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pH-Responsive Brush-Modified Silica Hybrids Synthesized by Surface-Initiated ARGET ATRP

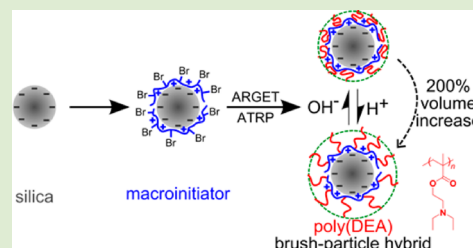
Benjamin T. Cheesman,[†] Joshua D. Willott,[†] Grant B. Webber,[†] Steve Edmondson,[‡] and Erica J. Wanless^{*,†}

[†]Priority Research Centre for Advanced Particle Processing and Transport, University of Newcastle, Callaghan, NSW 2308, Australia

[‡]Department of Materials, Loughborough University, Loughborough, LE11 3TU, United Kingdom

Supporting Information

ABSTRACT: Brush-modified silica hybrids have been synthesized by growing poly(2-(diethylamino)ethyl methacrylate) (poly(DEA)) brushes on 120 nm diameter silica particles by surface-initiated activators regenerated by electron transfer atom transfer radical polymerization (SI-ARGET ATRP). This is the first report of using SI-ARGET ATRP to synthesize poly(DEA) brushes. The kinetics of poly(DEA) brush growth in 4:1 v/v ethanol/water was monitored. The hydrodynamic diameter of the resulting brush-modified particles was dependent on the solution pH due to the weak polybasic nature of the brushes. Below the pK_a of poly(DEA), the hydrodynamic diameter of the brush-modified particles increased with decreasing pH as a consequence of brush protonation, rearrangement and solvent uptake. This pH-response of the brushes was reversible and the hybrid particles exhibited significant hydrodynamic volume changes of up to 200% when the solution pH was cycled from pH 7 to pH 4.



Polymer brushes, formed by end-tethering polymers to an interface have shown great promise in a growing number of applications including tertiary oil recovery.¹ Brush-modified solid surfaces can be designed to respond reversibly to external stimuli² such as temperature,^{3–7} solvent,^{8–10} pH,^{11–15} and electric fields.^{16,17} Surface-initiated polymerization (SIP), a “grafting from” approach, is often used to create well-controlled, densely grafted polymer brushes, which are unavailable by a “grafting to” approach due to the kinetic, steric, and entropic limitations associated with the latter technique.^{18,19} Surface-initiated atom transfer radical polymerization (SI-ATRP) has been extensively used for polymer brush growth, typically from planar oxidized silicon wafer substrates, using a variety of monomers.^{14,20,21}

Surface modification of particles can be used to dramatically improve colloidal stability through alteration of the particle surface charge, hydrophobicity or degree of steric stabilization.^{22–25} One such route to surface modification is to add a polymer brush to the particle, creating a brush-modified hybrid particle. Recently Ponnappati et al. found low concentrations of such a polyethylene oxide-silica nanocomposite to be effective at mobilizing residual oil in a porous sandstone as the dispersions were able to transport without adhering through the porous medium.¹ Modification of 300 nm silica particles with short weak polybasic polymer brushes has been shown to produce electrosterically stabilized particles below their isoelectric point (IEP) of around pH 8, representing a significant shift in the IEP (from approximately pH 2.1 for the unmodified silica particles) with only moderate addition of polymer (≤ 1 wt %).²³ Silica sols (120 nm) modified with longer weak polybasic brushes (13 wt %) exhibited a significant pH-response.

Decreasing the pH below the pK_a of the polymer resulted in an increase of approximately 50% in the particle hydrodynamic diameter due to polyelectrolyte protonation and swelling.²⁴

Activators regenerated by electron transfer (ARGET) ATRP is a recent ATRP variant, which uses reducing agents such as ascorbic acid or tin(II) 2-ethylhexanoate to generate the oxygen-sensitive Cu(I) catalyst species in situ from the Cu(II) deactivator.^{26,27} As the reducing agent is present in excess, it also imparts a degree of oxygen tolerance to the reaction. Consequently, less stringent conditions are required, and in comparison to conventional ATRP, ARGET ATRP uses significantly reduced copper catalyst concentration (down to ppm levels).^{26,27} As the concentration of the copper catalyst is lower, so too is the requirement for often difficult catalyst removal from ARGET ATRP products, making it a potentially more industrially attractive technique.^{26–29}

While SI-ATRP has been used frequently, there have been relatively few reports of using SI-ARGET ATRP to grow polymer brushes. The monomers investigated to date have been largely limited to hydrophobic or nonresponsive examples, such as methyl methacrylate or 2-hydroxyethyl methacrylate,^{27,30–34} with only a handful of reports of responsive monomers.^{35–37} Many of these ARGET ATRP polymer brush growth reactions are carried out in aprotic solvents such as anisole,^{27,30,31,35,36} although protic solvents and even water have been used.^{32,33} The most common protic solvents are alcohols, and methanol is often used. Ethanol,

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however, is a less hazardous and more environmentally benign alternative that has received little attention in the literature.

