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Accessible and sustainable Cu(0)-mediated radical polymerisation for the functionalisation of surfaces†

Oliver Frank Uttley, *[a] Leonie Alice Brummitt, [a] Stephen David Worrall [b] and Steve Edmondson [a]

Polymer brushes have great potential for use in functionalising surfaces due to their chemical and mechanical robustness, and wide variety of useful properties including antibacterial and antifouling behaviour. One such grafted polymer of interest is poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride (PMETAC), shown to have excellent antibacterial behaviour due to the presence of quaternary ammonium chloride groups (QACs). Previous studies have shown that increasing the density of QACs increases the efficacy of these surfaces, therefore the production of thick PMETAC brushes is highly desirable. *Cu(0)-mediated radical polymerisation* (CuRP) offers a simple route to the production of these surfaces. A movement towards more sustainable chemistry has led to research into polymerisations in environmentally benign solvent, with focus placed on recycled and easily accessible catalysts. In this study, the growth of PMETAC brushes up to 300 nm dry thickness (~425 nm water-swollen thickness) is demonstrated, thicker than any previous report we have found for this polymer brush. Furthermore, tap water is used as a cheap and readily available solvent, with a catalyst derived from copper wire. The use of copper wire, compared to the commonly used $CuBr_2$ catalyst, leads to thicker coatings which also display a lower swelling ratio, implying an increased grafting density. The protocol can be continuously cycled over a 7-day period without changing the monomer solution or catalyst, with numerous wafers being functionalised over the time period with no significant reduction in grafted amount. In addition, the polymerisation can be carried out in ambient (non-inert) conditions with no degassing steps, again without with significant detriment to grafting.

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1. Introduction

Due to their excellent mechanical and chemical robustness, *polymer brushes*, densely surface-tethered polymer chains, offer great potential for the functionalisation of surfaces for a broad range of applications including antifouling,[1,2] lubrication,[3,4] and thermo-responsive surfaces.[5] To date this type of functional surface coating has not been widely exploited, due to many applicable polymerisation methods being limited to small substrates and low-throughput batch processes due to inert atmosphere requirements of these oxygen sensitive chemistries. Poly[2-(methacryloyloxy) ethyl]trimethylammonium chloride (PMETAC) brushes have shown excellent antifouling and antibacterial properties in previous studies.[1,2] These properties are thought to derive from the cationic quaternary ammonium chloride groups (QACs), with antifouling and antibacterial properties increasing with greater polymer thickness and so charge density.[6,7] An accessible polymerisation route to thick PMETAC brushes, and so an increased surface density of QACs, is therefore of great interest.

When producing functionalised surfaces, especially those for biomedical applications, it is important to consider the synthesis procedure in order to reduce any hazards associated with both process and product, since solvent choice affects safety of both product and process, and production cost.[8] Water is a safe, environmentally benign and abundant solvent and is considered the "gold standard" solvent choice for reducing the environmental impact of industrial processes.[8,9] However, often water is required to be extensively purified, with deionized and ultrapure water used in many processes. The use of purified water is costly, and the energy associated with purification increases environmental impact.[8]

[a]*Department of Materials, School of Natural Sciences, University of Manchester, Oxford Road, Manchester, M13 9PL, UK. E-mail: oliver.uttley@manchester.ac.uk*
[b]*Aston Institute of Materials Research, School of Engineering and Applied Science, Aston University, Birmingham, B4 7ET, UK*

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In this paper, we demonstrate a process for synthesising antibacterial polymer brush coatings with unpurified tap water as solvent. Furthermore, we demonstrate recycling of the catalyst and polymerisation solution for multiple substrates (indeed in theory also compatibility with continuous processes such as roll-to-roll), making our process attractive for scale-up of brush synthesis with reduced costs, increased efficiency, and decreased hazards and environmental impacts compared to many existing procedures.

Various methods for the growth of polymer brushes have been detailed in previous work with *reversible addition–fragmentation chain transfer* (RAFT)[10,11] and *atom transfer radical polymerization* (ATRP)[12,13] being most popular due to both exhibiting excellent control over molecular weight, polydispersity and chain functionality. However, both have limitations: the *chain transfer agents* required for control in RAFT have limited commercial availability and relatively high cost.[14] ATRP, although a well-defined and controlled polymerisation,[15] can be highly oxygen sensitive, and is often carried out in undesirable or harmful solvents.[8] In 2007 Matyjaszewski *et al.*,[16] reported on *activators regenerated by electron transfer atom transfer radical polymerization* (ARGET ATRP) for the growth of polymer brushes, a method which offers a range of advantages over conventional ATRP including: reduced amounts of both metal catalyst and solubilising ligand; no addition of oxygen-sensitive and expensive Cu(I) catalysts due to it being formed *in situ* due to an addition of excess reducing agent; reduced oxygen sensitivity, with the reaction being able to proceed in ambient atmosphere. The risk of failure of the reaction is often decreased when an attempt to deoxygenate the solution is made.[16] These factors make ARGET ATRP more cost effective, environmentally friendly and safer than ATRP, making it desirable for the use of large-scale polymer brush synthesis, particularly in industry. ARGET ATRP has shown good results in the synthesis of various polymer brushes,[16–19] however, we were unable to find prior examples of the synthesis of PMETAC brushes *via* this route.

Recently, Mendonça *et al.*,[8] successfully showed the use of untreated water as solvent for solution-phase ATRP and ARGET ATRP. The synthesis of poly(ethylene glycol) methyl ether acrylate chains in solution was detailed, with kinetics and molecular weight obtained very similar for reactions in both ultrapure and untreated water. This research showed a more eco-friendly and sustainable solution polymerisation, when compared to other forms of ARGET ATRP. Extending this work to surface-initiated polymerisations to grow polymer brushes with unpurified water solvent while greatly reducing Cu(II) halide waste could be a significant step forward towards the cost effective and safe functionalisation of surfaces.

