



Substantially enhanced stability against degrafting of zwitterionic PMPC brushes by utilizing PGMA-linked initiators



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ABSTRACT

We present a simple method to prepare zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) brushes on silicon surfaces that exhibit excellent long term stability in aqueous environment. First, we attach poly(glycidyl methacrylate) (PGMA) to the substrate. Next, we couple 2-bromoisobutyryl bromide initiators to the modified substrate, which allows us to grow PMPC brushes using surface initiated atom transfer radical polymerization. Atomic force microscopy (AFM) is employed to evaluate the dry thickness of the PMPC brushes after incubation in water and solutions of various salts. The AFM results show that the PGMA-PMPC brushes are indeed very stable and that the brushes can stand being immersed for at least 4 weeks in physiological fluids (saline solution) and artificial sea water with only 1% decrease of their dry thickness. In view of potential applications, we demonstrate that the friction between these PGMA-PMPC brushes and a polystyrene colloid in water is extremely low: the friction coefficients are found to be 10^{-3} – 10^{-4} . Moreover, we show that our brushes keep their hydrophilic properties after immersion for 100,000 ppm hours in sodium hypochlorite solution, indicating their potential for employment as coatings on industrial membranes.

1. Introduction

Triggered by the recent increase in the demand of functional surface coatings [1,2], there has been a quickly growing scientific interest in polymer brushes [3–8]. These brushes are dense films of macromolecules that are attached with one end to a surface. Surfaces decorated with brushes can be employed for controlling surface wettability [9,10], adhesion [4,11–13] and friction [14–17], and can be utilized in sensing [18,19] and drug delivery [20,21], among others. In particular, zwitterionic polymer brushes, which bear both cationic and anionic groups in the same polymer chain, have drawn considerable attention, due to their excellent performance as lubricants [22–24] and low-fouling coatings [25–27]. Moreover, they are often bio-compatible [28,29], which makes them potential candidates for applications that are used in the human body, for example on the interface of artificial joints [29,30] and on catheters [31].

A well-studied example of a zwitterionic polymer is poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC). Brushes composed of such polymers show extremely low sliding friction, which is even lower than typical values found in human synovial joints [22]. A possible reason for this low frictional response is that water molecules can cooperatively bind with the zwitterionic moieties in the brushes resulting in a strong hydration [32]. As a consequence, the osmotic pressure in the polymer brush system is high and, therefore, the effective contact area is low, *i.e.* friction is low during single asperity sliding. Therefore, these brushes hold great

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potential for employment in devices or machines where low friction is required. However, a critical disadvantage, which has prevented application of the brushes, is that the polymers can be cleaved off the surface when being immersed in aqueous solutions for several days [33–35].

The degrafting of PMPC brushes and other brushes is in most cases caused by hydrolysis, which can be tension-induced or -enhanced and results in breaking of the bonds between the polymer and the grafting surface [36–38]. Strongly hydrated polymer brushes such as PMPC where the osmotic pressure and the stretching is high [34] are particularly sensitive to cleavage due to a better access of water to the hydrolysis sensitive bonds, but also due to the potential mechano-chemical shift in the hydrolysis equilibrium. In acidic and alkaline solutions [39,40], the cleavage of particular bonds can be accelerated even more. Which bond will break depends on the type of surface in combination with the type of anchor or polymerization-initiator used to prepare the brushes [37,41–45]. It has been shown using molecular dynamics simulations that the highest tension occurs at the bond closest to the surface [46]. This bond is, therefore, often considered to be the most likely candidate for breakage. However, other bonds in the brush-anchors, such as the common ester or amide bonds, can be sensitive to hydrolysis too [41,47]. Besides hydrolysis, the degrafting also can be intentionally achieved by trace amounts of HF formed in the solvent, which can partly etch the silicon-oxide grafting-surface [43] or the utilization of light-sensitive linkers between the polymer and the surface [48,49].

