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Control of pH- and Temperature-Responsive Behavior of mPEG-*b*-PDMAEMA Copolymers through Polymer Composition

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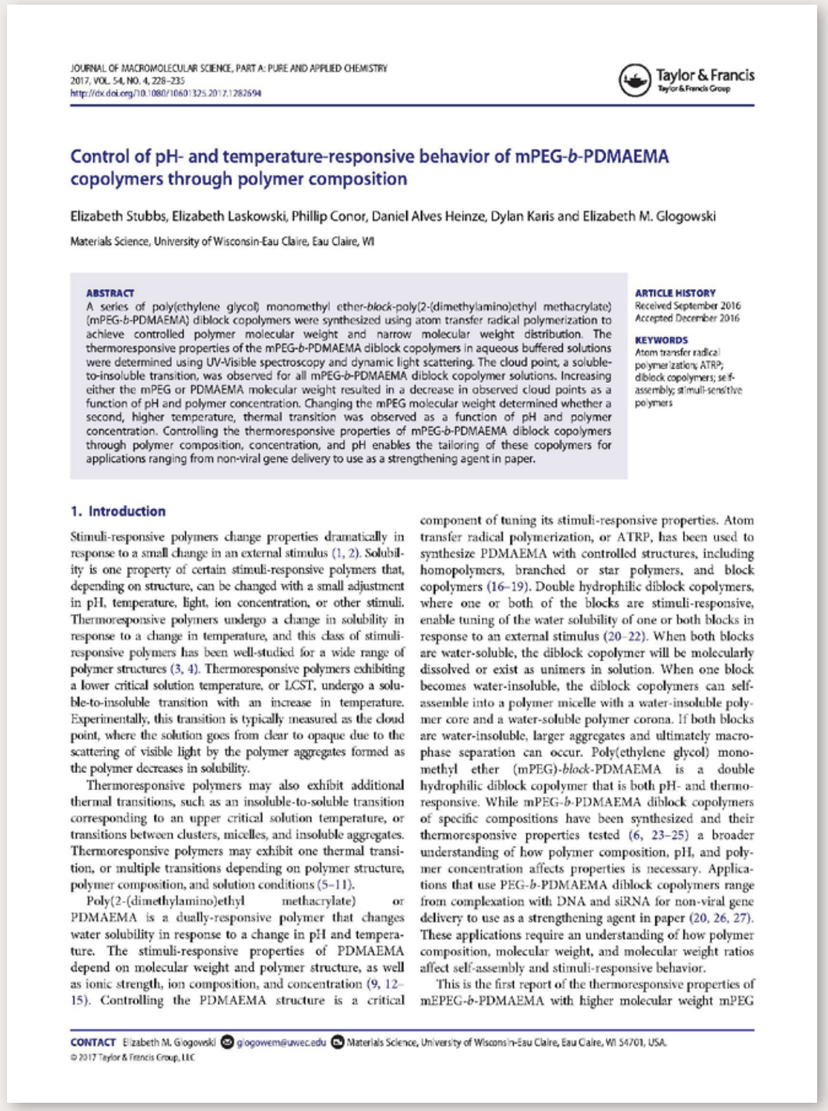
Smart polymers dramatically change properties in response to a small change in an external stimulus. Tuning of smart properties enables a wide range of possible applications from biomedical to oil and gas. This study describes how changing polymer structure directly affects the measured smart properties for the diblock copolymer mPEG-*b*-PDMAEMA. The observed smart behavior, specifically water solubility, depends on both pH and temperature. The solubility can be tuned by changing polymer composition and concentration to tailor this smart polymer material for applications ranging from DNA encapsulation to adaptable smart surfactants.



