Interplay of Composition, pH, and Temperature on the Conformation of Multi-stimulus-responsive Copolymer Brushes: Comparison of Experiment and Theory

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ABSTRACT: Poly(2-(2-methoxyethoxy)ethyl methacrylate) (PMEO₂MA), a thermoresponsive polymer with a lower critical solution temperature of ~28 °C, and poly(2-(diethylamino)ethyl methacrylate) (PDEA), a weak polyelectrolyte with an apparent pKₐ of ~7.5, have been statistically copolymerized using activators continuously regenerated via electron transfer atom transfer radical polymerization to form multi-stimulus-responsive polymer brushes. The stimulus-responsive behavior of these brushes has been investigated with ellipsometry and numerical self-consistent field (nSCF) theory. The pH- and thermoresponsive behaviors of a PDEA homopolymer brush were investigated experimentally in order to benchmark the nSCF theory calculations. nSCF theory was able to reproduce the responsive behavior of PDEA and PMEO₂MA homopolymer brushes. Three copolymer compositions (90:10, 70:30, and 50:50 mol % ME₂O₂MA:DEA) were investigated experimentally with pH ramps performed at low and high temperatures and temperature ramps performed at low and high pH. A broader range of compositions were investigated with nSCF theory and compared to the experimental results, with the nSCF calculations able to capture the general behavior of the homopolymer and copolymer brushes. The responsive behavior of each brush to a given stimulus (temperature or pH) was dependent on both the polymer composition and environment (temperature or pH). The influence of pH on the brush increased with higher DEA mol % with a copolymer brush response transitioning from temperature-dominant to pH-dominant. The temperature response of PMEO₂MA was completely masked at low and high pH values by the presence of at least 30 mol % polyelectrolyte in the copolymer.

INTRODUCTION

Stimulus-responsive macromolecules are ubiquitous in nature and are of particular interest for industrial and biomedical applications.¹,² A push toward synthetic polymers with properties that can be modified by the application of two or more stimuli has occurred in recent years because of their increased versatility and usage, particularly for medical applications such as cancer treatment.¹⁻⁶ Polymers of this nature are particularly attractive for biomedical applications where a variety of responses is advantageous as they are able to mimic multi-stimulus-responsive proteins and other biochemical molecules.⁷⁻⁻⁹ Grafting these polymers from a surface in a brush regime allows for the manufacture of responsive coatings with controllable interfacial properties.¹⁰,¹¹

Some homopolymers exhibit multi-stimulus-responsive behavior such as poly(2-(diethylamino)ethyl methacrylate) (PDEA), a weak polyelectrolyte, which exhibits pH-dependent thermoresponsive behavior.¹²,¹³ Thavanesan et al. investigated the thermoresponfive of a free PDEA polymer as a function of pH.¹² Although PDEA was insoluble in its uncharged state (pH > 7.5), there was a near linear increase in its lower critical solution temperature (LCST) when the pH was decreased below its apparent pKₐ and the polymer reached a maximum charged state.¹⁴ At pH < 6.5, where PDEA is considerably charged, its LCST was >70 °C. Copolymerization of different monomers can allow for a richer suite of responsive behaviors. In fact, through the combination of different monomers in different ratios and architectures, a wide variety of responsive copolymers with unique behaviors and properties can be synthesized. The reader is directed to a number of recent reviews covering the cornucopia of multi-stimulus-responsive copolymers including brushes.¹⁻⁻¹⁵⁻⁻¹⁷ A number of examples of multi-stimulus-responsive polymers are exemplified below to give direct context to the work presented here. The reader is further directed to a number of relevant multi-stimulus-responsive copolymer examples which are not discussed for brevity.¹⁵⁻⁻¹⁷

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Herein, an investigation into the synthesis and physical characterization of poly(2-(2-methoxyethoxy)ethyl methacrylate-stat-2-(diethylamino)ethyl methacrylate) (P(MEO2MA-stat-DEA)) brushes is presented. The chemical structure of homopolymer poly(2-(2-methoxyethoxy)ethyl methacrylate) (PMEO2MA) and PDEA is shown in Figure 1a. PMEO2MA is part of the poly(ethylene glycol)methylether methacrylate family of thermoresponsive polymers which vary in the length of their ethylene glycol sidechain \(^{16,17}\) and undergoes a first-order phase separation as the temperature is increased above its LCST of \(\sim 28^\circ C\) in aqueous solution. When end-tethered in a brush regime, the narrow LCST is broadened into a thermotransition which occurs over a large temperature range.\(^{18}\) The thermoresponse of PMEO2MA is independent of pH.

The interactions that govern the conformation of brushes are typically stronger for polyelectrolytes compared to neutral polymers because of their Coulombic origins. As such, the contribution of the neutral thermoresponsive polymers to the behavior of multi-stimulus-responsive copolymers is limited at only relatively low polyelectrolyte contents. Laloyaux et al. investigated the thermo- and pH-responsive behavior of poly(2-(2-methoxyethoxy)ethyl methacrylate)-stat-methacrylic acid (P(MEO2MA-stat-MAA)) copolymer brushes at a variety of compositions.\(^{19}\) They described the copolymers as either pH-modulated, thermoresponsive or temperature-modulated, pH-responsive brush. Interestingly, they observed that thermoresponsive behavior was not observed within their measured temperature range at only 14 mol % MAA. The hydrophobicity of the polyelectrolyte component in the pH- and thermoresponsive copolymers influences the composition at which the thermoresponsive properties are no longer observed.\(^{20}\) Lu et al. found that the thermoresponsive properties of PNIPAM were retained at lower mole fractions of NIPAM when copolymerized with a more hydrophobic weak polyelectrolyte monomer.\(^{20}\)

PMEO2MA and PDEA homopolymer brushes, as well as three compositions of P(MEO2MA-stat-PDEA) (PMEO2MA/PDEA 90:10, 70:30, and 50:50 mol %) multi-stimulus-responsive brushes, have been characterized herein. The copolymerization of MEPO2MA and DEA was achieved using surface-initiated activators continuously regenerated via electron transfer atom transfer radical polymerization (ARGET ATRP), and the brush thickness as a function of temperature and pH was measured with ellipsometry. Numerical self-consistent field (nSCF) theory gave monomer volume fraction profiles (among other quantities) as a function of temperature (effective monomer-water Flory Huggins parameters) and pH (concentration of H\(_3O^+\) ions) at a greater number of copolymer compositions and comparison to the ellipsometry measurements is made. A summary of the behavior of PDEA and PMEO2MA homopolymer brushes is illustrated in Figure 1b; these behaviors form the basis for the interpretation of copolymer response.