The use of Cu(0) based catalysts, such as copper wire, for polymer synthesis, has been documented before.[20–22] Copper wire is an excellent source of catalyst due to its ease of preparation, high observed reaction rates, predictability, tunability and importantly, reusability.[23] Zhang *et al.*,[24,25] previously detailed the growth of PMETAC brushes *via surface initiated Cu (0) controlled radical polymerisation* (Si-CuCRP). This procedure used recycled and readily available forms of copper as a catalyst (plates and coins), with a minimal amount of solution required for the polymerisation to proceed. The method showed excellent oxygen tolerance, and the polymerisation allowed for high grafting densities to be achieved. The copper plate was also reused for repeated reactions.

We detail the growth of PMETAC brushes, the thickest we have been able to find in literature, *via* an efficient and accessible aqueous Cu(0)-mediated radical polymerisation (CuRP) method based on a previous ARGET ATRP process, in which both the solvent and copper catalyst are abundant. Our method offers a low cost and efficient route to functionalising surfaces with thick cationic PMETAC brushes, which are ideal candidates for antibacterial surfaces. Both the reduction of solvent waste and reuse of reaction mixture are attractive for scale-up. We detail a method of reusing both the catalyst and monomer solution for a number of cycles to reduce solvent and metal catalyst waste. Our PMETAC brush polymerisation can be conducted in n ambient atmosphere with no deoxygenation steps required, significantly reducing experimental set up times and costs associated with purging reaction vessels. Interestingly, thicker PMETAC brushes are grown in ambient atmosphere, compared to an inert atmosphere, and we propose a secondary initiator present in the solution which may modify reaction kinetics.

2. Experimental section

2.1 Materials

Silicon wafers (⟨100⟩ orientation, boron-doped, 0–100 Ω cm) were purchased from PI-KEM (Tamworth, UK). Hydrogen peroxide (≥35 wt%) was supplied by VWR. 35 wt% ammonia solution (analytical reagent grade), ethanol, methanol (HPLC gradient grade), propan-2-ol, and cellulose dialysis bags (12 000 molecular weight cut-off (MWCO)) were supplied by Fisher Scientific (Leicestershire, UK). (3-Aminopropyl)triethoxysilane (≥98%), trimethylamine (laboratory reagent grade), tetrahydrofuran (HPLC reagent grade, ≥99.9%), 4 Å molecular sieves (8–12 mesh), 2-bromoisobutyryl bromide (98%), propionyl bromide (95%), [2-(methacryloyloxy)ethyl] trimethylammonium chloride solution (80 wt% in H_2O), copper(II) bromide (99%), copper wire (d = 1 mm, ≥99.9%), 2,2′-bipyridyl, ascorbic acid (99%) and deuterium oxide (99.9%) were supplied by Sigma Aldrich (St Louis, USA). Tap water was supplied from United Utilities, Manchester. Typical ion content as reported by supplier: calcium = 10.2 mg L^{-1}; chloride = 5.8 mg L^{-1}; magnesium = 1.21 mg L^{-1}; pH = 7.22; sodium = 5.23 mg L^{-1}; sulphate = 8.34 mg L^{-1}; hardness as calcium carbonate = 30 mg L^{-1}.

2.2 Sample preparation

2.2.1 Silicon wafer cleaning. Silicon strips of 1 cm width were cut from the supplied disk using gentle pressure to initiate cracks. Deionised (DI) water (71 mL) was heated to 70 °C on a hot plate. Hydrogen peroxide (15 mL) and

ammonia solution (15 mL) were added. Silicon strips were then added to the solution for 15 minutes. Strips were removed from the solution by flooding the crystalizing dish with water. The solution was decanted leaving enough to cover the silicon strips. The strips were then removed carefully and dried using a flow of nitrogen.[26]

2.2.2 APTES deposition. An aluminium weighing boat was filled with 10 drops of (3-aminopropyl)triethoxysilane (APTES) and placed in a vacuum desiccator. Cleaned silicon strips were placed around the aluminium boat. The desiccator was sealed, and a vacuum was applied for 5 minutes. The pressure was maintained in the vacuum desiccator for 30 minutes. Silicon strips were then removed and covered with foil before being placed into an oven at 110 °C for 30 minutes.[26] The thickness of the APTES coating on the silicon wafer was measured in ambient conditions *via* variable angle spectroscopic ellipsometry, detailed in section 2.3.1, and was found to be ~1 nm, corresponding to greater than monolayer coverage.[27–29]

2.2.3 Initiator grafting. Trimethylamine and tetrahydrofuran were dried using 4 Å molecular sieves for 2 hours prior to use. APTES coated silicon strips were placed individually in test tubes, sealed with a rubber septum and purged with nitrogen. A solution of tetrahydrofuran and triethylamine with a ratio (v/v) of 33 : 1 mL was added *via* syringe to cover the strip in the sample tube. Nitrogen pressure was applied to the tube throughout the procedure. 0.25 mL of 2-bromoisobutyryl bromide (BIBB) was then added for every 10 mL of tetrahydrofuran. The solution was left to react for 1 hour. The solution was removed, before tubes and silicon strips were washed with a series of 30 mL tetrahydrofuran and 30 mL methanol. The strips were then removed carefully with tweezers, rinsed with deionised water and dried with nitrogen. Successful initiator deposition was observed as a change in surface energy, with samples changing from hydrophilic to hydrophobic.

