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Abstract: Surface-active amphiphilic diblock copolymers, Si-EFS14 and Si-EFS71, consisting of a poly(dimethyl siloxane) block (degree of polymerisation 11) and a poly(4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene) block (average degree of polymerisation 14 and 71) were synthesised by ATRP. Films were prepared by incorporating each copolymer (4 wt%) into a PDMS matrix, which was then condensation cured. Bioassays were performed on the films using two barnacle species, Balanus amphitrite and Balanus improvisus, at different stages of their life cycles. The cyprids of B. improvisus settled on all test surfaces in higher numbers than those of B. amphitrite. However, the juveniles of B. improvisus were more easily removed from the films con-taining the copolymer Si-EFS14 than from those containing the copolymer Si-EFS71. An XPS analysis revealed that the near-surface region of copolymer Si-EFS71 was enriched in oxyethylenic chains and became even more populated by these hydrophilic chains after the films were immersed in water.

Dear Axel,

Please find enclosed our revised paper.
We thank the reviewers for their appreciation of our work and helpful comments. We accepted essentially all the suggestions from Reviewers 2 and 3 and changed the text accordingly; see our changes and answers in red.
As for Reviewer 1, let us insist that the main innovation resides in the complementary approach of the work by polymer chemistry, physics, surface science and biology, although individual aspects may not be fully original per se.
Therefore, we do believe that the paper is well suited for publication in Polymer to the benefit of the expert in the art and the general reader.

The paper is now in a better shape and we look forward to its final acceptance and publication.

Warm regards,

Giancarlo

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RESPONSE TO REVIEWERS

Reviewer #1:
The manuscript reports the anti-biofouling PDMS based films containing surface-active amphiphilic block copolymers which are surface-segregated onto film surface. This is a good work from the view angle of the preparation of a novel anti-biofouling surface. However, it contributes little on the science of polymer chemistry and physics. Actually, I think this manuscript is more suitable to be published in a journal about surface science or functional material.
In the work there was a good deal of chemistry and physico-chemical characterisation of what we believe are interesting amphiphilic polymers. Moreover, blend manipulation and formulation were necessary for film deposition and film surface engineering. Furthermore, this is the first known example of an application of coatings against different fouling barnacle species at early stages of their life cycles. Therefore, we do believe that the paper is well suited to appear in Polymer for the sake of the expert in the art and the general reader.

Reviewer #2:
The manuscript reports the synthesis of amphiphilic block copolymers used as additives in PDMS elastomer-based coatings. These coatings are developed to reduce the settlement of barnacles B. amphitrite and B. improvisus larvae and to increase the fouling release properties.
The literature biography is well documented. The data are relevant. The main characteristics of the prepared coatings have been investigated. The manuscript requires revisions.

My main concerns are the following ones:
1- Films for XPS measurements were prepared by spin coating a 3 wt% CHCl3 solution of each copolymer on glass slides at 5000 rpm (thickness ~300 nm). The procedure is different from preparing samples for bioassays. What is the influence of the substrate on the morphology of the spin-coated thin layer? Why XPS measurements were not investigated on thicker samples?
While we did not study the surface morphology, it is quite reasonable that in the present 'thick' films (>L0) the influence of the substrate is negligible, the dominant interfacial interactions being those at the polymer-air interface. This effect may be even amplified in the present block copolymers consisting of two low surface energy blocks. We added a sentence to better support this argument, page 9, line 17.
Unfortunately, XPS studies could not be performed on PDMS-based films because of outgassing

chemicals under the required high vacuum application which would seriously compromise analytical results and, much worse, contaminate XPS instrument as well.

2- What are the Mn and Đ values for Si-EFS14?
The values were added.

3- A thin top layer consisting of the block copolymer blended in a low amount (4 wt% with respect to PDMS) with the same PDMS matrix was spray-coated to modify the chemical surface composition at the nanoscale level of the coating. Does this last layer adhere strongly on the already crosslinked PDMS underlayer? Did the authors spray it before reaching a complete crosslinking of the 200µm-underlayer? Did the authors control the relative humidity during the crosslinking of the PDMS elastomer?
We understand the reviewer's concern and added a couple of sentences to better clarify the adhesion aspects, page 8, line 19.
Owing to the large number of the large-size specimens for bioassays it was not possible to deposit the films under controlled humidity, which was nevertheless monitored (70-80%). To specify this we inserted a statement in the Experimental Part, page 4, line 9 from bottom.
However, we have separately performed solid-state 29Si NMR investigations of the PDMS cross-linking reaction and clearly demonstrated that curing was complete under the adopted experimental conditions. These results will be published in a forthcoming paper.

4- The authors have shown from XPS analyses that the outer layer (~10 nm) of the Si-EFS71 film had a higher content of hydrophilic oxyethylenic units than the Si-EFS14 film, both before and after immersion in water. How could the authors explain that the surface free energy of Si-EFS14 and Si-EFS71 is independant of the amount of the amphihilic monomer 4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene (page 11, line 6)?
The seeming independence of the film surface of copolymer composition is due to the coexisting and contrasting effects on wettability of the block copolymer constituents, which compensate each other without producing an apparent different wettability. Subtle differences in surface chemistry were indeed evidenced by the reported XPS measurements and discussed in the paper. We added a couple of sentences to explain this better, page 9, line 7.

The addition of diblock copolymers in PDMS-based film does not modify the surface free energy of the coatings. The presence of EFS component of the diblock copolymers near the surface should lead to a decrease of the water contact angle and the increase of the surface free energy. Could the authors explain precisely the following sentence (page 11, line 7):
"Thus, the values of <theta>w and <gamma>S of the PDMS-based films were higher and lower, respectively, than those of the corresponding pristine block copolymers, indicating a poorer water wettability owing to location of the EFS component in the near-surface layers of the PDMS matrix."
This statement is consistent with our interpretation of the wettability results as has now been better clarified. To make this be even better understood we changed the sentence by emphasizing that the EFS groups were surface segregated but actually located in the molecular layers below the outer surface, page 9, line 12.

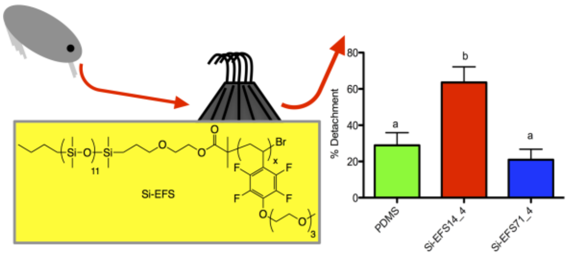
It would have been interesting to synthesize additional block copolymers with various molar compositions and to introduce different weight amounts of each block copolymer in PDMS elastomers to strengthen this paper.
As already mentioned in the paper, other block copolymer samples of this same structure were previously synthesised. However, they were not considered to be suitable for antifouling application and only the two reported block copolymers were newly investigated.

Minor issues:
1- Please replace Mw/Mn by Đ.
Done.

Reviewer #3:
This manuscript reported PDMS-based films containing surface-active amphiphilic block copolymers synthesized via ATRP to compat fouling from barnacles B. amphitrite and B. improvisus. Antifouling/fouling release properties against the two narnacle species have been investigated. I recommend the publication of this manuscript in the journal of Polymer after some minor revision as follows:
1.Fluorinated amphiphilic block copolymers synthesized via ATRP have been reported in some publications, such as Macromolecules 2008, 41, 6089-6093; J Polym Sci Part A: Polym Chem 2010, 48, 2076-2083; J Polym Sci Part A: Polym Chem 2011, 49, 1528-1534, etc. Such papers should be cited in the revision.
Some new references were added, page 7, line 14.