## MATERIALS AND METHODS

### Materials

Silicon wafers with a native oxide layer (Silicon Valley Microelectronics, USA) were used for ellipsometry experiments. 3-Aminopropyltriethoxysilane (>99%), triethylamine (Et\(_3\)N, 99%), and 2-bromoisobutyryl bromide (>99%) were purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (Honeywell Burdick and Jackson, >99%) was dried over 4 Å molecular sieves (Acros Organics) prior to use. Polymerization reagents copper(II) bromide (CuBr\(_2\), 99.999%), copper(II) chloride (CuCl\(_2\), 99.999%), 2,2-bipyridine (bipy, >99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), and sodium \(\text{t-ascorbate (} \geq 98\%\text{)}\) were purchased from Sigma-Aldrich and used as received. Monomers 2-(2-methoxyethoxy)ethyl methacrylate (MEO2MA, Sigma-Aldrich, 95%) and 2-(diethylamino)ethyl methacrylate (DEA, Sigma-Aldrich, 99%) were gravity-fed through a 10 cm long, 2 cm diameter alumina column (activated, basic) to remove the 100 ppm hydroquinone monomethylether and 1500 ppm monomethyl ether hydroquinone inhibitor, respectively, immediately prior to synthesis. Potassium nitrate (KNO\(_3\), >99.0%, Alfa Aesar) was used as received. pH adjustment was carried out using diluted nitric acid (HNO\(_3\)) (70%) to (97%), and sodium hydroxide (NaOH, pellet, Alpha Aesar) solutions. Methanol (Sigma-Aldrich, anhydrous, 99.8%) was used as received. Milli-Q water (Merck Millipore, 18.2 M\(\Omega\) cm at 25 \(^\circ\)C) was used throughout for physical measurements unless otherwise specified.

### Synthesis and Dry Brush Characterization

The silicon wafers were cleaned and the surface initiator was functionalized using our previously reported methods.\(^ {16}\) Following this, SI-ARGET ATRP was utilized to synthesize P(MEO2MA-stat-DEA) 90:10, 70:30, and 50:50 mol % brushes from the surface-bound bromine moieties.\(^ {18}\) A molar ratio of a monomer/Cu catalyst/ligand/reducing agent of 2500/1/10/10 was used throughout. The ratio of solvent-to-monomer was 1:1 v/v. For the monomer component of the synthesis, MEPO2MA and DEA were mixed in a 90:10, 70:30, and 50:50 mol/mol ratio prior to the addition to the polymerization mix. For the 90:10 mol % composition, a number of combinations of reagents were tried to find a polymerization environment which allowed for the production of a uniform brush surface on which ellipsometry could be performed. This is described further in Table S1 and Figure S1. It was found that using CuBr\(_2\) as a catalyst, bpy as a ligand, a 4:1 v/v mixture of MeOH/H\(_2\)O as a solvent, sodium ascorbate as a reducing agent, and a polymerization time of 1.5–2 h produced suitable surfaces. A PDEA homopolymer brush was also synthesized for ellipsometry experiments using the same polymerization recipe.\(^ {17}\) The exact mol % composition of the copolymer brushes could not be determined as there is insufficient polymer in the small area of the brush for postpolymerization degrafting and chemical analysis. Polymerization kinetics have been shown to vary between surface-initiated and free
polymer-initiated systems, which makes comparison to a free-solution analogue inaccurate.22,23 As such, the brush polymers are assumed to contain approximately 90:10, 70:30, and 50:50 mol %. Herein, the copolymers will be referred to by their monomer feed composition. Table 1 shows the dry brush thickness of each brush as determined by ellipsometry. It is important to note that grafting density and thickness can affect the swelling behavior of polymer brushes. As all brushes were prepared with the same methodology, we assume an equal grafting density for each composition.18,24,25,27

### Ellipsometry

Ellipsometry, all ellipsometry measurements were performed using a J.A. Woollam M-2000V spectroscopic ellipsometer (Lincoln, USA). Data analysis was carried out with the J.A. Woollam CompleteEASE software package (v 5.19). Dry brush thickness measurements were performed at 65, 70, and 75 °C at the vertical at three different locations over the brush-modified wafer. Aqueous experiments were conducted in a solid–liquid cell with cell windows set at 75° to the vertical. The cell internal volume was 5 mL. Measurements were made under a constant flow of electrolyte at ~3.5 mL min⁻¹. This rate was sufficient for rapid change of pH within the cell. The brush was initially exposed to pH 4, 10 mM KNO₃ solution. A small amount of the background electrolyte was used in order to promote charging of weak polyelectrolytes.26 KNO₃ was used as both ions are central in the Hofmeister series.26 The pH of the reservoir was adjusted as necessary throughout via dropwise addition of 0.1 and/or 0.01 M KOH or HNO₃ solutions. The cell was mounted on a temperature-controlled baseplate. Initially, each brush was cycled between 15 and 55 °C in pH 4, 10 mM KNO₃ to ensure the pH was adjusted to 9 and the brush was equilibrated at the set temperature for a minimum of 25 min. The pH was then readjusted to 4 and this process was repeated once to ensure that a reversible pH response in the brush was observed.

For all in situ studies, the ellipsometric quantities Ψ and Δ were recorded as a function of time (data point every 10 s) with data collected simultaneously over the spectral range of 370–1000 nm. Two types of experiments were then performed on each brush: (i) temperature ramps at constant pH; (ii) pH ramps at constant temperature. For the temperature ramps, the temperature was increased incrementally from 20 to 50 °C (lowest and highest achievable) and back to 20 °C in 2.5 °C steps throughout. The brush was equilibrated at the set temperature for a minimum of 25 min before moving onto the next temperature step. Temperature ramps were performed at pH 4 and pH 9 for the P(MEO2MA-stat-DEA) copolymer brushes. For the PDEA homopolymer brush, temperature ramps were performed at pH 4, 5.5, 6, 7, 8, and 9. For all measurements, the pH was monitored throughout and adjusted as necessary to ensure that the pH was maintained to within 0.1 of a unit. For all brushes, pH ramps were performed at 20 and 50 °C starting at pH 4 and increasing incrementally to pH 9 and then back to pH 4, in 1 pH unit intervals. The ellipsometric spectra were fitted using a multilayer model consisting of a 1 mm Si layer, a 1.5 nm SiO₂ layer, a linear effective medium approximation (EMA) layer of water, a polymer of unknown thickness and composition, and an ambient water layer. For Si, SiO₂, and water, dielectric values available within the software package were used. The refractive index, n, of the polymer was described using a Cauchy model and the brush layer was mixed with water to form an EMA layer.

\[
\frac{1}{n^2} = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}
\]

where \(\lambda\) is the wavelength in micrometers. Cauchy constants of \(A = 1.459, B = 0.006,\) and \(C = 0\) were used (measured from the dry brush, consistent across all brushes). Ellipsometric brush thicknesses were converted to ellipsometric swelling ratios by dividing the hydrated brush thickness by the dry brush thickness to allow for comparison between different brushes.

