

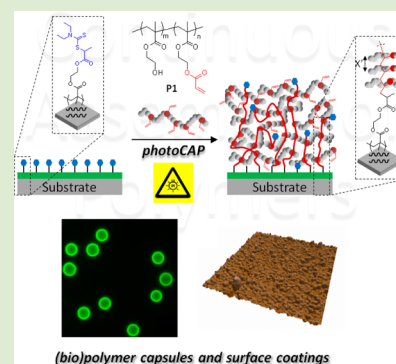
Phototriggered, Metal-Free Continuous Assembly of Polymers for the Fabrication of Ultrathin Films

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S Supporting Information

ABSTRACT: A facile and metal-free thin film fabrication technology based on the photoinduced continuous assembly of polymers (photoCAP) is described. The efficiency and versatility of this method is demonstrated by the formation of crosslinked and surface-confined nanoengineered thin films, in the form of surface coatings and hollow polymer capsules.



Over the past few decades, the development of highly efficient and versatile film fabrication methodologies has allowed for the development of advanced (bio)materials for a range of applications, including drug and gene carriers,^{1–3} electronic devices,^{4,5} and membrane purification units.⁶ Techniques such as polymer grafting-to^{7–9} and -from^{10–12} and layer-by-layer (LbL)^{13–15} assembly have been thus far widely used to prepare engineered nanoscale films. Recently, we introduced a new approach for thin film fabrication, termed continuous assembly of polymers (CAP), based on the chain-growth polymerization of prefunctionalized (bio)-macromolecules with pendant polymerizable groups (referred to as macrocrosslinkers) from initiator-anchored surfaces to form surface-confined and crosslinked ultrathin films in a single step.^{16,17} The CAP approach is described as a combination of both grafting-from and grafting-to processes. CAP offers the advantage of combining the robustness of the grafting-from approach to polymerize across the polymerizable moieties on the macrocrosslinker forming crosslinked materials and the compositional flexibility of the grafting-to approach to fabricate compositionally unique films that are not easily accessible via grafting-from methods alone. Previously, we demonstrated that ring-opening metathesis (CAP_{ROMP})¹⁶ and copper-mediated radical (CAP_{ATRP})¹⁷ polymerizations can be successfully employed to drive assembly of macrocrosslinkers into thin films of various compositions on both planar and spherical templates, yielding surface coatings and hollow polymer capsules, respectively. Depending on the method of polymerization used, different film properties (e.g., thickness, surface topography, and density) were obtained because of the inherent mechanistic differences between them. Therefore, given that the film properties are strongly influenced by the polymer-

ization technique and reaction conditions, the investigation of other polymerization protocols could provide new synthetic avenues and hence the design of unique films and polymeric capsules via the CAP process.

Herein, a photoinduced radical polymerization system for the CAP process (photoCAP) is described (Scheme 1). Dithiocarbamates, which are known to dissociate reversibly into pairs of carbon-centered radicals and dithiocarbamyl radicals (acting as the initiating and mediating species, respectively)^{18–21} upon UV irradiation (365 nm), were employed as the photoinitiators. The generated initiating species on the surface, as a result of the photocleavage of the dithiocarbamates, will react with the polymerizable moieties of the macrocrosslinkers, thus initiating the polymerization process while the dithiocarbamyl radicals would exclusively terminate/couple with the growing chains via a reversible activation/deactivation equilibrium (Scheme 1b). The application of dithiocarbamates in the photoCAP process was inspired by the earlier studies on the efficient photoinduced grafting-from polymerizations to synthesize functional polymeric brushes on surfaces.^{20–23}

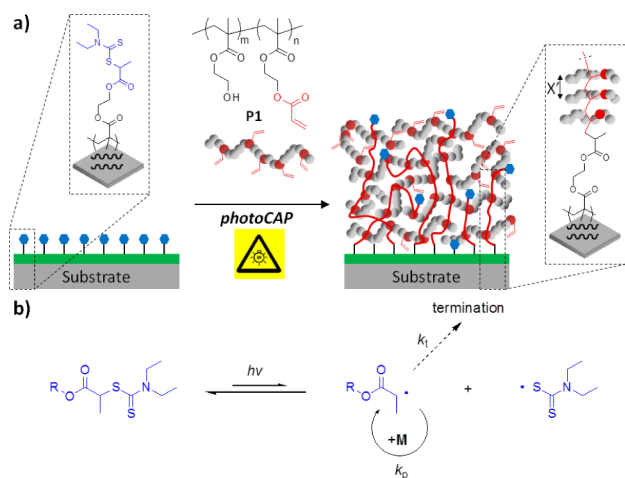
The strategic use of photochemistry enables the CAP reactions to proceed rapidly, reaching a maximum film thickness (ca. 5 nm on planar substrates) within minutes under mild conditions (i.e., at room temperature and without any potentially toxic metal catalysts). The efficiency of the photoCAP system is highlighted by the formation of ultrathin films on both planar Si wafers and SiO₂ particles, with the latter acting as templates to produce hollow capsules. The novelty of

