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Synthesis of α,*ω*-Bis Epoxy Oligo (1′H,1′H,2′H,2′H-Perfluoroalkyl Siloxane)s and Properties of Their Photo-Acid Cross-Linked Films

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Low-viscosity oligomers 1,9-bis[2′-(4-cyclohexenyl-1,2-epoxy)ethyl]-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)pentasiloxane (**VII**), 1,9-bis[2′-(4-cyclohexenyl-1,2-epoxy)ethyl]-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (**VIII**), and 1,9-bis[2′-(4-cyclohexenyl-1,2-epoxy)ethyl]decamethylpentasiloxane (**IX**) have been prepared by Pt-catalyzed hydrosilylation reactions of 4-vinylcyclohexene-1,2-epoxide with 1,9-dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)pentasiloxane (**IV**), 1,9-dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)-pentasiloxane (**V**), and 1,9-dihydridodecamethylpentasiloxane (**VI**), respectively. **IV**−**VI** were prepared by the triflic-acid-catalyzed ring-opening of 1,3,5-trimethyl-1,3,5-tris(1H,1H,2H,-2H-perfluorooctyl)cyclotrisiloxane (**I**), 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluoropropyl)cyclotrisiloxane (**II**), and hexamethylcyclotrisiloxane (D_3) (**III**), respectively, in 1,1,3,3-tetramethyldisiloxane (**TMDS**). Solutions of a UV-sensitive diaryliodonium salt (0.5 wt %) and oligomers **VII**−**IX** were cast as uniform layers onto clean glass microscope slides and steel coupons. UV irradiation of these liquid layers rapidly converted them to cross-linked films (**X**−**XII**). Thermal stability of these films was determined by thermogravimetric analysis (TGA). Glass transition temperatures (T_gs) were measured by dynamic mechanical thermal analysis (DMTA). Static contact angles of distilled water on the air−film interfaces of **X**−**XII** have been determined with a goniometer. Dynamic contact angle (DCA) measurements have also been carried out on free-standing films. Corrosion protection of steel coupons by **X**−**XII** was evaluated by electrochemical impedance spectroscopy (EIS) during exposure to 0.5 N NaCl. Antifoul and foul-release properties of **X**−**XII** were studied by settlement and removal tests with the barnacle *Balanus amphitrite* and with spores and sporelings of the green alga *Enteromorpha*.

Introduction

The purpose of the research described herein is the development of a synthetic strategy to prepare nontoxic foul-release coatings which are minimally adhesive to marine organisms and protect steel from corrosion. The attachment and accumulation of marine organisms on the surfaces of marine vessels and structures is known as biofouling. On a ship's hull, biofouling leads to an increase in hydrodynamic drag and, consequently, increased power requirements and decreased speed.[1] The conventional approach to inhibit fouling growth is by the release of biocides, e.g., organotin or copper compounds, from coatings.[2] However, increased concentrations of these biocides in marine waters have been noted and may be harmful to other marine life. Although there is no limitation of the use of copper biocides, organotin-based antifouling coatings were banned on small vessels in many countries at the end of the 1980s.[2] Thus, the development of nontoxic, environmentally benign polymer coatings which are minimally adhesive to marine organisms is a promising solution to biofouling.

Polysiloxanes have been shown to be effective nontoxic foul-release materials.[3,4] This has been attributed

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to their hydrophobicity as well as their low polarity, glass transition temperature, surface energy, and modulus.[5] Because the initial attachment of marine organisms to a substrate is strengthened by polar surface groups to which the organisms can hydrogen bond, hydrophobic polysiloxane surfaces are ideal for foul-release coatings.[6] The adhesion of marine organisms onto polysiloxane surfaces is sufficiently weak so that the joint is broken by the weight of the organism, movement of vessel through water, or a water jet.[7]

The use of fluorosilicones as antifouling coatings are of interest because the surface tension of a fluorosiloxane is lower than that of a corresponding siloxane.[8] However, some fluorosilicones exhibit inferior fouling-release properties compared to that of the corresponding polysiloxane. These results may be explained from previous observations in which a fluoroalkylsiloxane demonstrated higher peel adhesion with viscoelastic adhesives compared to a polysiloxane.[9] The softer (i.e., lower T_g) of the polysiloxanes allowed the adhesive to "slip" and thereby reduced adhesion strength.[9] In this regard, while poly(tetrafluoroethylene) (Teflon) has a lower surface energy than poly(dimethylsiloxane) (PDMS), it exhibits poor biofoul-release properties. Again, this may be credited to its T_g (130 °C) which is significantly higher than that of PDMS (T_g, −125 °C).[10] Also, polysiloxanes having pendant fluoroalkyl ether pendant groups were worse foul-release materials than the corresponding polysiloxanes.[11] Some fluorosilicones have demonstrated improved fouling-release properties compared to that of their silicone counterparts. For instance, polysiloxanes which contain pendant fluoroalkyl groups demonstrated superior fouling-release properties compared to polysiloxane controls.[12−14] Polysiloxanes have been shown to promote fouling joint failure by peel,[15] whereas fluoroalkyl groups promote failure by shear.[15]

Unfortunately, linear PDMS is mechanically weak and easily tears. Therefore, polysiloxanes must be cross-linked to form a film with sufficient mechanical integrity.[16] Moisture cure of silicone compositions by hydrolysis/condensation has been achieved with tin(IV) catalysis, e.g., dibutyltin dilaurate catalyzes the cure of $\alpha,\alpha,\omega,\omega$-tetra-alkoxy PDMS.[5] Tin(IV) catalyzed condensation of α,ω-disilanol PDMS and tetra-alkoxysilanes has also been demonstrated.[17,18] Alternatively, platinum-catalyzed hydrosilylation cross-linking between α,ω-divinyl PDMS and α,ω-dihydrido-oligosiloxanes or poly(methylsiloxane) has been utilized.[19] In the work described herein, we have prepared epoxy-terminated siloxane oligomers. Epoxy silicones have found utility as paper release coatings.[20] Epoxies are typically cross-linked with amines.[21] However, epoxy-terminated siloxane monomers have been photochemically cross-linked with UV irradiation.[22−24] In this study, we have utilized this later method to rapidly convert epoxy-terminated siloxane monomers to films.

Protection of steel, aluminum, or fiberglass ship hulls from biofouling typically requires a multilayer coating system. A biofoul-release siloxane coating is often applied over an anti-corrosion epoxy primer and possibly an amine-terminated siloxane tie coat.[25] In this study, we initially applied an epoxy-amine primer to some of the substrates (e.g., glass microscope slides and steel coupons) prior to coating with our epoxy-terminated siloxane oligomers (**VII**−**IX**).

We are interested in understanding the relationship between the chemical nature of polysiloxane coatings (e.g., surface energy, T_g, cross-linking chemistry) which produce foul-release properties. Toward this goal, we have produced three siloxane films (**X**−**XII**) whose pendant groups vary in the degree of fluorination: 1′H,1′H′,2′H,2′H-perfluorooctyl (**X**), 3′,3′,3′-trifluoropropyl (**XI**), and methyl (**XII**). Because the surface energies and T_g values of fluorosilicones are lower than those of siloxanes, the effect of coating surface energy and "softness" on fouling properties can be studied. Antifouling and foul-release tests are made using both hard foulers (barnacles) and soft foulers (algae). In addition, the ability of these coatings to protect steel against corrosion is evaluated.

