



The role of copolymer composition on the specific ion and thermo-response of ethylene glycol-based brushes

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ARTICLE INFO

Article history:

Received 7 December 2017

Received in revised form

15 January 2018

Accepted 19 January 2018

Keywords:

Thermoresponsive polymer

Poly oligo(ethylene glycol methacrylate)

Specific ion effect

ABSTRACT

Thermoresponsive ethylene glycol based comb-polymer brushes were studied as a function of copolymer composition in aqueous electrolyte solutions. Homopolymer poly oligo(ethylene glycol) methyl ether methacrylate (POEGMA₃₀₀) and statistical copolymer brushes with 60 mol% OEGMA₃₀₀ and 40 mol% (di(ethyleneglycol) methyl ether methacrylate) (MEO₂MA) underwent a monotonic swollen to collapsed transition with increasing temperature. Neutron reflectometry and ellipsometry measurements showed that the higher ethylene glycol content of the homopolymer brush led to a higher degree of swelling for a given temperature, with the transition occurring over a wider temperature range than the copolymer brush. Dynamic atomic force microscopy force measurements revealed minimal impact of probe velocity on normal interaction forces for the homopolymer brush. In contrast, a significant increase in both repulsion and adhesion was observed for the copolymer brush. Exposure to potassium thiocyanate solutions increased the degree of swelling at any given temperature while potassium acetate showed the opposite behaviour for both brush compositions. However, the homopolymer brushes displayed a greater increase in swelling due to thiocyanate and reduced collapse due to acetate.

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1. Introduction

Thermoresponsive polymers that undergo significant changes in physicochemical properties over a narrow temperature range form the basis of a large number of smart materials [1]. An emerging alternative to the most studied thermoresponsive polymer, poly(*N*-isopropylacrylamide) (PNIPAM), are the poly oligo(ethylene glycol) methyl ether methacrylates (POEGMAs), Fig. 1a [2]. Their lower critical solution temperature (LCST) is controlled by the average number of hydrophilic ethylene glycol side chain units (*n*) with values between 28 and 90 °C reported for *n*=2 and *n*~8.5 respectively. Copolymerisation of monomers with different side chain length allows the LCST to be tuned within this range.

Furthermore, POEGMAs do not exhibit the cytotoxicity or swelling hysteresis of PNIPAM [2]. These polymers have been utilised in a range of materials including bioconjugates, microgels and polymeric nanoparticles [3]. Thermoresponsive interfaces may be formed by densely end grafting POEGMAs to existing surfaces to form a polymer brush, Fig. 1b. A grafting from approach, where chains are polymerised directly from the surfaces, has previously been used to form thermo-switchable cell culture substrates [4], membranes [5] and chromatography supports [6].

Physical characterisation techniques provide a useful complement to biological studies with the molecular weight (MW), grafting density, composition, adhesion and surface hydrophilicity being linked to adsorption of proteins and cells [7–11]. The physical characteristics of POEGMA brushes in aqueous solution have previously been investigated using ellipsometry [12,13], atomic force microscopy (AFM) [11,13–17], contact angle [7–10,12,18,19], quartz crystal microbalance with dissipation monitoring (QCM-D) [18] and neutron reflectometry (NR) measurements [13,20].

Unlike the sharp LCST transition of free polymer chains, the degree of swelling of POEGMA brushes decrease gradually over a

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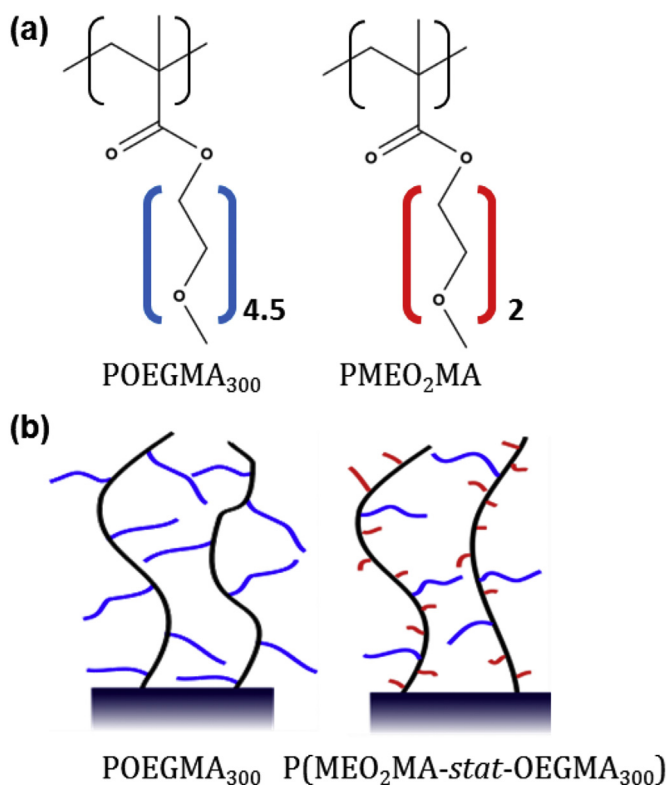


Fig. 1. (a) Members of POEGMA family used in this study. (b) Schematic representation of comb polymer brushes formed from POEGMA (co)polymers. Longer chain POEGMAs are commonly identified by the average molecular weight of the monomer; for example OEGMA₃₀₀ corresponds to $M_n = 300 \text{ g mol}^{-1}$.

