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Synthesis, characterization and surface analysis using dynamic contact angle measurements of graft copolymers: poly(methyl methacrylate)-g-poly(dimethylsiloxane) and poly(methyl methacrylate)-g-poly(trifluoropropylmethylsiloxane)

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Abstract

A series of poly(methyl methacrylate)-g-poly(dimethylsiloxane) and poly(methyl methacrylate)-g-poly(trifluoropropylmethylsiloxane) copolymers have been synthesized via the 'macromonomer' method by which monofunctional polysiloxane macromonomers are copolymerized with methyl methacrylate. The graft copolymers have been characterized by gel permeation chromatography, ^{1}H n.m.r. spectroscopy and differential scanning calorimetry. Dynamic contact angle (DCA) analysis afforded advancing and receding water contact angles over 15 days immersion in water. The initially hydrophobic polymer surfaces rapidly rearrange in the presence of water to more hydrophilic surfaces. The effects of varying the amount and type of siloxane in the copolymer on DCA results are discussed. The fouling and fouling release behaviour of coatings formulated from the graft copolymers have been evaluated in Chesapeake Bay. Fouling and fouling release behaviour are discussed in the light of DCA results. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Graft copolymers; Dynamic contact angle analysis; Fouling release behaviour

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1. Introduction

We are interested in developing polymeric materials which have minimally adhesive surfaces with respect to adhesion of marine organisms. These polymers are targeted for use in 'fouling release' or 'easy release' coatings, which are of interest from environmental and economic standpoints [1]. Currently used antifouling coatings release toxicants, e.g. tin or copper compounds, which may adversely affect non-target organisms. Thus, the development of alternative non-toxic coatings which are effective at minimizing the attachment of a broad spectrum of fouling species (silt, grasses, algae, barnacles, diatoms, etc.) to ship hulls and other underwater structures is desirable, but the fundamental surface properties which are needed to minimize adhesion are not well understood. The most effective non-toxic fouling release coatings thus far are silicone based [2]. Although marine organisms readily settle on polydimethylsiloxane elastomeric coatings, e.g. silicone RTV (Room Temperature Vulcanizing) resins, the surface may be cleaned, e.g. with a water jet.

Because RTV resins usually have poor durability and weak adhesion to substrates, we are exploring a multifunctional approach designed to combine the useful surface properties of silicones while improving toughness and adhesion. Toward this goal, we describe below the synthesis and characterization of two series of graft copolymers: poly(methyl methacrylate)-g-poly(dimethylsiloxane) and poly(methyl methacrylate)-g-poly(trifluoropropylmethylsiloxane). Comparison of poly(dimethylsiloxane) [PDMS] versus poly(trifluoropropylmethylsiloxane) [PTFPMS] grafts is aimed at elucidating the role of surface energy in these materials, since the solid surface tension (and thus the surface energy) of the fluorinated polysiloxane is lower than that of poly(dimethylsiloxane) [3,4].

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A number of efforts have been directed towards synthesizing alternative architectures for poly(dimethylsiloxane)-containing polymers [5]. Recent examples of block copolymers include polystyrene–polysiloxane diblock and triblocks [6], nylon-6–poly(dimethylsiloxane) block copolymers [7,8], bisphenol-A–polycarbonate–poly(dimethylsiloxane) random block copolymers [9], and various polyurethane–polysiloxane block copolymers [10,11]. Segmented copolymers of polyurethane–urea–poly(dimethylsiloxane) [12] and poly(imide-siloxane) [13] have also been synthesized. Recently reported syntheses of graft copolymers include poly(methyl methacrylate)-g-poly(dimethylsiloxane) [14] and poly(olefin sulfone)-g-poly(dimethylsiloxane) copolymers [15,16]. A recent patent describes a co-cured polyorganosiloxane/polyurethane, polyurea or poly(urethane-urea) [17], which presumably forms (at least in part) an interpenetrating polymer network. Epoxy thermosets which contain poly(dimethylsiloxane) segments have been reported [18,19], along with blends of various thermoplastic and thermoset materials with polysiloxanes [20,21].

Surface segregation in siloxane-containing polymers has been measured by techniques, e.g. Fourier transform infrared (*FT*i.r.) spectroscopy [either attenuated total reflectance (ATR) [9,21,22] or specular reflectance [22]], time-of-flight secondary ion mass spectrometry (TOFSIMS) [6,23], and angular-dependent X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) [8,9,11,14,16,21,23]. These techniques are useful in demonstrating qualitatively or semi-quantitatively the presence of low surface energy polymer at the surface in air or vacuum. Thus, we have used angle-resolved ESCA to depth profile poly(siloxane urea urethane)-segmented copolymers [24]. However, reconstruction of low-energy polymer surfaces often takes place in water and results in a partial replacement of the low energy phase with one of higher surface energy.