In the last years, many methods have been developed to slow down degrafting of brushes from the surfaces [33,34,41,50–52]. Examples include the use of dense bottle-brushes where the backbone attaches to the surface [53] and the employment of long hydrophobic alkyl-chains that reduce hydrolytic activity by preventing water molecules from reaching the surface-bond [54]. Alternatively, self-healing polymer coatings can be used to counter-act brush degradation by the polymer-reattachment [50]. In this article, we build on these developments, as well as on our own expertise in this area [33,55]. In a recent article, we have for example shown that the degrafting of neutral, water-soluble brushes is significantly slowed down by utilizing trimethoxysilane-based instead of monochlorosilane-based surface-initiated atom transfer radical polymerization (SI-ATRP) initiators [55]. The former silane can bind to the surrounding silanes and the surface creating more anchor-points. Moreover, an amide bond in the trimethoxysilane replaces the ester-bond in the monochlorosilane. The latter bond is considered to be slightly more hydrolysis-sensitive (at extreme pH and temperature) than the amide [56]. The method of Ref. [55], however, only works for neutral polymers. For more hydrophilic, charged or zwitterionic polymers such as PMPC, the brushes still detach [33,34,57]. For such very hydrophilic polymers, diblock copolymers systems have been proposed to obtain stable surface-coatings [33,52,58]. Yet, under particular solvent conditions these coatings can phase-separate creating a rough, heterogeneous surface [33].

In this article, we present a simple method to fabricate homogeneous and robust PMPC brushes, which show a substantial enhanced stability against degrafting in water and salt solutions. To do so, we modify the poly (glycidyl methacrylate) (PGMA)-macro-initiator method first reported by Liu et al. [59], where bromoacetic acid (BAA) initiators or 2-bromo-2-methylpropionic acid (BPA) [60] are coupled to the free epoxy groups on the silicon-oxide-bound PGMA molecule. Instead, we couple 2-bromo-2-methylpropionyl bromide (BIBB) initiators to the hydroxyl group that is formed when PGMA epoxy-groups react with hydroxyl groups on the silicon surface. This leaves the non-reacted epoxy groups intact, which reduces the chance that water molecules reach the hydrolysis-sensitive surface bonds. Our prepared PGMA-PMPC brushes show excellent lubricating properties and degrafting-resistance in both water and aqueous salt media: The height of the PMPC brushes reduces by less than 1% after immersion in physiological (saline) and marine (0.6 M sodium chloride) environments for 4 weeks, while the brushes degraft by only 48% after immersion for 100,000 ppm hours in sodium hypochlorite solution. Our brushes, therefore, hold great potential for application in e.g. biomedical engineering or as low-fouling membrane-coatings.

2. Materials and methods

2.1. Materials

Azobisisobutyronitrile (AIBN, Aldrich, 98%) was recrystallized twice in methanol, and dried in the oven for 12 h at room temperature. Next it was kept in an amber flask, and stored in the fridge. Copper (I) bromide (CuBr, Aldrich, 98%) was purified by stirring in acetic acid and filtered till the suspension solution was pale like. After washing with ethanol, the powder was dried in a vacuum oven at room temperature overnight. Poly (glycidyl methacrylate) (PGMA, $M_n = 1 \times 10^4$), 2-Methacryloyloxyethyl phosphorylcholine (MPC, 97%), 2,2'-Bipyridyl ($\geq 99\%$), triethylamine (TEA, $\geq 99\%$), 2-bromo-2-methylpropionyl bromide (BiBB, 98%), copper (II) bromide (CuBr₂, $\geq 99\%$), sodium fluoride (NaF, $\geq 99\%$), sodium chloride (NaCl, $\geq 99\%$), sodium iodide (NaI, $\geq 99.5\%$), sodium hypochlorite solution (NaOCl, 10%), CDCl₃ (99.8 atom% D) and D₂O (99.9 atom% D) were purchased from Sigma-Aldrich, and used as received without any purification. Methanol (absolute), sulfuric acid (95–97%), Methyl ethyl ketone (MEK) and dimethylformamide (DMF) were purchased from Biosolve. Hydrogen peroxide (H₂O₂) was purchased from Merck. MilliQ water was made from a MilliQ Advantage A 10 purification system (Millipore, Billerica, Ma, USA).