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Scheme 1. (a) The PhotoCAP Reaction is Based on the Photopolymerization of PHEMA Macrocrosslinker P1 from Surface-Functionalized Dithiocarbamate Initiators To Form Crosslinked Films via (b) the Reversible Radical Activation/Deactivation Mechanism^a



^a“X” represents the interlayer spacing.

this work resides in a facile strategy for thin film preparation that is metal-free and avoids the need for any additional additives, such as (organo)catalysts or radical sources. Metal-free thin film fabrication strategies are particularly attractive for the development of (bio)materials for environmental and biomedical applications, in which the presence of metals may be detrimental.^{24–26}

The dithiocarbamate initiators were primed directly onto negatively charged silica surfaces by electrostatic interactions. This simple method of deposition is achieved using a poly(2-(trimethylamino)ethyl methacrylate iodide) (PTMAEMAI)-based macroinitiator (P_{ini}) consisting of 75 mol % quaternary ammonium cation groups that act as the anchor, with the remaining 25 mol % bearing the dithiocarbamate initiating moieties (Supporting Information, SI). Ellipsometry measurements revealed an average initiator prelayer thickness of 1.3 nm when deposited onto Si wafers. The poly(2-hydroxyethyl methacrylate) (PHEMA)-based macrocrosslinker (P1) was prepared from a commercially available PHEMA, whereby the hydroxyl functionalities were partially converted into acrylate groups (15 mol %; SI).

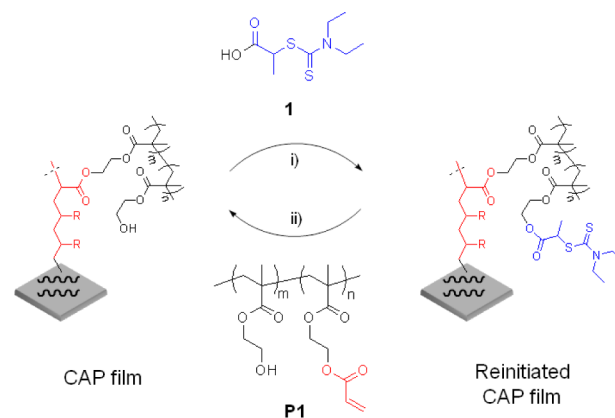
In examining the feasibility of the photoCAP system, initial studies were performed on dithiocarbamate-functionalized planar Si substrates. A thin film with a mean thickness of 4.5 nm, as determined via ellipsometry (excluding the initiator prelayer), was formed when the modified Si wafer was immersed in a solution of P1 in DMSO (4.6 mM) and irradiated with UV light ($\lambda = 365$ nm) for 30 min. This thickness was confirmed by atomic force microscopy (AFM) (Figure S1 in SI). During the photoCAP reaction, the initiating species tethered to the Si surface, propagates from the surface by controlled radical polymerization via the pendant polymerizable acrylate groups of the macrocrosslinkers as they approach the surface, forming a crosslinked film. In addition, the films are confined to the surface, as there was no observable polymerization of the macrocrosslinker in the solution. The molecular weight distributions of the macrocrosslinker P1 in solution before and after photoCAP were identical. This indicates that the integrity of P1 in solution during photoCAP is unaffected

and that film formation is confined to the surface. This allows subsequent reuse/recycling of the P1 solution for further photoCAP reactions. When reusing the same macrocrosslinker P1 solution for repeated photoCAP processes on freshly prepared Si wafers, the generated films displayed similar thicknesses with no apparent loss of functionality (Table S1 in SI), and the molecular weight distributions of P1 after each CAP reaction again remained unchanged (Figure S2 in SI). The recyclability of the macrocrosslinker proved economical while eliminating the need for tedious purification steps.

