



# Amphiphilic modified-styrene copolymer films: Antifouling/fouling release properties against the green alga *Ulva linza*

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## ABSTRACT

Surface-active copolymers of a styrene carrying a polysiloxane side chain (SSi) and a triethyleneglycol monomethyl ether-modified pentafluorostyrene (EFS) (39 and 77 mol% EFS) were prepared and incorporated (8 wt% loading) into a polydimethyl siloxane (PDMS) matrix to produce crosslinked blend films. The wettability of the surface-active copolymer films and PDMS-blend films was investigated by contact angle measurements. An angle-resolved X-ray photoelectron spectroscopy (XPS) of the surface chemical composition before and after immersion in water for 7 days enabled location of the hydrophilic oxyethylene segments of EFS within the top 10 nm from the film surface. Laboratory bioassays on the blend films against the marine green alga *Ulva linza* evidenced that the films containing the copolymer with the larger EFS content showed greater resistance to settlement of zoospores of *U. linza*, whereas both films had superior fouling-release properties of sporelings (young plants) compared to the PDMS standard films.

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## 1. Introduction

The biofouling of immersed man-made surfaces by the accumulation of proteins, cells and organisms is a worldwide problem, ranging from ship hulls [1] to water intake systems [2] and to biomedical implants and devices [3–5]. Specifically, marine biofouling causes a severe economic burden on maritime industries [6,7]. Antifouling paints containing biocides have long been effective in reducing biofouling [8], but their use is nowadays restricted because of potential toxicity to the marine environment [9–11]. Accordingly, more environmentally-friendly strategies are explored to replace traditional biocidal antifouling (AF) coatings, that prevent the settlement (attachment) of the colonizing stages of fouling organisms, with fouling release (FR) coatings, that reduce the adhesion strength of organisms so that they are removed hydrodynamically as a ship moves through the water [12].

Different approaches to producing novel AF/FR polymer coatings have been tested, including use of self-assembled copolymers with mesogenic side chains [13,14], zwitterionic polymers [15], phase-segregated polysiloxane-urethanes [16,17],

perfluoropolyether networks [18] and polymer nanocomposites [19,20]. Amphiphilic polymer films, which mix hydrophilic and hydrophobic components in the same surface, have also attracted interest in this field [21]. In particular, polyethylene glycols (PEGs) are hydrosoluble and biocompatible polymers largely used in biomedical applications owing to their ability to resist protein adsorption. On the other hand, fluorinated polymers are low surface energy materials suitable to reduce polar and hydrogen-bonding interactions with the bioadhesives used by fouling organisms. Such amphiphilic polymer films with AF/FR potential are produced by different strategies, such as multilayers of fluorinated/PEGylated polyions [25], UV photo-crosslinking of mixtures containing PEG and fluorinated macromonomers [23,24], crosslinking of PEG with hyperbranched fluoropolymers [22] and self-assembling of fluorinated/PEGylated copolymers blended with an elastomeric matrix [26–29]. The surfaces generated exhibit mixed hydrophilic and hydrophobic functionalities and feature (nano)scale heterogeneities that can deter the settlement of organisms and also minimize the interaction forces between biomolecules and substratum [30–32]. Moreover, the elastomer matrix provides independent control of the elastic property of the entire coating, an attribute that has been shown to be important for FR performance [33–35].

With the aim of combining these pre-requisite features into a single coating, we synthesized novel amphiphilic copolymers

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composed of styrene and pentafluorostyrene units modified in the *para* position with a hydrophobic polysiloxane and a hydrophilic triethyleneglycol monomethyl ether side chain, respectively, and used them as surface-active polymers to prepare PDMS-blend films. While different architectures of pentafluorostyrene/PEG polymers have been reported to have potential as marine antifouling surfaces [26,36], they have never been introduced as surface-active components in a PDMS matrix. The study of such systems may help to establish relationships between the polymer surface and its biological performance. In this context, we investigated the surfaces of the films prepared by contact angle and X-ray photoelectron spectroscopy (XPS) analyses, namely before and after immersion in water for 7 days. Biological performances were tested in laboratory bioassays with the marine alga *Ulva linza* by quantifying the number of zoospores that settled (attached) to the surfaces and evaluating the percent removal of sporelings (young plants) grown on the test films. A correlation was found between the biological performance of the films and the surface chemical composition of the copolymer blended, with both blend films showing improved FR compared to the PDMS standard films.

## 2. Materials and methods

### 2.1. Materials

Triethyleneglycol monomethyl ether (TEG), 4-vinylbenzoic acid, 2,3,4,5,6-pentafluorostyrene (PFS), bismuth neodecanoate (BiND), *N,N'*-dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) (all from Aldrich) were used as received. 2,2'-Azobisisobutyronitrile (AIBN) (from Fluka) was recrystallized from methanol. Dichloromethane was refluxed over CaH<sub>2</sub> for 4 h and distilled under nitrogen. Tetrahydrofuran (THF) was refluxed over Na/K alloy for 4 h and distilled under nitrogen. Anisole was kept at 100 °C over sodium for 4 h and then distilled under reduced pressure. Monocarinol-terminated poly(dimethyl siloxane) (PDMS-OH) ( $M_n = 1000 \text{ g mol}^{-1}$ ), bis(silanol)-terminated poly(dimethyl siloxane) (HO-PDMS-OH) ( $M_n = 26,000 \text{ g mol}^{-1}$ ), poly(diethoxy siloxane) (ES40) (all from ABCR) were used as received.