### Theoretical Approach

nSCF theory has been successfully applied to the study of weakly ionizable homopolymer and copolymer brushes,28–32 as well as neutral thermoresponsive polymers such as PNIPAM,33 with numerous predicted structures observed experimentally. nSCF calculations are computationally less demanding than molecular dynamics simulations and frequently align in their predictions.34 nSCF theory assumes that all species have the same dielectric permittivity are also temperature-dependent. In accordance with previous work,28 these are not implemented in the model. A swirled discussion is detailed later, the pH- and thermoresponsive of the PDEA homopolymer brush as well as the thermoresponsive behavior of the PMEO2MA homopolymer brush will first be established. These homopolymer brush systems will inform the parameters used to study the copolymer brushes. A discussion of the theoretical approximations that are relevant for the model employed can be found in the Supporting Information.30,31 Here, we discuss how the model is implemented to investigate homopolymer and copolymer brush systems.

### Model Implementation

The model has been implemented on a one-dimensional (1D) lattice with key parameters shown in Figure 2. The size of a single lattice site has been set at 0.5 nm (lattice volume of 0.125 nm³). The brushes are composed of polymer chains of length \(N = 302\) and grafted density (\(\sigma\)) of 0.025 chains per lattice site (corresponds to 0.1 nm⁻¹), well within the parameters of the brush regime.

When interpreting the Flory–Huggins parameter \(\chi\) as purely enthalpic, one finds an increase in solvent quality (reduction of \(\chi\)) with increasing temperature. However, with increasing temperature, the solvent quality of water for many polymers deteriorates (i.e., PDEA,33 ME02MA28 and PDEA39 exhibit LCST behavior in water). This behavior can only be captured in SCF theory using an ad hoc temperature dependence for the Flory–Huggins \(\chi(T)\) parameter. Previously, Alves et al.28 established such a relation between temperature and \(\chi\)polymer-solvent for poly(N-isopropylacrylamide) with \(\chi\)polymer-solvent(T) = \(A + \frac{B}{T}\) where \(A\) and \(B\) are experimentally derived constants representing enthalpic and entropic contributions, respectively.28 In our present work, in order to simulate the thermoresponsive behavior of the polymer brushes, a range of solvent qualities were investigated with \(\chi\)MEO2MA-water and \(\chi\)DEA-water. Varied linearly between 0 (good solvent) and 2.5 (very poor solvent) \(\chi\)polymer-solvent = 0.5 is the theta condition. Appropriate \(\chi\)MEO2MA-water and \(\chi\)DEA-water values were selected through comparison of the nSCF theory average brush thicknesses (calculated from the first moment of the end points) and the ellipsometric brush thicknesses. For both homopolymers, a linear change in \(\chi\)polymer-solvent was sufficient to capture the behavior of each brush. This is discussed in further detail in the Results and Discussion section. It is important to note that in reality, the electrostatic contribution to the segment potential and the dielectric permittivity are also temperature-dependent. In accordance with Alves et al. and because these dependences largely compensate each other,28 these are not implemented in the model.

The bulk ionic strength and pH in the system are set by fixing a volume fraction of positively charged co-ions, \(\phi_{+}\text{-ion} = \text{H}_2\text{O}^+\), respectively, while the number of counterions is set by an electroneutrality constraint. The \(\chi\)DEA and \(\chi\)MEO2MA ions were set equal to 0.5, that is, theta conditions. To convert the ion volume fraction to the salt molarity, it is necessary to multiply the volume fraction of ions by the molarity of bulk water (55 M). However, this value is a guide only due to the compromises involved in setting the lattice parameters. Neutron reflectometry studies of polyelectrolyte and...
neutral thermoresponsive polymer brushes have required thin, dense layers of the polymer near the substrate, prior to a diffuse tail, to adequately fit the reflectometry data.\(^{18,24,40–42}\) This region is often attributed to some interaction, either electrostatic or hydrophobic in origin, between the surface and polymer proximal to the surface. To incorporate this interaction into the current system, a solvent quality term for the surface, \(\chi\), is introduced consistent with our earlier work.\(^{29,32}\) The value of \(\chi\) has been set at 2, reflecting the hydrophobic nature of the initiator surface.\(^{21}\) Our calculations show no difference between a hydrophobic surface and a direct attractive interaction of the MEO\(_2\)MA and DEA monomers with water as set by Flory–Huggins interaction parameters, that is, \(\chi_{\text{MEO}2\text{MA–water}}\) and \(\chi_{\text{DEA–water}}\) where higher \(\chi\) values represent higher temperatures.

Figure 2. Schematic picture of the lattice-based Scheutjens–Fleer nSCF approach used. The example given is for the 80:20 mol % P(MEO\(_2\)MA-stat-DEA) copolymer brush. A one gradient (one-dimensional) planar lattice was used, and thus the only relevant coordinate is that perpendicular to the substrate (\(z\) direction). Each lattice layer parallel to the substrate contained a volume fraction of each species, that is, monomers (DEA or MEO\(_2\)MA), co-ions, counterions, and \(\text{H}_2\text{O}\), \(\text{H}_3\text{O}^+\), and \(\text{OH}^-\) ions, with the size of each species equal to the lattice size. The grafting density, \(\sigma\), (chains per lattice site) is fixed by the volume fraction of “polymer chain” grafting points in the first lattice layer after the substrate. All MEO\(_2\)MA monomers are uncharged and DEA monomers can be charged or uncharged. Changes in solution temperature are simulated as synchronous changes in the interaction of the MEO\(_2\)MA and DEA monomers with water as set by Flory–Huggins interaction parameters, that is, \(\chi_{\text{MEO}2\text{MA–water}}\) and \(\chi_{\text{DEA–water}}\) where higher \(\chi\) values represent higher temperatures.

