co*-AGE)) block copolymer was functionalised via thiol-ene click chemistry with a thiol-terminated peptoid composed of the aformentioned fluorinated and methoxyethyl *N*-glycine residues (Figure 20).[163] It was found that the number of the highly surface-active fluorinated moieties influenced the surface composition as well as the AF/FR performance (Figure 21). In particular, when the fluorinated moieties were located at the end of the peptoid chain the capability of the system to resist attachment of *U. linza* spores was lower than when they were located inside the chain. Neither the number of fluorinated residues nor the peptoid length appeared to play a significant role. However, these structural parameters were shown to influence the FR of sporelings, the best performers being the films with the lower amount of fluorinated units and shorter length of the peptoid chain. The biological properties of these amphiphilic polypeptoid films were correlated with their surface chemistry and composition, as investigated by sum frequency generation (SFG) vibrational spectroscopy.[164] The surface population of the hydrophilic residue in air was influenced by both the location and the amount of the hydrophobic fluorinated units in the peptoid chain and increased with decreasing

content of fluorine at the surface. Both SFG analysis and time-dependent water contact angle measurements revealed that the ability of the polymer film to form strongly hydrogen-bonded water was influenced by the position of fluorine in the chain and was correlated with their hydrophilicity and restructuring rate underwater. While surfaces with a larger concentration of hydrophilic moieties better disfavoured the adhesion of spores, films containing peptoid chain with only one fluorinated unit and capable of undergoing fast surface reconstruction were more effective in promoting the removal of sporelings.

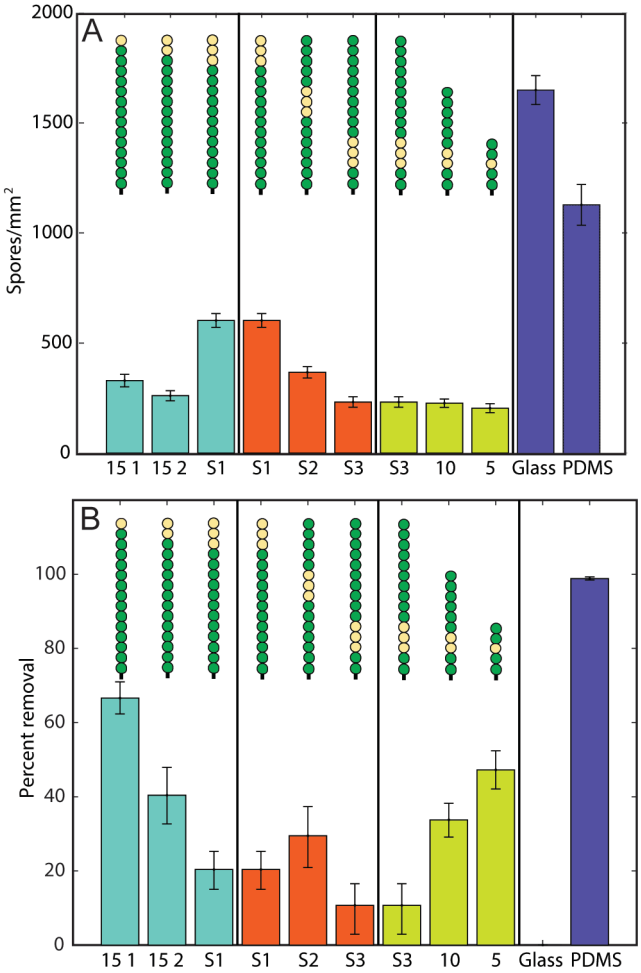

Figure 21. AF and FR assays on films of block copolymers functionalised with amphiphilic polypeptoid tethers with sequences of hydrophilic (green) and hydrophobic (yellow) *N*-glycine units: (A) Density of attached spores on surfaces after 45-min settlement. Each bar is the mean from 90 counts on three replicate slides. Bars show 95% confidence limits. (B) Percent removal of sporelings from the surfaces after exposure to an impact pressure of 160 kPa. Each bar shows the mean percentage removal of sporeling biomass from six replicate slides. Bars show standard error of the mean. Reprinted with permission from Ref.[163]. Copyright (2014) American Chemical Society.

10. Conclusions and outlook

'Green', i.e. non-biocidal non-toxic, chemical technologies under current exploration share the objective to prevent marine biofouling through manipulation of the superficial and interfacial properties of the coating, so that the organism either perceives the surface as non-conducive to settlement or the interaction forces between the surface and the polymeric adhesives produced by the fouling organism are weakened, promoting adhesive failure. The surface- and interface-structuring factors of activity, functionality, structure and reconstruction of a coating are highly relevant for potential application. Their synergistic combination would ultimately result in an enhanced AF/FR performance. According to exploitation of either one of these factors, several technologies of amphiphilic polymers have displayed unprecedented efficacy against individual fouling organisms in lab and field trial tests.