### 2.2. Monomers

Poly(dimethyl siloxane)propoxyethyl 4-vinylbenzoate (SSi) and 4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene (EFS) were synthesized by modifications of previous procedures in Refs. [37,38], respectively. The experimental details are given in [Supplementary Material](#).

### 2.3. General procedure for the preparation of copolymers SSi-EFSy

The copolymers SSi-EFSy were prepared by free-radical copolymerization with AIBN initiation in anisole at 65 °C (Scheme 1).

In a typical preparation, monomers SSi (0.707 g, 0.62 mmol) and EFS (0.800 g, 2.46 mmol), AIBN (2.6 mg) and anhydrous anisole (5 mL) were introduced into a Pyrex vial. The solution was outgassed by four freeze-pump-thaw cycles. The polymerization reaction was let to proceed under stirring at 65 °C for 40 h. The crude product was purified by several precipitations from chloroform

into methanol (yield 80%). The copolymer contained 77 mol% EFS counts and was named SSi-EFS77 ( $M_n = 52,000 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.9$ ).

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 0.1 (SiCH<sub>3</sub>), 0.5 (SiCH<sub>2</sub>), 0.9 (CH<sub>2</sub>CH<sub>3</sub>), 1.3 (CH<sub>2</sub>CH<sub>2</sub>Si), 1.6 (CH<sub>3</sub>CH<sub>2</sub>), 1.7–2.9 (CH<sub>2</sub>CHPh), 3.2–3.9 (OCH<sub>3</sub>, CH<sub>2</sub>O), 4.0–4.7 (COOCH<sub>2</sub>, PhOCH<sub>2</sub>), 6.2–8.0 (aromatic).

<sup>19</sup>F NMR (CDCl<sub>3</sub>/CF<sub>3</sub>COOH,  $\delta$  in ppm): –81 (2F, *m*-F), –67 (2F, *o*-F).

### 2.4. Preparation of films

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

The PDMS-blend films were prepared following a three-step procedure. (1) 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 layer. (2) 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 bottom layer. (3) Finally, a top layer was formed by spray-coating the same solution containing HO-PDMS-OH, ES40, BiND and the copolymer of choice (8 wt% with respect to PDMS). Eventual curing was at room temperature for 12 h and then at 120 °C for 12 h (overall thickness ~200  $\mu\text{m}$ ). The two PDMS-blend films are denoted as SSi-EFS39.8 and SSi-EFS77.8.

A film of PDMS alone was also prepared in the same way as a standard film.

Films of the pristine copolymers were prepared by spin-coating a 3 wt% solution in chloroform and drying at room temperature for 12 h and at 120 °C for 12 h.

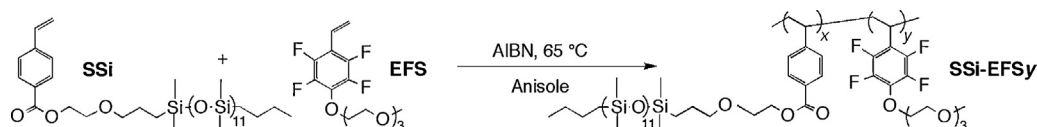
### 2.5. Characterization

<sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were recorded with a Varian Gemini VRX300 spectrometer on CDCl<sub>3</sub> and CDCl<sub>3</sub>/CF<sub>3</sub>COOH solutions, respectively. Gel permeation chromatography (GPC) analyses were carried out using a Jasco PU-1580 liquid chromatograph having two PL gel 5  $\mu\text{m}$  mixed-D columns, with a Jasco 830-RI refractive index detector. CHCl<sub>3</sub> was used as an eluent with a flow rate of 1 mL min<sup>-1</sup> and polystyrene standards were used for calibration.

Differential scanning calorimetry (DSC) analysis was performed with a Mettler DSC-30 instrument from –150 to 0 °C at heating/cooling rate of 10 °C min<sup>-1</sup> under a dry nitrogen flow. The glass transition temperature ( $T_g$ ) was taken as the inflection temperature in the second heating cycle.

Contact angles were measured by the sessile drop method with a FTA200 Camtel goniometer, using water ( $\theta_w$ ) (J.T. Baker, HPLC grade) and *n*-hexadecane ( $\theta_h$ ) (Aldrich product of the highest purity available) as wetting liquids. The measured values of  $\theta_w$  and  $\theta_h$  were then used to calculate the surface tension ( $\gamma_s$ ) of the polymer films using the Owens–Wendt–Kaelble approach with additive, dispersion  $\gamma_s^d$  and polar  $\gamma_s^p$ , components [39,40].

X-ray photoelectron spectroscopy (XPS) spectra were recorded by using a Perkin-Elmer PHI 5600 spectrometer with a standard Al-K $\alpha$  source (1486.6 eV) operating at 350 W. The working pressure was less than 10<sup>-8</sup> Pa. The spectrometer was calibrated by



Scheme 1. Synthesis of the surface-active copolymers SSi-EFSy.

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