Preparation and Physical Properties of Films Prepared by Crosslinking 1,9-Bis(glycidyloxypropyl)pentasiloxanes with α,ω-Bis(3-aminopropyl)polydimethylsiloxane and Their Settlement and Release Properties

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ABSTRACT: Six films were prepared by phenol-catalyzed crosslinking of 1,9-bis(glycidyloxypropyl)decamethylpentasiloxane (**I**) or 1,9-bis[glycidyloxypropyl]-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**II**) with α,ω-bis(3-aminopropyl)-PDMSs [M_n = 250 (**a**), 1700 (**b**), or 3200 (**c**)]. These films exhibited a wide range of glass transition temperatures (T_gs), high thermal stabilities, hydrophobicities, and fouling-release properties. Thermal stabilities were measured by thermogravimetric analysis. Surface properties were evaluated by static and dynamic contact angle measurements. Mechanical properties and T_gs were determined by dynamic mechanical thermal analysis. The fouling-release properties of films **Ia–Ic** and **IIa–IIc** toward spores and sporelings (young plants) of the green fouling macroalgae *Ulva* (syn. *Enteromorpha*) was also studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 751–757, 2006

Key words: crosslinking; films; fluoropolymers; silicones; fouling-release

INTRODUCTION

Polydimethylsiloxanes (PDMSs) have many desirable properties such as hydrophobicity (low surface energy), low T_g (backbone flexibility), thermal and oxidative stability, and a pronounced spreading tendency.[1,2] Despite these attractive properties, siloxane polymers have certain characteristics, which may limit their possible applications. Among these are low mechanical strength and the fact that they are often liquids. These limitations have been addressed by crosslinking siloxane polymers and/or by addition of reinforcing fillers.[3] Crosslinking is often achieved by free radical processes catalyzed by benzoyl peroxide and heat[4–7] or by Pt-catalyzed hydrosilylation reactions between polysiloxanes, which have vinyl groups and those with Si-H bonds.[8,9]

Silicone elastomers and fluoropolymers have been extensively studied for their potential use as nontoxic, fouling-release coatings. Low energy surfaces are consistent with poor adhesion of most fouling organisms and are easier to clean because of weaker binding at the substratum–liquid interface.[10–15] The flexibility of the PDMS backbone (T_g = −123°C) may minimize mechanical locking of adsorbed fouling organisms.

For these reasons, we have been interested in the formation of siloxane films. We have previously utilized both photoacid-catalyzed ring opening polymerization of α,ω-bis(epoxy)oligosiloxanes[16] and crosslinking of α,ω-bis(epoxy)oligosiloxanes with α,ω-diamines to prepare siloxane films.[17] Herein, we report our recent work on the preparation and properties of siloxane films produced by this latter approach.

We have previously reported the synthesis of both 1,9-bis(glycidyloxypropyl)decamethylpentasiloxane (**I**) and 1,9-bis[glycidyloxypropyl]-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**II**) (Fig. 1).[18] Herein, we describe the preparation and properties of films based on thermal crosslinking of **I** or **II** with commercially available α,ω-bis(aminopropyl)PDMSs [$H_2N—CH_2CH_2CH_2SiMe_2O(SiMe_2O)_n—SiMe_2CH_2CH_2CH_2NH_2$, where n = 0 (**a**), 20 (**b**), 40 (**c**)] (Fig. 2). Differences in physical properties of the films are expected since while the chain length of **I** and **II** are constant, the molecular weights of the α,ω-bis(aminopropyl)PDMSs differ. This difference affects the length between crosslinks.

Thermal stabilities of films **Ia–Ic** and **IIa–IIc** were evaluated by TGA. Storage (G') and loss moduli (G'') were measured by DMTA. Their surface energies were

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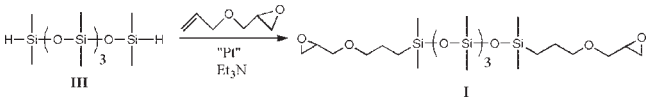

Figure 1 Hydrosilylation of **III**.

determined by both static and dynamic contact angle measurements.

