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Double Replication of Silica Colloidal Crystal Films

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Supporting Information

ABSTRACT: Inverse opals made by polymerizing vinyl monomers inside a colloidal crystal have lattice dimensions that are contracted relative to the original hard template. This effect was studied in order to investigate the possibility of making double replicas of varying pore sizes from different materials, and to gain a better understanding of the polymer contraction behavior during replication. The degree of lattice contraction was measured using colloidal crystal films formed from silica spheres with diameters in the range 33–225 nm, and polymers pEDMA [poly(1,2-ethanediol dimethacrylate)], pDVB [poly(divinylbenzene)], pHDMA [poly(1,6-hexanediol dimethacrylate)], pBDMA [poly-(1,4-butanediol dimethacrylate)], and a 5:4 copolymer mixture of pEDMA/pDVB. The degree of lattice contraction depended on



the alkyl chain length of the monomer, as well as the degree of cross-linking, with up to 32% contraction observed for pEDMA when the silica template was removed. However, filling the polymer inverse opals with silica or titania returned the lattice spacing closer to its original size, an effect that can be rationalized in terms of the driving forces for contraction. Double replication of both single-component and binary silica colloidal crystals therefore generated silica and titania replicas of the original lattice. Thus, double replication provides a pathway for accessing periodic structures that are difficult to synthesize directly from materials such as titania.

KEYWORDS: template, replication, colloidal crystal, silica, titania, polymer contraction

INTRODUCTION

Colloidal crystals, which are composed of periodically arranged particles that range from nanometers to microns in size, are attractive for structure-dependent property applications such as surface-enhanced Raman scattering, microfluidics, sensing, photonics, energy storage, electrocatalysis, and fabrication of inorganic materials in porous forms.^{1–11} In addition to size scalability, colloidal packing geometries are tunable, ranging from single-component face-centered cubic to complex binary or ternary component systems.^{12,13} The structural diversity of colloidal crystals makes them appealing candidates for template synthesis. Thus, the replication of colloidal crystals has been extensively studied, dating from early work on infiltrating silica or latex colloidal crystals with carbons and inorganic oxides, and soon thereafter expanded to many other materials including semiconductors, metals, quantum dots, and magnetic oxides.^{8,14–24}

Colloidal crystal replication with polymers follows the process flow shown in Figure 1. The template is first assembled by one of the several possible methods including sedimentation, evaporation, layer-by-layer assembly, floating layer or electric field deposition, or spin-coating (Figure 1a).^{25–32} Second, the colloidal crystal template voids are filled with the material of interest (Figure 1b). In Figure 1b, in situ polymerization was performed to obtain a cross-linked polymer replica. In addition to polymerization,^{33–35} other infiltration methods are available



Figure 1. Process flow: (a) 57 nm silica colloidal crystal film, (b) 5:4 pEDMA/pDVB polymer-infiltrated 57 nm silica template, and (c) 5:4 pEDMA/pDVB polymer inverse opal film cleaved cross-section.

and depend upon the infiltrant, such as electroless deposition or electroplating for metals, CVD/ALD (ALD, atomic layer deposition) for vapor phase reactants, and sol–gel processing for inorganic oxides.^{36–42} The template is finally removed

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chemically or thermally (Figure 1c) to leave an ordered inverse opal.

Despite the numerous possibilities for materials fabrication with colloidal crystal templates, there is a synthetic limitation set by the template itself. Replicas resulting from colloidal crystal templates may have only the dimensions, structural complexity, and degree of order of the original template. Colloidal crystal assembly has advanced considerably, but there is an ongoing challenge to develop a continuous range of templates to match the desired particle morphologies, packing geometries, and particle sizes. Structure and scale control are critical to materials research, and new methods of fabrication are needed in order to close the synthetic gap. Some studies have addressed this by infiltrating colloidal crystal templates with deformable polymers or sol-gels in order to manipulate the inverse opal structure. For example, Jiang and co-workers mechanically stretched polystyrene inverse opals, resulting in ovaloid pore spaces that would otherwise have been difficult or impossible to achieve by direct synthesis.³⁴ Phillips and coworkers achieved a similar shape effect by anisotropic shrinking of a hydrated silica inverse opal matrix with thermal treatment.43

