

Multilayer films composed of a thermoresponsive cationic diblock copolymer and a photoresponsive dye



Vincent S. Joseph^a, Soonhwa Kim^a, Qilu Zhang^b, Richard Hoogenboom^{b,**}, Jong-Dal Hong^{a,*}

^a Department of Chemistry, University of Incheon, 119 Academy-ro Yeonsu-gu, Incheon 406-772, Republic of Korea

^b Supramolecular Chemistry Group, Department of Organic Chemistry, Ghent University, Krijgslaan 281 S4, 9000 Ghent, Belgium

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ABSTRACT

This article describes the temperature-triggered self-assembly of poly[(2-dimethylamino)ethylmethacrylate]-block-poly[di(ethylene glycol) methyl ether methacrylate] (PDMAEMA₅₉-b-PDEGMA₃₁₈, PDD) unimers to aggregates in aqueous solution as a function of pH and temperature. Moreover, we examined the influence of the aggregate size of the thermoresponsive PDD diblock copolymer on the quantity and thickness of the multilayer films self-assembled layer-by-layer (LBL) with poly(styrenesulfonate) PSS on a substrate as a function of solution pH and temperature. The aggregation state of the PDD exhibited a significant influence on the deposition of the PDD/PSS bilayers, especially the first bilayer: The larger the aggregate size, the more loosely the aggregates were packed into the film with a higher surface roughness. The quantity and thickness of the multilayer films, however, grew linearly during the alternate sequential LBL-deposition of the PDD and PSS, irrespective of the aggregate size. Furthermore, loading a hydrophobic spiropyran dye into the multilayer films was realized to allow the multi-stimuli-responsive materials for separation and sensing applications.

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1. Introduction

Stimuli-responsive polymer films that control adhesion, wetting, and binding or release of functional molecules from surfaces are promising candidates for drug delivery, sensing, and tissue engineering applications. The property of stimuli-responsive polymers change dramatically in response to external conditions such as temperature [1–3], pH [4–6], light [7–10] and ionic strength [11]. Among the interesting features of responsive polymers is their reversible micellization in solution in response to external stimuli, e.g. changes in temperature [12–14] or pH [15,16]. Most of the commonly studied thermoresponsive polymers such as poly(*N*-isopropylacrylamide) (PNIPAM) [17–22], and poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA) [23], exhibit low critical solution temperature (LCST) behavior. POEGMA have been widely studied as alternatives to thermoresponsive PNIPAM [24–28], due to their excellent biocompatibility [29,30].

The electrostatic self-assembly via layer-by-layer (LBL) deposition of electrostatically charged monomolecular films on solid

substrates [31] has been developed into a powerful tool for constructing polymer membranes for controlled release and separation of functional guest molecules and ions [32] in response to external stimuli including pH [33], temperature [34,35], and light [36,37]. In recent years, amphiphilic block copolymers self-assembled into core-shell micelles have been used as a film constituent for improving functionality (the loading capacity of guest molecules) of polyelectrolyte multilayer (PEM) films. In aqueous medium, the diblock copolymer micelles consist of a water-soluble hydrophilic shell and a hydrophobic core. The core exhibits a tendency to incorporate hydrophobic guests, such as dyes [38] or inorganic particles [39]. Furthermore, multilayer films composed of diblock copolymer micelles with thermoresponsive cores exhibited largely reversible swelling transitions and a controlled retention and release of hydrophobic molecules from the core of the micelles in response to variations in temperature [40].

This article reports the preparation of multilayer films composed of a stimuli-responsive cationic diblock copolymer, poly[(2-dimethylamino)ethylmethacrylate]-block-poly[di(ethylene glycol) methylether methacrylate](PDMAEMA₅₉-b-PDEGMA₃₁₈, PDD) with a thermoresponsive PEG-methacrylate-modified polymer segment. The block copolymer PDD undergoes a temperature-induced LCST transition from individually dissolved polymers chains below the transition temperature to self-assembled aggregates with the thermoresponsive PDEGMA as hydrophobic domains and the positively

* Corresponding author. Tel.: +82 3 835 8234; fax: +82 32 8350762

** Corresponding author. Tel.: +32 9 264 4482; fax: +32 9 264 4998.

E-mail addresses: richard.hoogenboom@ugent.be (R. Hoogenboom), hong5506@incheon.ac.kr, hong5506@daum.net (J.-D. Hong).

charged stabilizing PDMAEMA above the transition temperature. The positively charged PDMAEMA block enables LBL-assembly of PDD into multilayer films with a negatively charged layer such as poly(4-styrene sulfonate) (PSS) or poly(acrylic acid) (PAA) as poly anion in both the dissolved and aggregated states of PDD. The LBL-deposition of PDD/PSS bilayers on solid substrate was investigated using UV–vis spectrometry, ellipsometry, and atomic force microscopy (AFM) as a function of temperature and pH in solution to examine the effect of polymer aggregation on the LBL-assembly. This paper also reports the incorporation of a hydrophobic photoresponsive guest, spiropyran (SP), into the hydrophobic domains of PDD above its transition temperature to yield photoresponsive SP-PDD/PAA multilayer films.