Ulva is the most common macroalgae that fouls ships and other man-made structures. Reproduction is through the release of vast numbers of motile, unicellular, pear-shaped zoospores, 5–8 μm in length, which attach rapidly to a surface.[19] The spores germinate and grow into young plants (sporelings), a few hundred microns in length, within a few days. Young sporelings (7–8 days old) are readily detached from fouling release PDMS elastomers.[20,21] Fouling-release properties of **Ia–Ic** and **IIa–IIc** were studied by subjecting sporelings (young, 10-day-old plants) of the fouling macroalgae *Ulva,* which has been cultured on the test surfaces to hydrodynamic forces generated in a flow channel apparatus. The ease of removal of laboratory-cultured *Ulva* sporelings indicates the potential for fouling release.[20,21] Quantification of the biomass of sporelings attached to the films before and after exposure in the flow channel allowed us to determine a relationship between physical properties and fouling release properties of the films.

EXPERIMENTAL

Materials

Pt-divinyltetramethyldisiloxane complex (Karstedt's catalyst) in xylene (2% Pt), hexamethylcyclotrisiloxane (D_3), 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluoropropyl)-cyclotrisiloxane (D_3^F), 1,3-bis(3-aminopropyl)tetramethyldisiloxane (**a**, redistilled before use), α,ω-bis(3-aminopropyl) PDMS (**b**, M_n = 1700 and **c**, M_n = 3200), tetramethyldisiloxane (TMDS), and hexamethyldisilazane (HMDZ) were obtained from Gelest (Morrisville, PA). The M_n of **a–c** were confirmed by end group analysis by ^{1}H and ^{29}Si NMR. Allyl glycidyl ether, triethylamine, triflic acid, phenol, and 2,4,6-tris-(dimethylaminomethyl)phenol (D-phenol) were purchased from Aldrich (St. Louis, MO). Corning (Midland, MI) microscope slides were used as substrates for coatings.

Monomer characterization

^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were acquired on a Bruker AMX-500 MHz spectrometer. Five percent weight-to-volume $CDCl_3$ solutions were used to obtain ^{1}H, ^{13}C, and ^{19}F NMR spectra. ^{29}Si NMR spectra were obtained from 25% w/v $CDCl_3$ solutions. ^{13}C NMR spectra were run with broadband proton decoupling. Off-resonance ^{13}C NMR spectra were obtained to determine the number of hydrogen atoms bonded to each carbon. A NONOE pulse sequence with a 60 s delay was used to acquire ^{29}Si NMR spectra.[22] Residual chloroform was used as an internal standard for ^{1}H and ^{13}C NMR. ^{19}F NMR spectra were referenced to internal $CFCl_3$. ^{29}Si NMR spectra were referenced to internal TMS. IR spectra of neat films on NaCl plates were recorded using a Perkin–Elmer Spectrum 2000 FTIR spectrometer.

Synthesis

1,9-Dihydridodecamethylpentasiloxane (**III**) was prepared by triflic acid-catalyzed ring opening of D_3 in TMDS.[23]

1,9-Dihydrido-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**IV**) was prepared by the triflic acid-catalyzed ring opening of D_3^F in TMDS.[16]

1,9-Bis[glycidyloxypropyl]decamethylpentasiloxane (**I**)[18] was obtained by Pt-catalyzed hydrosilylation of **III** and allyl glycidyl ether in the presence of a small amount of triethylamine. ^{1}H NMR δ: 0.03 (s, 12H), 0.05 (s, 6H), 0.07 (s, 12H), 0.52 (m, 4H), 1.61 (m, 4H), 2.61 (dd, 2H, J = 2.8, and 5.2 Hz), 2.79 (dd, 2H, J = 4.0, and 5.2 Hz), 3.14 (dddd, 1H, J = 2.8, 3.2, 4.0, and 5.6 Hz), 3.37 (dd 2H, J = 5.8, and 11.6 Hz), 3.42 (dt, 2H, J = 7.2, and 9.2 Hz), 3.46 (dt, 2H, J = 6.8, and 9.2 Hz), 3.69 (dd, 2H, J = 3.2, and 11.6 Hz) (Fig. 3). ^{13}C NMR δ: 74.42, 71.49, 50.96, 44.45, 23.50, 14.16, 1.26, 1.15, 0.18. ^{29}Si NMR δ: −22.20 (1Si), −21.42 (2Si), 7.74 (2Si). IR ν: 3046, 2960, 2938, 2873, 1476, 1438, 1409, 1341, 1255, 1185, 1153, 1102, 1032, 906, 841, 793, 704, 683, 664 cm^{-1}.