In order for a polymeric surface to function successfully in fouling release, we have postulated that the surface must: (1) have a low surface energy to minimize lipophilic and hydrogen bonding interactions; (2) have a low glass transition temperature, T_g, to minimize mechanical attachment; and (3) be temporally stable in water; i.e. conditions (1) and (2) must not change with immersion time in water. In contrast to static methods [14,16,23], one of the few techniques which can measure changes in the surface hydrophobicity (and thus surface composition) in the presence of water is time-dependent dynamic contact angle (DCA) analysis [25–28]. We have used this method to study the underwater surface dynamics of a poly(dimethylsiloxane-urethane-urea)-segmented block copolymer [29] and a crosslinked silicone RTV system [30]. In view of the utility of DCA analysis in evaluating surface dynamics in the presence of water, we have used this technique to evaluate the surface properties of the new graft copolymers described herein. In addition, the surface wettability as measured by time-dependent DCA is compared with field exposure tests to correlate ‘laboratory’ data to actual ‘real world’ coating behaviour.

2. Experimental

2.1. Materials

Hexamethylcyclotrisiloxane (United Chemical Technologies) was sublimed under vacuum. (3,3,3,-trifluoropropyl)Methylcyclosiloxane (United Chemical Technologies), which is a mix of the tri- and tetra-siloxanes, was distilled under reduced pressure to obtain a fraction consisting predominately of trisiloxane. *sec*-Butyllithium (1.3 M in cyclohexane, Aldrich) and 3-methacryloxypropyldimethylchlorosilane (Pfaltz and Bauer) were used as received. Methyl methacrylate (Aldrich) was distilled under reduced pressure. Azobis(isobutyronitrile) [AIBN] was recrystallized from acetone. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/potassium benzophenone ketyl and used immediately. Cyclohexane and toluene were purified by washing with concentrated H_2SO_4, water, saturated $NaHCO_3$ solution, and water, drying over $MgSO_4$, and then distilling under nitrogen over sodium; both were stored under nitrogen over fresh sodium. Acetone was dried and purified by refluxing under nitrogen over 4 Å molecular sieves followed by distillation and storage under nitrogen over fresh 4 Å molecular sieves.

2.2. Macromonomer synthesis

Mono-methyl methacrylate end-capped PDMS and PTFPMS macromonomers were synthesized via anionic polymerization (*s*-BuLi) in cyclohexane/THF of the corresponding cyclic trimers, followed by termination using 3-methacryloxypropyldimethylchlorosilane, according to the method of Smith et al. [14].

2.3. Graft copolymer synthesis

Free radical copolymerizations of methyl methacrylate with either PDMS macromonomer or PTFPMS macromonomer were carried out under nitrogen at 20 wt% solids in either deaerated toluene at ca. 70°C or deaerated refluxing acetone (56°C) for 50 h. The polymerizations were initiated using 0.1 wt% (based on methyl methacrylate) AIBN. The copolymers were isolated by precipitation in methanol, followed by Soxhlet extraction with hexanes to remove any unreacted polysiloxanes. Final drying was accomplished by heating the copolymers in vacuo to 60–70°C.

2.4. Polymer characterization

Molecular weights were determined by gel permeation chromatography (g.p.c.). The equipment consisted of a

Hewlett-Packard Series 1050 pump and two Altex μ-spherogel® columns (size 10^3 and 10^4 Å, respectively) connected in series. For the PDMS macromonomers, the solvent was toluene at 37°C; for all other polymers the solvent was THF at room temperature. Polymer content in the column effluent was detected with a Wyatt/Optilab 903 interferometric refractometer, and the average molecular weights were determined using polystyrene standards as references. ^{1}H n.m.r. spectra were recorded on a Bruker AM 300 spectrometer operating at 300 MHz. Polymer T_gs were measured using a Dupont 910 Differential Scanning Calorimeter (d.s.c.) controlled by a Dupont Thermal Analyst 2100 System. Experiments were performed under a nitrogen atmosphere at a heating rate of 10°C/min. T_g was taken as the midpoint of the transition.

2.5. Dynamic contact angle analysis

Polymer films were dip-coated onto glass cover slides ($24 \times 30 \times 0.2\ \mathrm{mm}^3$) from a 2 w/v% solution using reagent grade THF or $CHCl_3$ (for some PMMA samples). To enhance polymer adhesion, the cover slides were made hydrophobic by self-assembly of octadecyltrichlorosilane (Aldrich) prior to dip-coating the polymer. The films were air-dried for 24 h prior to measurement.

DCA measurements were performed on the coated slides using a Cahn DCA Model 312 analyzer (Cerritos, CA). Water for the DCA measurements was purified to Type I with a Barnstead Nanopure Bioresearch grade system and had an average resistivity of 18 MΩ-cm. The surface tension of the probe water was checked daily and had a typical value of 72.4 dynes/cm. The rates of immersion and withdrawal were 100 μm/s; the top and bottom dwell times were zero seconds.