Weak polybasic polymer brushes of tertiary amine methacrylate monomers exhibit pH-responsive behavior. Frequently the tertiary amine methacrylate monomer of choice has been 2-(dimethylamino)ethyl methacrylate (DMA).^{21,23,24,37} Poly(DMA) brushes have been grown by SI-ARGET-ATRP producing brush-modified surfaces with pH-dependent wettability and pH-dependent adsorption of weakly charged particles.³⁷ However, 2-(diethylamino)ethyl methacrylate (DEA) is a cheaper alternative,^{14,38} with a similar pK_a to DMA³⁹ that has received less attention owing to its increased hydrophobicity and limited solubility in aqueous solvents above pH 7. The synthesis of free poly(DEA) by ARGET ATRP has recently been reported,⁴⁰ but to the best of our knowledge, SI-ARGET ATRP of DEA has yet to be demonstrated.

In the present work, the surface of a silica particle was functionalized with initiator moieties by adsorption of a cationic poly[2-(dimethylamino)ethyl methacrylate-*co*-glycerol monomethacrylate]-based water-soluble macroinitiator, similar to that reported previously by Fielding et al. (see Supporting Information, Figure S1).¹⁴ Using a macroinitiator removes the need to synthesize halogen-containing silane species and subsequent functionalization of the silica surface which often requires at least one stringently water-free step.⁴¹ The use of a macroinitiator results in a polymer brush that is electrostatically attached to the silica surface, as opposed to being covalently bonded as in the case with silane initiators; however, the electrostatic interaction is sufficiently strong to support a number of brush swelling and collapse cycles.¹⁴ The macroinitiator used in this work had a higher ratio of positively charged binding sites to halogenated initiator sites than that used by Fielding et al. and, therefore, is expected to yield even more robust brushes. To minimize bridging flocculation, the macroinitiator molecular weight was relatively low.

The as-received silica had a scanning electron microscopy (SEM) diameter of 120 ± 7 nm and a hydrodynamic diameter of 124 ± 4 nm by dynamic light scattering (DLS). After adsorption, macroinitiator-modified silica was isolated from free macroinitiator by several wash cycles of centrifugation and redispersion in water. The macroinitiator adsorbed amount was estimated by thermogravimetric analysis (TGA) to be less than 1 wt % of the macroinitiator-modified silica, which equates to a maximum surface excess of 0.4 mg/m² based on the silica particle SEM diameter and density (1.9 g/cm³). Subsequently, poly(DEA) brushes were grown on the macroinitiator-modified silica particles by ARGET-ATRP using 2,2'-bipyridine (bpy) and ascorbic acid as ligand and reducing agent, respectively. The tertiary amine groups in the DEA monomer may possess some intrinsic reducing ability, as has been reported previously for DMA,³⁶ however, for the purposes of this study, the external reducing agent was included in accordance with most ARGET ATRP protocols in literature. Monomer and solvents were deoxygenated before use and polymerizations were carried out in 4:1 ethanol/water (by volume) at room temperature with an initial DEA/CuBr₂/bpy/ascorbic acid molar ratio of 2500:1:10:10.³³ Samples were withdrawn at specific intervals, and the brush-modified particles were washed by successive redispersion and centrifugation cycles before analysis. Further synthetic details are provided in the Supporting Information.

The growth of poly(DEA) brushes was confirmed by the infrared spectra of the resulting brush-modified particles, shown in Figure 1. The spectra show an increasing contribution from

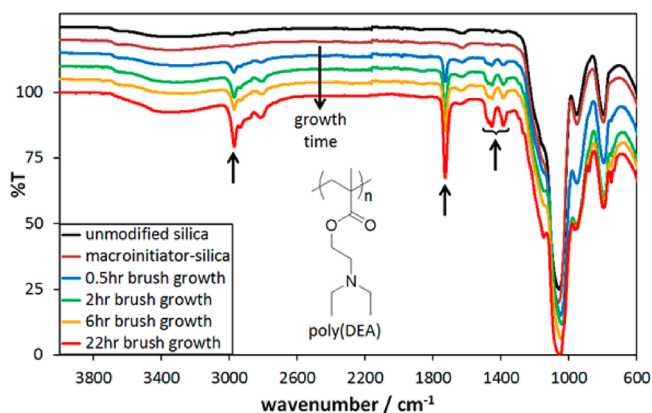


Figure 1. Infrared spectra of the unmodified silica, macroinitiator-modified silica, and poly(DEA) brush-modified silica particles showing the growth of peaks from the poly(DEA) brush as a function of time. Data have been vertically offset for clarity.