2.Fig. 4 showed the settlement percentage ±SE of B. Improvisus cyprids after 24 h (top) and 48 h (bottom). For comparison, the top and bottom images can be combined as only one. Similar defect occurred in Fig. 5.
Done.

*Graphical Abstract



PDMS-based films containing surface-active amphiphilic block copolymers to combat fouling from barnacles *B. amphitrite* and *B. improvisus*

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ABSTRACT

Surface-active amphiphilic diblock copolymers, Si-EFS14 and Si-EFS71, consisting of a poly(dimethyl siloxane) block (degree of polymerisation 11) and a poly(4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene) block (average degree of polymerisation 14 and 71) were synthesised by ATRP. Films were prepared by incorporating each copolymer (4 wt%) into a PDMS matrix, which was then condensation cured. Bioassays were performed on the films using two barnacle species, *Balanus amphitrite* and *Balanus improvisus*, at different stages of their life cycles. The cyprids of *B. improvisus* settled on all test surfaces in higher numbers than those of *B. amphitrite*. However, the juveniles of *B. improvisus* were more easily removed from the films containing the copolymer Si-EFS14 than from those containing the copolymer Si-EFS71. An XPS analysis revealed that the near-surface region of copolymer Si-EFS71 was enriched in oxyethylenic chains and became even more populated by these hydrophilic chains after the films were immersed in water.

Keywords: ATRP block copolymer, amphiphilic copolymer, surface-active copolymer, *Balanus amphitrite*, *Balanus improvisus*, antifouling.

1. Introduction

Biofouling, the colonisation of surfaces by the unwanted accumulation of proteins, cells and organisms, has a negative impact on many human activities and industries, spanning from membrane bioreactors [1] to biomedical implants [2], from aquaculture fish cages [3] to ship hulls [4]. In the marine environment particularly, the colonizing organisms are able to find optimal substrata by the detection of peculiar physicochemical cues [5–7]. Understanding the settling behaviour of fouling larvae during the initial stages of colonisation as well as the innate criteria they use to discriminate between surfaces [8–11] is a key factor in developing new environmentally friendly, i.e. non-toxic nonbiocidal antifouling (AF)/fouling-release (FR) coatings.

Several strategies to produce novel AF/FR coatings have been tested that use different polymer chemistries, including use of self-assembled copolymers with mesogenic side chains [12,13], zwitterionic polymers [14], phase-segregated polysiloxane-urethanes [15,16], and polymer nanocomposites [17–19]. Exploitation of amphiphilic polymer films, which combine hydrophilic and hydrophobic components in the same surface chemical structure, is currently regarded as one promising strategy to combat marine biofouling [20]. Amphiphilicity in such materials is produced by following different chemical approaches, such as curing blends of silica-reinforced silicones with poly(ethylene oxide)-polysiloxanes [21], modifying polymer scaffolds with glycine polypeptoids [22], UV photo-cross-linking of mixtures containing polyethylene glycol (PEG) and fluorinated macromonomers [23,24], cross-linking of PEG with hyperbranched fluoropolymers [25], multilayers of fluorinated/PEGylated polyions [26], fluoroalkyl-modified polysaccharides [27], and self-assembling of fluorinated/PEGylated copolymers dispersed in an elastomeric matrix [28,29]. The surface structures generated exhibit mixed hydrophilic and hydrophobic functionalities and feature (nano)scale heterogeneities that can deter the settlement of organisms and also minimise the interaction forces between biomolecules and substratum [30–32]. Moreover, the elastomeric matrix provides independent control of the elastic properties of the entire coating, an attribute that has been shown to be important for the FR performance [33–35].

In our approach to the macromolecular engineering of coating surfaces able to resist marine biofouling, we use amphiphilic block copolymers as surface-active agents in matrix polymer films [29,36–39]. Owing to the two-fold chemical character, their surface can rearrange and change chemistry and composition in response to the external environment, thereby preventing the settlement (AF) or promoting the removal (FR) of fouling organisms. In the present work, a new set of surface-active block copolymers composed of a polysiloxane first block and a poly(4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene) second block was dispersed and surface-segregated in a poly(dimethyl siloxane) (PDMS) matrix to ascertain their capability to reduce the colonisation or to facilitate the release of two different species of widespread marine macrofoulers, the barnacles *Balanus amphitrite* (= *Amphibalanus amphitrite*) and *Balanus improvisus* (= *Amphibalanus improvisus*) at different stages of their life cycles.

Fouling from different barnacle species, e.g. of ship hulls, is worldwide a cumbersome problem and much effort has been paid to solve it [40]. While *B. amphitrite* has been adopted as a widely-used model organism for assaying the AF/FR performances of test surfaces [20,41], the studies of settlement and adhesion of *B. improvisus* on experimental coatings lag far behind, see [42–46]. *B. amphitrite* and *B. improvisus* are cosmopolitan species, with overlapping distributions [47]. *B. amphitrite* is a tropical/sub tropical species, whereas *B. improvisus* can tolerate colder waters and lower salinities, extending to the upper reaches of estuaries [48]. *B. improvisus* and *B. amphitrite* were reported to settle on low-energy surface and negatively charged self-assembled monolayers (SAMs) [42]. However, a prevailing view has been that the cyprids from *B. amphitrite* would exhibit a preference for high-energy surfaces [49]. Therefore, surface chemistry may play a significant role for the two barnacle species [42,43], and the question of a difference in their surface selectivity is still open.

Starting from these apparent contrasting findings with antifouling surfaces, the present work made use of experimental coatings of PDMS-based films with different surface chemistry of a surface-active, amphiphilic block copolymer which is surface-segregated on a nanometer length scale with the aim to better understand how the cyprids and juveniles of the two different species of barnacles respond to the same surface.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF), ethyl acetate, anisole and triethyl amine were distilled under nitrogen prior to use. Monocarbinol-terminated poly(dimethyl siloxane) (Si-OH, $M_n = 1000$ g mol^{-1}, $M_w/M_n = 1.2$) (from Gelest), bis(silanol)-terminated poly(dimethyl siloxane) (HO-PDMS-OH) ($M_n = 26{,}000$ g mol^{-1}), poly(diethoxy siloxane) (ES40) ($M_n = 134$ g mol^{-1}), triethyleneglycol monomethyl ether (95%), bismuth neodecanoate (BiND), 2-bromo-isobutyryl bromide (BIBB, 98%), CuBr (99.9%) and 2,2'-bipyridine (bipy, 99%) (all from Sigma-Aldrich) were used without further purification.

Monomer 4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene (EFS) and poly(dimethyl siloxane) macroinitiator Si-Br were synthesised according to a previous procedure [37].

2.2. Synthesis of block copolymers Si-EFSx

In a typical block-copolymerisation, 0.084 g (0.07 mmol) of Si-Br, 1.416 g (4.37 mmol) of EFS, 32 mg (0.21 mmol) of bipy and 5 mL of anisole were introduced into a dry Schlenk flask. After four freeze-thaw pump cycles, 11 mg (0.15 mmol) of CuBr was added under nitrogen and the solution was deoxygenated by three further freeze-thaw pump cycles. The polymerisation was let to proceed under nitrogen for 64 h at 110 °C. The reaction mixture was diluted with chloroform and passed repeatedly on a neutral alumina column. The solvent was removed under vacuum and the polymer was purified by repeated precipitations in cold *n*-hexane (62% yield). The resulting block copolymer, with average degree of polymerisation *x* of the EFS block equal to 71, is denoted by Si-EFS71 ($M_{\mathrm{n,NMR}}$ = 25,200 g mol^{-1}, $M_{\mathrm{n,GPC}}$ = 12,300 g mol^{-1}, $Đ$ = 1.15). For Si-EFS14, $M_{\mathrm{n,NMR}}$ = 5,300 g mol^{-1}, $M_{\mathrm{n,GPC}}$ = 5,900 g mol^{-1}, $Đ$ = 1.17 were evaluated.