Samples were immersed in a 200 ppm sodium azide (NaN_3, Aldrich) solution, a known biocide, to prevent the growth of eucaryotic organisms which might affect the contact angle. To further prevent bacterial growth, the NaN_3 immersion solution was replaced once a week. The samples were removed at regular intervals and rinsed; advancing and receding water contact angles were recorded, then the samples were returned to the NaN_3 immersion solution. Several duplicate annealed (100°C/10 min) and non-annealed samples were run. Each advancing/receding contact angle data point is the average of the last three immersion/withdrawal cycles, each cycle probing a surface area of about 8 cm^2.

2.6. Field exposure tests

For coatings application, polymer solutions were formulated as 13–15 wt% solids in either 10/1 (v/v) toluene/propylene glycol methyl ether acetate (PMAc) [for PMMA and PMMA-g-PDMS copolymers] or 5/1 (v/v) THF/PMAc (for PMMA-g-PTFPMS copolymers). The solutions were applied to clean, dry acrylic panels in 5" × 5" test areas; the coated test panels were allowed to air dry one week prior to immersion.

Exposure tests were performed in the Chesapeake Bay at the Naval Research Laboratory, Chesapeake Bay Detachment, Chesapeake Beach, MD. The panels were immersed 1–5 feet underwater (depending upon tidal shifts of water depth), suspended off a pier located along the bank of the bay. The panels were removed from the water once a month (except over the winter), rinsed and cleaned with a sponge, evaluated for fouling and fouling release behaviour, and reimmersed. Results are reported after 1.5–2 years exposure.

3. Results and discussion

3.1. Polymer synthesis and characterization

Mono-methyl methacrylate end-capped PDMS and PTFPMS macromonomers were synthesized anionically, according to the method of Smith et al. [14]. Non-functional PDMS or PTFPMS was not separated from the macromonomer prior to characterization or use in graft copolymer syntheses; rather, the final copolymers were extracted to remove both non-functional and unreacted macromonomer. ^{1}H n.m.r. confirmed the presence of the methyl methacrylate endgroup in the macromonomers, but the peaks were too small for accurate quantitative integration. G.p.c. results for the macromonomers used in the graft copolymer syntheses are given in Table 1. DP(found) is the degree of polymerization derived from M_n; DP(calc.) is the degree of polymerization calculated from the experimental monomer to initiator ratio. Targeted molecular weights for the macromonomers were 10 000 and 20 000; it is seen that the molecular weights obtained are close to these values. The molecular weight distributions indicate macromonomers of low polydispersity ($M_w/M_n = 1.1–1.3$). Lower molecular weight materials have lower polydispersities. The PTFPMS macromonomer has a lower degree of polymerization (DP) than the PDMS macromonomer of comparable molecular

Table 1
G.p.c. results for PDMS and PTFPMS macromonomers

Macromonomer	M_w	M_n	M_w/M_n	DP(found)	DP(calc.)
11kPDMS	10 800	9700	1.1	128	132
22kPDMS	21 600	16 700	1.3	222	267
24kPTFPMS	23 800	18 200	1.3	115	127

weight (roughly half), due to added mass of fluorine in the side chain (Table 1). These observations are in agreement with a prior study which found similar molecular weight effects when synthesizing various mono-end-capped PDMS macromonomers [31].

The siloxane macromonomers were copolymerized free radically in solution with methyl methacrylate to give the desired graft copolymers. When using the PDMS macromonomers, the copolymerizations were carried out in toluene. Due to the low solubility of the PTFPMS macromonomer in toluene, only the graft copolymer with the lowest amount of PTFPMS could be synthesized in toluene; acetone was used in the syntheses of higher PTFPMS-content graft copolymers. As initially isolated, the copolymers were oily, waxy solids due to the presence of unreacted and non-reactive PDMS or PTFPMS coprecipitated with the graft copolymers. Soxhlet extraction with hexanes removed these siloxane species (isolated as oils), which were not covalently bonded to the PMMA backbone. After extraction, the pure graft copolymers no longer had an oily appearance; they ranged from hard to waxy solids, depending on the amount of PDMS or PTFPMS grafts. The characterization results for the graft copolymers are given in Table 2. The numbers preceding PDMS and PTFPMS denote the molecular weight (in thousands) of the siloxane moieties, and the numbers in parentheses after PDMS and PTFPMS refer to the weight percents of siloxane in the copolymers (determined using ^{1}H n.m.r.).

The T_g for PMMA synthesized in toluene (PMMA-tol, 98°C) is 29°C lower than PMMA prepared in acetone (PMMA-ac, 127°C). The surprisingly large difference in T_g is due to a solvent effect on tacticity, as PMMA T_g is strongly tacticity dependent [32]. An increase in PMMA syndiotactic content from 56 to 64% results in a T_g increase from 104 to 126°C [33]. The copolymerization temperature difference (70°C in toluene *versus* 56°C in acetone) may also have some small influence on PMMA tacticity [34].