wide temperature range, typically greater than 20°C [12,13,18]. The transitions of POEGMA brushes occur over a wider temperature range than PNIPAM brushes of the same grafting density, which is likely due to the absence of intramolecular hydrogen bonding in POEGMAs [13,21]. A broad transition is expected from self-consistent field theory as the brush undergoes cooperative conformational transition with decreasing solvent quality [22] (i.e. increasing temperature), which has been observed experimentally by NR on a poly(di(ethyleneglycol) methyl ether methacrylate) (PMEOMA, $n = 2$) brush [13]. Note that even a POEGMA₄₇₅ ($n = 8.5$, monomer $M_n = 475 \text{ g mol}^{-1}$) brush with a nominal LCST of 90°C displays a gradual collapse between at least 15 and 70°C [12]. However, techniques sensitive to the periphery of the brush such as contact angle [12,18] and AFM normal adhesion measurements [14–16] detect a sharper transition that occurs at a higher temperature relative to the bulk brush behaviour which is consistent with a bottom-up collapse [23]. Similar to free polymer chains, increasing the average ethylene glycol content will shift the thermoresponse to higher temperatures [18–20]. Composition also plays a significant role in performance of cell culture substrates with the relatively hydrophobic homopolymer PMEOMA showing limited temperature-dependent cell detachment below the LCST while copolymerisation with OEGMA₄₇₅ up to at least 8 mol% facilitates both attachment and detachment [8]. However, it has also been reported that copolymerisation with 5 mol% of OEGMA₄₇₅ is sufficient to have minimal protein adhesion at all temperatures [20].

The addition of salt is known to affect the LCST of both neutral and charged thermoresponsive polymers and therefore physical measurements of POEGMA based materials are often conducted in physiological buffer solutions [20,24,25]. These studies exhibit

salting out behaviour, i.e. lowering of the LCST by $\sim 3\text{--}4^\circ\text{C}$ relative to pure water [25]. The salting out effect may be understood through a larger body of work investigating specific ion effects on thermoresponsive polymers [26–28]. Specific ion effects include any phenomenon that is dependent on the identity of the ions present and are widely observed such as in bubble-bubble coalescence, solubility of proteins and the surface tension of the air-water interface [29]. In general strongly hydrated, hard anions are found to decrease the LCST, while softer and weakly hydrated anions raise the LCST around physiological concentrations [26]. This leads to a decrease or increase in the degree of swelling at any given temperature of the relatively broad transition of thermoresponsive polymer brushes [13,21,30,31]. The magnitude of increase or decrease in LCST is dependent on the degree of accumulation or exclusion of ions from the polymer surface [28]. Magnusson et al. hypothesised that the high interfacial structuring of the ethylene glycol side chains led to stronger salt effects for ungrafted POEGMA copolymers relative to PNIPAM [27]. We have previously reported an enhanced specific ion response of PMEOMA brushes relative to PNIPAM brushes in potassium acetate and thiocyanate solutions [13]. This was particularly evident for potassium thiocyanate, where the increase in the transition temperature at 250 mM being five times greater than for a PNIPAM brush of comparable thickness and grafting density.

This study builds on our previous work on PMEOMA ($n = 2$, LCST $\sim 28^\circ\text{C}$) to study how the composition of brushes from the POEGMA family affects both their thermoresponse and response to added ions [13]. The most hydrophilic brushes studied were homopolymer POEGMA₃₀₀ ($n = 4.5$, monomer $M_n = 300 \text{ g mol}^{-1}$) with a reported LCST of $\sim 65^\circ\text{C}$ for ungrafted chains [25]. Statistical copolymer brushes composed of 60 mol% MEO₂MA and 40 mol% OEGMA₃₀₀ (P(MEO₂MA-*stat*-OEGMA₃₀₀)), average $n = 3$) afforded brushes with an intermediate reported LCST of $\sim 45^\circ\text{C}$ [25]. Using a combination of ellipsometry, NR and AFM measurements on $\sim 175 \pm 35 \text{ \AA}$ dry thickness brushes it will be shown that higher concentrations of potassium thiocyanate lead to a greater degree of swelling of the brushes at any given temperature, while potassium acetate shows the opposite effect. Composition was found to have a significant effect on the relative magnitude of the salt response whereby increasing the average side chain length led to a greater impact of added thiocyanate and a reduced impact of acetate.

2. Experimental

2.1. Materials

Native oxide silicon wafers ($\sim 1 \text{ mm}$ thick) for ellipsometry and AFM and (10 mm thick, 100 mm diameter) for NR measurements were purchased from Silicon Valley Microelectronics (USA) and EL-CAT Inc. (USA) respectively. Surface functionalisation reagents potassium hydroxide (Chem-Supply Pty Ltd, AR grade), triethylamine (Eth₃N, Sigma-Aldrich, 99%) and (3-aminopropyl)triethoxysilane (APTES, Sigma-Aldrich > 99%) were used as received. Tetrahydrofuran (THF, Honeywell Burdick and Jackson, >99%) was dried over 4 Å molecular sieves (ACROS Organics) prior to use. Polymerisation reagents copper(II) bromide (CuBr₂, 99.999%), 2,2' bipyridine (bipy, $\geq 99\%$) and sodium L-ascorbate (>98%) were purchased from Sigma Aldrich and used as received. Monomers 2-(2-methoxyethoxy)ethyl methacrylate (MEO₂MA, Sigma-Aldrich, 95%) and oligo(ethylene glycol) methyl ether methacrylate (OEGMA₃₀₀, Sigma-Aldrich, 95%) were gravity fed through a 10 cm long, 2 cm diameter alumina column (activated, basic) to remove the 100 ppm hydroquinone monomethyl ether and 300 ppm butylated hydroxytoluene inhibitors immediately prior to synthesis. Methanol (Sigma Aldrich, anhydrous, 99.8%) was used as received. Electrolyte

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