Synthetic Approach. Herein, we report the preparation of novel cross-linked films prepared by the photoacid-catalyzed cross-linking of α,ω-bis epoxy oligo (1′H,1′H,2′H,2′H-perfluoroalkyl siloxane)s (**VII**−**IX**). The method consists of four steps: (1) the preparation of ring-strained cyclotrisiloxanes[26] (**I**−**III**), (2) triflic-acid-catalyzed ring-opening of **I**−**III** to yield α,ω-bis Si−H pentasiloxanes[27] (**IV**−**VI**), (3) Pt-catalyzed hydrosilylation reaction of **IV**−**VI** with 4-vinylcyclohexene-1,2-epoxide[28] to produce **VII**−**IX**, and (4) UV cure of **VII**−**IX** with photoacid catalyst[24] to produce films **X**−**XII**,

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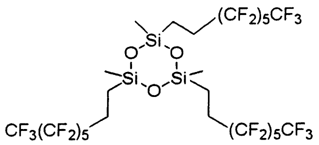
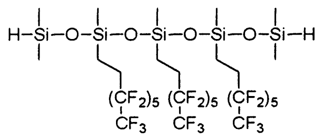
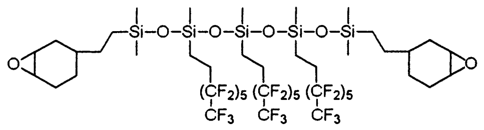
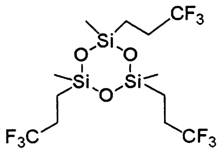
Table 1. Structures of Cyclotrisiloxanes (I–III), α,ω-bis Hydrido Oligosiloxanes (IV–VI), and α,ω-bis Epoxy-Alkyl Substituted Oligosiloxanes (VII–IX)


I


IV


VII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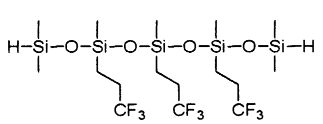
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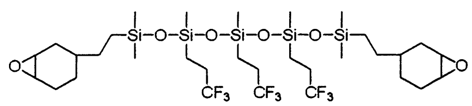
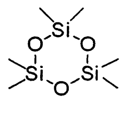
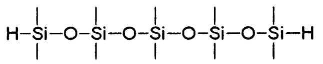
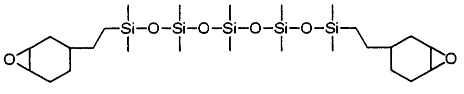

VIII


III


VI


IX

respectively. The structures of **I**–**IX** are represented in Table 1. Synthesis of **I** and film **X**–**XII** are depicted in Figures 1 and 2, respectively.

Cyclotrisiloxanes **II** and **III** are commercially available, whereas **I** required preparation. **I** was prepared by the reaction of 1H,1H,2H,2H-perfluorooctyldichlorosilane with dimethyl sulfoxide (DMSO) in the presence of zinc (Figure 1).[26] Solutions comprised of oligomer (**VII**, **VIII**, or **IX**) and a catalytic amount of a diaryliodonium salt were uniformly coated onto glass microscope slides or steel coupons. These liquid layers were then polymerized and cross-linked by irradiation with a 450-W medium-pressure Hanovia UV lamp to form films **X**–**XII**, respectively (Figure 2). Irradiation of diaryliodonium salts produced strong acid which catalyzes the ring-opening polymerization and cross-linking of **VII**–**IX** to produce films **X**–**XII**.

The thermal stabilities of films **X**–**XII** have been determined by TGA, and their T_g values were measured by DMTA in both bending and tensile modes. Static contact angles of distilled water at the air–film interface were determined with a goniometer. In addition, ascending and descending dynamic contact angles of free-standing films were determined by DCA analysis. Settlement and removal of *Balanus amphitrite* barnacles and *Enteromorpha* spores and sporelings were used to evaluate antifouling and fouling-release properties of **X**–**XII**. EIS was used to establish the ability of **X**–**XII** to provide corrosion protection for steel.

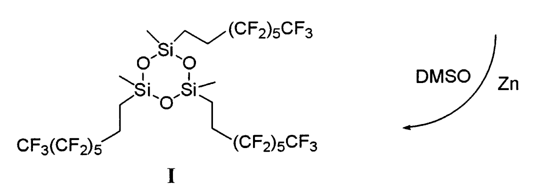


Figure 1. Synthesis of 1,3,5-trimethyl-1,3,5-tris(1′H,1′H,2′H,-2-H-perfluorooctyl)cyclotrisiloxane (**I**).

Experimental Section

Instrumentation. ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer operating in the FT mode. ^1H, ^{13}C, and ^{19}F NMR spectra of 5% w/v $CDCl_3$ solutions were obtained. ^{29}Si NMR spectra of 25% w/v $CDCl_3$ solutions were acquired. ^{13}C NMR spectra were obtained with broadband proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60-s delay was used to acquire ^{29}Si NMR spectra. Residual $CDCl_3$ was used as an internal standard for ^1H and ^{13}C NMR. ^{29}Si NMR spectra were referenced to internal TMS. ^{19}F spectra were referenced to internal $CFCl_3$. IR spectra of neat films on NaCl plates were recorded using a Perkin-Elmer Spectrum 2000 FTIR spectrometer. Refractive index (RI) measurements of liquids were determined using a Bauch & Lomb ABBE-3L refractometer at 22 °C.

High-resolution mass spectra were run at the University of California, Riverside, mass spectroscopy facility on a VG-7070 EHF instrument. Ionization was achieved by fast atom bombardment (FAB). Exact masses were determined by peak matching against known masses of perfluorokerosene.

TGA was performed on a Shimadzu TGA-50 instrument at a flow rate of 40 cm^3 of nitrogen per min. The temperature was increased 4 °C/min from 25 to 800 °C. Viscosity measurements were obtained with a Brookfield model DV-II viscometer at 22 °C with a shear rate of 12 s^{-1}.

Glass transition temperatures (T_gs) of films in a bending mode at frequencies of 1 and 5 Hz and at a strain level of 1 were determined using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) MkII. A standard single cantilever bending head was used. After equilibration at −130 °C, the temperature was increased at 4 °C/min to 100 °C. T_gs of these films were also determined in a tensile mode on a Rheometric Scientific DMTA V. The analysis was carried out at a frequency of 1 Hz at a strain level of 0.3%. After equilibration at −50 °C, the temperature was increased at a rate of 2 °C/min to 100 °C.