1,9-Bis[glycidyloxypropyl]-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpenta-siloxane (**II**) was prepared as above by reaction of **IV** and allyl glycidyl ether.[15] ^{1}H NMR δ: 0.08 (s, 3H), 0.09 (m, 12 H), 0.11 (m, 6H), 0.55 (m, 4H), 0.72 (m, 6H), 1.59 (m, 4H), 2.02 (m, 6H), 2.60 (p, 2H), 2.79 (dd, 2H, J = 5.0, and 5.2 Hz), 3.13 (m, 1H), 3.37 (ddd, 2H, J = 2.8, 5.6, and 11.4 Hz), 3.37 (m, 4H), 3.71 (dd, 2H, J = 2.8, and 11.6 Hz). ^{13}C NMR δ: −0.94 (m), −0.17 (m), 9.13, 14.02 (m), 23.37, 27.89 (m), 43.96 (m), 50.70, 71.43, 73.91 (m), 124.35, 126.55, 128.75, 130.94. ^{29}Si NMR δ: −22.26, −22.12, −22.00 (1 Si), −21.61, −21.46, −20.97 (2 Si), 7.45, 7.62, 7.70 (2 Si). ^{19}F

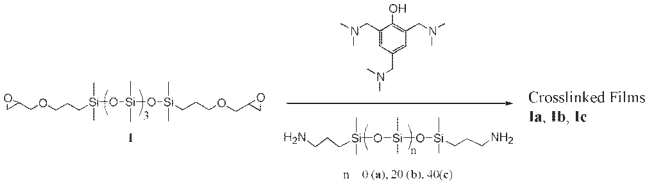

Figure 2 Crosslinking of **I**.

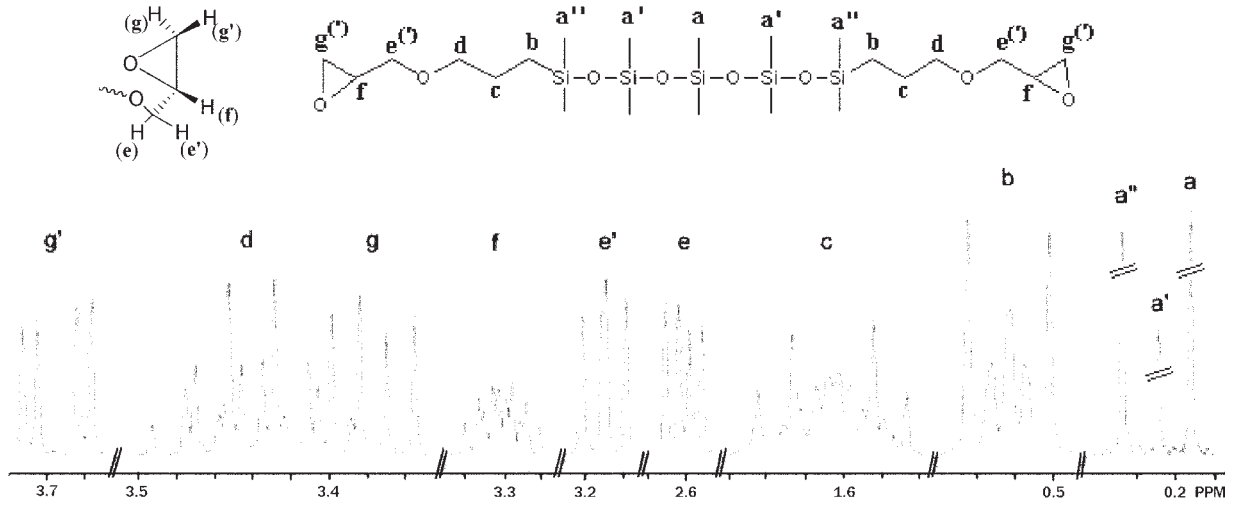

Figure 3 ^{1}H NMR of **I**.