To prove that the films result from photoCAP reactions, two separate control experiments were performed using (i) a Si wafer deposited with a pseudoinitiator prelayer (i.e., quaternized P_A, see SI) that contains no dithiocarbamates and (ii) by conducting the reaction in the dark. Both control experiments revealed negligible film growth (<0.3 nm), hence, validating the photoCAP process. Longer reaction times at 1 and 16 h did not increase the film thickness beyond 5 nm, indicating that the film thickness reached a plateau after 30 min of photolysis. Possible reasons for this plateau are that the surface confined propagating radical centers are either (i) “buried” within the film (due to steric hindrance) and are unable to propagate outward to the surface or (ii) undergo conventional cross termination reactions between one another, leading to the formation of unreactive carbon–carbon bonds, which is known for surface-initiated polymerization systems.²⁷ For further growth, the surface can be refunctionalized with new initiating groups followed by further film growth via sequential CAP reactions with the same or a different macrocrosslinker, similar to our previously reported CAP_{ROMP} and CAP_{ATRP} methods.^{16,17} Specifically, the available hydroxyl groups from the crosslinked films were reacted with acid-functionalized dithiocarbamate 1 via carbodiimide coupling chemistry, consequently regenerating fresh initiators on the surface (Scheme 2). Further film growth with the same macrocrosslinker (P1) as a result of subsequent reinitiation and photoCAP steps was monitored by ellipsometry (Figure 1a and Table S1 in SI), while the surface topography of the films was analyzed by AFM (Figure 1b).

Four reinitiation–film growth cycles were conducted. Each reinitiated film growth added about 4–5 nm of film, which is

Scheme 2. Refunctionalization of PHEMA Polymer Films with Fresh Initiator 1 Followed by Subsequent PhotoCAP Reaction^a



^aReagents and conditions: (i) 100 mM EDC, 10 mM DMAP, 25 °C, 30 min; (ii) $h\nu = 365$ nm, 25 °C, 30 min.

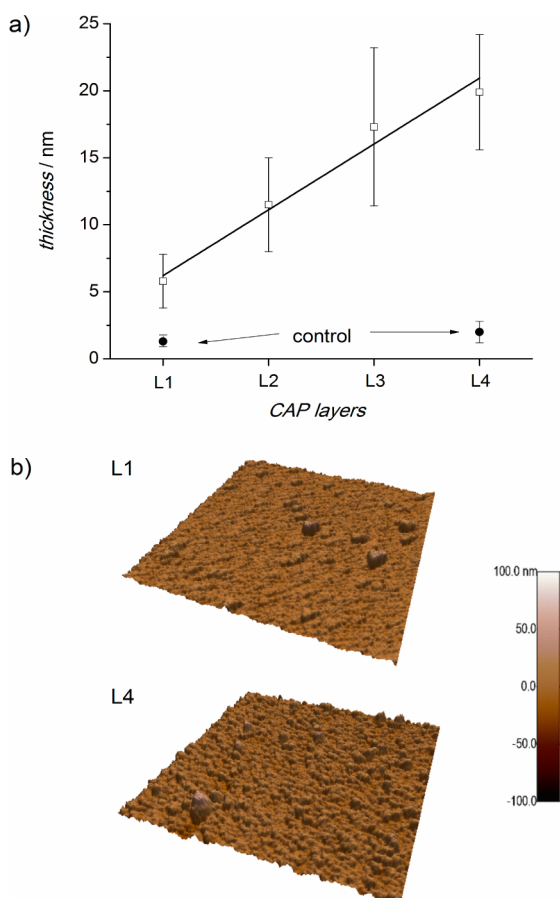


Figure 1. (a) PHEMA film thickness (as determined by ellipsometry) on a Si wafer after each reinitiation and photoCAP step; (b) $5 \times 5 \mu\text{m}$ 3D height mode AFM images of films as a result of one (L1) and four (L4) photoCAP reactions.

similar to the first layer from the Si surface. The final film thickness obtained after four consecutive CAP reactions was about 19 and 18 nm, as determined via ellipsometry and AFM (Figure S3 in SI), respectively. AFM imaging of the crosslinked films with different film layers revealed smooth and continuous film topographies (Figure 1b). The surface roughness of the films (as indicated by the root-mean-square (rms) values) increased from 4 to 7 nm as the number of initiator functionalization and photoCAP steps increased from one (L1) to four (L4), which is comparable to our previously described CAP_{ATRP} system.¹⁷ Because each reaction step (CAP followed by reinitiation) is relatively fast compared to earlier systems, the entire assembly process can be easily achieved within 6 h (vs 24 h).