Five \(\text{P(MEO}_2\text{MA-stat-DEA)}\) copolymer compositions (90:10, 80:20, 70:30, 60:40, and 50:50 mol %) were investigated with nSCF theory. Each polymer chain, regardless of composition, consisted of terminal MEO\(_2\)MA monomer graft and end point segments. Individual chains then consisted of 30 repeating 10 monomer unit sections with the ratio of MEO\(_2\)MA to DEA consistent with the desired composition. All periodic copolymer configurations studied are shown in Figure 3. The effect of chain configurations on the structure and responsive behavior of the brush will be explored in a later publication. It is possible, and indeed likely, that differences in reactivity ratios for the brushes investigated with ellipsometry would result in some degree of “blocky-ness” within the polymer chains and thus some deviation from the monomer feed ratios. However, it is again prudent to reiterate that the nSCF theory applied here is designed to be qualitative and thus the laterally consistent and periodic polymer configuration illustrated in Figure 3 is sufficient.

**RESULTS AND DISCUSSION**

This section covers two main topics. First, in order to set the foundations, the responsive behavior of the two homopolymers (PMEO\(_2\)MA and PDEA) will be established with comparisons made between ellipsometry and nSCF theory results. Second, the responsive behavior of \(\text{P(MEO}_2\text{MA-stat-DEA)}\) copolymer brushes of various compositions will be investigated. Using the results from the homopolymer section as a basis, nSCF theory will be used to investigate the change in brush thickness for each copolymer with changes in pH and temperature.

**Simulating the Experimental Behavior of PDEA and PMEO\(_2\)MA Homopolymer Brushes with nSCF Theory.**

The thermoresponsive behavior of the free PMEO\(_2\)MA polymer and brushes has been reported.\(^{10–11,43–46}\) For PMEO\(_2\)MA brushes in water, the favorable interactions between the water molecules and the polymer at low temperatures (\(\lesssim 28^\circ\text{C}\)) results in stretching of the polymer chains and the brush adopts a swollen conformation. As the temperature is increased, the hydrophobic portions of the...
polymer begin to have a greater influence on the overall solubility of the polymer chains and the brush collapses. To illustrate this, ellipsometry data from Murdoch et al. have been reproduced in Figure 4. At low temperatures (10 °C), the

brush is considerably swollen (swelling ratio 3). As temperature increases, the brush gradually collapses over a range of 25 °C. Above 35 °C, the brush undergoes no significant further change in thickness with temperature. The behavior of the PEO2MA brush reported by Murdoch et al. is comparable to that of other PEO2MA brushes, with differences in the swelling ratio attributed to slight variations in grafting density and dry brush thickness, as well as the different techniques (or models) used to measure the brush thickness.

nSCF theory was used to calculate the thermoresponsive behavior of a PEO2MA brush, see Figure 4. As the temperature increases, the overall solubility of the polymer, and thus polymer brush thickness, decreases. In order to simulate this reduction in solubility with increasing temperature, the Flory–Huggins parameter ($\chi_{\text{PEO2MA-water}}$) was varied between 0 and 1.4 in 0.1 unit intervals. The brush height at each value was taken as the moment of the end point and is plotted in Figure 4. Visually, the brush response to changes in pH as a function of temperature (blue circles, left y-axis) and thus polymer brush thickness, decreases. In order to simulate the thermoresponsive behavior of the copolymer brushes.

Influence of pH and Temperature on the Height of a PDEA Brush. The pH-induced swelling and collapse behavior of PDEA brushes at room temperature have been reported by Willett et al. We will briefly describe those results here to provide a context. At low pH, when the monomers are charged, electrostatic repulsion and an increase in osmotic pressure resulting from counterion and co-ion influx into the brush result in brush swelling. Above the apparent $p_K$ of PDEA, the brush charge is low and the hydrophobicity of the PDEA results in brush collapse. The behavior of weak polyelectrolytes such as PDEA is also strongly dependent on salt concentration as well as the identity of the salt ions. Herein, a background electrolyte of 10 mM KNO3 was used, which provides sufficient charge screening to induce significant brush swelling; for more detail on the influence of salt, please see ref 48. Here, this earlier work is expanded upon by investigating the pH response of a PDEA brush at a variety of temperatures and the thermoresponsive behavior at various pH values. Ellipsometry results are also compared to nSCF theory calculations.

Figure 4 shows the ellipsometric swelling ratio of a PDEA homopolymer brush as solution pH is increased (closed symbols) incrementally from $pH_{20°C} = 7.5$ and from the nSCF theory results, $pH_{20°C} = 6$. The same value of $pH_{20°C}$ is used throughout the entirety of this work.

For clarity and ease of comparisons between experiment and theory, a number of parameters are defined:

- $pH^*$ is the pH transition at a given temperature (or $X_{\text{polymer-solvent}}$ for theory). To calculate this value, a sigmoidal curve was fitted to the pH response of both the experimental ellipsometry data (decreasing pH) and the nSCF theory results and the pH at which the brush is half swollen is taken. An example of this is shown in Figure S2.
- $pH_{20°C}^*$ is the pH transition of a PDEA brush at 20 °C from ellipsometry or $X_{\text{PEO2MA-water}} = 0.83$ for theory. From the ellipsometry data, $pH_{20°C}^* = 7.5$ and from the nSCF theory results, $pH_{20°C}^* = 6$. The same value of $pH_{20°C}^*$ is used throughout the entirety of this work.
- $[pH–pH_{20°C}^*]$ is the pH relative to $pH_{20°C}^*$. Expressing pH as $[pH–pH_{20°C}^*]$ allows for direct comparison between ellipsometry and nSCF theory.