NMR δ: −69.37 (m). IR ν: 3057, 2954, 2863, 1444, 1417, 1366, 1312, 1266, 1207, 1126, 1073, 1022, 898, 841, 804, 774, 710 cm^{-1}.

Film preparation

Microscope slides as well as a single edged razor blade, used to remove films, were degreased by rinsing with reagent grade acetone followed by 50:50 (v/v) mixture of reagent grade hexane and dichloromethane. This is necessary since the presence of surface oil may significantly change contact angles. Degreased slides were stored in an oven (110°C) overnight and flamed immediately before coating. Homogeneous solutions were prepared from half a molar equivalent of α,ω-bis(amino)PDMS and one equivalent of **I** or **II**. Phenol (0.5 wt. %) was added to solutions of **II** while D-phenol (0.5 wt. %) was added to solutions of **I**. Homogeneous solutions (~1.2 mL) were applied to clean leveled microscope slides and allowed to spread for about 1 min. The coated slides were then transferred to a half-inch thick level glass plate in an oven at 110°C. Curing to a film (~0.5 mm thick) occurred over 24 h.

Film characterization

Thermal stabilities of the films in nitrogen or air were measured on a Shimadzu TGA-50 with a gas flow of 30 mL/min. The temperature of the TGA was raised from 25 to 800°C at a rate of 4°C/min (Fig. 4).

Film samples were cut to 14 × 5.6 mm^2 for the DMTA measurements, which were performed on a TA Instruments Q800 DMA 5 in dual-cantilever configuration at a frequency of 5 Hz. Storage and loss moduli were measured on a TA Instrument DMA Q800. After equilibration at −140°C for 5 min, the temperature was increased at a rate of 5°C/min to 30°C (Fig. 5).

Static (θ_{static}) as well as advancing (θ_{adv}) and receding (θ_{rec}) contact angles of distilled water at the air–film interface were measured with a First Ten Ångstroms 4000 optical contact angle measurement system (FTÅ) equipped with a video camera as well as drop shape analysis software. Conditions during time of measurements were 24°C and 58% relative humidity. θ_{static} of a sessile drop of distilled/deionized water (5 μL) was measured 3 s after the droplet was deposited onto the film surface. This time allows the droplet to equilibrate and form a defined shape.[24] Three measurements were performed on each film surface with a fresh water droplet and the values averaged. θ_{adv} and θ_{rec} contact angles were measured as follows. A 5 μL pendant droplet of distilled/deionized water was applied with a 10 μL syringe to the air–film interface. After equilibration, 2 μL of water was added to the droplet and the θ_{adv} determined. Addition of water causes the contact angle of the droplet to increase. θ_{rec} was measured by the removal of 4 μL from the same droplet with a microliter syringe. This causes the contact angle to recede. Measurements were repeated in triplicate and average values are reported.

Fouling-release bioassay

Zoospores were released from fertile *Ulva linza* plants and prepared for adhesion experiments.[19] Surface colonization occurs through the settlement and adhesion of motile *Ulva* spores.[19] Adhered spores (nonmotile) germinate into sporelings (young plants) and subsequently into mature plants. Six replicate microscope slides of **Ia–Ic**, **IIa–IIc**, were tested together with a PDMS standard, and acid-washed glass slides, which served as controls. Slides were initially leached for 8