2. Experimental

2.1. Materials

The copolymer PDD was synthesized in a two-step protocol by Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization using (4-cyanopentanoic acid)-4-dithiobenzoate (Sigma–Aldrich) as chain transfer agent (CTA) and azobutyronitrile (AIBN; Sigma–Aldrich; purified by recrystallization from methanol) as initiator (Scheme 1), in an analogous manner as recently reported for the synthesis of similar block copolymers [41,42]. In brief, DMAEMA (Sigma–Aldrich; purified by passing over neutral aluminum oxide) was first polymerized in toluene at 70 °C for 9 h up to ca. 60% conversion followed by precipitation in hexane/diethyl ether (50/50 in volume, Sigma–Aldrich) yielding the PDMAEMA macroCTA with a DP of 59, M_n of 8.07 kDa and \bar{D} of 1.20. This macroCTA was subsequently used for the polymerization of DEGMA (Sigma–Aldrich; purified by passing over neutral aluminum oxide) in toluene at 70 °C for 4 h upto ca. 80% conversion followed by precipitation in hexane/diethyl ether (50/50 in volume) yielding PDD with a M_n of 48 kDa and a \bar{D} of 1.4.

The synthesis and the characterization of SP dye were described in detail in our previous report [43]. Poly(styrenesulfonate, sodium salt) (PSS, M_w 70,000) and poly(acrylic acid) (PAA, M_w 250,000 g/mol; 25% aqueous solution) were purchased from Sigma–Aldrich, and used as received. Silicon wafers ($d = 100$ nm) were purchased from MEMC electronic materials Inc. (Malaysia). Besides, concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl, 35%), hydrogen peroxide (H_2O_2 , 30%), and ammonium hydroxide (29%) were obtained from PFP Osaka (Japan), OCI company Ltd. (Korea) and Mallinckrodt baker Inc. (Philipsburg, NJ), respectively. Ultrapure water (Millipore MilliQ Plus, 18.2 M Ω cm) was used for all the experiments including the preparation of the sample solutions, films and the cleaning steps.

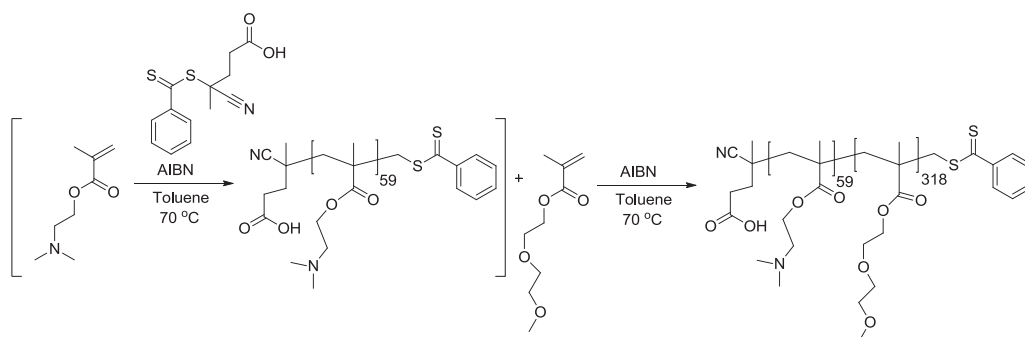
2.2. Methods

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Bruker (400 MHz) spectrometer. UV–vis absorption spectra were recorded on a spectrometer (Perkin–Elmer, Lambda 40) in order to monitor the LBL self-assembly of PDD and PSS layers on fused silica and also to investigate the photoisomerization of the SP-PDD/PAA multilayer films. The thickness of the multilayer film deposited on silicon wafers was measured using a real-time spectroscopic ellipsometer (Ellipso Technology, Elli-SE-F) with a Xe arc lamp (350–820 nm) equipped with a rotating polarizer, a liquid cell with optical access at an incidence angle of 60°, an analyzer, and a multichannel detection system. Employing a self-made computer program, the elliptical azimuth and phase angle were calculated for both the cleaned reference substrate and the multilayer films. Note that at least 3–5 sampling points were measured to obtain the average thickness. The AFM measurements were performed on a Si wafer in air at RT using a Nanoscope IV multimode microscope (Veeco). Using a 125 μ m long Si cantilever, with tip radius less than 10 nm, and a resonance frequency 261.42 kHz (Nanoworld) with a force constant of 42 N/m, topographic images were recorded in tapping mode (1 μ m \times 1 μ m size) at a scan rate of 0.50 Hz. Dynamic light scattering (DLS) measurements were carried out at varying temperatures with a Malvern Instrument Zetasizer Nano-ZS. The excitation light source was a He–Ne laser at 633 nm, and the intensity of the scattered light was measured at 173°. All samples were filtered through Millipore membranes with pore sizes of 0.2 μ m prior to measurement. Turbidity measurements were performed on a Cary 300 Bio UV–vis spectrophotometer at a wavelength of 600 nm. The transmittance was measured during two controlled heating/cooling cycles with various heating/cooling rates while stirring.

2.3. LBL-assembly of multilayer films composed of PDD/PSS bilayers

The multilayer assembly was performed with 10 mM PDD solution and 5 mM PSS solutions in deionized, ultrapure Millipore water (18 M Ω cm) (abbreviated as milliQ water), which were obtained after the filtration of the solutions using a sterile syringe nylon filter (0.45 μ m pore size, Fischer Scientific) to remove dust and/or impurities. The aqueous PDD solution in milliQ at pH 7.8 was adjusted to pH 4.5 using 0.1 N aqueous HCl, when needed. The substrates selected for the PEM buildup were fused silica and silicon wafer (12 \times 45 mm²).

Prior to the film deposition, the substrates (polished silicon wafers or fused silica slides) were cleaned by ultrasonication in piranha solution ($H_2SO_4/H_2O_2 = 7:3$) at 80 °C for 1 h. Subsequently, the cleaning operating was repeated in a mixture of $H_2O/H_2O_2/NH_3$ (5:1:1) at 80 °C for 1 h. The substrates were washed thoroughly with milliQ water after both the steps. The multilayer films were



Scheme 1. Synthetic route to PDD diblock copolymer by sequential RAFT polymerization.

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