Static contact angles (θ_{static}) were determined by placing a single drop of distilled water on each sample at the air–film interface. The contact angle was then measured with a goniometer. DCA analysis was performed by the Wilhelmy plate method with a Thermo Cahn DCA Analyzer 315. The

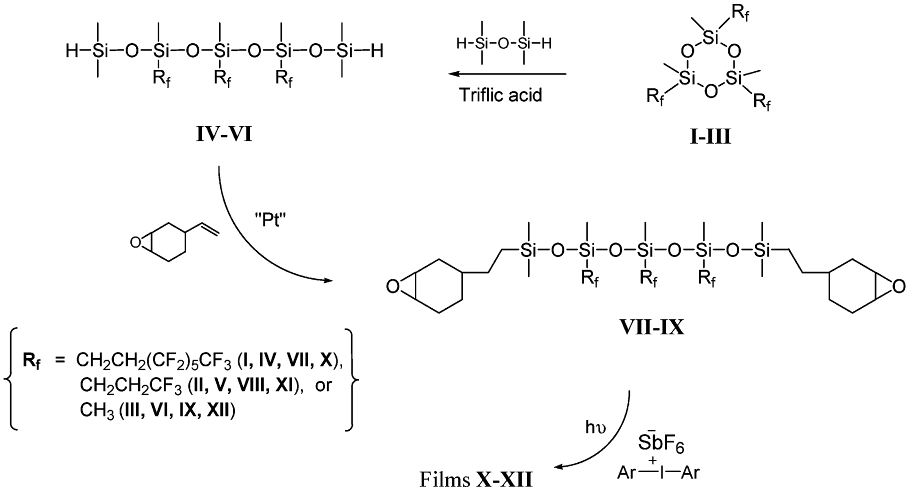


Figure 2. Synthesis of films **X**−**XII**.

probe liquid was prepared as follows. Sparklett's water, purified by deionization and/or reversed osmosis, was distilled twice in clean glassware under N_2. Two crystals of $KMnO_4$ were added to the water before the first distillation. During the second distillation, a gas trap filled with saturated aqueous NaOH was used to prevent CO_2 contamination. Last, the fresh, doubly distilled water was stored under N_2 in Pyrex glassware protected with a NaOH gas trap. All glassware used for DCA measurements was initially cleaned in saturated KOH in 2-propanol overnight and subsequently in aqueous HCl for at least 30 min. It was then rinsed several times with purified water and finally with reagent grade acetone. Glassware was then dried and stored in an oven (90 °C) before use. Films **X**−**XII** were removed from the microscope slides with a clean single-edged razor blade. The width and thickness of the samples were measured several times with digital calipers. Average values obtained were used for calculations. Typical dimensions were width 22 ± 1 mm and thickness 0.22 ± 0.02 mm. The films were immersed and withdrawn from the interrogating water three times with a stage speed of 100 μm/sec. Using the linear portion of the force−distance curve (fdc), the advancing contact angle (θ_{adv}) and the receding contact angle (θ_{rec}) could be calculated. The θ_{adv} and θ_{rec} were obtained from the first fdc curve. Subsequent cycles showed slightly decreased θ_{adv} as previously reported.[29,30] Contact angle hysteresis (θ_Δ) equals $\theta_{adv} - \theta_{rec}$.

Materials. bis(4-Dodecylphenyl)iodonium hexafluoroantimonate (GE UV 9380c), a photo-acid catalyst, was obtained from GE Silicones. 1H,1H,2H-Perfluoro-1-octene and 1,3,5-trimethyl-1,3,5-tris-(3′,3′,3′-trifluoropropyl)cyclotrisiloxane (**II**) were purchased from Lancaster. Triflic acid and Scotch-Weld Structural Adhesive Primer EC-1845 B/A were obtained from the 3M Corp. 1,3-Divinyltetramethyldisiloxane Pt complex (Karstedt Catalyst) in xylene (2% Pt) was purchased from United Chemical Technologies, Inc. Methyldichlorosilane, **III**, **TMDS**, and hexamethyldisilazane (**HMDZ**) were purchased from Gelest. Toluene, DMSO, 4-vinylcyclohexene-1,2-epoxide, triethylamine, THF, dichoromethane, and hexanes were acquired from Aldrich. Solvents were purified by distillation before use. Low-carbon, cold-rolled steel coupons (0.8 × 76 × 127 mm) which have a dull matte finish were received from the Paul N. Gardner Co., Inc.

Synthesis. All reactions were conducted in flame-dried glassware under argon. Reaction mixtures were agitated with Teflon-covered magnetic stir bars.

1H,1H,2H,2H-Perfluorooctylmethyldichlorosilane.[31] Methyldichlorosilane (20 g, 0.174 mol), 1H,1H,2H-perfluoro-1-octene (45 g, 0.130 mmol), and two drops of Karstedt's catalyst were placed in a 500-mL round-bottom flask sealed with a rubber septum. After stirring overnight, the contents of the flask were fractionally distilled through a 15-cm vacuum-jacketed Vigreux column under reduced pressure. A central fraction 45 g, 75% yield, bp = 90 °C/20 mm[26] was obtained. ^{1}H NMR δ: 0.88 (s, 3H), 1.44 (m, 2H), 2.36 (m, 2H). ^{13}C NMR δ: 4.96, 12.47, 25.83, (t, $J_{C-F} = 24$ Hz), 106.96−122.24 (m). ^{19}F NMR δ: −126.30 (m, 2F), −123.22 (s, 2F), −122.84 (s, 2F), −121.83 (s, 2F), −115.74 (br. s, 2F), −81.35 (t, 3F, $J_{F-F} = 10$ Hz). ^{29}Si NMR δ: 32.39. IR ν: 2982, 2954, 2913, 1444, 1364, 1318, 1241, 1210, 1197, 1146, 1072, 897, 830, 820, 811, 791 cm^{-1}.

1,3,5-Trimethyl-1,3,5-tris(1′H,1′H,2′H,2′H-perfluorooctyl)cyclotrisiloxane (I).[31] Compound **I** was prepared by reaction of 1H,1H,2H,2H-perfluorooctylmethyldichlorosilane and DMSO in the presence of zinc. A fraction bp = 57 °C/ 0.2 mm,[26] 40 g, 76% yield was obtained. ^{1}H NMR δ: 0.15 (s, 6H), 0.16 (s, 6H), 0.85 (m, 2H), 2.18 (m, 2H, $J_{H-F} = 18$ Hz). ^{13}C NMR δ: −0.68, 0.77, 0.92, 7.41, 25.86 (t, $J_{C-F} = 24$ Hz), 106−123 (m). ^{19}F NMR δ: −126.30 (m, 2F), −123.48 (br. s, 2F), −122.86 (br. s, 2F), −121.85 (br. s, 2F), −116.25 (t, 2F, $J_{F-F} =$ 17 Hz), −81.34 (t, 2F, $J_{F-F} = 10$ Hz). ^{29}Si NMR δ: −11.16, (1Si), −8.01 (2Si). IR ν: 2967, 2912, 1444, 1264, 1240, 1210, 1196, 1146, 1017, 813, 707 cm^{-1}.

1,9-Dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris-(1′H,1′H,2′H,2′H-perfluorooctyl)pentasiloxane (IV). **I** (7.0 g, 5.7 mmol) and **TMDS** (3.9 g, 29 mmol) were added to a 200-mL round-bottom flask. The flask was cooled in an ice bath, and triflic acid (150 mg, 90 μL) was added. After 17 min, the reaction was quenched with **HMDZ** (3.1 g, 4.0 mL). The solution was allowed to warm to room temperature. Salts were removed by filtration and the volatiles were removed by evaporation under reduced pressure. **IV** was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction bp 152 °C/0.2 mm, 7.3 g, 95% yield was obtained. ^{1}H NMR δ: 0.12 (s, 6H), 0.15 (s, 3H), 0.18 (d, 12H, $J = 2$ Hz), 0.75 (m, 6H), 2.05 (m, 6H), 4.70 (m, 2H). ^{13}C NMR δ: −0.99, −0.94, −0.68, 0.52, 6.81, 6.92, 25.16 (m), 109.17 (m), 111.32 (m), 113.07 (m), 116.30 (m), 118.59 (m), 120.44 (m). ^{19}F NMR δ: −126.87 (m, 2F), −124.08 (m, 2F), −123.55 (m, 2F), −122.59 (m, 2F), −116.91 (m, 2F), −81.57 (m, 3F). ^{29}Si NMR δ: −22.60 (m, 1Si), −21.40 (m, 2Si), −4.66 (d, 2Si, J_{Si-H} = 5 Hz). IR ν: 2965, 2911, 2131 (Si−H), 1238, 1195, 1143, 1069, 908, 809 cm^{-1}.