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.0 ($SiCH_3$), 0.5 ($SiCH_2$), 0.9 ($C\underline{H_2}CH_3$), 1.3 ($C\underline{H_2}CH_2Si$), 1.6 ($C\underline{H_3}CH_2$), 1.9 (CCH_3), 1.9–2.9 ($C\underline{H_2}C\underline{H}Ph$), 3.3 ($OCH_3$), 3.5–3.9 ($CH_2O$, $COOCH_2C\underline{H_2}OC\underline{H_2}$), 4.4 ($COOCH_2$, $PhOC\underline{H_2}$).

^{19}F NMR ($CDCl_3/CF_3COOH$): δ (ppm) = –82 (*m*-F), –68 (*o*-F).

The chemical composition of the copolymers was evaluated from the integrated areas of the ^{1}H NMR signals at 0.0 ppm ($SiCH_3$ of Si block) and 4.4 ppm (OCH_2 of EFS block). The attachment of the fluorinated block with the formation of a block copolymer was also confirmed by ^{19}F NMR spectroscopy investigations.

2.3. Preparation of PDMS-based films

Glass slides (76 × 26 mm^2) were cleaned with acetone and dried in an oven for 30 min.

The PDMS-based films were prepared following a three-step procedure which involved a sol–gel condensation cure reaction at (uncontrolled) 70–80 % relative humidity. Firstly, a solution of HO-PDMS-OH (5.0 g), ES40 (0.125 g) and BiND (50 mg) in ethyl acetate (25 mL) was spray-coated onto the glass slides using a Badger model 250 airbrush (50 psi air pressure). The films were dried at room temperature for a day and annealed at 120 °C for 12 h to form a thin bottom layer. Then, on top of it a solution of the same amounts of HO-PDMS-OH, ES40 and BiND was cast and cured at room temperature for a day and later at 120 °C for 12 h to give a thicker middle layer. Finally, a top layer was formed by spray-coating the same solution containing HO-PDMS-OH, ES40, BiND and the block copolymer of choice (4 wt% with respect to PDMS). Curing was at room temperature for 12 h and then at 120 °C for 12 h (overall thickness ~200 µm). The two PDMS-based films are denoted as Si-EFS14_4 and Si-EFS71_4.

A film of PDMS alone (no copolymer) was also prepared in the same way as a control film. Polystyrene was used as a standard material surface.

Films for XPS measurements were prepared by spin coating a 3 wt% $CHCl_3$ solution of each copolymer on glass slides at 5000 rpm (thickness ~300 nm).

2.4. Characterisation

^{1}H NMR (*vs* $CDCl_3$) and ^{19}F NMR (*vs* CF_3COOH) spectra were recorded with a Varian Gemini VRX300 spectrometer. The number and weight average molecular weights and dispersity of the polymers (M_n, M_w, $Đ$) were determined by gel permeation chromatography (GPC) with a Jasco PU-1580 liquid chromatograph equipped with two PL gel 5 μm Mixed-D columns and a Jasco 830-RI refractive index detector. Polystyrene standards (400–400,000 g mol^{-1}) were used for calibration.

Contact angles with water and *n*-hexadecane (θ_w and θ_h) were measured using the sessile drop method with a Camtel FTA200 goniometer at room temperature. They were then used to calculate the surface free energy (γ_S) of the polymer films using the Owens-Wendt-Kaelble method [50], as discussed in [51].

X-ray photoelectron spectroscopy (XPS) spectra were recorded by using a Perkin-Elmer PHI 5600 spectrometer with a standard Al-Kα source (1486.6 eV) operating at 350 W. The working pressure was less than 10^{-8} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f$_{7/2}$ line to be 84.0 eV with respect to the Fermi level. Extended (survey) spectra were collected in the range 0–1350 eV (187.85 eV pass energy, 0.4 eV step, 0.05 s step^{-1}). Detailed spectra were recorded for the following regions: C(1s), O(1s), F(1s) and Si(2p) (11.75 eV pass energy, 0.1 eV step, 0.1 eV s step^{-1}). The standard deviation in the BE values of the XPS line was 0.10 eV. The spectra were recorded at the photoemission angle ϕ (between the surface normal and the path taken by the photoelectrons) of 20°, corresponding to a sampling depth of ~10 nm. The atomic percentage, after a Shirley type background subtraction [52], was evaluated using the PHI sensitivity factors (□1% experimental error) [53]. To take into account charging problems, the C(1s) peak was considered at 285.0 eV and the peak BE differences were evaluated. The XPS peak fitting procedure was carried out, after a Shirley type background subtraction, by means of Voigt functions and the results were evaluated by the χ^2 function [54].

2.5. Biological assays

Settlement assays and removal by hydrodynamic shear tests were performed with cypris larvae and juveniles of *B. amphitrite* and *B. improvisus*, respectively.

2.5.1. Barnacle culture. Adult broodstock was supplied by the Duke University Marine Laboratory, North Carolina, USA, and reared at Newcastle University. For *B. amphitrite*, adults were maintained in semi-static culture, in natural seawater (exchanged daily), at 23 ± 2 °C and a salinity of 32. Nauplius larvae were released naturally and attracted to a point cold light source. Nauplii were stored in a beaker with a dilute concentration of *Tetraselmis suecica* until approximately 10,000 stage-1 nauplii had been collected (within 2–3 h), as described in [55]. Nauplii were then transferred into a bucket with 10 L of 0.7 μm filtered seawater, 36.5 mg L^{-1} of streptomycin sulphate and 21.9 mg L^{-1} of penicillin G and incubated at 28 °C. The larvae were fed daily with an excess of *T. suecica* until metamorphosis to the cyprid stage. Cyprids for settlement assays were collected by filtration and stored in 0.22 μm filtered natural seawater (FSW) at 6 °C for 3 days. After settlement assays, metamorphosed cyprids were cultured on the coated glass slides for 7 days before testing for ease of release in a fully turbulent flow cell. The juveniles were grown in 15 mL of FSW containing *T. suecica*. The water was changed and new food added every two days. During culture, the position of the juveniles was monitored and juveniles were removed as necessary to ensure that none were in contact so that they grew regularly.

The protocol used for *B. improvisus* culture and cyprid production was similar to that for *B. amphitrite*, with slight modifications: *B. improvisus* adults were maintained at 19 ± 2 °C, cyprids for settlement assay were used immediately after metamorphosis from nauplius stage (0-day cyprids). Aged cyprid settlement is not significantly different from 0-day cyprid settlement, except for 3- and 4-day cyprids which show a lower settlement if compared to newly metamorphosed ones [42].

2.5.2. Settlement assays. Settlement assays were carried out using coated glass slides placed in quadriPERM dishes (Sarstedt, Germany). Approximately 20 3-day-old cyprids were placed in a 1 mL drop of 0.22 μm FSW onto the surface of each coated slide, with six replicates per formulation. The lids were placed on the dishes to minimise water evaporation and incubation proceeded in the dark at 28 °C. Settlement was enumerated after 24 and 48 h and expressed as percentage settlement. Polystyrene 24-well plates, containing 2 mL of 0.22 μm FSW and 15 cyprids per well ($n = 6$ replicates), were used as a reference to check cyprid health and that settlement was at normal levels.

