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Photodirected assembly of polyelectrolyte complexes

Njideka H. Okoye [a, 1, 3], Udaka K. de Silva [a, 3], Justin A. Wengatz [a, 2], Yakov Lapitsky [a, b, *]

[a] Department of Chemical and Environmental Engineering, University of Toledo, Toledo, OH 43606, USA
[b] School of Green Chemistry and Engineering, University of Toledo, Toledo, OH 43606, USA

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ABSTRACT

When oppositely-charged polymers are mixed in water they self-assemble into polyelectrolyte complexes (PECs). These complexes have numerous technological applications that require control over their shape. To this end, we show how PEC geometry can be tailored through photodirected assembly. A commonly-used weak polycation, poly(allylamine) (PAH), was co-dissolved in a basic solution (significantly above its effective pKa) with a commonly-used polyanion, poly(styrene sulfonate) (PSS), and a photoacid generator (diphenyliodonium nitrate). The solution was then irradiated with UV light through photomasks to spatially control the protonation (and therefore the ionization) of PAH. The ionization resulted in the formation of insoluble PECs, whose shapes were predictably tuned by varying the photoirradiation pattern. Also analyzed were the phase behavior of PAH/PSS/diphenyliodonium nitrate mixtures, and the kinetics and spatial resolution limits of their photodirected assembly. This revealed that pH-mediated photodirected assembly works well for macroscopic structures (i.e., larger than about a millimeter in size), but is impeded by ion diffusion when smaller irradiation sites are used.

1. Introduction

Polyelectrolyte complexes (PECs) have numerous applications ranging from controlled release of bioactive payloads [1,2], to sensors [3,4], separations [5,6] and energy devices [7,8]. These varied uses require a broad spectrum of structures with well-defined shapes, which are prepared through methods such as layer-by-layer deposition [9], micromolding [10,11], microfluidics [12], and direct-write extrusion through microscopic nozzles [13]. As a simple and versatile alternative to these techniques, this article demonstrates photodirected assembly as a strategy for controlling PEC geometry.

The use of light to direct materials structure attracts widespread interest, which ranges from lithographic methods in the microelectronics industry [14,15], to the use of non-linear optics to form intricate 3-D structures through site-specific photopolymerization [16,17], crosslinking [18], etching [19] and colloidal assembly [20]. Recently, by using photoactive surfactants, Lee et al. have also demonstrated the use of light in tailoring the phase behavior and microstructure of surfactant/polyelectrolyte mixtures [21,22]. Similarly, two recent reports have demonstrated photodirected gelation of alginate via localized phototriggered release of crosslinking calcium ions [23,24]. The photodirected assembly of PECs (i.e., complexes between polyanions and polycations), however, has not yet been explored.

To this end, we have developed a photochemical method to direct the supramolecular assembly of a commonly used polyanion/polycation system – composed of the weak polycation, polyallylamine (PAH; effective pKa ≈ 8.5 [25]), and the strong polyanion, poly(styrene sulfonate) (PSS) – into insoluble structures whose shape is controlled by the photoirradiation pattern. This was achieved using a photoacid generator (PAG), which lowered the local pH upon its exposure to light. The use of PAGs, which generate acids through photolysis reactions [26–28], is common in the lithographic patterning of photoreactive polymers (e.g., in the microelectronics industry) [15,26,29,30]. Recently, their use has also been demonstrated in directing the self-assembly of pH-sensitive mixtures [24,31,32]. These photodirected assembly processes include the photogelation of dipeptide solutions [32], colloidal clay

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* Corresponding author. Department of Chemical and Environmental Engineering, University of Toledo, Toledo, OH 43606, USA. Tel.: +1 419 530 8254; fax: +1 419 530 8086.

E-mail address: yakov.lapitsky@utoledo.edu (Y. Lapitsky).

[1] Present address: Department of Chemical Engineering, Tennessee Tech University, 1020 Stadium Dr., Cookeville, TN 38505, USA.

[2] Present address: Rockwell Automation, 1 Allen-Bradley Dr., Cleveland, OH 44124, USA.

[3] These authors contributed equally.

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dispersions [31], and (through the acid-mediated dissolution of calcium) the photopatterned gelation of alginate [24].

Here, we show that PAGs can also be used for directing the assembly of custom-designed PECs. To achieve this, deprotonated PAH is co-dissolved at pH 11.6 with PSS and diphenyliodonium nitrate, which serves as the PAG. Upon photoirradiation with a UV lamp, the PAG undergoes a photolysis reaction that releases protons, and in turn protonates the PAH (see Scheme 1). This converts the near-neutral PAH molecule into a polycation and leads to its rapid and localized self-assembly with the polyanionic PSS at the photoirradiation site (Scheme 2). Using this method, we show that PECs with custom-designed shapes can be prepared through localized photochemical ionization of polymers in solution. We also probe the phase behavior and kinetics underlying this photopatterning process and relate them to the limitations in its spatial resolution.