The use of amphiphilic polymers allows the surface activity to be tuned at the molecular and higher level structures of the polymer platform. The control of the manifold character of an amphiphilic surface via the macromolecular engineering of hydrophilic/hydrophobic balance results in surface functionality suitable for specific responses to the water environment. Thus, the precision synthesis of polymer architectures in which amphiphilicity is incorporated by a systematic and modulated approach can address the question of a critical length scale in the proximity between opposite hydrophobic and hydrophilic functions for antifouling properties. Furthermore, the simultaneous occurrence of complex surface structures of the amphiphilic surface, like morphological, topographic and compositional nano-to-micro-scale cues, contributes to interfere with the mechanisms during colonisation and life cycle stages of the foulers. Several phenomena of surface reconstruction and surface segregation settle in over different time scales and can be exploited to improve fouling resistance.

Within the above four major driving factors, the rational design of amphiphilic polymers that function on specific mechanisms must address at least two, still largely unsolved, basic questions.[6] On the one hand, a major challenge in creating an effective fouling-resistant coating is that the diversity of foulers is vast and the range of adhesion mechanisms and bioadhesives[165] used is correspondingly great. Assuming that an organism has settled, the success of that organism in colonising a

surface depends on how firmly the bioadhesive secreted secures to the adhesive interface, which is determined by the interfacial molecular interactions that are in turn influenced by the properties of a surface at the molecular or nanoscale level. On the other hand, the colonising stages of fouling organisms range in size from micrometres (e.g. bacteria) to even millimetres (e.g. larvae of invertebrates). However, the critical length scale in determining settlement is not necessarily the size of the organism per se, but rather the size of the parts or structures involved in the sensing apparatus of an organism, which determines whether the organism selects a surface for attachment. Considerations of size are also relevant to engineer surface topographies that may deter the settlement of organisms.[6] As discussed, the majority of amphiphilic polymers developed so far rely on both the surface energy and surface segregation of the hydrophobic ingredient and the water responsiveness and protein resistance of the hydrophilic ingredient. This last property is associated with the strong affinity with water of the coating surface driven by electrostatic interactions and/or hydrogen bonding which forms a hydration layer near the surface. A physical and energetic barrier is thereby created which prevents protein adsorption on the surface. In the particular case of PEG-containing polymers, it is generally recognized that the removal of the water molecules from the hydration layer and the repulsive elastic force resulting from the compression of the PEG chains when a protein moves towards the surface are energetically unfavourable.[24] Moreover, the interfacial energy between PEG and water is already sufficiently low so that no thermodynamic advantage would be gained by protein adsorption. Different mechanisms seem to operate when the chemical and physical interactions between the fouler bioadhesives and the prospective amphiphilic polymer are weak. This may be caused by the confusing character of the surface owing to the combined-(positive and negative) charge nature of e.g. zwitterions and LbL assemblies or to the limited tendency to hydrogen bonding of e.g. polypeptoids (H-donors) as opposed to polypeptides (H-donors and acceptors). ‘Ambiguity’ of the amphiphilic polymer can be further amplified from the mixed morphology and topography of the nano-to-micro-structured surface, notably in the water-swollen state within the aquatic environment. The more or less homogeneous and regular structure of hydrophilic-hydrophobic domains of e.g. hyperbranched networks and surface-active polymer networks could in fact comply with a critical length scale proper to inhibit recognition of a colonising organism. The latter network systems moreover possess an elastomeric bulk which

favourably complements the surface amphiphilicity for an intended fouling-release property of the entire coating.

Such types of coatings pose also questions about mechanical robustness, stability, durability and resistance to damage for the deployment lifetime, ease of maintenance and compatibility with anticorrosion measures that have still to be better addressed. Ideal solutions would additionally be cost effective to perform under all marine operating conditions. At present it is quite difficult to foresee the advent of a universal coating which endures all fouling organisms and conditions and we consider it unlikely that non-biocidal solutions based on coating designs featuring a single attribute will be successful. A new emerging trend should aim at integrating multiple functionalities in one amphiphilic polymer platform that are each tailored to operate via a specific mechanism and to accomplish a particular task to impact in a synergistic dual-mode, i.e. active and passive, action on the secreted bioadhesive and the sensing size range of the colonising organisms.[166] Definitely, a more thorough knowledge of the necessary requirements to comprehend and control the intertwined surface features of amphiphilic polymers will aid the development of future guiding principles and design rules that can be used broadly for achieving breakthroughs in marine antibiofouling application. This will also help in solving global environmental problems caused by older chemical technologies.

Keywords: amphiphilic polymer; film; coating; surface property; marine antifouling.

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Amphiphilic Polymer Platforms: Surface Engineering for Marine Antibiofouling

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Amphiphilic polymers with diverse macromolecular architectures have been developed as low environmental impact coatings to combat marine biofouling. These novel 'green' technologies employ different building blocks to endow the polymer film with surface activity, functionality, structure, and reconstruction as a result of a tailored amphiphilic character of the polymer platform.