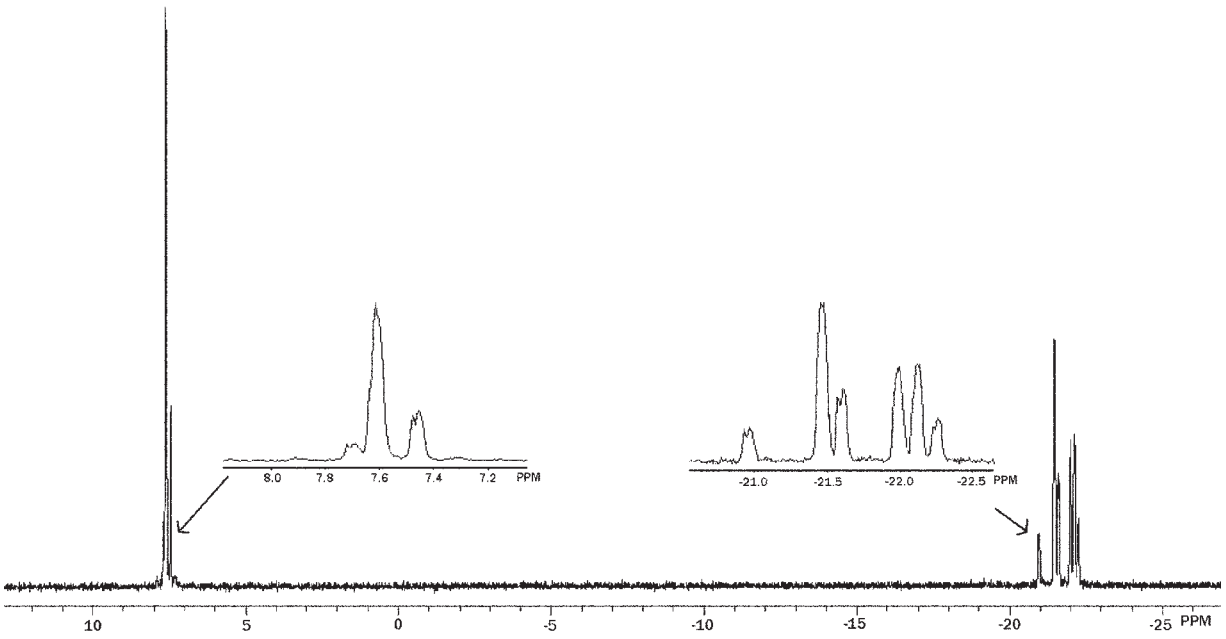

Figure 4 ^{29}Si NMR of **II**.

weeks in distilled water prior to testing. This served to remove any phenol, which may be toxic to the sporelings. All surfaces were immersed in artificial seawater for a minimum of 1 h before the bioassay commenced. Zoospores were allowed to settle for 1 h onto slide surfaces following standard methods.[25] After washing, the slides were transferred to dishes with enriched seawater culture medium and allowed to germinate and grow.[20,26] Sporelings were cultured on the slides for 10 days. The growth medium being refreshed every 2 days.

The quantity of sporelings that had grown on the surfaces was quantified as extracted chlorophyll. The biomass was scraped from half of each slide into a tube and quantified by extraction of chorophyll a into DMSO.[27] The data in Figure 7 show mean biomass per square centimeter. The bars show SEM (standard error of the mean). 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.[20,28] The sporeling biomass remaining was estimated by extraction of chlorophyll a as above. The mean quantity of biomass remaining after exposure in the flow channel was compared to the quantity of biomass before exposure in the flow channel. Results are expressed as percentage biomass removal. Error bars on percent removal data (Fig. 8) were obtained from arcsine transformed data.

Two standards were included in the sporeling bioassay as reference materials viz. acid-washed glass and Silastic T-2 (Dow-Corning) were prepared.[29] The latter was included as a standard PDMS elastomer with fouling-release properties.[30]

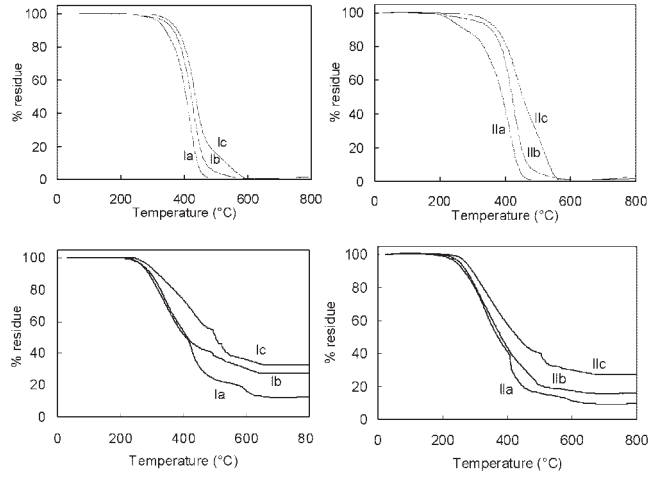

Figure 5 TGA in N_2 (top) and air (bottom).