1,9-Dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (V). Compound **V** was prepared by reaction of **II** (35.1 g, 75 mmol) and **TMDS** (25.2 g, 188 mmol) as above. A fraction, bp 112 °C/1.0 mm, 39.3 g, 87% yield was collected. ^{1}H NMR δ: 0.11 (s, 6H), 0.14 (s, 3H), 0.19

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(31) Paulasaari, J. K. Ph.D. Thesis, University of Southern California, Los Angeles, CA, 1999; p 194.

(d, 12H, $J = 2.5$ Hz), 0.74 (m, 6H), 2.04 (m, 6H), 4.72 (m, 2H). ^{13}C NMR δ: −0.96, −0.75, 0.63, 9.21, 9.30, 28.10 (m), 120.75 (m). ^{19}F NMR δ: −69.32 (m). ^{29}Si NMR δ: -22.96 (s, 1Si), −21.79 (s, 2Si), −4.84 (d, 2Si, $J = 4.5$ Hz). IR ν: 2961, 2902, 2127, 1265, 1208, 1130, 1069, 1016, 908, 809 cm^{-1}.

1,9-Dihydrido-1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane (VI). Compound **VI** was prepared as previously reported.[27]

1,9-bis[2′-(4-Cyclohexenyl-1,2-epoxy)ethyl]-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)-pentasiloxane (VII). **IV** (5.0 g, 3.7 mmol), Karstedt catalyst (10 drops), and triethylamine (3 drops) were placed in a 50-mL round-bottom flask. 4-Vinylcyclohexene-1,2-epoxide (1.4 g, 11 mmol) was placed in a pressure-equalizing addition funnel and was slowly added over 30 min. The mixture was allowed to stir overnight. THF (10 mL) was added and the solution was passed through a short silica gel column with additional THF to remove the Karstedt's catalyst. The volatiles were then removed under reduced pressure. **VII** (5.1 g, 86% yield) was obtained. ^{1}H NMR δ: 0.05 (s, 12H), 0.09 (s, 6H), 0.13 (s, 3H), 0.45−2.16 (m, 38H), 3.10 (m, 4H). ^{13}C NMR δ: −0.57, −0.02, 7.01, 15.06, 15.15, 23.77, 24.17, 25.22 (m), 25.47, 26.94, 29.75, 30.23, 30.56, 31.74, 32.47, 35.63, 38.99, 51.97, 52.08, 52.81, 53.36, 109.14 (m), 111.30 (m), 113.45 (m), 116.28 (m), 118.42 (m), 120.44 (m). ^{19}F NMR δ: −126.80 (m, 2F), −123.99 (m, 2F), −123.50 (m, 2F), −122.52 (m, 2F), −116.81 (m, 2F), −81.51 (m, 3F). ^{29}Si NMR δ: −23.13 (m, 2Si), −23.03 (m, 1Si), 10.08 (s, 2Si). IR ν: 2961, 2902, 1728, 1265, 1238, 1195, 1069, 1037, 908, 809 cm^{-1}. RI = 1.3872 ± 0.0002. Viscosity = 279 centipoise. High-resolution mass spectra: Calc. for $C_{47}H_{59}F_{39}O_6Si_5$ $(M + Na)^+$, 1623.2433; found, 1623.2367.

1,9-bis[2′-(4-Cyclohexenyl-1,2-epoxy)ethyl]-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane (VIII). Compound **VIII** was prepared from **V** (10.0 g, 16.6 mmol) and 4-vinylcyclohexene-1,2-epoxide (6.2 g, 50 mmol) as above. **VIII**, 13.7 g, 97% yield, was obtained. ^{1}H NMR δ: 0.52 (m, 21H), 0.45−2.17 (m, 38H), 3.11 (m, 4H). ^{13}C NMR δ: −0.48, 0.13, 1.20, 9.38, 15.05, 15.15, 23.77, 24.16, 25.48, 26.96, 28.16 (m), 29.72, 30.19, 30.52, 31.71, 32.45, 35.57, 52.02, 52.13, 52.86, 53.41, 126.60 (m), 128.79 (m). ^{19}F NMR δ: −69.25 (m, 1F), −69.35 (m, 2F). ^{29}Si NMR δ: −23.45 (s, 2Si), −21.87 (s, 1Si), 9.94 (s, 2Si). IR ν: 2958, 2923, 2853, 1639, 1367, 1261, 1208, 1130, 1069, 1016, 908, 809 cm^{-1}. RI = 1.4263 ± 0.0002. Viscosity = 63 centipoise. High-resolution mass spectra: Calc. for $C_{32}H_{59}F_9O_6Si_5$ $(M+Na)^+$, 873.2912; found, 873.2873.

1,9-bis[2′-(4-Cyclohexenyl-1,2-epoxy)ethyl]decamethylpentasiloxane (IX). Compound **IX** was prepared by reaction of **VI** (5.0 g, 14 mmol) and 4-vinylcyclohexene-1,2-epoxide (5.2 g, 42 mmol) as above. **IX**, 7.3 g, 86% yield, was obtained. ^{1}H NMR δ: 0.11 (s, 12H), 0.13 (s, 18H), 0.54−2.23 (m, 26H), 3.11 (m, 4H). ^{13}C NMR δ: −0.15, 0.87, 0.94, 14.76, 14.90, 23.44, 23.90, 25.27, 26.63, 29.37, 29.96, 30.30, 31.47, 32.04, 35.25, 51.26, 52.02, 52.55. ^{29}Si NMR δ: −22.32 (s, 1Si), −21.65 (s, 2Si), 7.66 (s, 2Si). IR ν: 2961, 2902, 1728, 1265, 1238, 1195, 1069, 1037, 908, 809 cm^{-1}. RI = 1.4330 ± 0.0002. Viscosity = 32 centipoise. High-resolution mass spectra: Calc. for $C_{26}H_{56}O_6Si_5$ $(M + Na)^+$, 627.2821; found, 627.2790.

Film X. To 5.0 g of **VII** was added 0.025 g (0.5 wt. %) of photoacid catalyst. The solution was passed through a 0.45-μm Whatman Polydisk filter to remove particulate impurities. Glass microscope slides were sequentially cleaned with acetone and a dichloromethane/hexane (50:50 vol) mixture. Steel coupons were initially rinsed with acetone and then vapor-degreased by suspension over a boiling mixture of dichloromethane/hexane (50:50 vol). Microscope slides and steel coupons were dried at 100 °C overnight after cleaning.

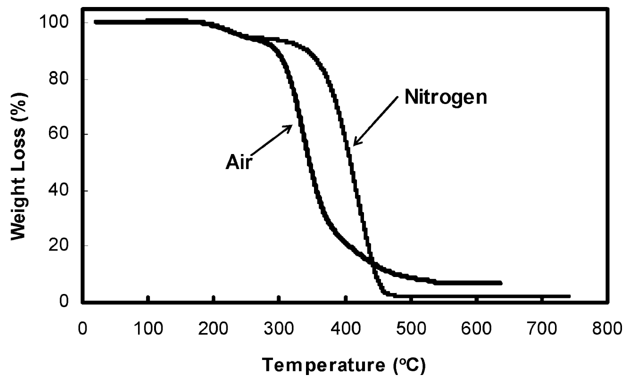

Figure 3. TGA of **X** in nitrogen and air.