The T_g for the PMMA phase in the copolymers follows a similar trend. The copolymer-tol compositions have PMMA phase T_gs in the range 94–98°C , while the corresponding values for copolymer-ac compositions are 125–126°C. Overall, the small or non-existent depressions in T_g suggest little or no phase mixing. PMMA-g-24kPTFPMS(12)-tol exhibits the maximum depression (4°C) which may indicate some slight miscibility of PTFPMS in PMMA. For PMMA-g-22kPDMS (32) a T_g could not be determined by DSC, presumably due to an insufficient amount of PMMA in the sample.

g.p.c. results show that all polymers have high molecular weights and polydispersities of 2.0 or less, which is typical for free-radically polymerized materials. The highest molecular weights are obtained for PMMA homopolymer. Using PDMS or PTFPMS macromonomers leads to copolymers with molecular weights lower than PMMA homopolymer. The decrease in molecular weight becomes greater with increasing siloxane macromonomer content, indicating that both the siloxane macromonomers are acting as either chain transfer agents or chain terminating agents, due to a difference in the reactivity ratios of methyl methacrylate and the methyl methacrylate end-capped macromonomers.

3.2. Dynamic contact angle analysis

To establish the dynamics of wettability for the graft copolymers, DCA analysis was used to measure advancing (θ_a) and receding (θ_r) contact angles and hysteresis ($\theta_\Delta = \theta_a - \theta_r$). DCA data for PMMA-tol films cast from $CHCl_3$ were collected for reference: θ_a , 99°; θ_r, 42°; θ_Δ, 57°. Van Damme et al. [27] reported DCA data for PMMA (T_g 120°C) films cast from toluene: θ_a , 95°; θ_r, 65°; θ_Δ, 30°, while Hogt et al. [28] reported values of θ_a , 80°; θ_r, 58°; θ_Δ, 22°. Results on commercial samples of PMMA determined by goniometry (most closely corresponding to θ_a) are in the range of 70–80° [35–37].

Surface roughness of PMMA films is a function of casting solvent, and θ_Δ is sensitive to surface roughness. The Wenzel equation [38] [Eq. (1)] provides an approach to correcting contact

$$\cos\theta_{app} = R\cos\theta_{true} \qquad (1)$$

angles for surface roughness, where θ_{app} is the observed or apparent contact angle, θ_{true} is the true contact angle, and R is the roughness factor [Eq. (2)].

$$R = \frac{\text{actual area}}{\text{apparent area}} \qquad (2)$$

Table 2
Characterization results for graft copolymers

Polymer	Polymerization solvent	T_g (°C)	M_w	M_n	M_w/M_n
PMMA	toluene	98	105 300	82 500	1.3
PMMA	acetone	127	139 300	84 800	1.7
PMMA-g-11kPDMS(10)	toluene	98	93 200	47 400	2.0
PMMA-g-11kPDMS(17)	toluene	97	96 200	65 400	1.5
PMMA-g-22kPDMS(32)	toluene	-	73 800	45 600	1.6
PMMA-g-24kPTFPMS(12)	toluene	94	101 900	65 400	1.6
PMMA-g-24kPTFPMS(30)	acetone	126	87 800	69 800	1.3
PMMA-g-24kPTFPMS(48)	acetone	125	67 600	33 100	2.0

Inspection of these equations shows that θ_Δ (or any angle above 90°) increases and θ_r (or any angle below 90°) decreases with surface roughness. This may be understood qualitatively by considering an advancing drop 'held back' and 'jumping' from peak to peak, while the receding drop 'clings' to valleys. Thus, previously reported data on PMMA-tol using THF solutions (θ_Δ, 134°; θ_r, 28°) [39] were influenced by surface roughness. DCA runs for PMMA-tol films from THF (Fig. 1a) and $CHCl_3$ (Fig. 1b) show the sensitivity of the technique to surface roughness. The THF film was opaque from light scattering due to surface roughness, while the $CHCl_3$ film was translucent.

Initial and final values for θ_a and θ_r for the graft copolymers over 15 days immersion in water are given in Tables 3 and 4, respectively. Annealing of the films tended to increase both the receding and advancing contact angles, since annealing increases the surface content of the lower surface energy siloxane grafts. Figs 2 and 3, respectively, show initial and final values of θ_a and θ_r for annealed samples as a function of composition. The high values for θ_a and low values for θ_r suggest that surface roughness is influencing the data. However, certain trends are apparent. For PMMA-g-PDMS compositions, the wettability decreases with increased siloxane content, as demonstrated by the increase in all water contact angles with increased siloxane content. For PMMA-g-PTFPMS compositions, the results differ. The advancing water contact angles appear to decrease slightly, while the receding water contact angles appear to increase slightly with increased siloxane content. Considering experimental error (note the standard deviations included in Tables 3 and 4), the data for PMMA-g-PTFPMS compositions may well be fairly invariant with respect to changes in the siloxane content.