2.2.4 Typical synthesis of PMETAC brushes *via* $CuBr_2$ catalysed ARGET ATRP. Initiator-grafted silicon wafers were placed in a test tube and sealed. The tubes were purged with nitrogen gas. 75 wt% METAC solution (30.4 g, 109.8 mmol METAC, 0.4 mol H_2O) and water (19.1 g, 1.1 mol) were mixed in a sealed vessel. The solution was bubbled with nitrogen for 30 minutes. 2,2′-Bipyridyl (bpy) (68 mg, 435.4 μmol), ascorbic acid (77.4 mg, 439.5 μmol) and $CuBr_2$ (9.8 mg, 43.9 μmol) were added to the METAC solution and the flask was resealed and bubbled again for 5 minutes. The flask was sonicated until all contents were dissolved. The PMETAC solution was syringed over the silicon wafers until they were covered. A positive nitrogen pressure was applied to the tube during the polymerization. Samples were left for the desired polymerisation time then removed, washed with DI H_2O and dried with a nitrogen flow.

2.2.5 Synthesis of PMETAC brushes *via* Cu(0)-mediated radical polymerisation. Initiator grafted silicon wafers and coiled copper wire (l = 10 cm, d = 1 mm) were placed in a test tube, sealed and purged with nitrogen. To vary the amount of copper ends the 10 cm length of wire was cut into equal fraction (*i.e.* 8 ends = 4 lengths of 2.5 cm). METAC solution was prepared as described above (section 2.2.4), however no $CuBr_2$ was added. The METAC solution was syringed over the silicon wafers until they were covered. A positive nitrogen pressure was applied to the tube during the polymerization. Samples were left for the desired polymerisation time and samples were cleaned as mentioned previously (section 2.2.4).

2.2.6 Synthesis of PMETAC brushes in ambient atmosphere. Initiator grafted silicon wafers were placed in a test tube and sealed. For samples that used copper wire as a catalyst coiled copper wire (l = 10 cm, d = 1 mm) was added to each tube. METAC solution was prepared as described previously (section 2.2.4). METAC solution was syringed over the silicon wafers until they were covered. Samples were left for the desired polymerisation time and samples were cleaned as mentioned above (section 2.2.4).

2.2.7 Re-usable reaction mixture for the sustainable synthesis of PMETAC brushes. For the re-usable solution method both METAC solution and tubes containing wafers were prepared as detailed in the previous steps (section 2.2.4). $CuBr_2$ was omitted. A copper wire catalyst was used (8 pieces at l = 1.25 cm, d = 1 mm). The sealed tubes were placed in an oil bath maintained at 20 °C for the duration of the experiment. PMETAC solution was syringed over the silicon wafers and copper wire until they were covered whilst in the oil bath. For polymerisation in a nitrogen atmosphere a positive nitrogen pressure was applied to the tube during the polymerization. After 24 hours the nitrogen pressure was removed from the tube. A flow of nitrogen was applied over the top of the tube and the rubber septum was removed. The sample was removed from the tube and replaced with a new initiator grafted sample. The tube was resealed, and a nitrogen pressure was re-applied. This process was repeated every 24 hours.

2.3 Analysis

2.3.1 Ellipsometry. Analysis of the polymer brushes was conducted on an M-2000 variable angle ellipsometer (J. A. Woollam) with a spot size of 30 μm. Dry measurements were taken at incidence angles of 60°, 70° and 80° at wavelengths 250–1000 nm. A custom made liquid cell with quartz windows with a 1.25 mm light path (Hellma analytics, Germany) was used for wet measurements. CompleteEase software (J. A. Woollam) was used to analyse the results. For ambient/dry measurements the model consisted of: a silicon substrate with optical constants taken from Herzinger *et al.*;[30] a 2 nm thick native oxide layer with optical constants taken from Herzinger *et al.*;[30] a Cauchy layer with Cauchy A and Cauchy B values were derived from fitting the thickest sample (1440 minutes polymerisation) measured in the dry state which gave values of 1.491 and 0.00589 μm^{-2}, respectively. A Cauchy C term was not required for good fits. For wet measurements spectra were acquired at an incidence angle of 70°. The ellipsometric model consisted of the following layers: a silicon substrate with optical constants taken from Herzinger *et al.*;[30] a 2 nm thick native oxide layer with optical constants taken from Herzinger *et al.*;[30] 4 linear effective medium approximation (EMA) layers of fitted thickness with the thick-

ness of the four layers constrained to be equal; water as the ambient medium. The EMA layers had a fitted volume fraction of polymer with the remainder water. Polymer was represented by a Cauchy model. The Cauchy A, B and C values were the same as those used in the ambient model. The optical constants for H_2O were taken from Palik.[31] An angle offset was also fitted in each case. The Δ-offset due to the windows of the liquid cell was measured but found to be negligible and was therefore not included in the model. A schematic representation of the model is shown in Fig. S1 (ESI†). The wet thickness (h_{wet}) of brushes was calculated using eqn (1):

$$h_{wet} = 2\left(\frac{\int_0^d \phi(z) z \mathrm{d}z}{\int_0^d \phi(z) \mathrm{d}z}\right) \quad (1)$$

where d is the total thickness of the 4 layers used in the model, z is the distance from the substrate surface and ϕ is the polymer density within the layer:

$$\phi(z) = \begin{cases} \phi_1, & 0 < x < \frac{d}{4} \\ \phi_2, & \frac{d}{4} < x < \frac{d}{2} \\ \phi_3, & \frac{d}{2} < x < \frac{3d}{4} \\ \phi_4, & \frac{3d}{4} < x < d \end{cases} \quad (2)$$