2.5.3. Flow cell. Removal of permanently attached juveniles (7 days post metamorphosis) from coated slides ($n = 6$ per formulation) by hydrodynamic shear was carried out using a fully turbulent flow cell [56]. The flow cell simulates the turbulent boundary layer created by ships when underway. Juvenile barnacles on the coated slides were located, counted and exposed to a shear stress of 90 Pa for 180 seconds. Juveniles still anchored on the slides were located and counted.

2.5.4. Data analysis. Results related to settlement and flow cell tests are presented as means ± standard error (SE). Settlement assays were examined by non-parametric analysis of variance

(Kruskal-Wallis) with Dunn's test using GraphPad Prism. Larval detachment assay was examined by one-way analysis of variance (ANOVA) with Tukey's pairwise comparisons using GraphPad Prism. In any case an alpha level of 0.05 was accepted as significant.

3. Results

3.1. Synthesis of block copolymers

The two block copolymers Si-EFS14 and Si-EFS71 were prepared by atom transfer radical polymerisation (ATRP) of the amphihilic monomer 4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene (EFS) starting from one same bromo-terminated PDMS macroinitiator (Si-Br, number average degree of polymerisation 11) (Figure 1). By taking advantage of the controlled nature of the ATRP, it was possible to synthesise the two block copolymers with different number average degree of polymerisation (x) of the EFS block by increasing the monomer/macroinitiator feed mole ratio from 15 to 60, while keeping constant the reaction time (66 h). Various types of amphiphilic block copolymers with different fluorinated polymer blocks were previously prepared by ATRP [57]. Each of the obtained copolymers was then dispersed in a PDMS matrix (4 wt% with respect to PDMS) to create antifouling/fouling-release films.

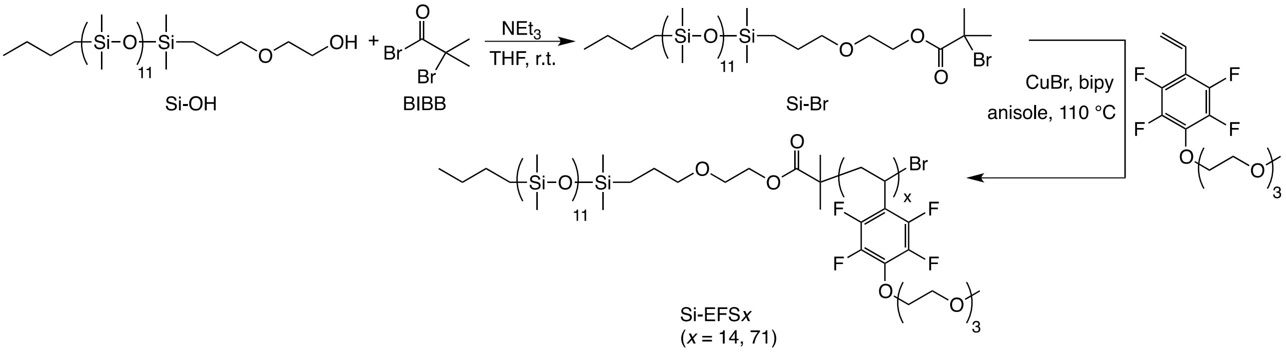

Fig. 1. Reaction pathway for the synthesis of block copolymers Si-EFSx (x = 14, 71).

3.2. Preparation of PDMS-based films

The PDMS-based films were prepared following a three-step procedure. Initially, a glass slide was spray-coated with a thin bottom layer (~2 μm) of PDMS which was then cross-linked. The firm anchorage of the film to the substrate was ensured by the covalent reaction between the silanol groups of glass and the PDMS matrix and cross-linker. Then, a thicker PDMS layer (~200 μm) was cast on top of the bottom one to secure bonding. Such a middle layer was able to impart a relatively high bulk thickness (>100 μm) and low elastic (*E* <2 MPa) modulus to the overall system. These properties have been shown to favour the release of several macrofoulers, including *U. linza* [33] and *B. amphitrite* [58]. PDMS-based films similar to those of this work exhibited tensile modulus values as low as 0.2 MPa [59]. Finally, a thin top layer (~2 μm) consisting of the block copolymer blended in a low amount (4 wt% with respect to PDMS) with the same PDMS matrix was spray-coated to modify the chemical surface composition at the nanoscale level. In fact, the incorporation of low amounts of copolymer in the top layer has been proven not to significantly affect the elastomeric behaviour of the entire film [60]. Therefore, the copolymer is ultimately responsible for the surface and interface properties of the final film only. According to this approach, the surface-active copolymer additive was physically dispersed within the PDMS cross-linked network. The Si block improved the chemical compatibility of both copolymers with the PDMS matrix and homogeneous transparent films were obtained at the investigated 4 wt% loading.

In all of the three steps, the cross-linking reaction of PDMS partially occurred at room temperature via a condensation sol-gel process that was catalysed by BiND. This enabled strong adhesion between the polymer layers and with the substrate and prevented delamination during the subsequent tests. BiND has recently been shown to be less toxic than traditional tin-catalysts in laboratory assays against several marine species [61]. Final cure was carried out at 120 °C to facilitate the block copolymer migration to the film surface. Traceable leachates out of the films were never detected in extraction experiments with water.

3.3. Surface analyses

The static contact angles of the PDMS-based films were measured using the two wetting liquids, water and *n*-hexadecane (Table 1). A marked hydrophobic (θ_w ~112°) and a poor lipophobic (θ_h ~30°) behaviour was observed, independent of the copolymer composition included in the film and similar to that of the PDMS control. Accordingly, relatively low values of surface tension, γ_S ~23–24 mN m^{-1}, were calculated close to that of the PDMS control (Table 1). The only contribution to γ_S was the dispersion component γ_S^d ($\gamma_S^p = 0$ mN m^{-1}), owing to an essentially apolar nature of the film surface. Block copolymers Si-EFS14 and Si-EFS71 displayed θ_w, θ_h and γ_S values of ~89°, ~32° and ~28 mN m^{-1} respectively, which were basically independent of their chemical composition. This suggests that a competition existed for surface segregation of the Si and EFS blocks. Moreover, the latter could provide contrasting contributions to wettability from their inherent hydrophobic and hydrophilic groups. Thus, the values of θ_w and γ_S of the PDMS-based films were higher and lower, respectively, than those of the corresponding pristine block copolymers, indicating a poorer water wettability owing to location of the EFS component in the layers underneath the surface of the PDMS matrix.

Table 1

Contact angles and surface tensions for the PDMS-based films and PDMS control.

Film	θ_w[a] (°)	θ_h[a] (°)	γ_S^{d}[b] (mN m^{-1})	γ_S^{p}[b] (mN m^{-1})	γ_S[b] (mN m^{-1})
Si-EFS14_4	112 ± 2	30 ± 2[c]	24.0	0.0	24.0
Si-EFS71_4	112 ± 1	34 ± 1[c]	23.1	0.0	23.1
PDMS	110 ± 1	33 ± 2[c]	23.3	0.0	23.3

(a) Measured with water and n-hexadecane. (b) Calculated with the Owens-Wendt-Kaelble method: γ_S^d dispersion component, γ_S^p polar component. (c) Not accurate, decreasing with time.