RESULTS AND DISCUSSION

Synthesis of monomer

Pt-catalyzed hydrosilylation reactions of allyl glycidyl ether with **III** or **IV** gives **I** or **II**, respectively. Addition of small amounts of triethylamine is necessary to prevent premature ring-opening of epoxides by acidic impurities during the hydrosilylation. Completion of the reaction was confirmed by IR analysis of **I** and **II**, which showed no absorbance at ~2100 cm^{-1} due to unreacted Si—H bonds of **III** or **IV**.

^{29}Si NMR spectra of **I** show expected three signals at −22.20 (1 Si) (central O—$SiMe_2$—O), −21.42 (2 Si)

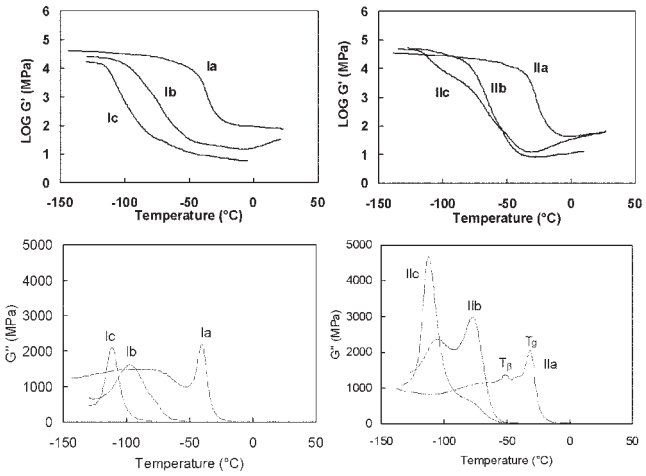

Figure 6 Storage (top) and loss modulus (bottom).

(O—$SiMe_2$—O), and 7.74 (2 Si) (terminal O—$SiMe_2$—). However, the ^{29}Si NMR of **II** is more complicated due to the presence of chiral centers. The 3′,3′,3′-trifluoropropyl-methylsiloxy units are chiral. The relationship between the chiral silyl center and the two adjacent silyl centers can be (RR′R, SS′S), (RR′S, SS′R), or (RS′R, SR′S). Thus, there are three magnetically nonequivalent diastereotopic environments, which result in the three peaks for each silyl signal (Fig. 4).

Properties of the films

Thermal stability

The thermal stability in N_2 or air of films **Ia–Ic** and **IIa–IIc** increased with the length of the α,ω-bis(amino)PDMS (Fig. 5). Thus, **Ic** is more thermally stable than **Ib**, which in turn is more stable than **Ia**. Likewise, **IIc** is more thermally stable than **IIb**, which is more stable than **IIa**. In N_2, films **Ia–Ic** are stable to 300°C, at which point catastrophic decomposition occurs. On the other hand, both **IIa** and **IIb** experience an initial weight loss starting at ~180°C. This amounts to 10% for **IIa** and 5% for **IIb**. No weight loss for **IIc** is observed below 300°C. This is followed by catastrophic decomposition of **IIa–IIc** at 300°C in N_2 (Fig. 5, top). It is known that poly(trifluoropropylmethyl-)siloxane is less stable than the PDMS in both inert and oxidizing conditions.[31] The lower thermal stability of films **IIa** and **IIb** may result from the lower number of the dimethylsiloxy units from the α,ω-bis(3-aminopropyl)-PDMS in comparison to **IIc**. The onset of thermal degradation in N_2 of the nonfluorinated films (**Ia–Ic**) is 230–240 °C and that of the fluorinated films (**IIa–IIc**) is 210–230°C (Fig. 5, bottom). In air, all of the films leave significant residue. **Ic** leaves more residue than **Ib** and **Ia** leaves the least residue. Similarly, **IIc** leaves more residue than **IIb**, which in turn leaves more residue than **IIa**. Films **Ia–Ic** leave more residue than the corresponding films **IIa–IIc** (Fig. 5, bottom).