poly(DEA) with longer brush growth time, seen by evolution of peaks around 1400, 1730, and 2980 cm⁻¹, which are not present in the spectra of either the unmodified or macroinitiator-modified silica. These peaks are assigned to the C–N, C=O, and C–H bonds of the polymer brush, respectively.

Figure 2 shows SEM images of the brush-particle hybrids which exhibit a distinct change in the dried morphology with increasing growth time. The unmodified silica is shown in Figure 2a. For short brush growth times, the images are consistent with a thin brush coating (Figure 2b), whereas particles modified with brushes grown for longer times show amorphous polymer containing embedded particles (Figure 2c). The amorphous nature of the dried polymer with longer growth times is due to the low glass transition temperature (T_g) of poly(DEA), allowing intermixing of the polymer chains from neighboring brush-modified particles when there is sufficient polymer to form a film between the core silica particles upon drying.⁴² However, it should be noted that all polymer–particle hybrids could be dispersed in aqueous solution as single particles, irrespective of polymer brush growth time.

TGA and DLS measurements demonstrated a sustained increase in the polymer content and Stokes diameter of the brush-modified particles with longer polymerization times, as shown in Figure 3. Brush growth proceeded rapidly in the early stages of the polymerization, producing a hybrid particle containing 19 wt % polymer (as determined by TGA) after just 30 min growth, which steadily increased to 46 wt % after 22 h growth. These polymer compositions correspond to geometrically calculated dry brush thicknesses of 6 and 12 nm for 30 min and 22 h growth times, respectively. When dispersed in ethanol, a good solvent for poly(DEA), the profile of the Stokes diameter as a function of growth time followed a similar trend to the TGA data. In both data a fast initial growth is evident, followed by sustained growth over 22 h albeit at a slower rate. This nonlinear kinetic profile is indicative of either the reaction deviating from living character (i.e., chain termination occurring) or catalyst deactivation.⁴³ However, another factor that may contribute to the nonlinear kinetics observed in Figure 3 would be the effect of the increasing volume available for chains to occupy as the distance from the particle surface increases, as has been observed experimentally.⁴⁴ That is to say, as the chains extend further from the curved silica interface, the steric hindrance between chains decreases, allowing individual chains to adopt a more coiled conformation. For this reason,

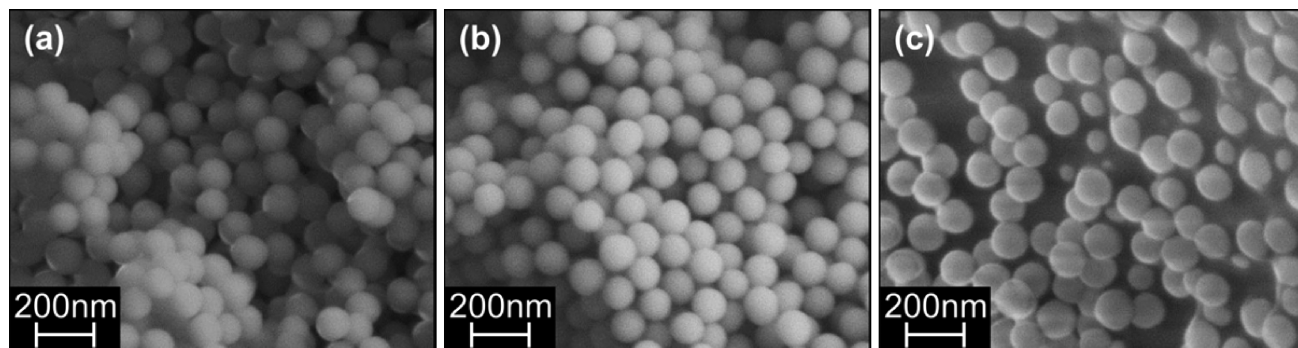


Figure 2. Scanning electron micrographs of (a) the unmodified 120 nm silica particles, and hybrid particles grown for (b) 0.5 h (19 wt % polymer) and (c) 22 h (46 wt % polymer). The image in (b) is consistent with discrete hybrid particles with only a thin shell of polymer, while the hybrid particles in (c) contain sufficient polymer to form a film between the core silica particles.