Figure 5a shows the ellipsometric swelling ratio of a PDEA homopolymer brush as solution pH is increased (closed symbols) incrementally from $[pH–pH_{20°C}^*] = –3.5$ (pH 4, ellipsometry) through 1.5 (pH 9, ellipsometry) and then decreased (open symbols) across the same pH range at 20 and 50 °C. At 20 °C (blue circles), the brush response to changes in pH is similar to that reported by Willett et al. with the brush in its most swollen state at $[pH–pH_{20°C}^*] = 3.5$ through –0.5 because of the protonation of the tertiary amine groups. At $[pH–pH_{20°C}^*] = 1.5$, the hydrophobic PDEA dominates chain solubility as the fraction of charged monomers is significantly reduced and thus the PDEA homopolymer brush collapses. Note that the brush does not collapse to the same extent as the PEO2MA homopolymer brush, that is, the swelling ratio is higher. This higher degree of solvation is attributed to residual charge within the brush as a result of the broad pH transition of weak polyelectrolytes.

The brush thickness at $[pH–pH_{20°C}^*] = –0.5$ and 0.5 is dependent on the direction of the pH change with a large hysteresis observed between brush swelling (open symbols) and collapse (filled symbols). It is likely that with
temperature, the brush thickness at low pH values is slightly lower than it was at 20 °C. There is also less hysteresis between the swelling (decreasing pH) and collapse (increasing pH) transitions at 50 °C. Willett et al. have previously shown that the hydrophobicity of weak polybasic monomers affects the brush pH transition with poly(2-(diisopropylamino)ethyl methacrylate), the more hydrophobic analogue of PDEA, undergoing its swelling/collapse transition at lower pH values. In Figure 5a, the increase in solution temperature can be effectively described as an increase in $\chi_{\text{DEA-water}}$ (the brush is effectively more hydrophobic), which results in a decrease in pH*. The reduction in hysteresis is also consistent with this increase in hydrophobicity with the brush preferring to adopt either a swollen or collapsed brush conformation.

nSCF theory was used to simulate the pH response of a PDEA homopolymer brush at different temperatures, where increasing values of $\chi_{\text{DEA-water}}$ simulate an increase in solution temperature. Figure 5a shows the pH ramps at $\chi_{\text{DEA-water}} = 0.83$ and 2.4 and these capture the pH transitions observed by ellipsometry at 20 and 50 °C, respectively. These $\chi_{\text{DEA-water}}$ values are also consistent with the $\chi_{\text{polymer-solvent}}$ ramps which will be discussed below. It is worth noting that the theory gives the thermodynamically most favorable brush structure for a given parameter set and thus cannot reproduce the hysteresis observed in experimental measurements. Interestingly, the nSCF theory best captures the swelling (reducing [pH–pH20 °C]) behavior of the ellipsometry data, suggesting that during collapse, the brush is kinetically trapped and unable to reach an equilibrium state. Although the model employed is not quantitative, it is again undeniable that it is able to capture the overall trends observed in the ellipsometry measurements on a PDEA homopolymer brush. Figure S3 shows a complete suite of pH ramps for $\chi_{\text{DEA-water}}$ equals 0.3 through 2.4. Increasing values of $\chi_{\text{DEA-water}}$ shifts pH* to lower pH values, that is, a greater degree of protonation is required in order to promote brush swelling, consistent with the ellipsometry results mentioned above.

Figure 5b shows the change in ellipsometric swelling ratio of the PDEA homopolymer brush as a function of temperature at various pH values. At $[\text{pH–pH}_{20 \degree C}] = -2$, the brush is fully swollen and the thickness does not change significantly with increasing temperature, that is, the brush is not thermoresponsive. At $[\text{pH–pH}_{20 \degree C}] = -0.5$, the brush height is significantly affected by temperature and the brush is truly thermoresponsive. Here, at 20 °C, the brush swelling ratio is lower than at lower pH, compared with $[\text{pH–pH}_{20 \degree C}] = -2$. The brush thickness is unaffected by temperature between 20 and 25 °C but gradually collapses between 30 and 35 °C with a ~20% decrease in brush thickness across this temperature range (swelling ratio 3.1 reduced to 2.5). Interestingly, for $[\text{pH–pH}_{20 \degree C}] = -0.5$, above 35 °C, the swelling of the brush is rather insensitive to changes in temperature. At this pH, there is still significant protonation of the DEAMA monomers which oppose the collapse of the brush at high temperature. At higher pH values ($[\text{pH–pH}_{20 \degree C}]$ of 0.5 and 1.5), the brush is significantly collapsed at all measured temperatures. Here, a slight reduction in brush swelling is observed between 20 and 22.5 °C, while at higher temperatures, the swelling does not change significantly.

The thermoresponsive behavior of the PDEA homopolymer brush is simulated by varying $\chi_{\text{DEA-water}}$ between 0.0 and 2.5; increasing pH, the brush is kinetically trapped and resists collapse until higher pH values ($[\text{pH–pH}_{20 \degree C}] \approx 1.5$).

PDEA in solution has been shown to undergo a temperature-induced phase separation with increasing temperature, with the LCST dependent on solution pH. Figure 5a shows that the pH-responsive behavior of the PDEA brush is sensitive to temperature with the pH transition (or pH*) of the PDEA homopolymer brush shifted to a lower pH value at 50 °C; $[\text{pH–pH}_{20 \degree C}] = -1.7$ (pH 5.8). At this elevated

Figure 5. (a) Ellipsometric swelling ratio of a PDEA homopolymer brush as a function of pH and $[\text{pH–pH}_{20 \degree C}]$ at 20 °C (blue circles) and 50 °C (red squares). Filled symbols are increasing pH and open symbols are decreasing pH. Dotted lines are the predicted brush height (nSCF theory) of a PDEA homopolymer brush at various $[\text{pH–pH}_{20 \degree C}]$ values. Please refer to the main text for definition of pH20 °C.*
see Figure Sb for $\chi_{DEA-solvent} = 0.83 - 2.4$ and Figure S3 for the full data set. This was performed at fixed pH values between $[pH-pH_{20C}] = -3.5$ and 1.5. Decreasing the pH increases the brush thickness at a given $\chi_{DEA-water}$ value and shifts the temperature transition to higher $\chi_{DEA-water}$ values. As with Figure 5a, the comparison in Figure Sb shows that nSCF theory is able to capture the experimental swelling behavior of the PDEA homopolymer brush as a function of solution temperature. Deviations between the ellipsometry results and the nSCF theory seen at high temperature can be modeled by an increase in $\chi_{DEA-water}$ and this results in a reduction in brush thickness. The pH transition of a PDEA brush is dependent on temperature with elevated temperatures shifting the pH transition (pH*) to lower pH values because of the increased effective hydrophobicity of the brush. Equally, the thermoresponsive behavior of PDEA is dependent on pH. At low and high pH values (far from the apparent brush $pK_a$), there is no significant influence of temperature on brush thickness as the brush is either considerably charged or largely uncharged and hydrophobic, respectively. At intermediate pH values (closer to the apparent brush $pK_a$), the brush can be considered truly thermoresponsive, where solution temperature has a significant influence on the brush thickness. Importantly, both the pH-responsive (at various temperatures) and thermoresponsive (at various pH values) behaviors of the PDEA homopolymer brush are captured by nSCF theory.