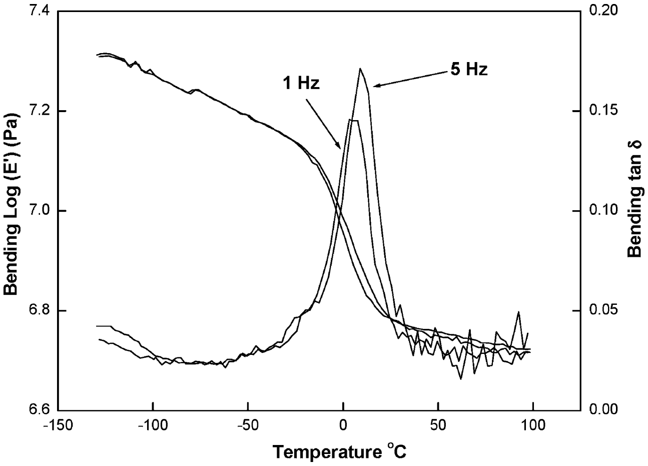

Figure 4. DMTA of **X**.

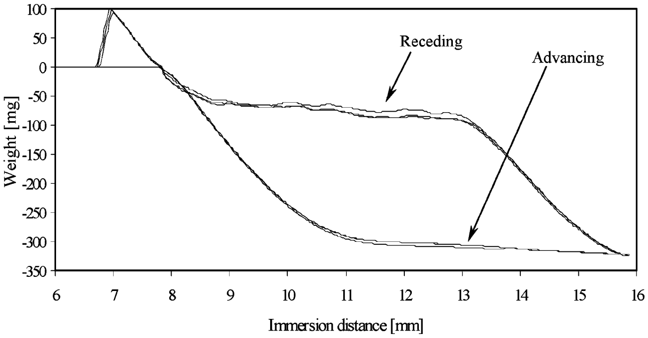

Figure 5. DCA force−distance curves of **X** run in purified water.

A 10-mil (0.25 mm) thick liquid layer of the above solution was cast uniformly on a clean smooth microscope glass slide using a Gardner drawdown bar. The coated slide was then exposed to UV radiation from a 450-W medium-pressure Hanovia mercury lamp for 5 min. During this exposure, a transparent cross-linked film was produced. These films were removed from the glass substrate with a clean razor blade prior to DMTA, TGA, and DCA measurements. Their thickness (~0.2 mm) after curing was measured with a micrometer. By TGA, **X** is stable to 300 °C in nitrogen, and to 275 °C in air (Figure 3). By DMTA, the T_g of **X**, in a bending mode at a strain level of 1, is 5 °C at 1 Hz and 9 °C at 5 Hz (Figure 4). DCA analysis on **X** with probe water produced an initial fdc with θ_{adv} of 112°, θ_{rec} of 78°, and $\theta_{\Delta} = 34°$ (Figure 5). The θ_{static} of distilled water on the air−film interface of **X** was 121°. Coated glass microscope slides were similarly prepared for biotesting. Some microscope slides for biotesting were initially dip-coated with the liquid primer and allowed to dry for 24 h. These "primed" glass slides were then coated as above.

Steel coupons for corrosion testing were prepared as follows. The liquid primer was cast uniformly onto the steel panel at a 2-mil thickness using a Gardner drawdown bar. The primer was allowed to dry 24 h at room temperature and then placed in a 100 °C oven for one h. The above liquid solution was uniformly cast at 5-mil thickness as above. The coated steel coupons were irradiated for 5 min to produce transparent cross-linked films.

Film XI. A solution of **VIII** and photoacid catalyst was prepared as above. After filtration, this solution was uniformly cast on glass microscope slides at a thickness of 10 mil (0.25

mm). Subsequent cross-linking of the liquid layer by exposure to UV radiation produced a film (**XI**). The cured film **XI**, ~0.2-mm thickness, was removed from the glass slides as above. By TGA, **XI** is stable to 300 °C in nitrogen, and to 275 °C in air. Its T_g was 14 °C by DMTA in a bending mode at 1 Hz, whereas its T_g was 18 °C at 5 Hz. Its T_g by DMTA in a tensile mode is 24 °C. DCA analysis on **XI** with probe water produced an initial fdc with θ_{adv} of 107°, θ_{rec} of 75°, and $\theta_\Delta = 32°$. The θ_{static} of a droplet of distilled water on the air−film interface of **XI** was 101°. Coated microscope slides for biotesting were prepared with and without an initial primer layer as above. Coated steel panels were also prepared for corrosion testing as above.

Film XII. A solution of **IX** and photoacid catalyst was prepared as above. Cured films, ~0.2-mm thick, were prepared as above for DMTA, DCA, and TGA. By TGA, **XII** is stable to 325 °C in nitrogen and to 275 °C in air. Its T_g by DMTA in a bending mode at 1 Hz was 55 °C. A beta transition of −20 °C at 1 Hz or −25 °C at 5 Hz was also observed. Its T_g by DMTA in a tensile mode was 83 °C. DCA analysis on **XI** with probe water produced an initial fdc with θ_{adv} of 105°, θ_{rec} of 77°, and $\theta_\Delta = 28°$. The θ_{static} of a droplet of distilled water on the air−film interface of **XII** was 102°. Coated microscope slides for biotesting were prepared with and without an initial primer layer as above. Coated steel coupons were also prepared for corrosion testing as above.

Biotesting using the Barnacle *Balanus*. Three replicate microscope slides of **X**−**XII** were evaluated along with uncoated glass and commercial PDMS which served as controls. The slides were soaked in seawater for 7 days to remove any leachate. Next, approximately 30−50 *Balanus* larvae were suspended directly on the surface of the coatings in approximately 1 mL of filtered seawater. After approximately 60 h, ~50% of the larvae settled on the uncoated glass slides. The numbers of larvae attached and metamorphosed onto the coated slide surfaces were counted. Error bars on percent settlement data (Figure 9) represent one standard error. Uncoated glass surfaces are favorably colonized by larvae of *Balanus amphitrite*.

Newly metamorphosed barnacles were transferred on their respective slides to growth chambers where they were fed the unicellular alga *Dunaliella* sp. and the diatom *Skeletonema costratum* for two weeks. Naupliar larvae of *Artemia* sp. were then added to the above diet. Juveniles were maintained in an incubator at 25 °C on a 12-h light/dark cycle for ~8 weeks, which is the time required for the juveniles to achieve a basal plate diameter of 3−5 mm (the minimum size necessary for force gauge tests by ASTM D 5618).

Procedures for critical removal stress followed ASTM D 5618 except that the force-measuring device was operated by a motorized stand to ensure a constant force dislodgement of the barnacles from coatings. The procedure was further modified in that all animals were dislodged under water. The apparatus consisted of an IMADA AXT 70 digital force gauge (4.4 lb) mounted on an IMADA SV-5 motorized stand. The slides were clamped in a Plexiglas chamber that allowed their complete submersion. Only healthy juvenile barnacles that were attached at least 5 mm from the edges of the slides were tested. Other barnacles in close proximity to the test subject were removed. The basal diameter of the barnacle was measured with calipers in two perpendicular directions. Basal area of attachment to the coating was estimated: area $(A) = \pi\,(0.5d_1)(0.5d_2)$. A shear force was applied with a force gauge to the barnacle's base parallel to the coated slide surface at a rate of ~4.5 N/s (1 lb./s) until the organism detached from the coating or broke from its basal plate. The critical removal stress is equal to removal force divided by the area of attachment.