An initial XPS analysis of the block copolymer films had pointed out significant differences in their surface chemistry [37], which later appeared to be relevant to the interpretation of the biological results reported here. Therefore, new additional XPS experiments were performed on the block copolymer films to understand their surface segregation and reconstruction in response to exposure to different outer environments. In fact, in the present relatively thick films the dominant interfacial interactions occurred at the polymer–air interface for dry surfaces and polymer–water interface for underwater surfaces. This effect mIn addition to the main expected XPS signals for Si(2s) at ~153 eV, F(1s) at ~689 eV and O(1s) at ~533 eV (Figure 2) it was found that the C(1s) signal at ~287 eV had a complex shape and could be resolved in at least three overlapping contributions from different C-moieties centred at 285 eV ($SiCH_3$, CH, CH_2), 287 eV ($\underline{C}CF$, CH_2O) and 288 eV (CF) (Figure 3). Their relative intensity clearly depended on the composition of the block copolymer and its being immersed in water for a relatively long period of time (7 days). The intensity of the peak due to the CH_2O group was higher for Si-EFS71 than for Si-EFS14 both before and after immersion in water (Table 2). Moreover, for both polymer surfaces the intensity of peaks due to CH_2O and $SiCH_3$ groups increased and decreased, respectively, upon immersion in water (Table 2), as a result of the amphiphilic nature of the EFS units. For example, for Si-EFS71 the former increased from 35% to 43%, while the latter decreased from 62 to 53%. On the other hand, the integrated area of the CF peak remained unchanged before and after water immersion (3% and

4%, respectively).

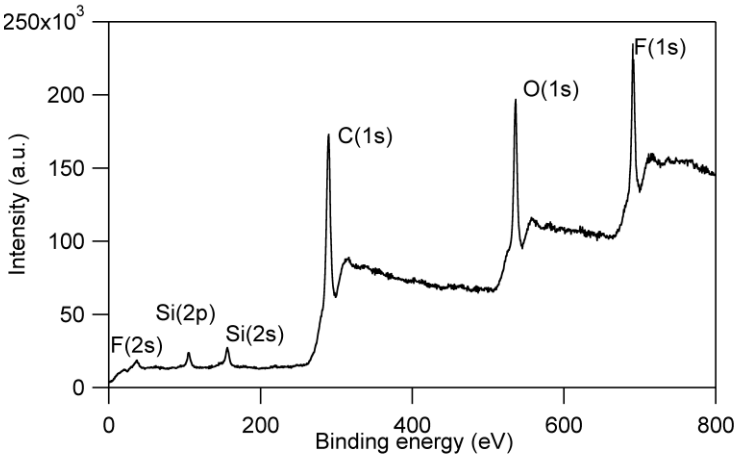

Fig. 2. XPS survey spectrum of the block copolymer film Si-EFS71 (ϕ = 20°) after immersion in water for 7 days.

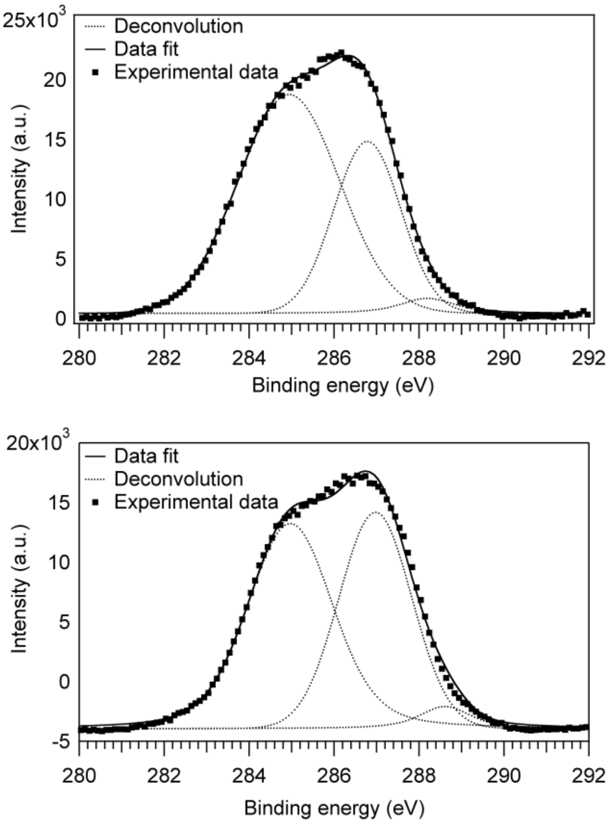

Fig. 3. Deconvolution of the XPS C(1s) signal of block copolymer film Si-EFS71 (ϕ = 20°) before (top) and after (bottom) immersion in water for 7 days.

Table 2

XPS C(1s) deconvolution data ($\phi = 20°$) for the block copolymer films before and after immersion in water for 7 days.

Film	Peak 285 eV (%)		Peak 287 eV (%)		Peak 288 eV (%)	
	Before	After	Before	After	Before	After
Si-EFS14	62	56	31	38	7	6
Si-EFS71	62	53	35	43	3	4

3.4. Settlement of cyprids

Settlement (attachment) of cypris larvae was assessed after 24 h- and 48 h-incubation times.

The amphiphilic film Si-EFS14_4 displayed a low (<2%) percentage of settlement of *B. improvisus* cyprids after 24 h, whereas no settlement was detected on Si-EFS71_4 (Figure 4). After 48 h, the settlement of cyprids significantly increased on all surfaces, up to a maximum percentage of 46% for PDMS surfaces (data not shown). Although settlement was lower on Si-EFS71_4 compared to PDMS control and Si-EFS14_4, this difference was not significant ($p > 0.05$).

The films Si-EFS14_4 showed very little settlement (<1%) of *B. amphitrite* cyprids after 24 h, similar to that of the PDMS control, while no settlement was detected on Si-EFS71_4 (Figure 5). After 48 h the amphiphilic films also showed a low settlement percentage (<2%), lower than that on PDMS even though this difference was not significant ($p > 0.05$).

Preliminary settlement assays were performed on 24-well polystyrene plates with both *B. amphitrite* and *B. improvisus*. A high number of cyprids for *B. amphitrite* settled after 48 h-incubation, whereas quite a few settled for *B. improvisus* (Figures 4 and 5). Such a low settlement percentage of *B. improvisus* was probably due to a phenomenon of “floating cyprids” [42]. This phenomenon is particularly problematic in assays with *B. improvisus* where very low percentages (<10%) of cyprids are able to explore the well bottom of the 24-well polystyrene plate.

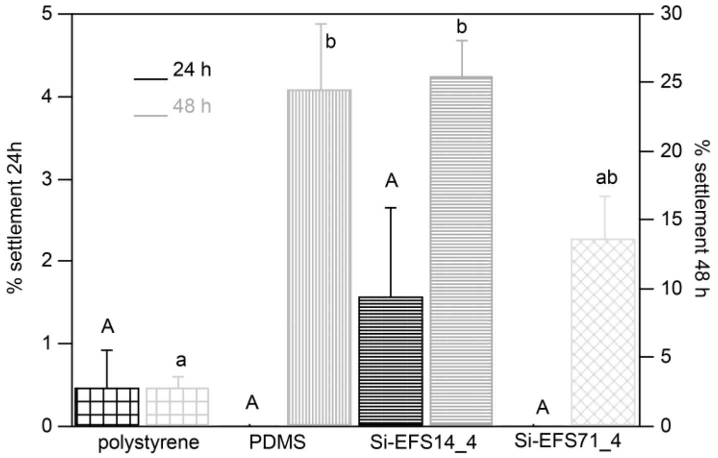

Fig. 4. Settlement percentage ± SE of *B. improvisus* cyprids after 24 h and 48 h. Each bar is the mean of six replicates. Comparisons were performed by non-parametric analysis of variance (Kruskal-Wallis) (Dunn's test, $p \leq 0.05$). Means that do not share a letter are significantly different (uppercase for 24 h settlement, lowercase for 48 h settlement).