**Behavior of P(MEO₂MA-stat-DEA) Copolymer Brushes: Ellipsometry and nSCF Theory.** *Experimental Results.* The swelling behavior of three P(MEO₂MA-stat-DEA) copolymer brushes of differing monomer compositions to changes in solution pH and temperature were studied using in situ ellipsometry. The ellipsometric swelling behavior of the three copolymer brushes (90:10, 70:30, and 50:50 mol % MEO₂MA:DEA) is shown in Figure 6. To facilitate comparison to theory, the pH is again expressed relative to pH₂₀C* which is calculated from the pH φ* of the PDEA homopolymer brush.

The P(MEO₂MA-stat-DEA) 90:10 mol % brush contains the lowest mol % of the weakly polybasic DEA monomers; however, the brush thickness is still distinctly responsive to changes in pH at both 20 and 50 °C (Figure 6a). At 20 °C, the brush is the most swollen at the lowest pH ($([pH-pH_{20C*}] = -3.5)$. As the pH increases, the 90:10 mol % brush gradually collapses across the entire pH range. Unlike the PDEA homopolymer, which collapses to a swelling ratio of ~1.8 at the highest pH ($([pH-pH_{20C*}] = 1.5)$ (Figure 5a), the 90:10 mol % copolymer remains much more hydrated with a swelling ratio of ~2.5 because of the higher solubility of PMEO₂MA at 20 °C. When the pH is decreased, the 90:10 mol % brush swells with considerably less hysteresis than seen for the PDEA homopolymer brush. As with the PDEA homopolymer brush, increasing the temperature to 50 °C shifts the pH transition of the 90:10 mol % brush to lower pH values. Relative to the PDEA homopolymer brush, the copolymer brush is less swollen at the elevated temperature (at all pH values) because of the presence of PMEO₂MA within the brush.

Looking at Figure 6d, at low and high pH ($([pH-pH_{20C*}] = -3.5$ and 1.5, respectively), it is clear that increasing the temperature decreases swelling. At the high pH, the swelling ratio decreases from ~3 at 20 °C to ~2 at 35 °C, and then, above 35 °C, the brush becomes unresponsive to temperature. There is very little hysteresis between the swelling and the collapse of the brush with temperature. As the PDEA homopolymer brush exhibited effectively no thermoresponsiveness at high pH, any thermoresponsive behavior of the copolymer brush at high pH can be attributed to changes in the solvent quality for the PMEO₂MA sections of the brush. Two key differences are found when comparing the thermoresponsiveness of this copolymer brush at high pH (where DEA monomers are uncharged) to that of the PMEO₂MA homopolymer brush (see Figure 4). First, the copolymer brush reaches its least swollen conformation at a lower temperature, 35 °C compared to 40 °C for the PMEO₂MA homopolymer, which can be attributed to the more hydrophobic DEA monomers within the copolymer brush. Second, in the least swollen state, the
swelling ratio of the copolymer brush is larger than that of the PMEO2MA homopolymer brush (compare a swelling ratio of 2 vs 1.3 at 40 °C). This increased hydration of the copolymer brush when collapsed (as compared to PMEO2MA) is likely due to a low fraction of DEA monomers that remain charged. At low pH, the DEA monomers are now charged and overall, this increases brush swelling. Here, the 90:10 mol % brush is more hydrated at all temperatures compared to that at high pH, with the brush remaining considerably hydrated even at 50 °C. The charging of the brush at low pH also shifts its thermotransition to higher temperature.

Unsurprisingly, as the DEA content of the copolymers is increased to 30 mol % (Figure 6b,e) and then further to 50 mol % (Figure 6c,f), the brushes become increasingly more sensitive to pH, with the swelling transition (pH*) shifting to higher pH values. At 50:50 mol %, the pH* value matches that of the PDEA homopolymer. Also as expected, increasing the mol % of DEA also makes the brushes less sensitive to temperature.

To summarize the abovementioned experimental behavior of the P(MEO2MA-stat-DEA) copolymer brushes, as the DEA content in the copolymer brush increases (from 10 to 50 mol %), the pH-responsive behavior of these brushes increasingly resembles that of the PDEA homopolymer brush. Moreover, at higher DEA contents, when the pH is significantly greater or lower than pH20°C*, the temperature response is lost. However, when the pH is closer to pH20°C*, the behavior of the brush is still influenced by temperature. Even the 70:30 mol % copolymer brush behaves more like a PDEA brush than a PMEO2MA brush. For the pH and temperature ranges studied here, the 50:50 mol % copolymer brush behaves essentially the same as a PDEA brush.

On a similar topic, Ge and Liu reported that for micellization of P(MEO2MA-block-DEA) copolymers in solution, the thermoresponsive and pH-responsive behaviors act in parallel, with no clear effect of one stimulus on the other. This is not what is seen in our current study as here, clearly the statistical copolymerization of the two monomers invokes a strong interplay between the stimuli. For temperature- and pH-responsive copolymers, the composition plays a critical role in determining the effect of pH and temperature on the brush thickness as well as the effect each stimulus has on the other. Importantly, we see that only a small mol % of a charged monomer is required to dominate the overall behavior of multi-stimulus-responsive polymers. Furthermore, monomer characteristics, such as the hydrophobicity, are important. Using the terminology established by Lalyaux et al., both the 50:50 and 70:30 mol % copolymer brushes would be described as temperature-modulated, pH-responsive copolymer brushes while the 90:10 mol % brush would be described as a pH-modulated, thermoresponsive brush.