Figs 4 and 5 show the water contact angle data versus immersion time in water for two of the annealed graft copolymers—their behaviour is representative of all of the graft copolymers studied. The decline in receding contact angle is most likely caused by surface reorganization leading to hydrophilic PMMA patches on the otherwise hydrophobic polysiloxane surface. As immersion time in

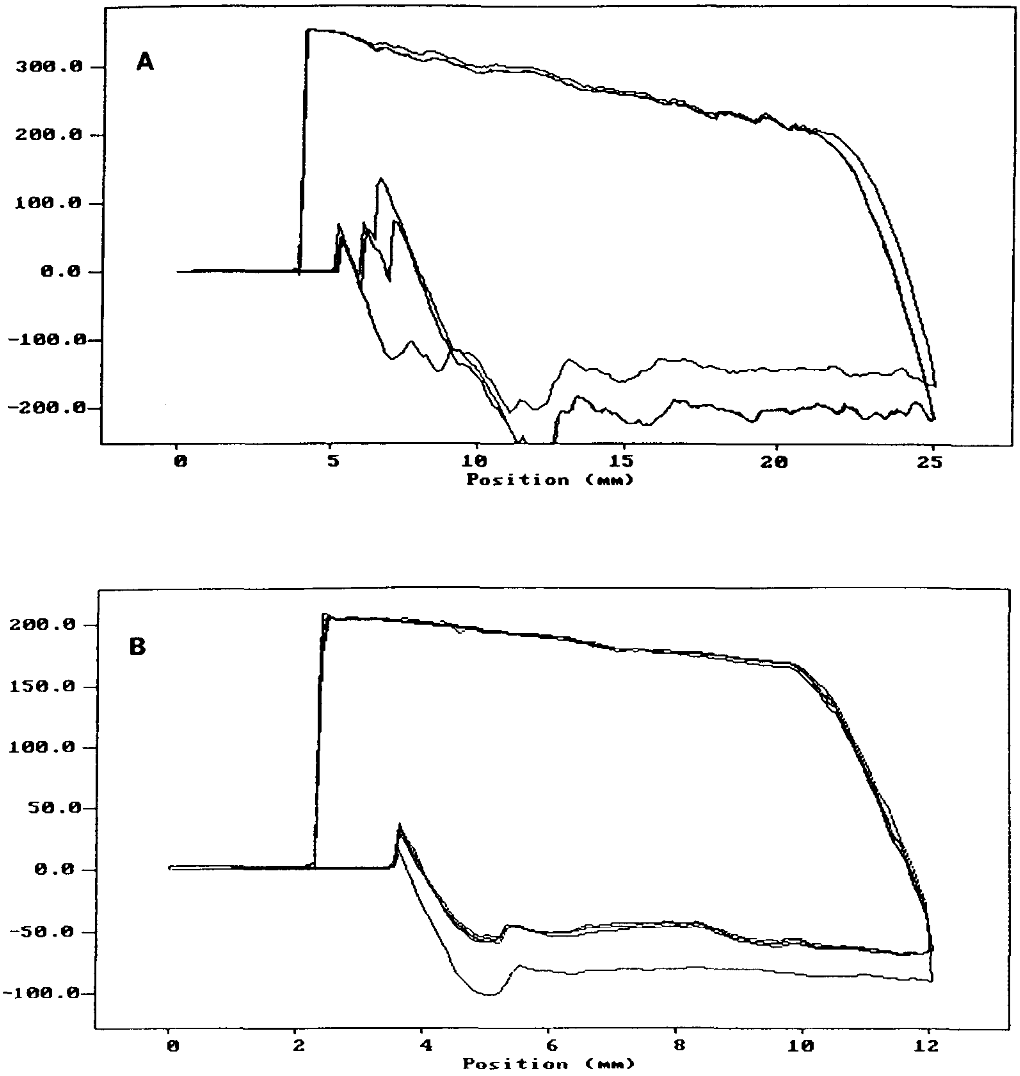

Fig. 1. DCA traces for PMMA: (A) cast from THF solution; (B) cast from $CHCl_3$ solution.