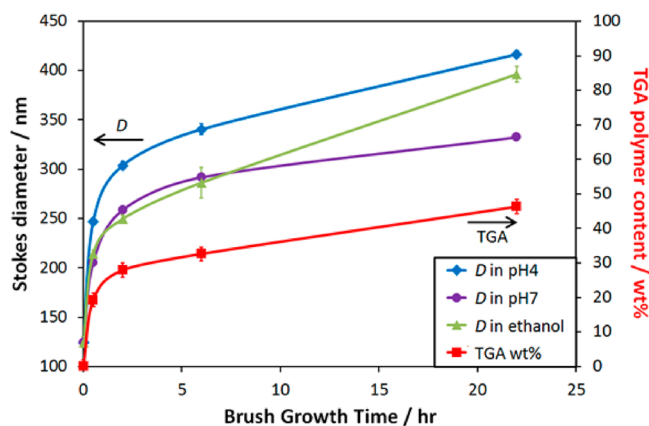


Figure 3. Evolution of the Stokes diameter (measured by DLS) and TGA polymer content of poly(DEA) brush-modified particles as a function of brush growth time. Error bars are shown on all data, although some are smaller than the symbol size.

even a perfectly living polymerization would show curvature in a growth kinetics plot in the form of Figure 3.

The hydrodynamic diameters of the brush-modified particles grown for short times were similar in both neutral (pH 7) aqueous solution and when dispersed in ethanol. This indicates that the brush is equally solvated in pH 7 aqueous solution as in ethanol. This equivalent solvation is reasonable considering the pK_a of 7.3 for free poly(DEA),³⁹ so that at pH 7 more than half the tertiary amine groups are protonated, giving good solubility. Ellipsometry measurements of similar brushes grown on planar silica surfaces indicate the brush layer contains around 15% polymer and 85% solvent in pH 7 aqueous solution, calculated by fitting the refractive index of the swollen layer.

Over the pH range investigated, the hydrodynamic diameters of the brush-particle hybrids were greatest at pH 4 for all polymer thicknesses (see Figure 3). This is due to the polybasic nature of the poly(DEA) brushes, which become more protonated in more acidic environments. The resulting electrostatic repulsion between neighboring charged chains and associated counterion osmotic pressure forces them into an extended conformation, which is observed as an increased hydrodynamic diameter.⁴⁵

The ratio of the wet (pH 4)/dry brush thickness was relatively constant and independent of polymerization time, maintaining a value of 9.2 ± 0.5 for the growth times studied. This suggests that there is not a dramatic decrease in chain density toward the outside of the brush layer, which might be

expected if there was high dispersity resulting from a large amount of termination. For the same unswollen layer thickness reported by TGA, it is likely that a disperse brush would show a greater degree of swelling because the steric constraint in the outermost (longest) chains in the wet state is reduced, allowing greater stretching when solvated.^{46,47} However, the effect of dispersity and consequent brush profiles on the hydrodynamic diameter observed by DLS may be complex, so care should be exercised in interpreting these swelling results. We believe, however, that it is indirect evidence for a low termination rate during the polymerization, suggesting that the decrease in polymerization rate with time may be in part due to other factors such as catalyst deactivation.

The poly(DEA) brush-modified particles demonstrate typical pH-responsive polybasic behavior, as shown in Figure 4. The

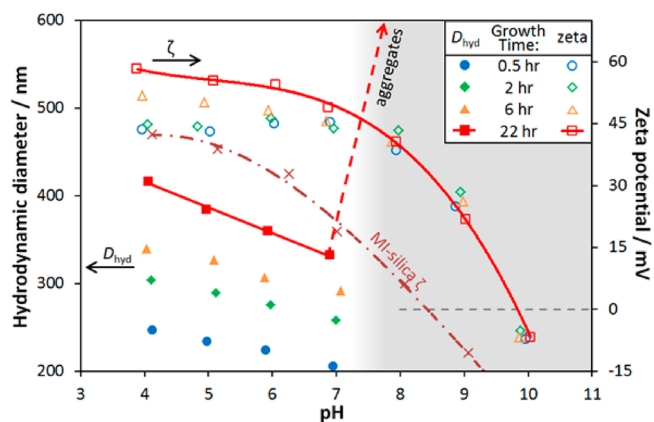


Figure 4. Hydrodynamic diameter and zeta potential of poly(DEA) brush-modified particles as a function of pH. The shaded area denotes hybrid particle aggregation, the cross symbols and chained line are the zeta potential of the macroinitiator-modified silica (MI-silica). The hydrodynamic diameters of the unmodified silica and MI-silica were 124 ± 4 and 126 ± 3 nm, respectively.