2.3.2 Atomic force microscopy. Atomic force microscopy (AFM) was performed using a Multimode 8 Atomic Force Microscope (Bruker, USA), operating in non-contact mode with ScanAsyst activated in ambient conditions. RTESPA-300 antimony nitrogen doped cantilevers with a resonant frequency (f_0) of 300 kHz and a nominal spring constant of 40 N m^{-1} were used with the tips mounted inside an MFMA cell. Images were acquired at a resolution of 512 × 512 pixels over a scanning area of 50 × 50 μm^2 at a scan frequency of 0.301 Hz. All images were analysed using Gwyddion (Department of Nanometrology, Czech Metrology Institute) to acquire values for average surface roughness (R_a) and root mean square surface roughness (R_q). Rows were aligned by the median and 2 degrees of horizontal and vertical polynomial background were removed.

2.3.3 Nuclear magnetic resonance spectroscopy. All ^{1}H nuclear magnetic resonance (NMR) spectra were obtained using a 400 MHz Bruker Avance III NMR instrument. All spectra were obtained at ambient temperature. The chemical shifts (δ) and coupling constants (J) were recorded in parts per million (ppm) and Hertz (Hz) respectively. The residual peak of D_2O was used as a reference and spectra was recorded relative to it. 0.1 mL of the relevant reaction solution was added to 0.5 mL D_2O and mixed thoroughly for analysis. MestRenova software (Version 14.1.0) was used to analyse all data.

2.3.4 Ion chromatography. Ion chromatography was conducted on a Dionex ICS5000 Analytical Ion Exchange Ion Chromatographer, at a flow rate of 15 μL min^{-1}. Isocratic 34 mM potassium hydroxide was used as a mobile phase. Samples were filtered down using a 0.2 μm filter before analysis and both chloride and bromide ion content was measured.

3. Results and discussion

3.1. Surface initiated ARGET ATRP and CuRP in water

Before studying the effectiveness of a copper wire as a source of catalyst, it is first important to look at the growth of PMETAC brushes *via* a more typical method. The effectiveness of both *activators regenerated by electron transfer atom transfer radical polymerisation* (ARGET ATRP), using a copper(II) halide catalyst, and *Copper(0)-mediated radical polymerisation* (CuRP) (Fig. 1A), using copper wire as a source of catalyst were compared. Further to this, the solvent was also investigated, with deionised (purified) and tap (non-purified) waters being assessed.

Ion chromatography was performed to analyse chloride and bromide ion content of both water sources. A chloride and bromide ion content of 0.13 mg L^{-1} and <0.05 mg L^{-1}, respectively, was observed for DI water. Tap water had a chloride and bromide ion content of 7.56 mg L^{-1} and <0.05 mg mL^{-1}, respectively, in line with quoted values from the utilities company.

For all reactions, aqueous solutions of [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC), 2,2′-bipiridyl (Bpy) and ascorbic acid were made with a molar ratio of 3400 : 250 : 1 : 1, respectively. For ARGET ATRP reactions with copper(II) halide, a molar ratio of 1 : 0.1 for ascorbic acid to $CuBr_2$ was used. For CuRP, a coiled piece of copper wire (l = 10 cm, d = 1 mm) was used. All reactions were carried out at ambient temperature in a nitrogen atmosphere. It is important to note that due to the ionic structure of METAC with a Cl^- counterion, the addition of an extra halide salt to improve control is not needed, as noted in previous work.[8] Polymer growth kinetics are shown in Fig. 1B.

The results show that replacing deionized water (DI) with tap water has no detrimental effect on the growth of PMETAC brushes, and so tap water is suitable for use in both ARGET ATRP and CuRP in future work, successfully translating results from Mendonça *et al.*,[8] on solution polymerization to the surface initiated growth of polymer brushes. This finding should be of benefit for scale-up and industrial application of these brushes, with no requirement for solvent or reagent purification in order for the growth of polymer brushes to proceed efficiently.

$CuBr_2$ and other copper(II) halide compounds are often used for the catalyst complex in ARGET ATRP,[16] however, these compounds lead to the production of halogen-containing waste which can be difficult to properly and safely dispose of.[32,33] The use of copper wire as a source of catalyst for reactions has been detailed before,[20,34] however, importance was placed on control of molecular weight control and polydisper-