Dynamic mechanical thermal analysis

Improved mechanical strength seems to correlate with shorter chain length of the α,ω-bis(3-aminopropyl)PDMS unit. This is expected since shorter chains lead to higher crosslink density. The storage modulus of films **Ia**, **Ib**, and **Ic** start to decrease at around −40, −100, and −110°C, respectively, (Fig. 6, top). This corresponds to the observed order of T_gs (Table I) from the loss modulus (Fig. 6, bottom). The storage modulus of **IIa**, **IIb**, and **IIc** deteriorate at around −30, −80, and −110°C, respectively. This also agrees with the decrease in the loss modulus. As the number of dimethylsiloxy units increases, the films more closely resemble PDMS, which is well known to have low mechanical strength. For comparison, the T_g of PDMS is −123°C, whereas the T_g of PTFPMS is −80°C. This has been attributed to electronic repulsion between adjacent CF_3 groups, which leads to side chain rigidity.[32] The T_gs, determined from the maximum of the loss modulus, of both sets of films **Ia–Ic** and **IIa–IIc** decrease with the increase in molecular weight of the α,ω-bis(amino)PDMS component. The T_gs of **Ic** and **IIc** both approach that of PDMS. An increase in T_gs of fluorinated films **IIa–IIc** is anticipated versus nonfluorinated films **Ia–Ic**. However, **IIc** stands out as an exception (T_g = −112°C). This may be due to the dominant role of the PDMS units compared to the fluorine content. Overall, a linear decrease in T_g is observed as the α,ω-bis(amino)PDMS unit grows in length. T_β, a second maximum in the loss modulus, is usually higher than T_g.[33] Since T_β is only observed in the fluorinated films **IIa–IIc**, it may be due to side chain mobility (Fig. 6, bottom).[33]

Contact-angle analysis

Both sets of films, **Ia–Ic** and **IIa–IIc**, show similar values of θ_{static} and θ_{adv}. This agrees with comparable surface energies of PDMS and PTFPMS (water contact angle of 108° and 104°, respectively).[1] Also, θ_{static} and θ_{adv} of both types of films show little deviation from

TABLE I
Properties of Films

Films	T_g (°C)	T_β (°C)	θ_{stat} (°)	θ_{adv} (°)	θ_{rec} (°)	θ_{hys} (°)
Ia	−40	—	103	103	73	30
Ib	−97	—	116	115	86	29
Ic	−111	—	115	115	88	27
IIa	−32	−56	105	103	80	23
IIb	−77	−105	101	101	80	21
IIc	−112	—	112	112	91	21

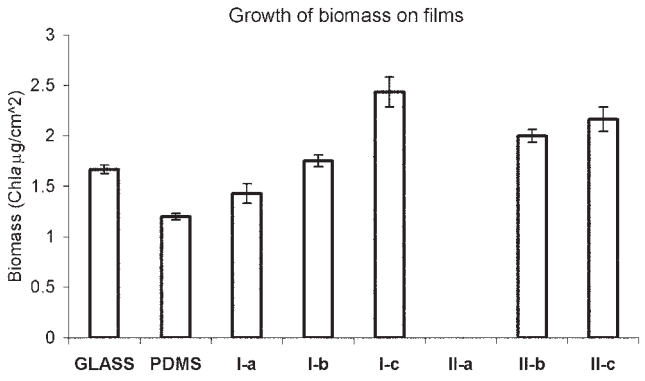

Figure 7 The biomass of *Ulva* sporelings after 10 days, quantified as chlorophyll a/cm^2 of test surface. Each point is the mean of six replicates. Error bars shown one standard error of the mean. PDMS is Silastic T2.

one another (Table I). These films are hydrophobic at the air–film interface. The θ_{rec} are all significantly lower. This causes significant hysteresis ($\theta_{adv} - \theta_{rec}$) observed in all the films.