Biotesting with *Enteromorpha* Spores and Sporelings. Surface colonization is through the settlement and adhesion of motile spores.[32] Adhered spores (nonmotile) germinate into sporelings and subsequently into mature plants. Zoospores were released from fertile *Enteromorpha linza* plants and prepared for adhesion experiments.[32] Six replicate microscope slides of **X**−**XII** and acid-washed uncoated glass slides which served as the controls were tested. Slides were initially leached for 24 h in stirred distilled water. Settlement of zoospores over 4 h onto slide surfaces was done according to standard methods.[33] The spores that had not adhered to the slides during the settlement period were exposed to light to observe their motility and determine leachate toxicity. Spores that had adhered to the slides were counted on three replicates with a Zeiss Kontron 3000 image capture analysis system attached to a Zeiss epiflourescence microscope.[34] The remaining three replicate slides with adhered spores were subjected to an automated water jet with a surface pressure of 71 kPa on a 5 cm² area for 5 min.[33,35] The number of spores remaining attached were counted with the imaging system described above. Percentage spore removal after exposure to the water jet was calculated.[33]

Five replicate microscope slides each of **X**−**XII** coated over an initial primer layer were used to evaluate *Enteromorpha* sporeling attachment. Uncoated glass slides and slides coated only with primer were included as standards. Slides were initially leached for 24 h in stirred distilled water. Zoospores were released and spores were allowed to settle onto surfaces as above. Unattached spores were monitored for motility. Sporeling growth and attachment was carried out according to standard methods.[36] Sporelings were cultured on the slides for 8 days. The sporeling biofilm was scraped from half of each slide into a tube and quantified by extraction of chorophyll *a* into DMSO.[37] The remaining sporelings on the other half of each slide were exposed to a wall shear stress of 53 Pa for 5 min in a turbulent channel flow apparatus.[38] The sporeling biomass remaining was estimated by extraction of chlorophyll *a* as above. Percentage biomass removal after exposure to shear was calculated. Error bars on percent removal data (Figure 10) were obtained from arcsine transformed data. Significance was tested using 1-way ANOVA and when significant differences were found, the means were compared using Tukey's test.

Evaluation of Corrosion Protection with EIS. Samples of **X**−**XII** with a coating over a primer layer on steel coupons were placed in a three-electrode electrochemical cell 0.5 N NaCl (open to air) at room temperature. Samples with only a primer coat were also tested. The exposed area of the working electrode was ~5 cm². A stainless steel electrode was used as counter electrode, while a saturated calomel reference electrode (SCE) served as reference electrode. EIS data were obtained at the open-circuit or corrosion potential in a frequency range between 100 kHz and 5 mHz using a Gamry PCI4/300 potentiostat or a BAS-Zahner IM6 impedance analyzer. The amplitude of the applied ac signal was 25 mV. The exposure period was approximately two weeks. The impedance spectra are displayed as Bode-plots in which the logarithm of the impedance modulus ($|Z|$) and phase angle (Φ) are plotted vs the frequency (f) of the applied signal.

Discussion

Synthesis. Ring-opening of D_3 derivatives in **TMDS** requires rapid quenching to avoid acid-catalyzed equilibration of the resulting pentasiloxanes. The IR spectra of α,ω-dihydridopentasiloxanes (**IV**−**VI**) all show a strong band at ~2130 cm^{-1} due to the Si−H bonds. As expected, three resonances in a 1:2:2 intensity ratio were detected in the ^{29}Si NMR. The terminal silicon reso-

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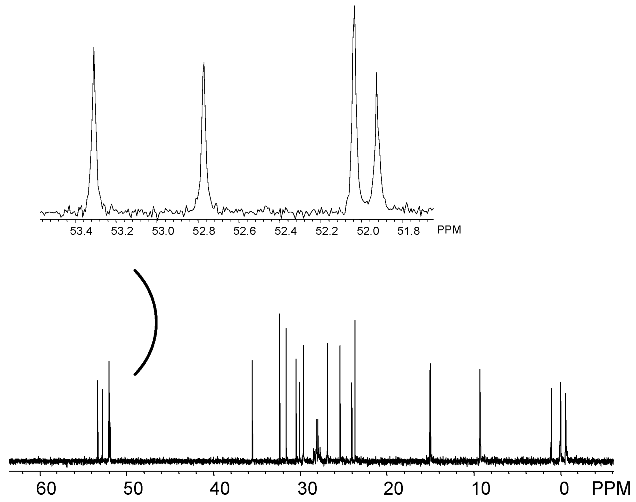

Figure 6. ^{13}C NMR of **VIII**.

nance at ~ -4.75 ppm is split to a doublet ($J_{\mathrm{Si-H}} = \sim 5$ Hz) by the hydrogen directly bonded to silicon. Likewise, in the ^{1}H NMR, three signals in a ratio of 2:1:4 are observed due to chemically distinct $Si-CH_3$ groups. The signal due to the $Si-CH_3$ groups is split to a doublet ($J = \sim 2.5$ Hz) by the hydrogen which is directly bonded to silicon. In the ^{19}F NMR spectra of **IV** and **V**, signals due to the terminal trifluoromethyl group are found at -82 ppm for **IV** and -69 ppm for **V**. Five multiplets due to the five distinct difluoromethylene units of **IV** are detected between -127 and -117 ppm.

It is critical to add a small amount of triethylamine to the Pt-catalyzed hydrosilylation reaction of 4-vinylcyclohexene-1,2-epoxide with the α,ω-dihydridopentasiloxanes (**IV**–**VI**) to prevent ring-opening of the epoxide by acidic impurities.

The ^{29}Si NMR spectra of the α,ω-bis[2′-(4-cyclohexanyl,1,2-expoxy)ethyl]pentasiloxanes (**VII**–**IX**) each have three distinct silicon resonances in a 2:1:2 ratio. Two of these, between -23 and -21 ppm, are due to the central silicon atoms which are each bonded to two oxygen atoms. On the other hand, the terminal silicon atoms, which are each bonded to only one oxygen atom, give rise to a signal between 10 and 7.6 ppm. This is reasonable considering the ^{29}Si NMR signal of trimethylsilyloxy groups is usually found at $\sim$10 ppm.

The ^{19}F signals due to terminal trifluoromethyl groups are found at -81.5 ppm for **VII** and -69 ppm for **VIII**. In addition, five multiplets due to the distinct difluoromethylene groups of **VII** are found in the ^{19}F NMR between -127 and -117 ppm. In the ^{13}C NMR of **VII**, six multiplets are detected between 109 and 120 ppm due to the terminal trifluoromethyl groups and the five distinct difluoromethylene groups. These multiplets for the carbons bonded to fluorine atoms arise from ^{13}C–^{19}F coupling. Thus, whereas the ^{13}C NMR is run with broad band proton decoupling, we are unable to simultaneously decouple the fluorine atoms. Four signals between $\sim$52 and 53.5 ppm are detected in the ^{13}C NMR of both **VII** and **VIII** (Figure 6). These are due to the chemically unique carbons of the epoxy moieties. The two epoxy carbons are nonequivalent because of the unsymmetrical substitution of the cyclohexane ring and the presence of both isomers in which the epoxy group and the ethyl group are cis or trans to one another. An additional 21 ^{13}C NMR signals are observed for **VII** and **VIII** because the 1,2-epoxy group and the 4-silyl substituted ethyl unit of the cyclohexane ring can either have a cis or a trans relationship (Figure 7). On the basis of this analysis, a total of 22 resonances are predicted for **VII** and **VIII**. However, in fact, only 21 are observed. Apparently two of these ^{13}C NMR signals fortuitously overlap. Consistent with this interpretation, a total of 16 signals are observed in the ^{13}C NMR spectrum of 4-vinylcyclohexene-1,2-epoxide. Thus, the vinyl group and the epoxide moiety can have either a cis or trans relationship to one another.