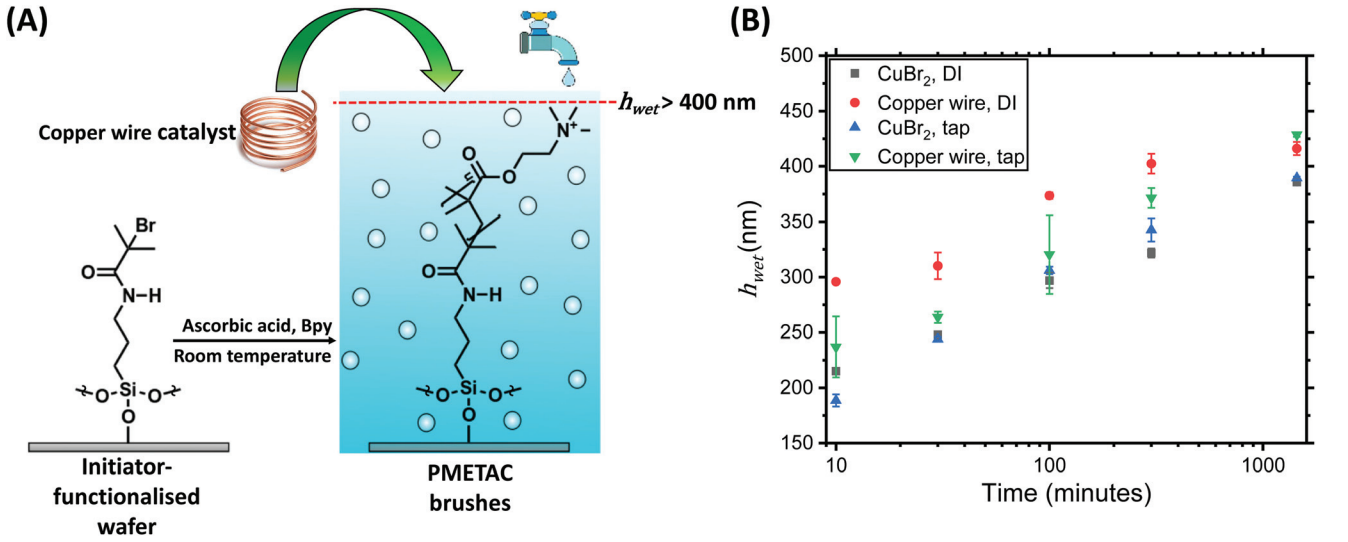

Fig. 1 (A) A scheme showing growth of PMETAC brushes using a copper wire catalyst in tap water and an excess of reducing agent. (B) A kinetics plot of the wet thickness (h_{wet}) of PMETAC brushes grown *via* activators regenerated by electron transfer – atom transfer radical polymerisation and Copper(0)-mediated radical polymerisation over a 24 hours period at ambient temperature. The effect of solvent type was investigated.

sity of chains grown in solution. Further to this, prior work has not applied an environmentally benign solvent, such as H_2O.

Our results (Fig. 1B) clearly demonstrate the growth of thicker PMETAC brushes (up to 30–40 nm greater wet thickness at each time step), when using copper wire catalysed CuRP compared with $CuBr_2$ catalysed ARGET. A maximum dry and wet thickness of 300 nm and 428.7 nm was observed, respectively, from CuRP as shown in Table 1. To our knowledge these are the thickest PMETAC brushes grown in the current literature, with previous work by Zhang *et al.*,[24,25] detailing a method of growing PMETAC brushes with a dry thickness of ~230 nm *via surface-initiated – Cu(0)-mediated controlled radical polymerisation* (SI-CuCRP). PMETAC and other polycationic brushes have shown excellent antibacterial behaviour due to the presence of charged QAC groups.[1,35] A key advantage both our work and the work by Zhang *et al.*,[24,25] was that no copper halide catalyst was required. Copper wire is a readily available, easily accessible and reusable alternative to compounds such as $CuBr_2$ in controlled radical polymerisations. Our results show a clear step forward towards the production of thick PMETAC brush functionalised surfaces *via* a low energy, cost effective and green polymerisation.

Although we have shown growth of thicker PMETAC brushes than previously, it is important to additionally assess both the swelling ratio (SR) and roughness of brushes in order to assess the grafting density and the homogeneity of surfaces. Table 1 shows the swelling ratio of brushes which is calculated as h_{wet}/h_{dry}. Both the average roughness (R_a) and root mean square roughness (R_q) were calculated from 2500 μm^2 scans of the surface *via* AFM, as a means of measuring homogeneity. Representative images can be found in the ESI (Fig. S2†).

Recently Oh *et al.*,[2] attempted to estimate the grafting density (σ) (defined here as chains nm^{-2}) of PMETAC brushes, however, their calculation was derived from a scaling law for *neutral* brushes:[36] $h_{wet} \propto N\sigma^{\frac{1}{3}}$, where N is the degree of polymerization. We believe this approach is not valid and instead, any estimation of σ for PMETAC should begin with the predicted scaling law for strong polyelectrolyte brushes in the osmotic regime, where wet thickness is independent of grafting density:[36,37]

$$h_{wet} \propto N\sigma^{0}. \quad (3)$$

When brushes, either charged or neutral are in the dry state, thickness is directly proportional to grafting density:[38]

$$h_{dry} \propto N\sigma^{1}. \quad (4)$$

If swelling ratio (SR) is defined as the wet thickness divided by the dry thickness for one sample (*i.e.* with the

Table 1 The dry and wet thickness, swelling ratio and roughness of PMETAC brush coatings on silicon wafers grown *via* ARGET ATRP and CuRP in various water types as solvent and with different sources of copper catalysts. Standard error values were taken from data from 3 separate samples

	Catalyst	h_{dry} (nm)	h_{wet} (nm)	Swelling ratio (SR)	R_a (nm)	R_q (nm)
DI	$CuBr_2$ (ARGET)	179.8 ± 1.0	385.6 ± 1.4	2.14	1.19 ± 0.39	1.95 ± 0.27
Tap	$CuBr_2$ (ARGET)	187.2 ± 0.7	389.4 ± 0.6	2.08	0.91 ± 0.20	1.37 ± 0.21
DI	Copper wire (CuRP)	300.1 ± 19.3	416.2 ± 3.0	1.39	2.25 ± 0.23	4.26 ± 0.87
Tap	Copper wire (CuRP)	282.3 ± 4.9	428.6 ± 0.9	1.52	1.36 ± 0.04	2.00 ± 0.04

same degree of polymerization, N), we can relate grafting density to swelling ratio, for brushes of the same monomer structure:

$$\mathrm{SR} = \frac{h_{\mathrm{wet}}}{h_{\mathrm{dry}}} \propto \frac{N\sigma^0}{N\sigma^1} \propto \sigma^{-1}. \quad (5)$$

Therefore, differences in SR between samples of strong polyelectrolyte brushes with the same structure should provide a good estimate of the difference in σ, being inversely proportional to SR.