Understanding how polymer properties (such as composition and hydrophobicity) affect the interplay of stimuli on controlling the behavior of multi-stimulus-responsive brushes requires a systematic and rigorous approach. One would expect, much like the PDEA homopolymer brush, that at intermediate pH values, the copolymer brushes would exhibit clear thermoresponsive properties. Characterizing these brushes experimentally over this entire pH range would be challenging because of sample degradation and/or contamination, and thus, nSCF theory can help to study and elucidate this interplay between pH, temperature, and brush composition for such copolymer brushes.

nSCF Theory Results. Five different P(MEO2MA-stat-DEA) copolymer compositions ranging from 90:10 to 50:50 mol % were examined using nSCF theory. Values of χMEO2MA−water and χDEA−water determined for the homopolymer brushes were used to simulate the influence of temperature for all the copolymer brushes. The full range of χMEO2MA−water and χDEA−water values used and the correspondingly equivalent temperatures are shown in Table S2, and again, it is important to stress that these interaction parameters are obtained from a qualitative comparison between the experiment and nSCF theory. The temperature equivalents were acquired through comparison of the experimental and nSCF theory data presented in Figures 4 and 6. In this section, we first study how temperature affects the pH response and then vice versa. Second, we look at the effect of temperature and pH on the swelling transition of the copolymer brushes.

Interplay of Temperature and pH on the Magnitude of the Multistimulus-Responsive Behavior of the Copolymer Brushes. Figure S6 shows pH ramps at varying χMEO2MA−water and χDEA−water values and temperature ramps at various pH values for the five copolymer brushes. Again, to facilitate comparison, pH is expressed relative to pH20°C*. Overall, at
low pH values, all copolymer brushes are more swollen than at high pH, regardless of temperature or composition. Similarly, at all pH values, the brush is more swollen at lower temperatures than at higher temperatures. The difference in brush thickness between the lowest and highest pH, as shown in Figure S6, is shown in Figure 7a. First, as the DEA mol %

function of pH is shown in Figure 7b. At lower pH values, all the brushes resist collapse until higher temperatures, compared to higher pH values. However, above 30 mol % DEA, the copolymer brushes are the most responsive to changes in temperature at 1 pH unit lower than pH₂⁰°C. By comparing Figures S6 with S5, it can be seen that at higher DEA mol %, the responsive behavior of the copolymer brush gradually shifts toward the behavior of the PDEA homopolymer brush (Figure 5b), with reduced thermoresponsive behavior at the lowest and highest pH values but thermoresponsive properties at intermediate pH values.

Overall, the nSCF theory implemented here is able to capture the trends observed in the ellipsometry results of Figure 6. Generally, higher DEA content in the copolymer brush results in a greater influence of pH on the brush thickness, while the influence of temperature is reduced at the high and low pH extremes.

Interplay of Temperature and pH on the Transition Values of the Multistimulus-Responsive Copolymer Brushes. The abovementioned section examined the change in copolymer brush thickness with pH and temperature. The pH transitions (pH*) and temperature transitions of the copolymer brushes (Figure S6) are summarized in Figure 8 and will now be discussed. Figure 8a shows how the pH transition (pH*) shifts as a function of temperature (χ_MEO₂MA−water and χ_DEA−water) and also copolymer composition, while Figure 8b shows how the temperature transition changes in copolymer brush compositions at increasing χ_polymer−solvent values. Here, a negative value indicates a brush that requires a lower pH in order to undergo its pH swelling transition relative to the PDEA homopolymer. (b) χ_MEO₂MA−water and χ_DEA−water at the temperature transition for the five copolymer brush compositions at various [pH−pH₂⁰°C*] values.
as a function of pH and composition. In Figure 8a, the pH transition or pH* is expressed relative to pH\textsubscript{20°C} and thus

- pH\textsuperscript{*}−pH\textsubscript{20°C} = 0 is the pH where a PDEA homopolymer brush is half swollen (half height of sigmoidal fit to brush height data) at 20 °C.
- If pH\textsuperscript{*}−pH\textsubscript{20°C} < 0, the copolymer brush requires a greater degree of protonation (charge) in order to swell compared to the PDEA homopolymer brush at 20 °C.
- Conversely, if pH\textsuperscript{*}−pH\textsubscript{20°C} > 0, the brush swells more readily upon protonation.

By increasing $\chi_{\text{polymer-solvent}}$ (increase in temperature), the solubility of both the PMEO\textsubscript{MA} and PDEA segments is reduced within the copolymer brush. This results in a decrease in pH\textsuperscript{*}−pH\textsubscript{20°C} (Figure 7a), which means that the copolymer brush requires a larger degree of charge in order to swell. At lower DEA compositions, the influence of temperature ($\chi_{\text{polymer-solvent}}$) on the pH* of the copolymer brushes is greater. Temperature has the greatest influence on the shift in the pH transition (pH*) for the 90:10 mol % copolymer brush. This is expected as it has the largest mole fraction of the thermoresponsive MEO\textsubscript{2MA} monomer.\textsuperscript{19}

Figure 8b shows the temperature transitions ($\chi_{\text{MEO-MA-water}}$ left axis, $\chi_{\text{DEA-water}}$ right axis) of the five copolymer brushes as a function of pH. From Figure 4, the temperature transition of PMEO\textsubscript{MA} from nSCF theory is at $\chi_{\text{MEO-MA-water}} = 0.5$. Therefore, if the temperature transition of the copolymers is greater than 0.5, the brush is more hydrophilic, while if the temperature transition is below 0.5, it is more hydrophobic than PMEO\textsubscript{MA}. The 90:10 mol % copolymer brush has the lowest DEA mol % and accordingly pH has the least influence on its temperature transition. At low pH ($[\text{pH}−\text{pH}\textsubscript{20°C}] ∼ -2$), the temperature transition of the 90:10 mol % copolymer brush is at $\chi_{\text{MEO-MA-water}} \sim 0.75$, meaning that the copolymer brush remains more hydrated until higher temperatures. This is consistent with the ellipsometry results in Figure 6d which shows that at [pH−pH\textsubscript{20°C}] $= -3.5$, the 90:10 mol % brush remains significantly solvated until $\sim 50 °C$. Upon increasing pH (increasing [pH−pH\textsubscript{20°C}] values), the temperature transition decreases to $\chi_{\text{MEO-MA-water}}$ values $< 0.4$, that is, to lower than the PMEO\textsubscript{MA} homopolymer brush. At elevated pH, the lack of charge and the hydrophobicity of the DEA monomers shifts the temperature transition to very low values of $\chi_{\text{MEO-MA-water}}$ (and implicitly lower $\chi_{\text{DEA-water}}$ values). Overall, the elevation of the temperature transition at low pH values and its depression at high values is also seen for the other four copolymer compositions.