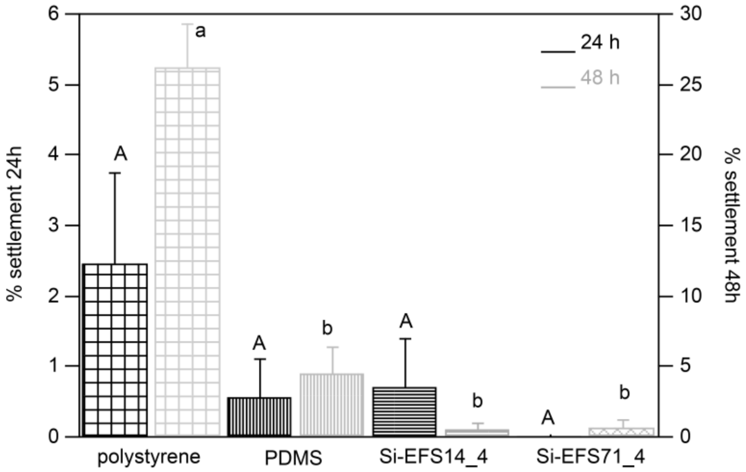

Fig. 5. Settlement percentage ± SE of *B. amphitrite* cyprids after 24 h and 48 h. Each bar is the mean of six replicates. Comparisons were performed by non-parametric analysis of variance (Kruskal-Wallis) (Dunn's test, $p \leq 0.05$). Means that do not share a letter are significantly different (uppercase for 24 h settlement, lowercase for 48 h settlement).

3.5. Removal of juveniles

Attached larvae of *B. improvisus* were grown on for 7 days post-metamorphosis to the juvenile barnacles. The percentage removal by exposure to a 90 Pa wall shear stress in the flow channel is shown in Figure 6. Films of Si-EFS14_4 performed significantly better than Si-EFS71_4 ($p < 0.05$), that in turn seemed to perform worse than the PDMS control, although the comparison was not significant ($p > 0.05$). A detachment assay with *B. amphitrite* juveniles was also performed but is not included here as too few juveniles settled on the films incorporated with any block copolymer, even after repeated settlement trials (<2% after 24 h-incubation and <5% after 48 h-incubation for both Si-EFS14_4 and Si-EFS71_4).

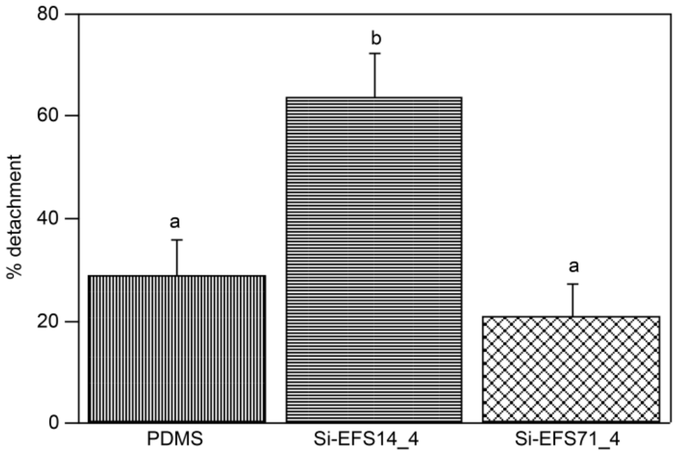

Fig. 6. Percentage removal ± SE of juveniles of *B. improvisus* following exposure to a wall shear stress of 90 Pa. Experiments were run in six replicates. Means were compared by ANOVA (Tukey's pairwise comparison assay, $p \leq 0.05$). Means that do not share a letter are significantly different.

4. Discussion

Two block copolymers, Si-EFS14 and Si-EFS71, which differed in the length of the amphiphilic EFS block, and consequently for the inherent hydrophilic/hydrophobic balance, were dispersed within a condensation-curing PDMS matrix in a low proportion (4 wt% with respect to PDMS). The surface-active block copolymers were designed to have a siloxane block to facilitate the dispersion of the copolymer itself in the elastomeric matrix and avoid phase separation, along with a block of fluorostyrene functionalised in the *para* position with a triethylene glycol chain to modify the surface chemistry of the PDMS and impart a responsive behaviour when in contact with water.

The surface segregation and responsiveness of the block copolymers were proved by XPS measurements carried out on the same copolymer surfaces before and after immersion in water for 7 days. Both copolymers underwent surface reconstruction upon contact with water and their surface became enriched in oxyethylenic CH_2O groups, whereas it was depleted of siloxane $SiCH_3$ groups after immersion in water. On the other hand, the content of CF_2 groups remained essentially unchanged. The *para* oxyethylenic side chains were driven by the low surface energy fluorinated styrene units to the near-surface region when the polymer was in contact with air. Consequently, they could readily expand outward after immersion in water to maximise their contact with water. Conversely, the methyl groups of the siloxane block, which populated the dry surface, moved back into inner regions as a result of their hydrophobicity. Such a dynamic restructuring of the amphiphilic block copolymer should play a role in affecting the AF/FR ability of the films.

B. improvisus cyprids settled in a higher number compared to *B. amphitrite* on all PDMS-based surfaces. Moreover, both species at the larval stage seemed to 'prefer' to settle on films containing Si-EFS14 rather than on those containing Si-EFS71. XPS analysis revealed that the outer layer (~10 nm) of the Si-EFS71 film had a higher content of hydrophilic oxyethylenic units than the Si-EFS14 film, both before and after immersion in water. This result is in agreement with previous findings on the settlement of cyprids of *B. improvisus* [42] and *B. amphitrite* [43] on a series of model SAMs with different wettability properties. Both species of cyprids preferentially attached on more hydrophobic, CH_3-terminated SAMs than on more hydrophilic, OH-terminated SAMs. More recently, it has been shown that the overall pattern of settlement for both species was similar on hydrophilic SAMs, with settlement to a higher degree being observed on charged surfaces and to a lower degree on neutral and zwitterionic surfaces [45].

The juveniles of *B. improvisus* were more easily released from films of Si-EFS14_4 compared to Si-EFS71_4, indicating that the removal was favoured when a lower amount of oxyethylenic units was located at the surface. By contrast too few *B. amphitrite* juveniles settled on any film incorporated with any block copolymer, even after repeated settlement trials. The settlement percentage of *B. amphitrite* only increased on PDMS after 48 h-incubation. Nonetheless, cyprids from the same culture successfully settled on polystyrene plate (>25%) in a separate assay that was carried out in the same conditions that are normally used for assays of *B. amphitrite* settlement [43,62,63]. Recently it has been shown that the removal of *B. amphitrite* juveniles from PDMS-based films loaded with copolymers with increasing amounts of polyethylene glycol side chains was low from more hydrophilic surfaces, but high from less hydrophilic surfaces [38].

4. Conclusions

Amphiphilic block copolymers with controlled and tailored chemical structure are effective surface-active materials for surface segregation and responsiveness to the outer environment. Their dispersion in PDMS-based films is a tool to enhance the overall resistance to fouling from barnacle species *B. amphitrite* and *B. improvisus*. Several reports have dealt with assaying either the two species separately on different types of surfaces, or on testing only the settlement of cypris larvae, this work compares the behaviour of the individual species at two stages of their life cycles on sets of the same films. Whilst the antifouling capacity is not much affected by the chemistry of the surface-active amphiphilic additive, the fouling-release properties depend on its hydrophilic/hydrophobic balance. Removal of *B. improvisus* juveniles is facilitated by incorporation of the less hydrophilic block copolymer.