From Table 1 it is clear to see that polymerisations containing copper wire as a catalyst source (CuRP) led to lower SR and hence a higher grafting density being achieved than with ARGET. Further to this, water type has little influence on SR, further confirming that tap water is suitable for use as a solvent in these polymerizations. However, the use of copper wire as a catalyst leads to higher values of both R_a and R_q. The increase in roughness values may simply be due to the increase in overall brush thickness, with the roughness as a percentage of dry brush thickness being similar for all samples (~0.5%). It was noted that the use of a copper wire catalyst led to visibly less homogenous sample surfaces with variation in thin-film colours being seen across the silicon wafer, with samples grown using a $CuBr_2$ catalyst showing a uniform gold thin-film colour over each ~1 cm^2 sample.

3.2. Cu(0)-mediated radical polymerisation

Interestingly, during reactions it was observed that leaching of a red colour was seen from each end of the copper wire, presumed to be the dissolution of copper ions. The effect of both the length and number of exposed ends of copper wire on the growth over a 24-hour period was investigated (Fig. 2). Previous work by Magenau *et al.*,[20] investigated the effect of copper wire on reaction kinetics of methyl methacrylate (MMA) *via* ATRP, with rate dependent and increasing with surface area of copper wire, and thus copper catalyst concentration. However, copper wire was used with a small amount of $CuBr_2$ in this prior work, in order to gain better control of polydispersity and reaction kinetics, and the reaction was a solution polymerisation of MMA chains.

In our work, the length of copper wire is seen to have no significant effect on the swollen brush thickness (and so degree of polymerization) with a small increase in swelling ratio observed with wire length (Fig. 2A).

In order to change the number of exposed ends, a 10 cm length of copper wire was cut into equal sizes (*i.e.* 8 ends = 2.5 cm lengths). The exposed end area was calculated as the number of ends multiplied by πr^2 (r = 0.5 mm). Remarkably, with increasing exposed end area all growths produced brushes with near-identical wet thickness (~425 nm) suggesting near-identical molecular weight, while smoothly increasing dry thickness and so grafting density. Controlling grafting density independently of molecular weight is highly desirable in polymer brush fabrication, allowing surface properties to be more precisely tailored and investigated. The tuning of Cu(0) ion concentration, through the simple method of cutting wire into more pieces, is therefore a powerful tool for precise surface grafting.

It is likely that due to the increased exposed end area, more copper ions can dissolve at the beginning of the reaction, meaning more catalyst complex is present, allowing for a higher early rate of initiation. The polymerisation can therefore occur from more active initiator sites, increasing the grafting density. Previous studies on copper mediated ATRP of PMETAC brushes have shown that altering catalyst concentration allows for the control of grafting density.[39] Magenau *et al.*,[20] showed that increasing the surface area of copper wire as a catalyst source in the solution ATRP of MMA lead to increased initial reaction rates, agreeing with our results. It is likely that significant copper dissolution only occurs at the freshly-cut ends of the wire due to lack of a protective oxidised layer. This slow release of copper ions from the exposed ends allows for sensitive tuning of the initial reaction rate, thus allowing for increased initiation, and in turn increasing grafting density. To a first approximation, the degree of polymerisation in a surface-initiated controlled radical polymerisation should not depend on either initiator concentration or catalyst concentration, as observed in our experiments.

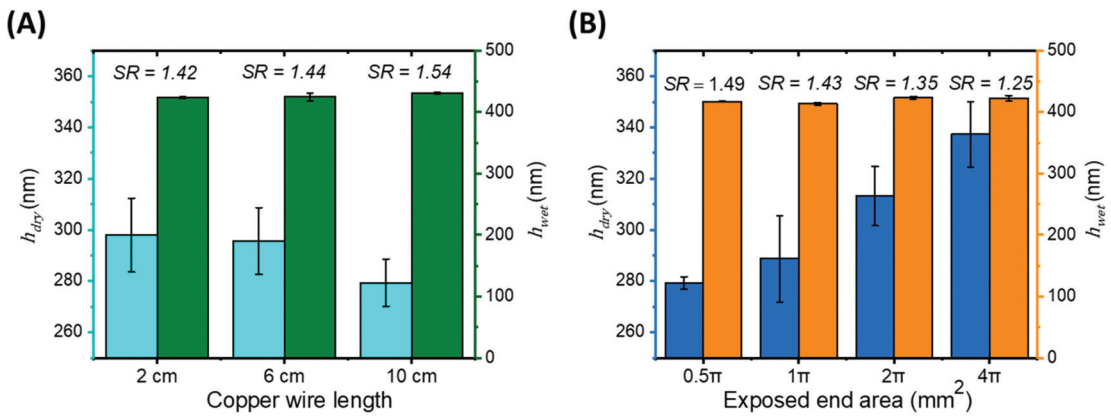

Fig. 2 The effect of both the (A) length of copper wire and (B) number of exposed ends of copper wire on the dry thickness (h_{dry}), wet thickness (h_{wet}) and swelling ratio (SR) of PMETAC brushes grown for 24 hours *via* CuRP in tap water.