2. Materials and methods

2.1. Materials

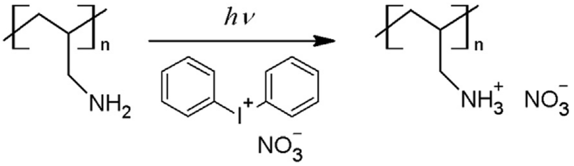
All experiments were performed using 18.2 MΩ cm Millipore Direct-Q water. PSS (nominal MW ~ 70,000), Triton X-100 (TX-100) and low-electroendosmosis agarose (Type 1) were purchased from Sigma–Aldrich (St. Louis, MO). PAH (nominal MW ~ 15,000) was obtained from Polysciences Inc. (Warrington, PA). Diphenyliodonium nitrate, which served as the PAG, was acquired from TCI America (Portland, OR). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from VWR (West Chester, PA). All materials were used as received.

2.2. Precursor solution preparation

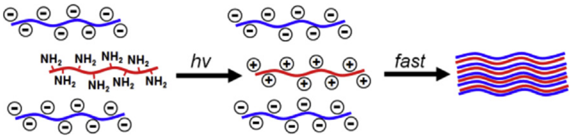
The precursor solutions for the photodirected assembly process were prepared using 0.008–0.064 M PAG, 0.048–0.601 M PAH and 0.241 M PSS. Furthermore, because the photoirradiation of the PAG leads to the formation of hydrophobic byproducts (such as 4-iodobiphenyl and biphenyl [33]), 0.077 M of nonionic surfactant (TX-100) was added, at a concentration significantly above its critical micelle concentration (CMC $\approx 2 \times 10^{-4}$ M [34]), to keep them dissolved. To prevent PEC formation prior to photoirradiation, the pH of these solutions was adjusted to 11.6 using NaOH (i.e., so that the PAH would be mostly deprotonated). Additionally, to confirm that the insoluble structures formed upon photoirradiation were PECs rather than precipitates of PAG byproducts, PSS-free control samples (which were unable to form PECs) were prepared in the same manner at matching PAH, PAG and TX-100 concentrations.

2.3. Photodirected assembly of PECs

To prepare photopatterned PECs, 60-μL aliquots of precursor solution were inserted into chambered microscope slides (which were built by applying double-sided 3M Scotch™ tape as spacers to the edges of standard microscope slides, and covering the slides with 200-μm glass cover slips). The slides were then covered with homemade aluminum foil photomasks (with shapes of stars, circles and the letters “UT” cut out) and irradiated for 1 h using a UVP Blak-Ray® B-100AP High Intensity UV lamp (λ = 365 nm; nominal intensity = 21,700 μW/cm^2) at a 10-cm distance. The patterns that formed upon photoirradiation were imaged without magnification via regular digital photography and at 5× magnification using an Ernst Leitz Wetzlar GMBH optical microscope (Solms, Germany) equipped with an Infinity2-2C camera. Furthermore, to confirm that the PEC structures were continuous rather than composed of many dispersed particles, 3 ml of precursor solution were placed in a petri dish (with an optically-clear cover to prevent evaporation). The samples were then irradiated with UV light for 3 h (the required irradiation time here was longer due to the greater sample thickness), whereupon PECs were obtained and handled with tweezers to confirm their continuity.



Scheme 1. Photoactivated ionization of PAH by the PAG (diphenyliodonium nitrate).



Scheme 2. Photodirected assembly of polyelectrolyte complexes between PAH and PSS.

2.4. Elemental analysis

The presence of both PAH and PSS in the photopatterned structures was confirmed through the elemental analysis of complexes prepared using 0.481 M PAH, 0.241 M PSS and 0.048 M PAG. These PECs were prepared using microscope slides without photomasks, so that the entire sample would undergo photodirected assembly. The resulting complexes were then collected from the microscope slides and washed, once for 10 min in 0.077 M TX-100 solutions (to remove any hydrophobic PAG byproducts), and then twice for 20 min in DI water (to extract the surfactant and unassociated PAH and PSS molecules). After each washing step, the PECs were centrifuged for 20 min at 5000 rpm using an Eppendorf 5804R (Hauppauge, NY) centrifuge to separate them from the supernatant. The solid PEC pellets were then dried for 1 h on a Labconco FreeZone 2.5 lyophilizer and analyzed for nitrogen and sulfur at the Galbraith Laboratories (Knoxville, TN) using GLI Procedures ME-3 and E16-2. To ensure reproducibility, the elemental analysis was repeated twice.

2.5. Phase studies

To determine the pH-values where insoluble PECs began forming at each polymer and PAG concentration, phase studies were performed. Here, precursor solutions containing 0.048 M PAG and either 0.242–0.962 M PAH or 0.482 M PSS were prepared at pH-levels ranging between 10.3 and 11.3 (separated by 0.05-unit pH increments). The PAH and PSS solutions were then mixed in 1:1 volumetric ratios (so that the final PAH concentration ranged between 0.121 and 0.481 M, and the final PSS and PAG concentrations were fixed at 0.241 and 0.048 M), whereupon the final mixture pH was measured again. The mixture pH where insoluble PECs began forming was then determined visually (immediately upon mixing), based on a sudden increase in turbidity. Furthermore, to test the effect of PAG concentration on the PAH/PSS phase behavior, this procedure was repeated while varying the PAG concentration from 0.012 to 0.048 M (while keeping the PAH and PSS concentrations in the final PAH/PSS/PAG mixtures fixed at 0.481 and 0.241 M, respectively).