Earlier work in our group showed that polymer replicas of silica colloidal crystals contracted significantly upon template removal, effectively reducing the pore size while maintaining order. The contracted inverse opal polymer pores filled incompletely with a single infiltration of silica sol-gel in that study; thus, double replication in reduced dimensions was not confirmed, and the contraction phenomenon remained poorly understood.³⁵ The mechanism of lattice contraction is likely due to a combination of factors, including volumetric contraction of the polymer during curing and the surface free energy at the template-polymer interface. Volume contraction typically occurs in addition polymerization when van der Waals contacts between monomers convert to covalent bonds in the polymer network.^{34,35,44-54} This inherent tensile stress can be relieved by polymer chain coiling or flow when the hard template is removed. Similarly, if there are strong noncovalent interactions between a polar polymer and the hard template, the surface energy should increase when the template is removed, resulting in contraction.

Polymer contraction during template replication has been noted in several studies as a side effect of the polymerization process, but it has been unexplored as a tool for intentionally tuning inverse opal structures following initial reports of the effect.^{34,35,55} One might imagine the potential that double replication could result in a hard template of reduced dimensions, and that multiple cycles of replication could access very small pore dimensions. However, as we show below, the contraction process is reversed when the contracted polymer pores are refilled during double replication. Studying polymer inverse opal contraction and re-expansion is of fundamental interest for attaining a better understanding of double replication synthetic procedures.

In this study, we further investigated colloidal crystal filling with polymers that undergo different degrees of contraction when the hard template is removed. We quantified the pore contraction of several polymer inverse opals and measured the lattice spacing of double replicas cast from them. Double replicas were made from face-centered cubic colloidal crystals, as well as from structurally more complex binary colloidal crystals. Lattice contraction was monitored as a function of colloid size, polymer nanomechanical properties, and polymer composition. To do this, we used silicon-wafer-supported silica colloidal crystal films assembled by the vertical evaporation method, which produces films with long-range order. The silica colloidal crystal films were subsequently infiltrated by in situ radical polymerization with pEDMA [poly(1,2-ethanediol dimethacrylate)], pDVB [poly(divinylbenzene)], pHDMA [poly(hexanediol dimethacrylate)], pBDMA [poly(butanediol dimethacrylate)], and a 5:4 copolymer blend of pEDMA/ pDVB.

EXPERIMENTAL METHODS

Silica Colloid Synthesis. All reagents were used as received from commercial sources. Amino-acid-stabilized silica nanoparticles of 32.9 \pm 2.2 nm diameter were prepared by following a modified Hartlen method.⁵⁶ Briefly, approximately 23 nm diameter seed particles were prepared by stirring a mixture of 0.52 mmol of L-arginine (Sigma-Aldrich, \geq 98%) and 3.8 mol of nanopure water below a floating layer of 0.042 mol of cyclohexane (anhydrous, 99.5%) and 0.025 mol of tetraethyl orthosilicate (hereafter referred to as TEOS; Sigma-Aldrich, 98%). This biphasic mixture was reacted for 20 h at 60 °C. Regrown nanoparticles were prepared by mixing 20 mL of the 23 nm diameter seeds with 4.0 mol of nanopure water, with a floating layer of 0.031 mol of tetraethyl orthosilicate and 0.093 mol of cyclohexane. This was further reacted for 30 h at 60 °C. The 56.7 \pm 2.8 nm diameter silica was prepared by reacting the same 23 nm seed particles for 4 days instead of 20 h, reaching a 39 nm diameter, followed by the same seed regrowth reaction for another 4 days instead of 30 h in order to reach 57 nm.

The 112.6 \pm 3.2 nm and 225.5 \pm 4.8 nm diameter silica colloids were prepared by following the Watanabe method directly for their 100 and 250 nm syntheses, with all quantities scaled by half.⁵⁷ The synthesis of colloids of all sizes began with a 14 nm seed synthesis, in which 0.5 mmol of L-arginine was dissolved in 4.85 mol of nanopure water and reacted with 25 mmol of TEOS at 70 °C for 24 h. Then, for 112.6 nm particles, 0.26 g of seed solution (cooled to room temperature) was added to 1.15 mol of water, 0.5 mmol of arginine, 1.45 mol of ethanol (Koptec, anhydrous 200 proof) and then reacted with 24.94 mmol of TEOS for 24 h at 70 °C. The 226 nm particles were prepared in a similar manner using the same seed preparation, but with the regrowth reactants in the following amounts: 44 mg of seed solution, 25 mmol of TEOS, 0.75 mmol of L-arginine, 1.45 mol of ethanol, and 1.15 mol of water.