hydrodynamic diameter of the brush-modified particles steadily decreased as the pH increased from pH 4 to pH 7. Between pH 7 and 8 the brush-modified particles became colloiddally unstable and aggregation was observed, concordant with the pK_a of free poly(DEA)³⁹ and the poor aqueous solubility of poly(DEA) above this value.⁴⁸ It is interesting to note that the particles aggregated at pH 8 while they were still significantly charged ($\sim +40$ mV), suggesting the aggregation was driven by the hydrophobicity of poly(DEA).⁴⁹

The unmodified silica was negatively charged over the pH range studied as expected,⁵⁰ and adsorption of the macro-initiator reversed the charge on the particles to +40 mV at pH 4 with an IEP of pH 8.4. As shown in Figure 4, the brush-modified particles were more positively charged than the macroinitiator-modified particles over the studied range reaching an IEP just below pH 10. This is expected behavior given that poly(DEA) is a weak polybase. Below the pK_a of poly(DEA) the charge on the brush-modified particles was greater in magnitude for longer growth times, ranging from +44 mV for 0.5 h growth to +58 mV for 22 h growth at pH 4. This trend is thought to be due to increasing surface charge density with growth time, and the existence of an IEP indicates the underlying silica surface charge is detected through the unprotonated brush.

The pH-response of the brush-modified particles was seen to be robust and highly reversible when the pH was cycled between pH 4 and 7, shown in Figure 5. Each of the brush-

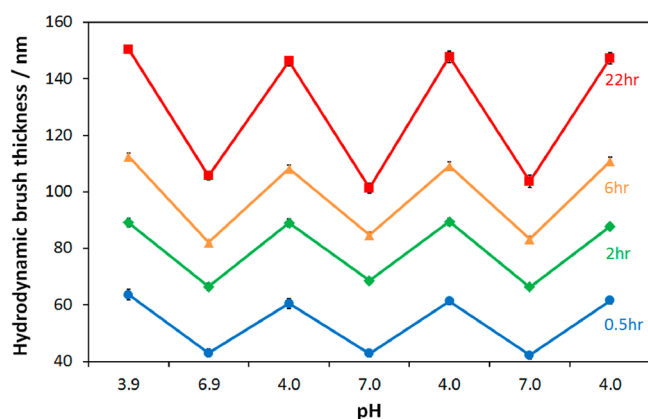


Figure 5. Hydrodynamic brush thicknesses of poly(DEA) brush-modified particles as the pH was cycled between 4 and 7.

modified particles exhibited a substantial volume increase upon further protonation of the poly(DEA) chains below pH 7. For example, using the pH 7 average as a baseline particle volume, the particle modified with a brush grown for 0.5 h increased in volume by 164% upon swelling in acidic solution at pH 4. The brush-modified particle grown for 22 h exhibited the largest volumetric swelling of 200% at pH 4 compared to pH 7. All of the volumetric swelling shown in Figure 5 are significantly greater than the approximately 50% volume increase previously reported by Chen et al. for silica particles modified with poly(2-(dimethylamino)ethyl methacrylate) brushes.²⁴ In the next stage of our research we intend to harness this considerable pH-response through investigation of the rheological properties of brush-modified particle suspensions. The ability to rapidly double the hydrodynamic volume of the modified particle by application of a pH switch is an attractive prospect, given that the high shear relative viscosity of a particulate suspension increases exponentially with volume fraction in the Krieger–Dougherty equation.⁵¹

In conclusion, pH-responsive brush-modified particles have been produced by growing poly(DEA) brushes on 120 nm silica particles by surface-initiated ARGET ATRP. This is thought to be the first report of using SI-ARGET ATRP to grow poly(DEA) brushes. The hydrodynamic diameter and zeta-potential of the brush-modified particles has been shown to be pH-dependent; below the pK_a of poly(DEA) the

hydrodynamic diameter increased with decreasing pH due to the weak polybasic nature of the brushes. This pH-response is reversible and the modified particles exhibit volume changes of up to 200% when the solution pH was changed from pH 7 to pH 4. Thus, we provide proof-of-concept hybrid particles for deployment as in situ rheology modifying agents.

■ ASSOCIATED CONTENT

§ Supporting Information

Materials, instrumentation, and experimental conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: erica.wanless@newcastle.edu.au.

Notes

The authors declare no competing financial interest.

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