Table 3
Advancing water contact angle data

Advancing angles	Initial (day = 0)		Final (day = 15)	
	Non-annealed	Annealed	Non-annealed	Annealed
PMMA	98.7 ± 0.9	92.8 ± 3.7		
PMMA-g-11kPDMS(10)	106.9 ± 2.7	110.4 ± 7.5	95.9 ± 4.9	100.0 ± 13.0
PMMA-g-11kPDMS(17)	121.4 ± 8.5	123.8 ± 2.9	104.5 ± 3.5	100.2 ± 8.0
PMMA-g-22kPDMS(32)	110.6 ± 2.2	114.2 ± 1.3	109.5 ± 5.0	118.6 ± 3.5
PMMA-g-24kPTFPMS(12)	137.4 ± 2.8	142.3 ± 15.0	137.6 ± 0.1	130.1 ± 3.1
PMMA-g-24kPTFPMS(30)	131.3 ± 0.4	133.2 ± 1.6	121.2 ± 3.9	125.2 ± 4.2
PMMA-g-24kPTFPMS(48)	136.3 ± 4.3	128.4 ± 5.3	109.2 ± 5.2	113.1 ± 6.3

Values were determined by averaging the raw advancing water contact angle data for day = 0 and day = 15

water increases, the area fraction of hydrophilic patches on the surface increases, leading to a continual decline of the receding contact angle.

As an approach to factor out the effects of surface roughness, the mean contact angle was calculated for the copolymer samples. The rationale for this approach is that θ_a and θ_r are similarly, but oppositely, effected by surface roughness. Eq. (3) was used for this calculation, where θ_m is the mean contact angle [40].

$$\cos\theta_m = (\cos\theta_a + \cos\theta_r)/2 \qquad (3)$$

Table 5 summarizes the results of θ_m *versus* immersion time. Figs 6 and 7, respectively, show initial and final values of θ_m for annealed samples as a function of composition. The change in θ_m versus immersion time for the two representative compositions is also included in Figs 4 and 5.

From the θ_m data, some new information is apparent. PMMA displays a θ_m of 73°, in the range of the water contact angles measured by goniometry. The decreased wettability of PMMA-g-PDMS compositions with higher siloxane content is more pronounced utilizing θ_m, both before and after immersion in water. The PMMA-g-PTFPMS copolymers exhibited higher values for θ_m than the non-fluorinated polymers at lower siloxane contents; however, this trend disappears or possibly reverses at higher siloxane contents. As noted for θ_a and θ_r data, θ_m values for PMMA-g-PTFPMS compositions show little correlation with siloxane content, and are most probably invariant within experimental error.

The observations that θ_m after immersion increases with increasing PDMS content, remains constant or slightly decreases with increasing PTFPMS content, and is greater for PDMS grafts versus PTFPMS grafts at higher siloxane percentages, implies three points. (1) At low siloxane concentrations, PTFPMS grafts are more effective at providing a hydrophobic surface than PDMS grafts. (2) At high siloxane percentages, PDMS grafts afford a more stable hydrophobic surface than PTFPMS grafts. (3) The correlation between pure siloxane surface tension and surface wettability of the graft copolymers is not straightforward. The solid surface tension of PTFPMS is lower than that of PDMS, which correlates with wettability at low siloxane graft concentrations. However, the liquid surface tension of PDMS is lower than that of PTFPMS [3], which correlates with wettability at high siloxane graft concentrations. In our graft copolymers, at high siloxane percentages, the siloxane moieties may be acting more like a liquid layer on the surface of the polymer film, giving the PTFPMS-grafted copolymers a higher surface tension, and thus a higher degree of wettability. The lack of side chain ordering and acccssibility of water to the relatively acidic CH_2 groups adjacent to the CF_3 group may account for this observation.

3.3. Field exposure tests

Our protocol for evaluation of fouling release involves: (1) qualitative evaluation of small coated panels in Chesapeake Bay exposure; and (2) if promising results are obtained, semi-quantitative evaluation of hard fouling

Table 4
Receding water contact angle data

Receding angles	Initial (day = 0)		Final (day = 15)	
	Non-annealed	Annealed	Non-annealed	Annealed
PMMA	41.5 ± 0.3	48.2 ± 7.0		
PMMA-g-11kPDMS(10)	63.4 ± 2.1	67.7 ± 1.5	38.2 ± 9.7	42.5 ± 12.5
PMMA-g-11kPDMS(17)	57.4 ± 8.0	65.0 ± 5.3	36.7 ± 7.4	40.7 ± 7.2
PMMA-g-22kPDMS(32)	76.8 ± 2.0	83.1 ± 3.2	51.6 ± 2.5	58.4 ± 3.9
PMMA-g-24kPTFPMS(12)	62.0 ± 1.3	52.1 ± 1.4	44.6 ± 0.9	37.1 ± 7.4
PMMA-g-24kPTFPMS(30)	52.1 ± 0.6	53.1 ± 2.7	37.7 ± 1.3	42.2 ± 3.4
PMMA-g-24kPTFPMS(48)	65.4 ± 1.8	66.0 ± 4.5	31.5 ± 2.5	45.6 ± 2.9

Values were determined by averaging the raw receding water contact angle data for day = 0 and day = 15