Acknowledgements

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References

[1] S. P. Hong, T. H. Bae, T. M. Tak, S. Hong, A. Randall, Desalination, 2002, **143**, 219–228.
[2] M. Bianco, V. Guarino, G. Maruccio, G. Galli, E. Martinelli, G. Montani, R. Rinaldi, V. Arima, Sci. Adv. Mater., 2015, **7**, 1387–1394.
[3] J. K. Greene, R. E. Grizzle, Aquaculture, 2007, **262**, 289–301.
[4] M. P. Schultz, J. A. Bendick, E. R. Holm, W. M. Hertel, Biofouling, 2011, **27**, 87–98.
[5] N. Aldred, L. K. Ista, M. E. Callow, J. A. Callow, G. P. Lopez, A. S. Clare, J. R. Soc. Interface, 2006, **3**, 37–43.
[6] J. Bielecki, B. K. K. Chan, J. T. Hoeg, A. Sari, Biofouling, 2009, **25**, 203–214.
[7] R. J. Stewart, T. C. Ransom, V. Hlady, J. Polym. Sci. Polym. Phys. Ed., 2011, **49**, 757–771.
[8] K. Matsumura, S. Mori, M. Nagano, N. Fusetani, J. Exp. Zool., 1998, **280**, 213–219.
[9] M. Andersson, K. M. Berntsson, P. R. Jonsson, P. Gatenholm, Biofouling, 1999, **14**, 167–178.
[10] K. M. Berntsson, P. R. Jonsson, A. I. Larsson, S. Holdt, Mar. Ecol. Prog. Ser., 2004, **275**, 199–210.
[11] T. Murosaki, T. Noguchi, A. Kakugo, A. Putra, T. Kurokawa, H. Furukawa, Y. Osada, J. P. Gong, Y. Nogata, K. Matsumura, Biofouling, 2009, **25**, 313–320.
[12] G. Galli, E. Martinelli, E. Chiellini, C. K. Ober, A. Glisenti, Mol. Cryst. Liq. Cryst., 2005, **441**, 211–226.
[13] S. Krishnan, N. Wang, C. K. Ober, J. A. Finlay, M. E. Callow, J. A. Callow, A. Hexemer, K. E. Sohn, E. J. Kramer, D. A. Fischer, Biomacromolecules, 2006, **7**, 1449–1462.
[14] S. Jiang, Z. Cao, Adv. Mater., 2010, **22**, 920–932.
[15] P. Majumdar, S. Stafslien, J. Daniels, D. C. Webster, J. Coat. Technol. Res., 2007, **4**, 131–138.
[16] S. Sommer, A. Ekin, D. C. Webster, S. J. Stafslien, J. Daniels, L. J. Van der Wal, S. E. M. Thompson, M. E. Callow, J. A. Callow, Biofouling, 2010, **26**, 961–972.
[17]]A. Beigbeder, P. Degee, S. L. Conlan, R. J. Mutton, A. S. Clare, M. E. Pettitt, M. E. Callow, J. A. Callow, P. Dubois, Biofouling, 2008, **24**, 291–302.
[18] M. Wouters, C. Rentrop, P. Willemsen, Progr. Org. Coat., 2010, **68**, 4–11.
[19] C. Carl, A. J. Poole, M. J. Vucko, M. R. Williams, S. Whalan, R. de Nys, Biofouling, 2012, **28**, 1077–1091.
[20] J. A. Callow, M. E. Callow, Nat. Commun., 2012, **2**, DOI:10.1038/ncomms1251.
[21] F. Faÿ, M. L. Hawkins, K. Rehel, M. A. Grunlan, I. Linossier, Green Materials, 2016, DOI: 10.1680/jgrma.16.00003.
[22] W. van Zoelen, H. G. Buss, N. C. Ellebracht, N. A. Lynd, D. A. Fischer, J. Finlay, S. Hill, M. E. Callow. J. A. Callow, E. J. Kramer, R. N. Zuckermann, R. A. Segalman, ACS Macro Lett., 2014, **3**, 364−368.
[23] E. Martinelli, I. Del Moro, G. Galli, M. Barbaglia, C. Bibbiani, E. Mennillo, M. Oliva, C. Pretti, D. Antonioli, M. Laus, ACS Appl. Mater. Interfaces, 2015, **7**, 8293–8301.

[24] Y. Wang, D. E. Betts, J. A. Finlay, L. Brewer, M. E. Callow, J. A. Callow, D. E. Wendt, J. M. De Simone, Macromolecules, 2011, **44**, 878–885.
[25] C. S. Gudipati, C. M. Greenlief, J. A. Johnson, P. Prayongpan, K. L. Wooley, J. Polym. Sci. Part A: Polym. Chem., 2004, **42**, 6193–6208.
[26] X. Zhu, S. Guo, D. Jańczewski, F. J. P. Velandia, S. L.-M. Teo, G. J. Vancso, Langmuir, 2014, **30**, 288–296.
[27] S. Bauer, M. Alles, M. P. Arpa-Sancet, E. Ralston, G. W. Swain, N. Aldred, A. S. Clare, J. A. Finlay, M. E. Callow, J. A. Callow, A. Rosenhahn, Biomacromolecules, 2016, **17**, 897−904.
[28] B. H. Tan, H. Hussain, K. C. Chaw, G. H. Dickinson, C. S. Gudipati, W. R. Birch, S. L. M. Teo, C. He, Y. Liu, T. P. Davis, Polym. Chem., 2010, **1**, 276–279.
[29] E. Martinelli, S. D. Hill, B. M. J. A. Finlay, M. E. Callow, J. A. Callow, A. Glisenti, G. Galli, Progr. Org. Coat., 2016, **90**, 235–242.
[30] M. L. Hawkins, F. Fay, K. Rehel, I. Linossier, M. A. Grunlan, Biofouling, 2014, **30**, 247–258.
[31] C. S. Gudipati, J. A. Finlay, J. A. Callow, M. E. Callow, K. L. Wooley, Langmuir, 2005, **21**, 3044–3053.
[32] E. Martinelli, M. Suffredini, G. Galli, A. Glisenti, M. E. Pettitt, M. E. Callow, J. A. Callow, D. Williams, G. Lyall, Biofouling, 2011, **27**, 529–541.
[33] M. K. Chaudhury, J. A. Finlay, J. Y. Chung, M. E. Callow, J. A. Callow, Biofouling, 2005, **21**, 41–48.
[34] J. Kim, B. J. Chisholm, J. Bahr, Biofouling, 2007, **23**, 113–120.
[35] K. A. Pollack, P. M. Imbesi, J. E. Raymond, K. L. Wooley, ACS Appl. Mater. Interfaces, 2014, **6,** 19265–19274.
[36] E. Martinelli, E. Guazzelli, C. Bartoli, M. Gazzarri, F. Chiellini, G. Galli, M. E. Callow, J. A. Callow, J. A. Finlay, S. Hill, J. Polym. Sci. Part A: Polym. Chem., 2015, **53**, 1213–1225.
[37] E. Martinelli, G. Pelusio, B. R. Yasani, A. Glisenti, G. Galli, Macromol. Chem. Phys., 2015, **216**, 2086–2094.
[38] E. Martinelli, D. Gunes, B. M. Wenning, C. K. Ober, J. A. Finlay, M. E. Callow, J. A. Callow, A. Di Fino, A. S. Clare, G. Galli, Biofouling, 2016, **32**, 81–93.
[39] E. Martinelli, M. K. Sarvothaman, M. Alderighi, G. Galli, E. Mielczarski, J. A. Mielczarski, J. Polym. Sci. Part A: Polym. Chem., 2012, **50**, 2677–2686; E. Martinelli, M. K Sarvothaman, G. Galli, M. E Pettitt, M. E Callow, J. A. Callow, S. L. Conlan, A. S. Clare, A. B. Sugiharto, C. Davies, D. Williams, Biofouling, 2012, **28**, 571–582.
[40] V. Thiyagarajan, V. P. Venugopalan, K. V. K. Nair, T. Subramoniam, J. Indian Inst. Sci., 1999, **79**, 399-414; K. Kamino, Biofouling, 2013, **29**, 735–749.
[41] N. Aldred, A. S. Clare, Biofouling, 2008, **24**, 351–363.
[42] A. Di Fino, L. Petrone, N. Aldred, T. Ederth, B. Liedberg, A. S. Clare, Biofouling, 2014, **30**, 143–152 and references therein.
[43] L. Petrone, A. Di Fino, N. Aldred, P. Sukkaew, T. Ederth, A. S. Clare, B. Liedberg, Biofouling, 2011, **27**, 1043–1055.
[44] E. Pinori, M. Berglin, L. M. Brive, M. Hulander, M. Dahlström, H. Elwing, Biofouling, 2011, **27**, 941–953.
[45] W. Yandi, S. Mieszkin, A. Di Fino, P. Martin-Tanchereau, M. E. Callow, J. A. Callow, L. Tyson, A. S. Clare, T. Ederth, Biofouling, 2016, **32**, 609–625.
[46] R. Trepos, G. Cervin, C. Pile, H. Pavia, C. Hellio, J. Svenson, Biofouling, 2015, **31**, 393–403.
[47] H. B. Moore, A. C. Frue, Bull. Mar. Sci., 1959, **9**, 421–440; H. B. Moore, A. C. Frue, J. Exp. Zool., 1959, **280**, 213–219.
[48] J. T. Carlton, W. A. Newman, F. B. Pitombo, In: *In the Wrong Place – Alien Marine Crustaceans: Distribution, Biology and Impacts*, B. S. Galil, P. F. Clark, J. T. Carlton (Eds.), 2011, Springer: Dordrecht, p.159–213.
[49] J. A. Finlay, S. M. Bennett, L. H. Brewer, A. Sokolova, G. Clay, N. Gunari, A. E. Meyer, G. C. Walker, D. E. Wendt, M. E. Callow, J. A. Callow, M. R. Detty, Biofouling, 2010, **26**, 657–