2.2. Methods

2.2.1. Synthesis of PGMA-PMPC

First, the silicon substrate surfaces were activated with Piranha solution. Then, the PGMA thin film was deposited on the cleaned substrates by dip coating in a concentration of 0.1% of PGMA in MEK solution, and dried in air. As reported before [59], increasing the aging time before annealing improved the thickness of PGMA film on the substrates. Here, all the samples were kept in petri-dish for the aging time of 48 h and then annealed for 30 min at 110 °C. The physically attached macromolecular film was removed by

multiple washing-cycles with chloroform and sonication such that a permanently bonded PGMA layer was obtained. To modify the surfaces with the atom transfer radical polymerization (ATRP) initiator, a one-step initiator grafting reaction was conducted. The PGMA coated substrates were immersed in a cold DMF solution (30 mL), and triethylamine (0.1 mL) and 2-bromo-2-methylpropionyl bromide (0.1 mL) were added drop by drop. Next, the reaction was allowed to react for one night with violently stirring. Next, ATRP was used to grow the brushes from the surface [61]. In a round bottom flask, MPC monomers (2 g, 6.8 mmol) and 2,2'-bipyridyl (50 mg, 0.3 mmol) were dissolved in a MilliQ water (2 mL) and methanol (2 mL) mixture, and purged with argon for 15 min. Meanwhile, CuBr (16.2 mg, 0.1 mmol) and CuBr₂ (7.5 mg, 0.03 mmol) were also flushed with argon in another flask for 15 min. After that, the monomer solution was combined with the catalyst and bubbled with argon for another 15 min. Later, the mixture combining monomer, ligand, and catalyst was transferred into the flask with the substrates, which had been flushed with argon for at least 20 min before. The polymerization was allowed to proceed for 4 h at room temperature under argon atmosphere. 30 mL MilliQ water was injected into the flask to stop the reaction. Finally, the substrates were rinsed in water and ethanol solution to remove the physically adsorbed polymer.

2.2.2. Synthesis of free PMPC polymer

PMPC was polymerized via free radical polymerization utilizing a recipe modified from Ref. [62]. In a round bottom flask, MPC (1 g, 3.4 mmol), AIBN (14 mg, 0.09 mmol) were added sequentially. Then 5 mL methanol was added and stirred violently under nitrogen gas. The polymerization was allowed to proceed for 8 h at 60 °C. After that, the reaction was stopped by cooling down, and exposure to air. Diethyl ether was used to precipitate the polymer. After filtering, the precipitant was dissolved in a small amount of water and freeze dried for 24 h.

2.3. Characterization

Static Contact Angle measurements were conducted on an optical contact angle device equipped with an electronic syringe unit (OCA15, Dataphysics, Germany). The pictures of the droplet were captured by a charge-coupled device (CCD) video camera, and the drop contour was fitted by the Young-Laplace equation. At least three droplets were analyzed to determine the contact angle of specimens after each modification step. The results are shown in Table S1.

X-ray Photoelectron Spectroscopy (XPS) was used to determine the chemical composition of the substrates after each modification step. The measurements were carried out on a Quantera Scanning XPS Microprobe from Physical Electronics with a monochromatic Al K α X-ray source (1486.6 eV photons). All binding energies were referenced to the C_{1s} hydrocarbon peak at 284.8 eV. The spectra show the correct elemental peaks after the reaction, which indicates a successful chemical modification for each step. Fig. 1(a) shows

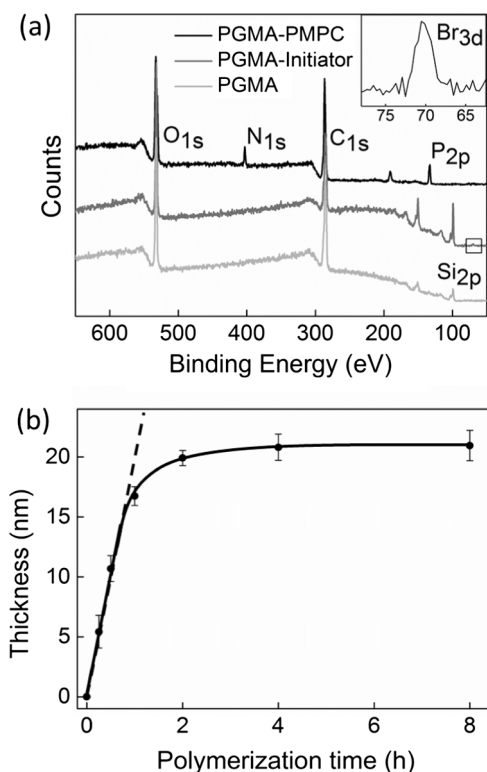


Fig. 1. (a) XPS spectra of the surface after each modification step of the PGMA-macro-initiator method: PGMA layer, initiator grafted PGMA layer, and PGMA-PMPC brush; (b) evolution of PGMA-PMPC brush dry thickness by varying polymerization time.

the XPS spectra of the surfaces after each modification step.

Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Bruker Vertex 70v spectrometer to get the specific group signals of the grafted polymer brushes. Before the measurements of the substrates with brushes, a bare silicon substrate was first scanned and used as a background to be subtracted from the brush-spectra. The PMPC brush spectrum (Fig. S1) shows characteristic infrared absorption peak at 1680 cm^{-1} (C=O), 1260 cm^{-1} (POCH₂), 985 cm^{-1} (N(CH₃)₃) [63,64]. The observed absorption peaks indicate that the PMPC brushes were successfully grafted from the substrates.

¹H NMR was conducted on a Bruker Avance 400 MHz instrument, in D₂O. For determination of the molecular weight of PMPC, the PMPC polymers were grown from sacrificial propargyl 2-bromoisoobutyrate initiator dissolved in D₂O at a concentration of 10 mg/mL. The repeat unit number of PMPC was estimated using the obtained spectra (Fig. S2). The stability of bulk PMPC in NaF was tested by comparing the spectra of a mixture of PMPC (10 mg/mL) and 0.1 M NaF in D₂O before and after long-time incubation (2 and 4 weeks).

The thickness of the PGMA thin layer was measured using a Variable Angle Spectroscopic Ellipsometer (VASE, J.A. Woollam). Measurements were performed as a function of photon energy (0.8–4.0 eV, corresponding to a wavelength range of 276–1550 nm) with a step size of 0.1 eV. The experiments were performed at room temperature (25 °C) in air. Spectra on samples were captured at three different angles of incidence (65, 70 and 75°). The ellipsometry data was fitted to the traditional Cauchy model, in which thickness *d*, and Cauchy parameters *A* and *B* were varied; the Cauchy parameter *C* was set to 0 (for more information on the fitting procedure see Ref. [65]).

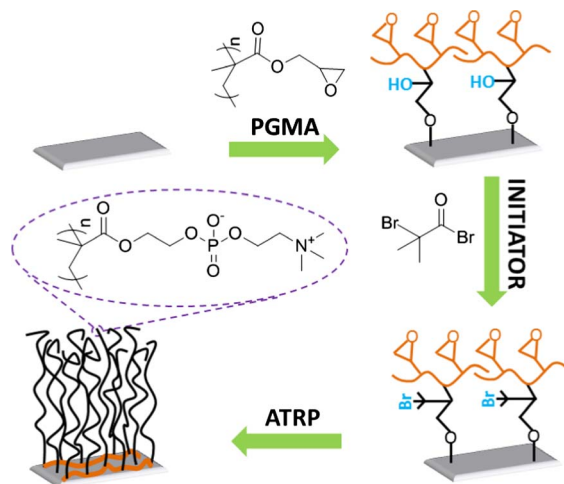
AFM imaging of the brush height was carried out on a Multimode 8 AFM, with a NanoScope V controller, and a JV vertical engage scanner using tapping mode. Aluminum-coated cantilevers were purchased from Olympus. The resonance frequency of the cantilevers was around 70 kHz, with the force constant of 2 N/m. All the samples were gently scratched on several positions by tweezers to expose the silicon surface underneath, which allowed for measuring the height. The brush specimens that had been separately immersed in water, 0.1 M NaF, NaCl and NaI aqueous solution for various times, were rinsed with water and ethanol sequentially, and dried with nitrogen before AFM height measurement. Generally, three different positions of the surface were measured and the average height was taken. The friction was measured by sliding the cantilever through the samples in the lateral direction (with the scan angle: 90°) over a sliding size 10 μm using a velocity of 10 μm/s. The cantilever is calibrated using the noncontact method [66] resulting in a torsional conversion factor of $S_{\theta} = 3.5 \times 10^{-8}\text{ N/V}$.

2.3.1. Stability test

To study the degrafting-kinetics of PMPC brushes, 0.1 M NaF, NaCl, NaI and 1000 ppm hypochlorite solutions were prepared. After immersing of the sample in MilliQ water or one of the solutions for a certain time, the sample was rinsed with water and ethanol sequentially and then dried with nitrogen gas. Next, the height of the brush was measured. Afterwards, the samples were re-immersed in fresh solutions to prevent changes in the pH.