Substrate Preparation. p-type <100> silicon wafers (1–10 Ω cm with native oxide layer present, obtained from University Wafer) were cleaved into approximately 2.5 cm \times 1.0 cm rectangles. The Si substrates were immersed in freshly prepared piranha solution (3:1 concentrated sulfuric acid and 30% v/v hydrogen peroxide) for 30 min to clean the surface and to render their surface sufficiently hydrophilic. [Caution: piranha solution is dangerous and reacts violently with organic substances!] The cleaned substrates were rinsed copiously with nanopure water.

Colloidal Crystal Film Deposition. Silica colloidal solutions were diluted in water and assembled into colloidal crystals using static vertical evaporation at 40 $^{\circ}$ C and approximately 80–85% humidity onto silicon substrates.^{28,58} Films were sintered at 600 $^{\circ}$ C for 2 h prior to polymer infiltration.

Polymer Preparation. Reagents were used as received: divinylbenzene (DVB; 80%, Sigma-Aldrich), 1,2-ethanediol dimethacrylate (EDMA; 98%, Sigma-Aldrich), 1,4-butanediol dimethacrylate (BDMA; 95%, Sigma-Aldrich), 1,6-hexanediol dimethacrylate (HDMA; \geq 90%, Sigma-Aldrich), and azobisisobutyronitrile (AIBN; 98%, Sigma-Aldrich). Monomer solutions were prepared by mixing 2 wt % AIBN with monomer. Monomer–AIBN mixtures were deoxygenated and cured at 70 °C for 12 h. Silica colloidal crystal films (~1 cm²) were infiltrated with monomer–AIBN solutions by pipetting the monomer solution directly onto the colloidal crystal films prior to deoxygenating and curing in situ. The 5:4 pEDMA/pDVB copolymer was prepared by mixing the monomers in a 5:4 molar ratio.



Figure 2. SEM micrographs of a 112.6 nm silica colloidal crystal film, and polymer inverse opals made from it, after etching out the silica template. Inset images are all at the same scale for comparison.

Inverse Opal Preparation. Polymer inverse opal films were obtained by etching out the silica template with 10% hydrofluoric acid (diluted from 48%, Sigma-Aldrich). [Danger: Hydrofluoric acid is toxic; wear appropriate protection while handling hydrofluoric acid!] The films were rinsed several times with nanopure water to remove residual hydrofluoric acid. The films were then dried in air at ambient temperature.

Characterization. Colloidal particles were sized and films imaged by scanning electron microscopy using a Zeiss SIGMA VP-FESEM and a Zeiss Merlin SEM. We imaged all films at lower accelerating voltages and without the use of metal coatings. Young's modulus measurements were performed with a Bruker Dimension Icon AFM on thin films (>200 nm thick) of polymers cast on silicon wafers with soft indentations of 2 nm. Softer polymer measurements (Young's modulus < 2 GPa) were performed with a Tap150A probe calibrated by the absolute method (tip geometry at indentation depth, spring constant, and deflection sensitivity were all defined). Stiffer polymers (Young's modulus > 2 GPa) were indented with an OTESPA probe calibrated relative to a polystyrene film standard (PSFilm-12M, elastic modulus 2.7 GPa). Moduli were calculated with the Hertz fit using Bruker NanoScope analysis data processing software. Replicate measurements were recorded from different points for each polymer. Poisson's ratio was unknown for the tested sample films, so a ratio of 0.35 was assumed for all.

RESULTS AND DISCUSSION

Polymer Replication of Colloidal Crystal Films. Silica colloidal crystal templates ranging from 32.9 to 225.5 nm diameter were infiltrated with pDVB, pEDMA, 5:4 molar mixture of pEDMA/pDVB, pHDMA, and pBDMA. By minimally wetting the colloidal crystals, template filling was achieved by capillary action, and there was minimal polymer overgrowth obstructing the top surface. Minimization of the overlayer was key to successful silica etching and subsequent inverse opal infiltration in later steps. This also allowed top surface imaging of most polymer films. The thickness and overall quality of the original colloidal template was critical to film integrity with infiltration/etching steps. If the colloidal crystal was too thick (greater than approximately $1-1.5 \ \mu m$ for 32.9 nm colloids) and severely cracked, the film delaminated during the silica template etching step. The critical thickness varied by silica colloid size and layer count. This was due to the widening of cracks and partial lift-off of the silica colloidal

crystal film, allowing the infiltrating polymer to wedge the film apart from the substrate.