666

[50] D. K. Owens, R. C. Wendt, J. Appl. Polym. Sci., 1969, **13**, 1741–1747; D. H. Kaelble, J. Adhesion, 1970, **2**, 66–81.

[51] Y. Y. Durmaz, E. L. Sahkulubey, Y. Yagci, E. Martinelli, G. Galli, J. Polym. Sci. Part A: Polym. Chem., 2012, **50**, 4911–4919.

[52] D. A. Shirley, Phys. Rev. B, 1972, **5**, 4709–4714.

[53] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, 1992, Physical Electronics: Eden Prairie (MN).

[54] N. S. McIntyre, T. C. Chan, In: *Practical Surface Analysis 1*, D. Briggs, M. P. Seah (Eds.), 2nd ed., 1990, Wiley: Chichester, UK.

[55] P. D. Elbourne, R. A. Veater, A. S. Clare, Biofouling, 2008, **24**, 87–96.

[56] M. E. Callow, J. A. Callow, S. Conlan, A. S. Clare, S. Stafslien, In: *Biofouling Methods*, S. Dobretsov, D. N. Williams, J. Thomason (Eds.), 2014, Wiley-Blackwell: Chichester, p.291–316.

[57] For examples, see (a) K. Jankova, S. Hvilsted, Macromolecules, 2003, 36, 1753–1758; (b) Y. Zhu, W. T. Ford, Macromolecules, 2008, **41**, 6089–6093; (c) W. Guo, X. Tang, J. Xu, X. Wang, Y. Chen, F. Yu, M. Pei, J. Polym. Chem. Part A: Polym. Chem., 2011, **49**, 1528–1534.

[58] N. Ahmed, T. Murosaki, A. Kakugo, T. Kurokawa, J. P. Gong, Y. Nogata, Soft Matter, 2011, **7**, 7281–7290.

[59] B. R. Yasani, E. Martinelli, G. Galli, A. Glisenti, S. Mieszkin, M. E. Callow, J. A. Callow, Biofouling, 2014, **30**, 387–399.

[60] I. Marabotti, A. Morelli, L. M. Orsini, E. Martinelli, G. Galli, E. Chiellini, E. M. Lien, M. E. Pettitt, M. E. Callow, J. A. Callow, S. L. Conlan, R. J. Mutton, A. S. Clare, A. Kocijan, C. Donik, M. Jenko, Biofouling, 2009, **25**, 481–493.

[61] C. Pretti, M. Oliva, E. Mennillo, M. Barbaglia, M. Funel, B. R. Yasani, E. Martinelli, G. Galli, Ecotoxicol. Environ. Saf., 2013, **98**, 250–256.

[62] L. Petrone, S. C. C. Lee, S. L. M. Teo, W. R. Birch, Biofouling, 2013, **29**, 213-221.

[63] N. Aldred, G. Z. Li, Y. Gao, A. S. Clare, S. Y. Jiang, Biofouling, 2010, **26**, 673-683.

Fig. 1. Reaction pathway for the synthesis of block copolymers Si-EFSx (x = 14, 71).

Fig. 2. XPS survey spectrum of the block copolymer film Si-EFS71 ($\phi = 20°$) after immersion in water for 7 days.

Fig. 3. Deconvolution of the XPS C(1s) signal of block copolymer film Si-EFS71 ($\phi = 20°$) before (top) and after (bottom) immersion in water for 7 days.

Fig. 4. Settlement percentage ± SE of *B. improvisus* cyprids after 24 h and 48 h. Each bar is the mean of six replicates. Comparisons were performed by non-parametric analysis of variance (Kruskal-Wallis) (Dunn's test, $p \leq 0.05$). Means that do not share a letter are significantly different (uppercase for 24 h settlement, lowercase for 48 h settlement).

Fig. 5. Settlement percentage ± SE of *B. amphitrite* cyprids after 24 h and 48 h. Each bar is the mean of six replicates. Comparisons were performed by non-parametric analysis of variance (Kruskal-Wallis) (Dunn's test, $p \leq 0.05$). Means that do not share a letter are significantly different (uppercase for 24 h settlement, lowercase for 48 h settlement).

Fig. 6. Percentage removal ± SE of juveniles of *B. improvisus* following exposure to a wall shear stress of 90 Pa. Experiments were run in six replicates. Means were compared by ANOVA (Tukey's pairwise comparison assay, $p \leq 0.05$). Means that do not share a letter are significantly different.

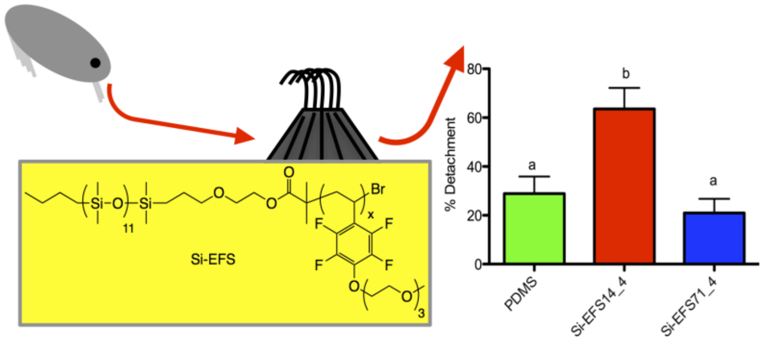
Table 1

Contact angles and surface tensions for the PDMS-based films and PDMS control.

Table 2

XPS C(1s) deconvolution data ($\phi = 20°$) for the block copolymer films before and after immersion in water for 7 days.

Graphical Abstract



Highlights

Surface-active amphiphilic block copolymers prepared by ATRP

PDMS-based films incorporating amphiphilic block copolymers

Surface chemistry investigated by XPS before and after water immersion

Antifouling/fouling release properties against two barnacle species

***Highlights**

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