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Control of pH- and temperature-responsive behavior of mPEG-*b*-PDMAEMA copolymers through polymer composition

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ABSTRACT

A series of poly(ethylene glycol) monomethyl ether-*block*-poly(2-(dimethylamino)ethyl methacrylate) (mPEG-*b*-PDMAEMA) diblock copolymers were synthesized using atom transfer radical polymerization to achieve controlled polymer molecular weight and narrow molecular weight distribution. The thermoresponsive properties of the mPEG-*b*-PDMAEMA diblock copolymers in aqueous buffered solutions were determined using UV-Visible spectroscopy and dynamic light scattering. The cloud point, a soluble-to-insoluble transition, was observed for all mPEG-*b*-PDMAEMA diblock copolymer solutions. Increasing either the mPEG or PDMAEMA molecular weight resulted in a decrease in observed cloud points as a function of pH and polymer concentration. Changing the mPEG molecular weight determined whether a second, higher temperature, thermal transition was observed as a function of pH and polymer concentration. Controlling the thermoresponsive properties of mPEG-*b*-PDMAEMA diblock copolymers through polymer composition, concentration, and pH enables the tailoring of these copolymers for applications ranging from non-viral gene delivery to use as a strengthening agent in paper.

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Atom transfer radical polymerization; ATRP; diblock copolymers; self-assembly; stimuli-sensitive polymers

1. Introduction

Stimuli-responsive polymers change properties dramatically in response to a small change in an external stimulus (1, 2). Solubility is one property of certain stimuli-responsive polymers that, depending on structure, can be changed with a small adjustment in pH, temperature, light, ion concentration, or other stimuli. Thermoresponsive polymers undergo a change in solubility in response to a change in temperature, and this class of stimuli-responsive polymers has been well-studied for a wide range of polymer structures (3, 4). Thermoresponsive polymers exhibiting a lower critical solution temperature, or LCST, undergo a soluble-to-insoluble transition with an increase in temperature. Experimentally, this transition is typically measured as the cloud point, where the solution goes from clear to opaque due to the scattering of visible light by the polymer aggregates formed as the polymer decreases in solubility.

Thermoresponsive polymers may also exhibit additional thermal transitions, such as an insoluble-to-soluble transition corresponding to an upper critical solution temperature, or transitions between clusters, micelles, and insoluble aggregates. Thermoresponsive polymers may exhibit one thermal transition, or multiple transitions depending on polymer structure, polymer composition, and solution conditions (5–11).

Poly(2-(dimethylamino)ethyl methacrylate) or PDMAEMA is a dually-responsive polymer that changes water solubility in response to a change in pH and temperature. The stimuli-responsive properties of PDMAEMA depend on molecular weight and polymer structure, as well as ionic strength, ion composition, and concentration (9, 12–15). Controlling the PDMAEMA structure is a critical component of tuning its stimuli-responsive properties. Atom transfer radical polymerization, or ATRP, has been used to synthesize PDMAEMA with controlled structures, including homopolymers, branched or star polymers, and block copolymers (16–19). Double hydrophilic diblock copolymers, where one or both of the blocks are stimuli-responsive, enable tuning of the water solubility of one or both blocks in response to an external stimulus (20–22). When both blocks are water-soluble, the diblock copolymer will be molecularly dissolved or exist as unimers in solution. When one block becomes water-insoluble, the diblock copolymers can self-assemble into a polymer micelle with a water-insoluble polymer core and a water-soluble polymer corona. If both blocks are water-insoluble, larger aggregates and ultimately macrophase separation can occur. Poly(ethylene glycol) monomethyl ether (mPEG)-*block*-PDMAEMA is a double hydrophilic diblock copolymer that is both pH- and thermoresponsive. While mPEG-*b*-PDMAEMA diblock copolymers of specific compositions have been synthesized and their thermoresponsive properties tested (6, 23–25) a broader understanding of how polymer composition, pH, and polymer concentration affects properties is necessary. Applications that use PEG-*b*-PDMAEMA diblock copolymers range from complexation with DNA and siRNA for non-viral gene delivery to use as a strengthening agent in paper (20, 26, 27). These applications require an understanding of how polymer composition, molecular weight, and molecular weight ratios affect self-assembly and stimuli-responsive behavior.

This is the first report of the thermoresponsive properties of mEPEG-*b*-PDMAEMA with higher molecular weight mPEG

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