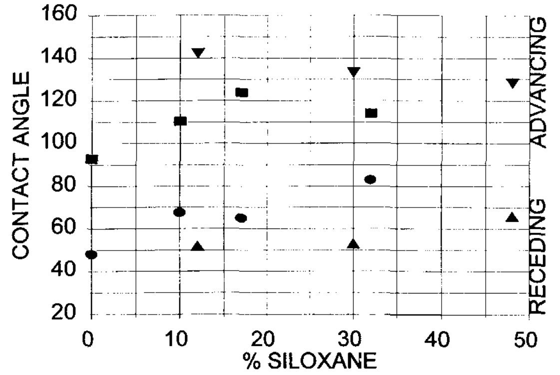

Fig. 2. Plot of initial advancing and receding water contact angles versus wt% siloxane in the graft copolymers. Key: ■ PMMA-g-PDMS advancing; ▼ PMMA-g-PTFPMS advancing; ● PMMA-g-PDMS receding; ▲ PMMA-g-PTFPMS receding.

release of larger coated panels in Indian River Lagoon, Melbourne, FL exposure [41]. We report the results of the first part of this protocol below.

Seven coatings were subjected to field exposure tests: PMMA-tol, PMMA-g-11kPDMS(10), PMMA-g-11kPDMS(17), PMMA-g-22kPDMS(32), PMMA-g-24kPTFPMS(12), PMMA-g-24kPTFPMS(30) and PMMA-g-24kPTFPMS(48). After 13 months, one coating, PMMA-g-24kPTFPMS(48), showed signs of microcracking, which worsened with time, while all the others exhibited no changes in appearance over 1.5–2 years exposure. PMMA-g-24kPTFPMS(48) copolymer has the lowest amount of PMMA and the lowest molecular weight of the six copolymers, indicating that one or both of these factors impact long term coating performance in water. During the exposure, all coatings fouled equally; but there were some differences in the ease of removal of fouling. The coatings containing PTFPMS were somewhat easier to clean than those with PDMS, which in turn were easier to clean than PMMA. Increasing the siloxane content in the copolymer had little effect, if any, on increasing the ease of removal of fouling.

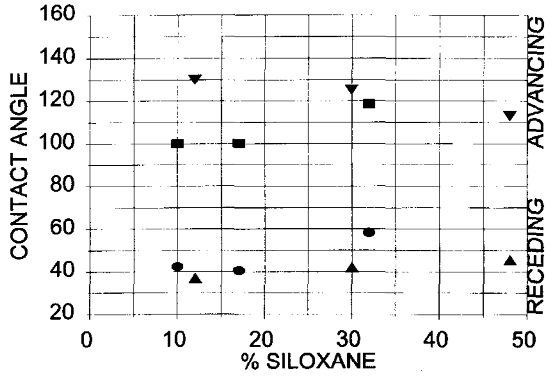

Fig. 3. Plot of final (after 15 days immersion in water) advancing and receding water contact angles versus wt% siloxane in the graft copolymers. Key: same as Fig. 2.

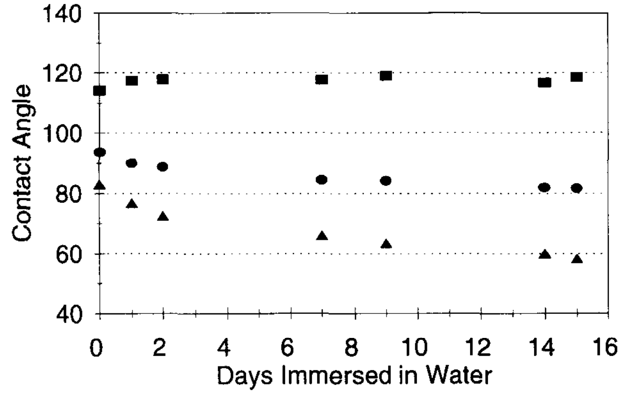

Fig. 4. Water contact angle data versus immersion time in water for PMMA-g-22kPDMS(32). Key: ■ advancing; ● mean; ▲ receding.

4. Conclusions

A series of PMMA copolymers grafted with PDMS and PTFPMS were synthesized via the 'macromonomer' method by which monofunctional polysiloxane macromonomers are copolymerized with methyl methacrylate. The goal of this work was to assess surface stability of the hydrophobic soft phase for this polymer architecture. DCA analysis of the copolymers shows that the materials initially possess hydrophobic surfaces, but become increasingly hydrophilic in the presence of water. Increasing the siloxane content of the copolymers increased the initial advancing and receding contact angles for PDMS grafts, but had little effect on initial advancing and receding contact angles for PTFPMS grafts. After 15 days immersion in water, the mean contact angle, which is a measure of wettability, increases with increasing PDMS content, and decreases slightly or remains invariant with increasing PTFPMS content, indicating that the PDMS-grafted materials are somewhat more resistant to surface reconstruction than the PTFPMS-grafted materials.