3.3. Ambient atmosphere Cu(0)-mediated radical polymerisation

To further probe the robustness and sustainability of the CuRP system, polymerizations were carried out in ambient atmosphere with all deoxygenation steps removed. Commonly in Cu-catalysed polymerisations, an attempt to thoroughly deoxygenate the solution is made, and polymerisation is carried out under an inert atmosphere in order to improve polymerisation consistency and extent.[8,34,40] However deoxygenation procedures are costly, time consuming and rely on access to specialised equipment, such as Schlenk lines.[22]

Methods to reduce oxygen sensitivity and oxygen content within a reaction, such as the addition of a reducing agent,[16,41] the use of a glucose oxidase enzyme (GOx),[42] and limiting headspace,[22] have been employed to tackle this problem. To reduce the oxygen sensitivity of our procedure, excess ascorbic acid was added as an oxygen scavenger, due to it being low cost, easily-obtainable and non-toxic. The kinetics for reactions in both ambient and nitrogen atmospheres are shown in Fig. 3.

Over the 24-hour growth period, PMETAC brushes grew to a very similar thickness in both atmospheres, with no significant difference in dry thickness observed (Table 2). The swelling ratio was also identical, indicating the same grafting density was achieved.

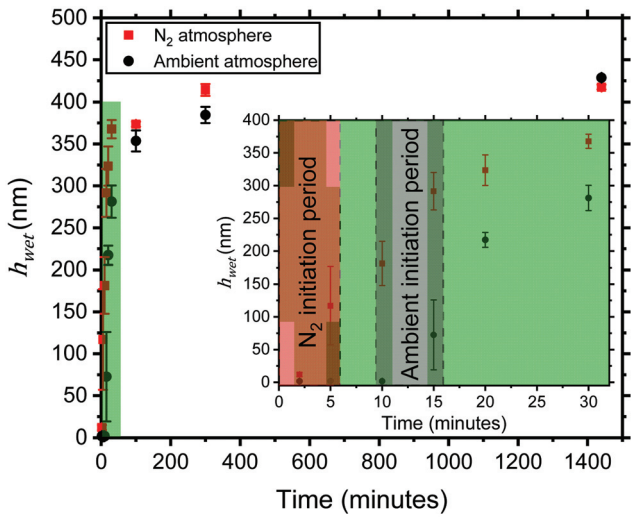

Fig. 3 A kinetics plot of PMETAC brushes grown *via* CuRP in both a nitrogen and ambient atmosphere in tap water using a coiled copper wire catalyst (l = 10 cm, d = 1 mm) for 24 hours. The inset shows the kinetics plot for PMETAC brushes grown in both atmospheres during the initial 30 minutes of CuRP.

During the polymerisation time, it was observed that the solution exposed to oxygen in ambient atmosphere became more viscous (ESI, Fig. S3†). It was also noted that an inhibition period was observed during the first 10 minutes of the reaction in ambient atmosphere (Fig. 3 inset), with little growth of PMETAC brushes observed. Both the increase in viscosity of the polymerisation solution and inhibition period are indicative of a secondary reaction in solution. ^{1}H NMR spectroscopy of the polymerisation solution from both atmospheres was carried out in order to identify a possible secondary polymerisation (Fig. 4).

A broad peak between 1.3 and 0.9 ppm was observed for samples from both atmospheres, indicative of a methacrylic backbone, consistent with previous literature.[43] Furthermore, spectra displayed other peaks corresponding to PMETAC chains in solution, assigned according to literature.[43] Although it is possible that the NMR spectra observed is due to chains de-grafting from the silicon surface rather than secondary polymerisation occurring in solution, the polymer concentration produced by degrafting is likely to be far below the sensitivity of NMR, even if complete degrafting is assumed.

Previous work by Reyhani *et al.*,[44] showed a method of initiating a RAFT polymerisation using a Fenton reaction. Fe^{2+} ions were used to generate hydroxyl radicals from hydrogen peroxide, allowing for initiation. They found that there was an induction period during which oxygen is preferentially consumed, followed by a well-controlled and rapid polymerisation.[45]

Although no H_2O_2 is present in, or added to, our reaction it is likely that the presence of Cu(I) ions can lead to hydroxyl radical production, from any oxygen and H_2O present.[15] This has been observed in previous literature, where a reaction between glucose, glucose oxidase and oxygen with Cu(I) species leading to the production of hydroxyl radicals, which acted as an initiating species.[46] It is important to note that our reactions contained a small amount of ascorbic acid. Previous studies have shown the formation of hydroxyl radicals and H_2O_2 from the oxidation of ascorbic acid by oxygen in copper catalysed reactions.[47,48] It is likely that a combination of these reactions is allowing for the formation of radicasl, and therefore, the initiation of the solution polymerisation.

To further validate that a secondary polymerisation was occurring and initiating from non-grafted species, CuRP reaction mixtures were made as above, and left for 24 hours without addition of an initiator-coated silicon wafer. If the polymerisation is surface-confined, no polymerization should occur, and the monomer solution should remain unchanged. ^{1}H NMR data can be found in the ESI (Fig. S4†). NMR shows a distinct peak between 1.3 and 0.9 ppm for both oxygenated

Table 2 Table to show the thickness, swelling ratio and roughness of PMETAC brush coating on silicon wafers grown *via* CuRP in tap water using a coiled copper wire catalyst (l = 10 cm, d = 1 mm) in both nitrogen and ambient atmosphere for 24 hours

Atmosphere	h_{dry} (nm)	h_{wet} (nm)	Swelling ratio (SR)	R_a (nm)	R_q (nm)
Nitrogen	282.3 ± 4.9	417.4 ± 2.9	1.52	1.36 ± 0.04	2.00 ± 0.04
Ambient	274.7 ± 8.1	428.6 ± 0.9	1.52	1.93 ± 0.67	2.56 ± 0.71