Fouling-release properties

There was no detectable toxicity to swimming *Ulva* zoospores associated with leachates collected from slides. Spores that attached to the test surfaces germinated and grew normally except for those settled on **IIa**. Spores germinated only slowly on this surface and did not develop into robust sporelings, hence there was insufficient biomass to quantify. The reason for the inhibition of the growth of the sporelings on this surface is not known. Two slides of **IIb** blistered during the course of the experiment, which detached during the exposure to water flow. All other coatings remained attached to the glass slides during the experiment.

The biomass growth is expressed as chlorophyll a μg/cm^2 (Chl a μg/cm^2). On all the coatings except for film **IIa**, the growth of sporelings was similar or better than on glass and PDMS (Fig. 7). Both the nonfluorinated (**Ia–Ic**) and fluorinated (**IIa–IIc**) sample sets showed decreasing sporeling growth and increasing sporeling removal with decreasing crosslinker chain length (Figs. 7 and 8). Sporeling detachment from the **Ia** (~60%), **Ib** (~45%), and **IIb** (~35%) was intermediate between that of glass (~20%) and PDMS (~90%). Removal of biomass from the **Ic** and **IIc** coatings was similar to that from glass (<20%). These two coatings also showed the highest sporeling growth. Thus, coatings crosslinked with the shorter crosslinker showed the best fouling-release of the experimental coatings, although it was not as good as the standard PDMS (Silastic T2).

CONCLUSIONS

The objective of this work was to assess the relationship between physical/chemical properties of crosslinked films with their bio-foul release properties. Based on contact angle measurements, all films were hydrophobic at the air-film interface ($\theta_{static} \geq 101°$)[34] and exhibited significant hysteresis (21°–30°). They were thermally stable. High crosslink density and high T_g, which both result from shorter crosslinker chain length (Table I), correlate with increased fouling release property (Fig. 8).

Antifouling properties demonstrated by the film **IIa** is very interesting because physical properties of the film **IIa** are not particularly exceptional (Table I). In terms of physical properties, **IIa** is very similar to **Ia**. Film **Ia**, however, does experience growth of biomass that is comparable to that of PDMS standard. The only difference between the two films is the presence of trifluoropropyl group on the pentasiloxane backbone. Therefore, surface reorganization of the trifluoropropyl group in a prolonged contact with water seems likely. Because all contact angle measurements are done within seconds, surface reorganization in water may have not been observed. During the fouling-release studies, however, all the slides were soaked in water for 8 weeks before testing. This may have allowed some surface reorganization of the pendant groups. Such reorganizations would be true for all fluorinated films (**IIa–IIc**). But the exceptional property observed with **IIa** may be due to its dimension. It is possible that the ratio of trifluoropropyl group to the dimethylsiloxy region in **IIb** is preventing the settlement of the sporelings, whereas two other films with longer crosslinkers do not exhibit such inhibition. We have demonstrated a change only in pendant group making a significant response in fouling-release properties.

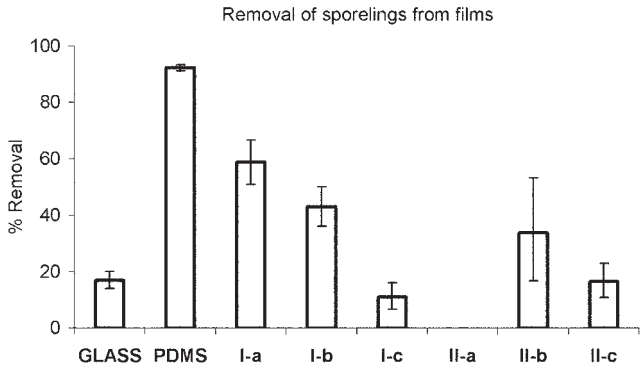

Figure 8 Percentage removal of *Ulva* sporelings after exposure to a wall shear stress of 53 Pa. Each bar represents the mean of six replicate determinations apart from **IIb**, which is the mean of four replicates. Error bars show one standard error of the mean calculated from arcsine transformed data. Biomass and hence percentage removal could not determined on **IIa**. PDMS is Silastic T2.

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