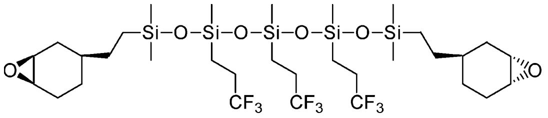

Figure 7. Stereochemistry of **VIII**.

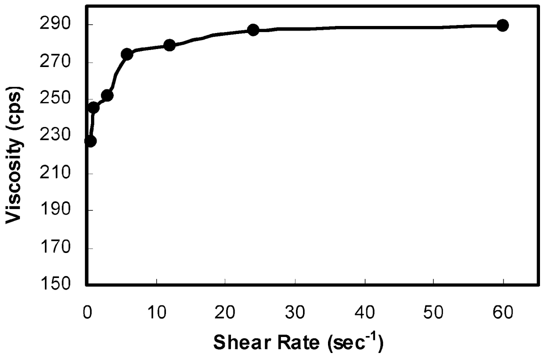

Figure 8. Viscosity versus shear rate of **VII**.

The refractive index values of oligomers (**VII**–**IX**) decrease as the amount of fluorine in the oligomeric pentasiloxane increases (from 1.387 to 1.433 for **VII** to **IX**). Viscosity was found to increase with increasing shear rate until a plateau region was reached. Viscosities reported at 12 s^{-1} are from the plateau region (Figure 8).

Thorough cleaning of glass microscope slides and steel coupons surfaces was required to achieve films with good quality and adhesion. The glass or steel surfaces must not be wiped with tissues to avoid transfer of silicon contaminants. During the 8 days of immersion in seawater to culture *Enteromorpha* sporelings onto the film surface, some detachment of **X**–**XII** from the slides was noted. For this reason, microscope slides were first dip-coated into primer to improve adhesion of films **X**–**XII** to the glass during sporeling evaluation. Steel coupons were also initially coated with a 2-mil liquid layer of primer to improve adhesion.

Solutions of diaryliodonium salt and oligomers **VII**–**IX** were prepared. These solutions were then coated at a thickness of 10 mil (250 μm) onto glass microscope slides or at a thickness of 5 mil onto steel coupons using a Gardner drawdown bar. Films **X**–**XII** were produced by the acid-catalyzed ring-opening polymerization and cross-linking of **VII**–**IX,** respectively. A strong acid catalyst was generated by UV irradiation of the diaryliodonium salt[24] using a 450-W medium-pressure Hanovia mercury lamp. When a 2.0 wt. % mixture of diaryliodonium salt catalyst and **VII**–**IX** was used, a "wrinkled" film surface of **X**–**XII** resulted. Reduction of the catalyst concentration to 0.5 wt. % produced smooth film surfaces.

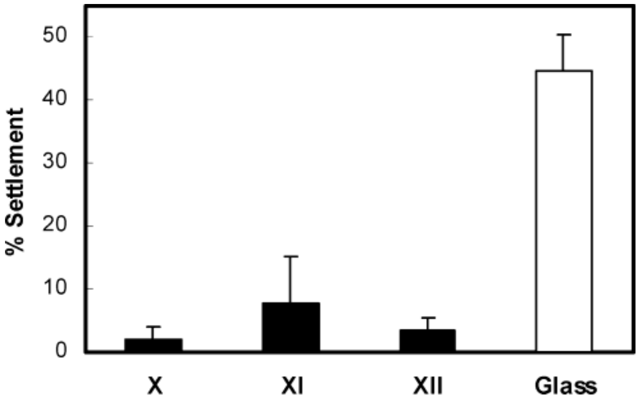

Figure 9. Percent settlement of *Balanus amphitrite* larvae on **X**−**XII**.

Films **X**−**XII** are all quite thermally stable by TGA. This may be a result of their high degree of polymerization and/or cross-link density.

Low surface energies (high contact angles) and low T_g values have been correlated with good biofoul-release properties.[5] On the basis of our analysis, all films (**X**−**XII**) are hydrophobic at the air−film interface ($\theta_{static} \geq 101°$). The DCA measurements provide more information than do static contact angle measurements. For instance, the θ_{adv} may provide information regarding the hydrophobic (low surface energy) properties of the surface, whereas the hydrophilic nature of the surface may be derived from the θ_{rec}.[39] The DCA measurements of **XII** can be compared to those of coatings prepared from α,ω-dihydroxy PDMS cured with tetraethoxysilane.[29] Likewise, DCA measurements of **X** and **XI** may be compared with those obtained from surfaces prepared by cross-linking α,ω-dihydroxy PDMS with 1H,1H,2H,-2H-tridecafluorooctyltriethoxysilane.[30,40] Increased hysteresis, θ_Δ, with increased fluorination was observed for **X**−**XII**. Although these films (**X**−**XII**) have low surface energies, their T_gs, as measured by DMTA, are significantly higher than that of PDMS.

Biotesting. The barnacle *Balanus amphitrite* is a prevalent ship and pier fouling organism that is cosmopolitan in subtropical and warm temperate environments.[41] In our settlement assays, cyprid larvae remained active during their 6−7 day exposure to films **X**−**XII** and there were no apparent differences in behavior compared to that of glass controls. This indicates neither the coating nor any leachate was toxic. Stopping the assays after approximately 50% of the larvae hadsettled onto the uncoated glass slides provided a measure of antifouling characteristics of the films. Larvae settlement was significantly lower for **X**−**XII** compared to that of uncoated glass (Figure 9). Because of the low settlement rate, the larvae were given an additional 4 days to settle on the surfaces to provide sufficient settled barnacles for the force gauge testing. The average force required to remove barnacles from a commercial silicone was 0.083 N/mm^2. However, the force required to remove them from **X**−**XII** ruptured the barnacles from their baseplates, which subsequently remained attached to the film. Thus, the force required to break the adhesive bond of the barnacle to **X**−**XII** exceeded the cohesive force of the barnacles themselves.

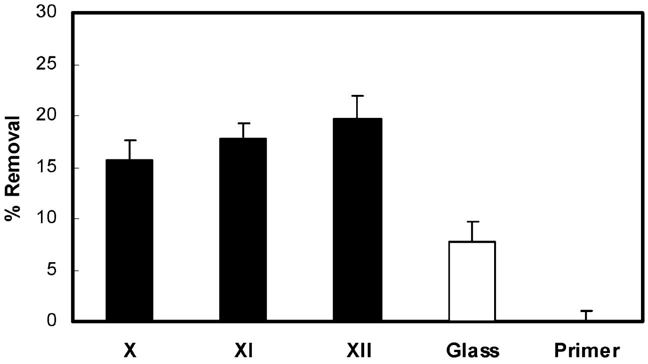

Figure 10. Percent removal of *Enteromorphora* sporeling biomass from **X**−**XII**.