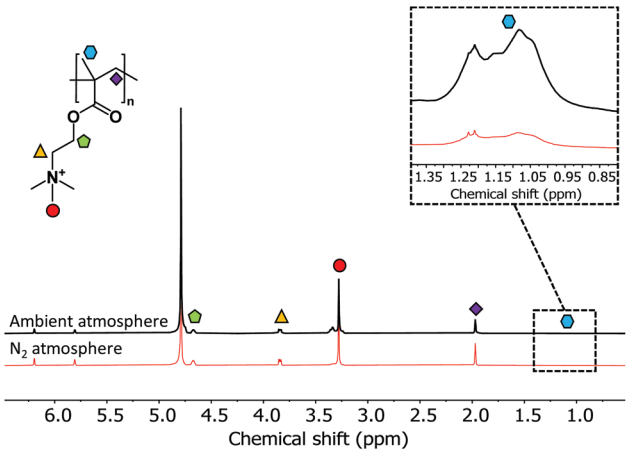

Fig. 4 ^{1}H NMR spectra taken for both METAC solution that was degassed and used under nitrogen pressure and solution that was not degassed and used in ambient conditions after 24 hours.

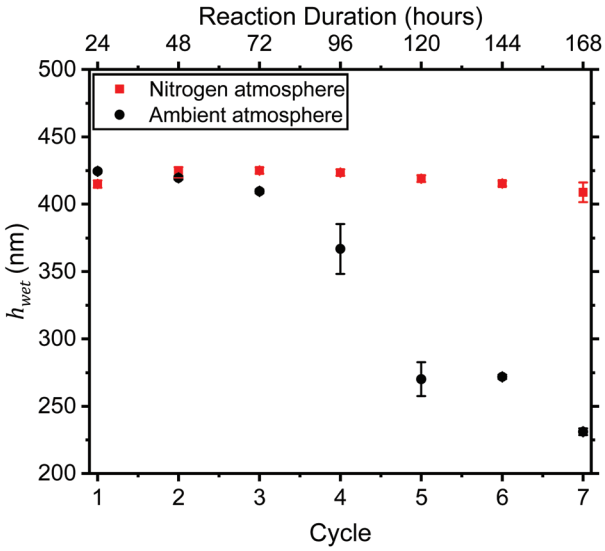

Fig. 5 The wet thickness (h_{wet}) of PMETAC brushes grown for 24 hours *via* Cu(0)-mediated radical polymerisation in nitrogen and ambient atmospheres in DI water using a 10 cm long copper wire catalyst cut into 8 equal pieces of 1.25 cm length with 16 exposed ends (d = 1 mm). After each 24 hours cycle the silicon wafer was removed and replaced with a new initiator functionalised silicon wafer.

and deoxygenated samples confirming that a secondary polymerisation is indeed occurring. Even for deoxygenated monomer solutions it is likely that a small amount of oxygen remains, with the NMR peaks present with much lower intensity. The growth of PMETAC brushes *via* CuRP in ambient conditions offers a robust route to the synthesis of thick PMETAC brushes, however, there may be implications for efficiency and repeatability due to secondary polymerisation in solution.

3.4. Multiple cycle Cu(0)-mediated radical polymerisation

To our knowledge, there are few literature examples of reusing monomer solution for repeated and/or continuous surface-initiated polymerisations cycles (see, for example Zhang *et al.*,[24]). After a surface-initiated polymerisation has been carried out, the remaining solution is usually disposed of immediately, regardless of its potential for use in another reaction and if any monomer remains. Since most surface-initiated polymerisations are carried out with a vast excess of monomer, it is likely that monomer remains. The potential for recycling solution and copper wire catalyst was assessed (Fig. 5). Each polymerization cycle was run for 24 hours, after which the functionalised wafer was removed, replaced with a new initiator-coated sample and left for another 24-hour period, for a total of 7 cycles. The results show clearly that monomer remains after for the duration of the experiment with a wet thickness of ~425 nm being grown for 7 consecutive cycles over a total of 168 hours in a nitrogen atmosphere. It is likely that this process could continue for more cycles, with little drop-off in grown thickness being seen. This result is beneficial for scale-up and high-throughput industrial application, drastically reducing waste amounts and increasing process efficiency compared to individual polymerisations. Furthermore, this result may pave the way for continuous processing (*e.g.* roll-to-roll).

For solution left in ambient conditions and not degassed, a clear drop in grown thickness is observed after the third cycle. By this time, as reported above, the viscosity of the solution had increased significantly. It is likely that either monomer had been consumed in a side Fenton reaction, and/or the resultant high viscosity has significantly affected reagent diffusion and so polymerization kinetics.

4. Conclusions

We have successfully functionalised silicon wafers with thick PMETAC brushes of water-swollen 425 nm thickness, *via* a more environmentally benign and sustainable Cu(0)-mediated radical polymerisation route that requires no added copper halide catalyst. We detail a system with a cheap and readily-available copper wire catalyst, which can easily be reused. The method was also carried out in tap water, extending previous research by Mendonça *et al.*,[8] to surface-initiated polymer brushes. Further, we have reused the solution over multiple cycles, significantly increasing the number of samples that can be prepared from the same amount of polymerisation solution, making this method of polymerisation highly material- and time-efficient. We demonstrate that our polymerizations work well in ambient conditions, drastically reducing the times involved with deoxygenating solution and the glassware required for polymerisation. However, it is important to note that a side Fenton-type is observed in the presence of oxygen, reducing the method's effectiveness over multiple cycles when in contact with oxygen. It is vital that our system is translated across to other monomer systems in order to help minimise the contribution of polymer chemistry to the environmental crisis and aid the growth of a true bio-economy that is currently strived for.

Conflicts of interest

There are no conflicts to declare.

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