Figure 2 shows electron micrographs of a face-centered cubic template made from 112.6 nm diameter silica spheres and replicas made from it using five different polymers. Figure 3



Figure 3. (a) Monomer molecular structures. (b) % lattice contraction of inverse polymers vs silica template diameter. Abbreviations: E = pEDMA, B = pBDMA, H = pHDMA, M = 5:4 pEDMA/pDVB, D = pDVB.

plots the percent contraction of the polymer inverse opal lattice versus original silica colloid diameter, up to $32.4\% \pm 3.0\%$ with pEDMA. The percent lattice contraction in Figure 3 was calculated from the spacing between inverse opal pores and the spacing of spheres in the original colloidal crystal (distance between neighboring pore or particle centers). Direct pore diameter measurements are also reported in Table S1 in the

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Supporting Information for comparison. In all cases, the apparent contraction in pore diameter was greater than the percent contraction in lattice spacing. This is likely due to the thickening of pore walls as well as to systematic error in measuring distances in a 2-dimensional projection of a 3-dimensional lattice.

Consistent with the results of Johnson et al.,³⁵ we found that inverse opal polymer thin films contracted most with increasing amounts of pEDMA relative to pDVB. The contraction of pHDMA and pBDMA inverse opals was intermediate between those of pDVB and pEDMA films. The three polymers, pEDMA, pBDMA, and pHDMA, differ only in their aliphatic backbone chain length. The degree of lattice contraction increased monotonically as the chain length decreased. This trend agrees with other studies on dimethacrylate polymerization, which also found less contraction with increasing molecular weight or aliphatic chain length. Several causes have been proposed for this trend, including molecular weight effects on monomer diffusion during polymerization, and the increased degrees of freedom that longer chains have for uncoiling in the process of polymerization.^{59,60}

The pore size distributions in the inverse opals were the widest in the most contracted polymer, pEDMA. This was due to a higher incidence of deformation defects occurring either randomly or at sites of film damage, or uneven contraction-induced tension, as well as instability under the electron beam while imaging. (Pores typically widened when overexposed, resulting in an overestimation of pore diameter; see Figure S2 in the Supporting Information.) Less contraction was sometimes observed at the perimeter of the films where colloids had fewer neighbors, allowing more deformation of the polymer replica than in the bulk of the film. Film integrity could be disrupted by polymer curing, with contraction causing delamination and film cracking to relieve strain at the polymer–substrate interface. This effect could be reduced by minimizing polymer overlayer growth.

Polymer Contraction versus Template Size. Silica colloidal crystal templates of different periodicities were filled with polymers to determine how the template size and crystal structure affected the resulting lattice contraction. The template colloid size/packing geometry defines the void space that the curing polymers fill. The polymers experience greater contraction stress upon curing as the number of walls increases because the cured polymer is pinned to the wall surface.^{46,51} In Figure 4, face-centered cubic colloidal crystals grown from 225.5 nm diameter silica templates were filled with pDVB, pEDMA, and 5:4 pEDMA/pDVB. In Figure 5, 56.7 and 32.9 nm templates were infiltrated with 5:4 pEDMA/pDVB for comparison.

As seen in the data plotted in Figure 3, the percent contraction was comparable within a few percent for all 5:4 pEDMA/pDVB polymer replicas. This was also corroborated by the similar percent contractions of pDVB and pEDMA in the 112.6 and 225.5 nm templates. There is a general trend of less contraction with increasing template size, but the 112.6 nm 5:4 pEDMA/pDVB polymer film deviated from the trend. Since all the templates in these examples were cubic close-packed, the geometry and relative void-to-solid volume ratio (~26% void for ideal FCC packing) were comparable for all template sizes. The trend suggests that the polymer has more freedom to deform during curing in larger particle templates. Previous studies on polymer composites mixed with disordered filler particles also suggest some small size and shape

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Figure 4. SEM micrographs of 225.5 nm diameter silica colloidal crystal template and its polymer inverse opals after etching. Inset images are all at the same scale for comparison.