3. Results and discussion

Scheme 1 shows the fabrication method described here to prepare PMPC brushes by SI-ATRP [61] using initiators linked to a polymeric film [67]. We have chosen PGMA as a polymeric film because of the relatively high contact angle (54°) for water droplets on surfaces covered with PGMA, which reduces the chance of water reaching the hydrolysis-sensitive bonds. In the first step, the PGMA is coupled to a piranha-activated silicon substrate using dip-coating (24 h aging time) followed by annealing for 30 min at 110 °C. Via a ring-opening reaction of the epoxy groups with the hydroxyl groups on the SiO₂, the PGMA is covalently bonded to the surface resulting in a $4 \pm 1\text{ nm}$ thick PGMA film as measured by ellipsometry after sonication in chloroform for 1 min such that physisorbed



Scheme 1. Synthetic route for preparing PMPC brushes using the PGMA-macro-initiator method.

PGMA is removed. The thickness of the chemically bound PGMA film indicates that only parts of the PGMA are linked to the silicon surface. In the second step, the BIBB is coupled in a DMF solution (30 mL with 0.1 mL triethylamine and 0.1 mL BIBB) to the hydroxyl groups that are formed during the ring opening reaction. In contrast to the BAA or BPA used in Luzonov's papers [59,60], for which the hydroxyl group of these molecules can open the epoxy ring, our BIBB will not react with the epoxy groups on the PGMA. We note that BIBB can react with leftover hydroxyl groups on the silicon surface. However, most of these hydroxyl groups will have oxidized or reacted during annealing. In the final preparation step, the PMPC brushes are grafted from the surface using a well-established recipe [68]. The brushes so obtained are smooth and homogeneous as shown in the AFM images (Fig. S4). The successful completion of the surface modification steps are tested by contact angle [69] (Table S1) and X-ray photoelectron spectroscopy (XPS) measurements (Fig. 1(a)).

After the first step, for the grafted PGMA layer (light gray curve), C_{1s} (284.7 eV) and O_{1s} (532.9 eV) peaks dominate the spectrum. Also, a Si_{2p} peak is visible at 99.6 eV, which arises from the SiO_2 surface underneath the thin PGMA film. The reaction of epoxy groups on the silicon substrates is confirmed by the appearance of the C-OH peak at 285.89 eV (Fig. S5). Though it is clear from the peak at 286.84 eV that most epoxy groups did not react. After the second step, when the initiator molecules have been grafted to the surface (dark grey curve), a characteristic Br_{3d} peak appears at 70.5 eV (see also inset), while the C_{1s} , O_{1s} and Si_{2p} peaks are still present. After the third step, when the PMPC brushes are grafted from the surface (black curve), the Br_{3d} and Si_{2p} peaks have vanished and new peaks can be observed. The new peak at 402.5 eV is assigned to N_{1s} arising from the positively charged N^+ in the polymer's side chain. The peak at 133.3 eV is assigned to P_{2p} and can be attributed to the P^- in PMPC. The elemental fractions for each modification step are shown in Table S2.

The PMPC growth kinetics for our macro-initiator method is shown in Fig. 1(b). The dry brush height for PGMA-PMPC is linearly increasing during the first hour and after 2 h of polymerization, it reaches a plateau. The grafting density of PGMA-PMPC brush is calculated using the dry height of test samples (around 11 nm) measured by AFM and the molar mass ($M_n = 5 \pm 0.3 \times 10^4$ g/mol) as determined by nuclear magnetic resonance (1H NMR) measurements of polymers grown from sacrificial propargyl 2-bromoisobutyrate initiator molecules free in solution during the polymerization [70,71] (spectrum in Fig. S2), resulting in a PGMA-PMPC grafting density of 0.18 chains/nm².

The stability of the PGMA-PMPC brushes is evaluated in aqueous solutions. Fig. 2 shows the dry height of the PGMA-PMPC brush normalized by the initial dry height (typically 20 nm) as a function of the immersion time of the samples in MilliQ water (upward triangles), 0.15 M sodium fluoride (NaF, downward triangles), sodium chloride (NaCl, circles) and sodium iodide (NaI, squares). The height is measured by AFM using tapping mode. Before each height measurement, the brushes are washed with water and ethanol to remove the salt and then dried in a stream of nitrogen gas. After the measurements, the brushes are placed back into a freshly prepared aqueous solution.