Differences in ease of removal of fouling in the first stage of a test protocol do not correlate directly with the results from wettability studies. Removal of fouling from both

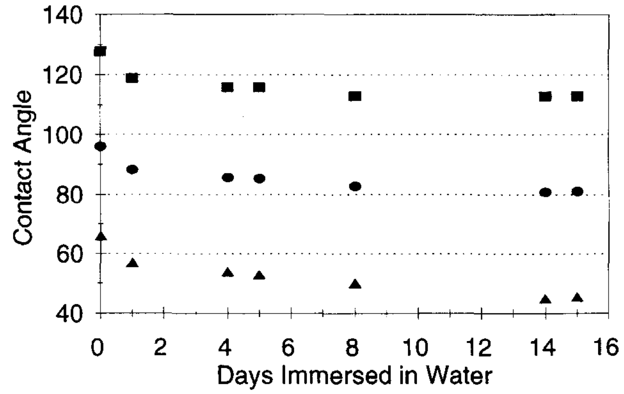

Fig. 5. Water contact angle data versus immersion time in water for PMMA-g-24kPTFPMS(48). Key: same as Fig. 4.

Table 5
Mean water contact angle data

Equilibrium angles	Initial (day = 0)		Final (day = 15)	
	Non-annealed	Annealed	Non-annealed	Annealed
PMMA	72.6 ± 0.5	72.1 ± 0.9		
PMMA-g-11kPDMS(10)	85.5 ± 1.4	82.0 ± 2.8	70.2 ± 5.8	73.6 ± 11.0
PMMA-g-11kPDMS(17)	89.5 ± 2.0	93.8 ± 2.1	74.1 ± 1.0	73.2 ± 1.8
PMMA-g-22kPDMS(32)	93.6 ± 0.4	98.3 ± 2.1	81.7 ± 2.8	88.7 ± 0.2
PMMA-g-24kPTFPMS(12)	97.7 ± 1.6	94.7 ± 4.1	90.8 ± 0.4	85.5 ± 1.2
PMMA-g-24kPTFPMS(30)	91.3 ± 0.4	92.4 ± 1.5	82.1 ± 2.1	85.3 ± 2.8
PMMA-g-24kPTFPMS(48)	98.8 ± 0.8	96.1 ± 4.0	74.8 ± 3.2	81.1 ± 3.4

Values were determined by averaging the cosines of the advancing and receding water contact angles for day = 0 and 15

PDMS and PTFPMS coatings was more facile than from PMMA, but PTFPMS materials were somewhat more easily cleaned than those containing PDMS. At the present time, we are not pursuing the second phase of our test protocol. Firstly, the fouling release characteristics of these graft copolymers deteriorate with time, and secondly, the fouling release characteristics at best are qualitatively inferior to both silicone alkoxy-cured networks and PDMS networks cured via hydrosilation [41]. Further research is needed on other polymeric systems, possibly on copolymers consisting of a more hydrophobic polymeric backbone, to expand the database and determine if there truly are any correlations between DCA 'laboratory' data and actual 'real world' coating behaviour.

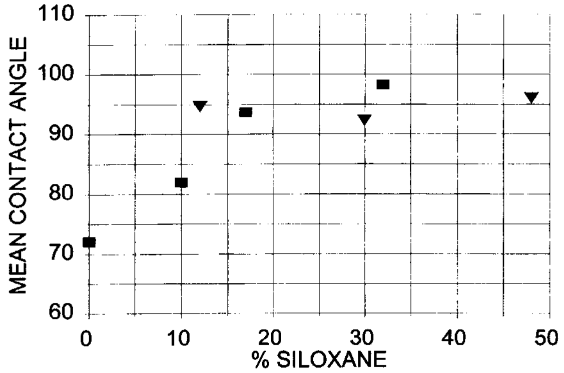

Fig. 6. Plot of initial mean water contact angle versus wt% siloxane in the graft copolymers. Key: ■ PMMA-g-PDMS; ▼ PMMA-g-PTFPMS.

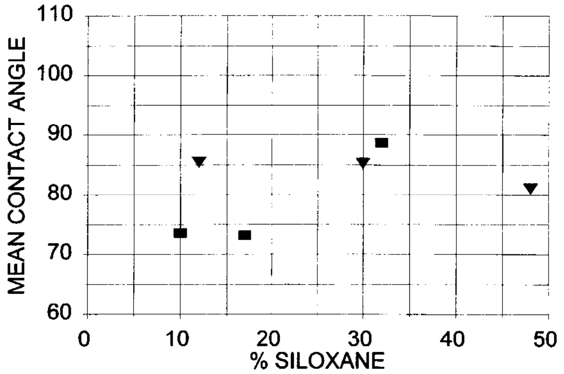

Fig. 7. Plot of final (after 15 days immersion in water) mean water contact angle versus wt% siloxane in the graft copolymers. Key: same as Fig. 6.

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