Fully describing the behavior of stimulus-responsive and multi-stimulus-responsive polymers is often difficult. For polymers where only a single stimulus has a significant effect on the polymer conformation, describing the behavior is easy. For example, PNIPAM and PMEO\textsubscript{MA} are undeniably thermoresponsive polymers. Describing the behavior of polymers that are sensitive to multiple stimuli becomes difficult, especially when one considers the interplay of the various stimuli. Laloyaux et al.\textsuperscript{19} approached this problem by describing multi-stimulus-responsive copolymer brushes with regard to a dominant and modulating response. At low polyelectrolyte composition, they described the pH and temperature poly(di(ethylene glycol) methyl ether methacrylate-stat-methacrylic acid) copolymers as pH-modulating, while at high polyelectrolyte compositions, these copolymers displayed temperature-modulating pH-responsive behavior.

Although the Laloyaux et al. terminology is more than adequate to describe their experimentally investigated system, it is insufficient to fully describe the responsive behavior of the P(MEO\textsubscript{2MA}-stat-DEA) copolymer brushes investigated here. Figures 6 and S7 show that as the mol % of DEA increases, pH increasingly becomes the dominant stimulus and the influence of temperature becomes less pronounced at high and low pH values. At intermediate pH values, however, around the apparent pK\textsubscript{a} of PDEA ([pH−pH\textsubscript{20°C}] = −1 and 0), the change in brush thickness across the examined temperature range increases (i.e., at these intermediate pH values, the copolymer brushes are more thermoresponsive at higher DEA mol %). This shows clearly that the higher DEA mol % copolymer brushes are still thermoresponsive. Thus, we describe these polymers by the stimulus which has the largest impact on the brush, that is, the 90:10 and 80:20 mol % copolymer brush are temperature-dominant, multi-stimulus-responsive copolymer brushes, while the 70:30, 60:40, and 50:50 mol % brushes are pH-dominant, multi-stimulus-responsive copolymer brushes. This new terminology is important because when one considers the two limiting cases, it reveals that at a certain composition, an equally responsive copolymer must therefore exist. From Figure S6, temperature and pH (qualitatively) appear to have approximately equal contributions to the 70:30 mol % copolymer brush thickness for the ranges investigated; however, a more robust analysis would be required to determine the composition that exactly balances these two rather different environmental stimuli.

In summary, Figure 8a shows that as temperature increases, the swelling transition of the copolymer brushes shifts to lower pH values. Figure 8b shows that as pH decreases, the brush swelling transition moves to higher temperatures, and oppositely, as pH increases, the swelling transition shifts to lower temperatures. These general behaviors are modulated by copolymer composition. Overall, the swelling of multi-stimulus-responsive P(MEO\textsubscript{2MA}-stat-DEA) copolymer brushes is determined by the interplay of pH, temperature, and the composition of the copolymer. nSCF theory has been applied to model the pH and thermoresponsive behavior of a number of copolymer brushes at various compositions (Figures S6 and 8) and has been able to reproduce the experimentally observed trends (Figure 6). At low pH, all the copolymers were more swollen than at high pH because of the protonation of the DEA monomers. Increasing the temperature resulted in a reduction in brush thickness, with the broad thermotransition shifted to higher temperatures at lower pH. As the mol % of DEA in the copolymer increased, the brush behaved more like the PDEA homopolymer, with a more dominant influence of pH on the brush thickness, and a reduction in thermoresponsive behavior at extreme pH values. This is concordant with the ellipsometry results presented above and with the behavior of previously studied pH and thermoresponsive copolymers.\textsuperscript{1,15,19,20}

### CONCLUSIONS

Ellipsometry and nSCF theory have been combined to investigate the responsive behavior of various multi-stimulus-responsive P(MEO\textsubscript{2MA}-stat-DEA) copolymers. The responsive behavior of PMEO\textsubscript{2MA} and PDEA homopolymers synthesized using surface-initiated ARGET ATRP was investigated to form the foundations for copolymer experi-
ments. By varying the Flory–Huggins parameter from low values (good solvent conditions) to high values (poor solvent conditions), the responsive behavior of a PMEO₂MA brush to changes in temperature was captured with nSCF theory. The pH- and thermoresponsive behavior of a PDEA homopolymer brush as measured by ellipsometry was also captured with nSCF theory, with temperature significantly influencing the brush thickness at pH values near its pH transition (pH_{20{°}C}^*)

Multi-stimulus-responsive P(MEO₂MA-stat-DEA) copolymer brushes at 90:10, 70:30, and 50:50 mol % were also synthesized using surface-initiated ARGET ATRP and their pH- and thermoresponsive behaviors were tracked with ellipsometry. The composition of the copolymer is important with higher DEa mol % decreasing the sensitivity of the brush changes in temperature at pH values far from pH_{20{°}C}^*. Above 30 mol % DEa, the temperature responsiveness of the brush is effectively turned off at very high or very low pH.

nSCF theory was able to capture this behavior, showing the same trends that were observed experimentally and providing greater detail on the response of the brushes to variations in temperature and pH. At intermediate pH values, all copolymer brushes showed thermoresponsive behavior. At one pH unit lower than pH_{20{°}C}^*, the change in brush thickness with temperature increased with higher DEa mol %, that is, increasing the DEa mol % decreases how thermoresponsive the brush is at low and high pH but increases the influence of temperature at intermediate pH values. Two distinct regimes existed for the multi-stimulus-responsive P(MEO₂MA-stat-DEA) copolymer brushes. At low DEa mol %, the responsive behavior of the brushes is described as temperature-dominant, while at higher DEa mol %, the brushes are classified as pH-dominant. The 70:30 mol % brush qualitatively appears to be equally responsive to both temperature and pH; however, a more detailed analysis is required for this to be quantitatively determined.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c00424.

Synthetic optimization conditions, example calculation of pH_{20{°}C}^*, nSCF theory pH and temperature ramps at a greater number of conditions for the PDEA homopolymer, fraction of charged monomers for a PDEA brush (as calculated from nSCF theory) as a function of pH and temperature, calculated pK_a values of the PDEA homopolymer, equivalent X_{MEO₂MA-water}/X_{DEA-water} and temperatures, and the copolymer brush response to changes in temperature and pH as calculated from nSCF theory (PDF)

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Notes

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