From the stability test results shown in Fig. 2, it is clear that the degrafting of PGMA-PMPC brushes is substantially reduced. While PMPC brushes grown from silane-based surface-linkers typically degraft in water within a couple of days [33–35], PGMA-PMPC brushes are stable for several weeks. After 25 days, the dry height of the brushes has decreased only by 14% in NaF solution, by 10% in NaCl solution, by 5% in NaI solution and by 3% in pure water. One reason for the enhanced stability can be the existence of Si–O–C surface bonds instead of the Si–O–Si surface bonds for silane-PMPC. The former is less sensitive to hydrolysis [72]. Another important reason can be the protection of the PGMA (contact angle 54 degrees), which lowers the chance of water molecules and ions reaching the hydrolysis sensitive surface bonds (the Si–O–C and ester bonds). In NaF, there is more degrafting than in the other ionic solutions. This can be attributed to small amounts of HF formed in solution [43], which can slowly etch the silicon oxide surface when it reaches the surface. Degradation of PMPC in the NaF solution has been ruled out as a reason for the height decrease by H NMR measurements, which do not show any changes in the proton peaks. All the spectra are shown in Fig. S3, and indicate there is no degradation of PMPC in NaF solution.

To demonstrate the long-term protection by the PGMA layer, we also test the stability of exposed epoxy groups using FTIR measurements: to study if the epoxy groups have been hydrolyzed the FTIR spectra are captured and compared before and after immersion of the substrates with annealed PGMA in H₂O and 0.15 M NaCl for 4 weeks. Fig. S6 shows that there is no signal of

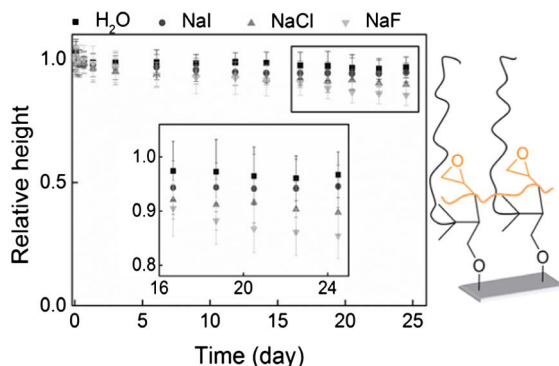


Fig. 2. Stability of PGMA-PMPC in MilliQ water, 0.15 M NaF, NaCl, NaI solution. The inset shows a magnification of the height over the last measurement week in which a small degrafting is observed. The height is normalized by the initial height (typically around 20 nm).

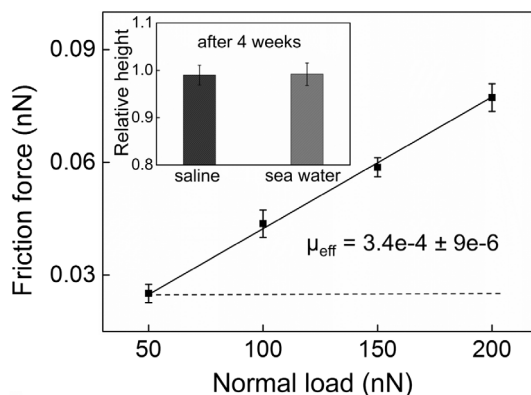


Fig. 3. Friction force between PGMA-PMPC brush and PS colloid at different normal loads. The inset shows the stability of PMPC brush in saline solution and in sea water (0.6 M NaCl) before and after 4 weeks.

hydroxyl groups appearing at 3400 cm^{-1} after the brush has been incubated in NaCl. Moreover, the height of the peak characteristic for epoxies is also constant. This demonstrates that the epoxy-groups do not degrade and can effectively prevent the water and ions from reaching the anchor points over long periods of time such that the degrafting of the brush can be substantially slowed down.