Enteromorpha, the most prevalent ship-fouling macroalga, is found in the upper intertidal seashores of the world.[42,43] Spores settled normally and all nonsettled spores remained motile, indicating the leachate was nontoxic. Spore attachment was tested on **X**−**XII** coated directly over glass slides, whereas sporeling attachment was tested on **X**−**XII** with a primer undercoat. Spore settlement was significantly higher on **XI** than on the other surfaces ($P < 0.05$). After exposure to surface pressure from the water jet, however, **XI** showed a higher percent removal of spores compared to that of all other surfaces ($P < 0.05$). Growth of sporelings on **X**−**XII** (coated over a primer layer), on uncoated glass, and on slides coated only with primer was not significantly different ($P > 0.05$). **XII** showed the highest percent removal of sporeling biomass after exposure to shear stress by the water channel (Figure 10). Although **X**−**XII** all showed higher percent removal compared to that of uncoated glass slides and slides coated only with primer, there was no significant difference between any of the coatings when the data were analyzed by ANOVA. The percentage removal of sporeling biomass from **X**−**XII** was also much lower than that from the commercial foul-release coating Veridian (International Coatings).[36] The lack of optimal foul-release properties of these films (**X**−**XII**) seems to indicate that both low surface energy and low T_g need to be simultaneously achieved.

Representative EIS data for **X**−**XII** and for the primer control on steel coupons are shown in Bode-plots (Figure 11). For **X**−**XII**, EIS data remained capacitive during the entire exposure time. EIS spectra for **XI** (Figure 11b) and **XII** (Figure 11c) remained essentially unchanged with exposure, whereas impedance increased for **X** (Figure 11a). This increase may be due to blocking of coating pores by corrosion products and/or reactions of the coating components with the steel surface. Additionally, impedance values increased with increased fluorination, with **X** exhibiting the highest impedance. Films **X**−**XII** demonstrated significant improvements in protective properties compared to steel coupons coated only with primer, for which the impedance decreased significantly with time (Figure 11d). The observation that the capacitance of **X**−**XII** coatings did

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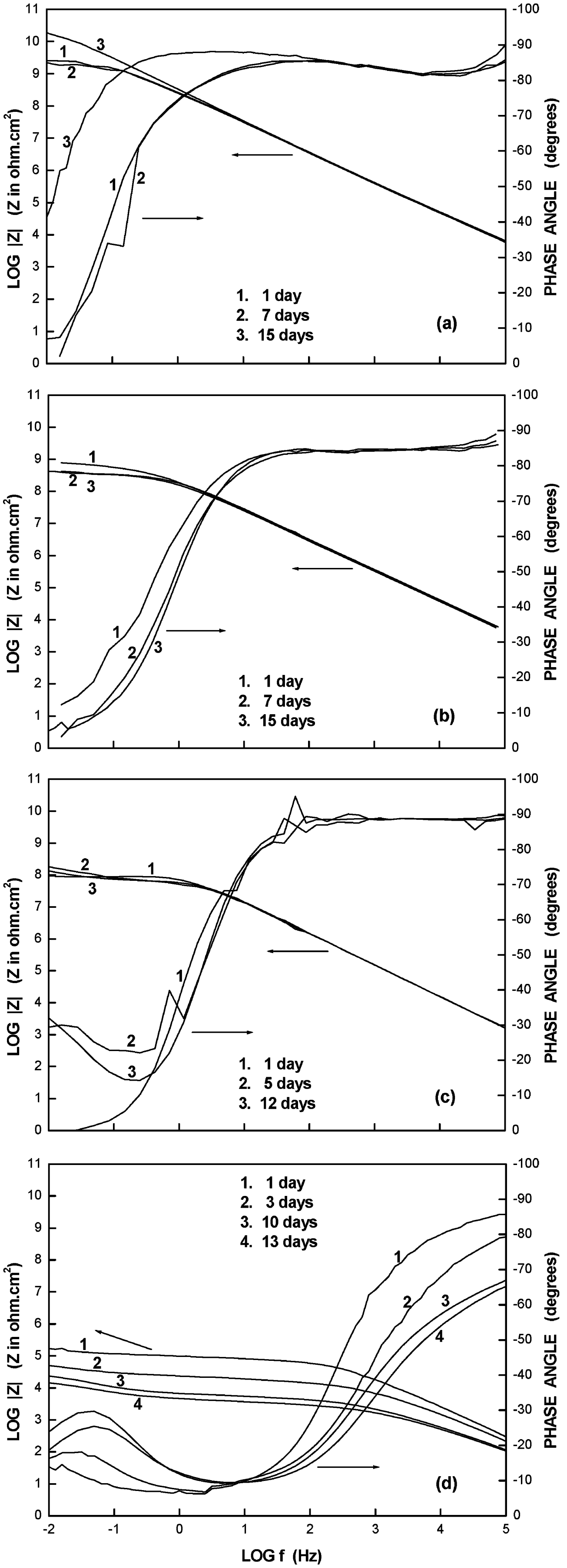

Figure 11. Bode-plots for steel coupons coated with with (a) **X**, (b) **XI**, (c) **XII**, and (d) primer only.

not significantly increase with time suggests that they did not take up much water.[44]

Conclusions

The procedures reported herein allow the synthesis of low-viscosity epoxy-terminated pentasiloxane oligomers (**VII**−**IX**) which may be photochemically cross-linked to rapidly form films (**X**−**XII**). These films are of interest as foul-release coatings due to their nontoxicity, low polarity, hydrophobicity, and low surface energies. The synthesis is highly versatile which allows for the fine-tuning of properties to suit particular demands by selection of a number of parameters. Among these are the number of fluoroalkyl chains, chain length, type and amount of epoxide used, and choice of cationic initiation.

The objective of this work was to assess the relationship between physical properties of films and antifoul and foul-release properties as well as corrosion resistance. All films were hydrophobic (low surface energy) at the air−film interface ($\theta_{\text{static}} \geq 101°$).[45] The highly fluorinated film **X**, bearing pendant 1′H,1′H,2′H,2′H-perfluorooctyl groups, possessed the lowest T_g (5−9 °C) and lowest surface energy ($\theta_{\text{static}} = 121°$). Film **X** demonstrated superior antifouling resistance to barnacle *Balanus amphitrite* (hard foulers) compared to **XI** and **XII**. However, adhesion of the barnacles to **X**−**XII** was too high for them to be removed without breakage from their baseplates. Films **X**−**XII** did not inhibit settlement of *Enteromorpha* spores or the growth of sporelings (soft foulers). Removal of spores was greatest from **XI**. Sporeling growth on **X**−**XII** (coated over a primer layer) was similar to that on uncoated glass and slides coated only with primer. The highest percentage of sporelings was released from the nonfluorinated surface of film **XII** which possessed the relatively highest T_g (50 °C) and surface energy ($\theta_{\text{static}} = 102°$). These results indicate that foul-release properties of siloxane coatings may vary with respect to a hard or soft fouler. A coating which could provide both foul-release properties and corrosion protection would be desirable. In this regard, electrochemical impedance data for **X**−**XII** showed no deviation from capacitive behavior during exposure, which indicates that these coatings were very protective. In fact, an increase in impedance values was observed with higher fluorine content of films.

The results reported herein may provide guidance for the future design and synthesis of improved antifoul and foul-release coatings for marine applications. Namely, the combination of *both* low surface energy and low T_g (modulus) appears to be critical to achieve adequate foul-release properties. Although the coatings described in this study have low surface energies (high contact angles), their T_gs are high compared to that of PDMS. We anticipate that a reduction in the T_gs of the coatings described herein would produce superior foul-release behavior. This may be achieved by a reduction in cross-link density of the films.

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