The photoCAP process was successfully implemented on particle templates. Nonporous SiO₂ particles (5 μm diameter) coated with P_{ini} were subjected to photoCAP reactions in the same way as the Si wafers. As with the planar system, sequential reinitiation and photoCAP steps were repeated on the SiO₂ particles. After different reinitiation-film growth steps, dissolution of the SiO₂ core afforded free-standing films in the form of hollow polymer capsules. AFM, fluorescence and differential interference contrast (DIC) microscopy images (Figure 2) provided direct evidence of capsules. From AFM analysis (Figures S4–S6 and Table S1 in SI), an increase in the capsule wall thickness was observed, corresponding to additional reinitiation and photoCAP steps, similar to the

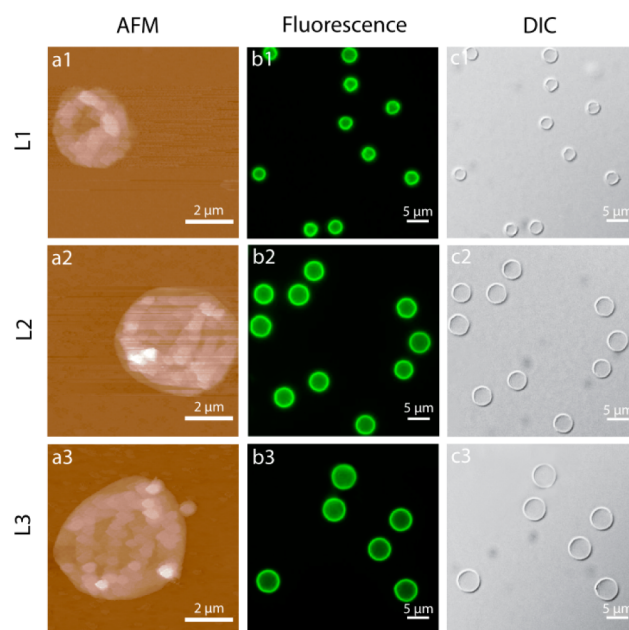


Figure 2. AFM (a1–3), fluorescence microscopy (b1–3), and DIC microscopy (c1–3) images of PHEMA polymer capsules after 1, 2, and 3 reinitiation and photoCAP steps, respectively. SiO₂ particles (5 μm diameter) were used as templates.

crosslinked films formed on Si wafers. The average single-wall thickness of the formed capsules after three photoCAP reactions was about 18 nm. The fluorescently labeled capsules (fluorescently tagged macrocrosslinker P2 was used in place of P1, see SI) are also clearly visible by fluorescence microscopy. DIC microscopy further confirmed the formation of capsules. To prove that formation of polymer capsules was due to the photoCAP process, the same experiment was performed using a pseudoinitiator prelayer as above. Under these conditions, no capsule formation was observed via microscopy upon dissolution of the silica core. Capsules with higher mechanical stability (L2 and L3, Figure 2) as a result of greater film thicknesses and possibly increased crosslinking density exhibited limited shrinkage ($\leq 10\%$) compared to those formed after only a single photoCAP reaction (ca. 50% shrinkage). This is not surprising, as often more than four polymer deposition steps are required in conventional LbL processes before stable and robust capsules are obtained.^{2,14,28} To the best of our knowledge, such capsule formation via photoCAP is the first example of one-step phototriggered formation of crosslinked films on particle templates.

In conclusion, a novel and versatile film fabrication methodology, referred to as photoCAP, is demonstrated. The photoCAP approach, which is metal-free and tolerant to numerous functional groups, can be applied to form crosslinked ultrathin films as surface coatings or hollow polymer capsules. The generated films are confined to the surface, which allows the macrocrosslinker solution to be recycled. Noteworthy is the ability to produce crosslinked and surface-confined films in one step, which complements other efficient (photo)crosslinkable systems,^{29,30} thus, providing scientists an alternative approach for film fabrication. Different macrocrosslinkers can be applied to different reinitiation/film growth steps, potentially forming composite film structures. Furthermore, the photocontrolled film formation could potentially be applied in photolithography

to allow patterned film structure formation, which can be integrated in designed photoCAP layers.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed experimental and characterization procedures as well as AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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