PMPC has been shown to be biocompatible [73]. Therefore, we anticipate that PMPC brushes can be applied as low-friction and low-fouling coatings in the human body, e.g. on artificial joints. Other applications could be in marine environments. Hence, we test the stability of our PGMA-PMPC brushes in saline solution and artificial seawater. As shown in Fig. 3, the PGMA-PMPC brushes are extremely stable over long times and there is as little as 1% polymer detachment after immersion for 4 weeks. These results indicate (by linear extrapolation) that the brushes will not significantly degraft ($> 50\%$) for immersion times of 4 years. However, we emphasize that this needs to be confirmed with measurements, since we do not know a priori how the degrafting will evolve in time. These results also indicate that the small degrafting observed for the brushes of Fig. 2 can in part be induced by the shear stress that has been regularly applied during rinsing and drying the samples. When we measure the dry thickness of the brush after incubation in salt solution week by week, there is much less degrafting compared to the frequently measured case. But, more importantly, our results show that our PGMA-PMPC brushes hold great potential for application in biomedical applications and marine antifouling coatings. Moreover, the synthesized PGMA-PMPC brushes in relative sliding motion with a PS colloid exhibit extremely low friction coefficients of 10^{-3} – 10^{-4} . This is similar to friction coefficients reported for brushes prepared with silane-based initiators [22], which show severe degrafting in aqueous solutions. We obtain similar results for silicon colloids as a counter surface, which suggests that the low-friction properties of PMPC could be insensitive to the choice of counter surface. However, to confirm low-friction for the counter surface that is relevant for the applications we have in mind, further testing is required. The low friction coefficient and substantially enhanced stability demonstrate that PGMA-PMPC brushes are promising systems that can potentially be applied on the surface of artificial joint and catheter. Moreover, this simple method to produce stable PMPC brushes can be applied to other polymers that need to be stable and robust in their good solvents too.

In industry, the modification of membranes by coating can enable low fouling [74], responsive [75], ion and solvent selective properties [76,77]. However, unstable grafts on the membranes prevents a long-term application of such membranes in liquid media due to the gradual degradation of the coating [78]. As a reference system [78,79], oxidative solution (1000 ppm NaOCl, pH = 8) can be used to evaluate the lifetime of the membrane coating layer. Here, we test the stability of our PGMA-PMPC brushes in 1000 ppm NaOCl solution for various immersion times, which is shown in Fig. 4. The change in height is plotted against the immersion time in ppm hours (as is common in membrane science [74–79]), since the degradation depends on both the NaOCl concentration and the

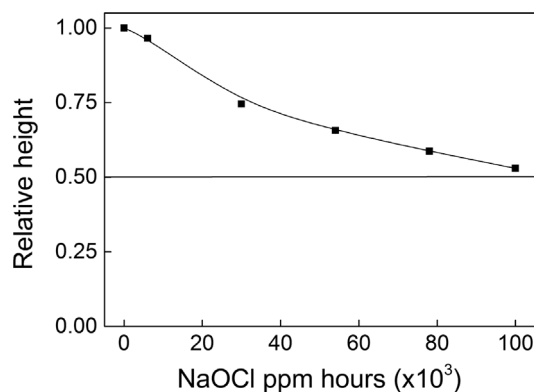


Fig. 4. The relative height of PGMA-PMPC brushes as a function of time incubated in 1000 ppm NaOCl (pH = 8) solution.

immersion time. At the first 6000 ppm hours, there is a slight degrafting of the brush, then with a gradual degradation of the brush with more incubating time. After 100,000 ppm hours, there is still 52% of the brush grafted on the surface, which represents that the PGMA-PMPC brushes can effectively resist the oxidation by NaOCl. Analysis by FTIR and contact angle measurements indicates that the PMPC polymer itself does not degrade (see SI). A typical membrane that last for 5 years tends to break down after 100,000 ppm hours of NaOCl treatment. Our brush keeps about half of its mass over that time, indicating that the brush might be able to withstand 5 years of operation [78]. Therefore, the stable PGMA-PMPC brush can potentially be applied in industrial applications where membrane coating with a long-time durability and performance are critical.

4. Conclusions

In summary, we have shown that zwitterionic PMPC brushes can be successfully grafted from PGMA that is covalently bonded to a silicon surface. To enable initiation of the polymerization we couple BIBB initiator molecules to the hydroxyl groups within the linker between the PGMA and the SiO₂ surface. Our PGMA-PMPC brushes are shown to be very stable in pure water and salt solutions. Only 1% of the polymers detach after immersion for 4 weeks in saline solution or in artificial seawater. Moreover, the synthesized PMPC brushes show extremely low friction coefficient in aqueous solution, and have potential application in biomedical engineering and as functional coatings on membranes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2017.02.033>.

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