Figure 5. SEM micrographs of 32.9 and 56.7 nm silica colloidal crystal templates and their polymer inverse opals.

dependence on contraction, with larger particles causing less contraction. 61

Polymer Nanomechanical Properties. Polymer pore contraction was compared with the relative stiffness of bulk polymer thin films, and the results are summarized in Figure 6. Young's moduli were measured by AFM nanoindentation and

Figure 6. Young's moduli of the 5 different polymers plotted against % lattice contraction of the polymer inverse opals prepared from 112.6 nm silica colloidal crystal film templates.

calculated with the Hertzian fit on the force–separation plots as described in the Experimental Methods section. The technique and fit, as well as their limitations, have been described elsewhere.^{62,63} AFM indentation force–separation curves for each polymer sample are shown in Figure S3. Because of the peak forces necessary to indent each film (see the highest *y*-value force on the red approach curves in Figure S3), it was also qualitatively evident which samples are more deformable than others without the modulus calculations.

In the series of pDVB, pEDMA, and 5:4 mixture of pEDMA/ pDVB, the moduli increased linearly with higher amounts of pDVB relative to pEDMA. This follows since pDVB is a crosslinker and is the stiffest polymer due to its aromatic rings. A similar linear trend was reported in previous work with mixtures in this polymer series.³⁵ In the pEDMA, pBDMA, and pHDMA series, the modulus decreased as the molecular weight increased. It is interesting to note that, in this series (with no cross-linker present), the most mechanically deformable polymers were not the ones that experienced the most contraction as inverse opals. The most contracted polymer was pEDMA, which has a higher modulus than the other two dimethacrylate polymers. The softest, most elastic pHDMA polymer experienced relatively little contraction. There is often an inverse correlation between polymer stiffness and volumetric contraction, but some polymers deviate from this trend, depending on their molecular structure and degree of conversion from monomer to polymer.^{50,64} In this case, we can rationalize the greater contraction of pEDMA in terms of the favorable interaction between the polar ester groups and the silica surface; the tension that results in contraction is a result of increasing polymer surface energy when the template is removed. pHDMA is a less polar polymer, with lower surface energy, and the hexyl chain also has more degrees of freedom for uncoiling to relieve strain than the ethyl chain in pEDMA.

The consideration of both modulus and contraction has significance for designing future porous materials in which pore contraction is desired. The combination of properties affects the polymerization stress on the inverse opal polymer structure and how well the film will handle the stress upon template removal. This in turn affects film adhesion and cracking, and so a polymer with a moderate balance of contraction and deformability would be ideal. In this study, the best contraction to modulus compromise was in the pBDMA and 5:4 pEDMA/ pDVB films, which both contracted and retained larger areas of film for further replication steps and analysis (sol–gel infiltration, dissection for SEM imaging).

A notable source of experimental error in the modulus measurements is localized variations in sample roughness, which affect the measured indentation depth (observed in AFM topography imaging, Figure S4). Additionally, there are local variations in stiffness (hard or soft spots) and adhesion. The standard deviations were highest for the pDVB, pEDMA, and 5:4 mixture films, which had the largest bulk moduli.

Double Replica Silica Opals. The contracted polymer inverse opals were filled with inorganic sol-gels in order to investigate the possibility of making second-generation replicas with a range of reduced (from the original template size) particle sizes. The polymer was first wetted with 1 M hydrochloric acid (HCl) and then immersed in TEOS in order to prepare silica double replicas. The samples wetted with TEOS were stored overnight in a closed container, dried in a 60 °C oven, and then wetted with HCl and then TEOS again. This method required 3–7 filling cycles depending on the pore size

(larger pores required more filling steps) and usually produced a significant silica overlayer. The final film was calcined at 450 $^{\circ}$ C to remove the polymer template. Initial experiments infiltrated a mixture of TEOS with water and catalyst (HCl acid or ammonia base were each tried); however, the process was more difficult to control in those cases because of the faster reaction rate.

The most significant finding was that, in almost all cases, the lattice spacing expanded in the resulting silica double replicas. The results are summarized in Table 1. Figure 7 compares the

Table 1. Silica Opals Templated from Polymer Inverse Opals

polymer inverse opal type	silica template lattice spacing (nm)	polymer pore spacing (nm)	second-generation silica lattice spacing (nm)
pEDMA	122.6 ± 4.7	82.9 ± 7.0	103.0 ± 7.4
pDVB	122.6 ± 4.7	114.7 ± 2.9	108.5 ± 6.5
5:4 pEDMA/pDVB	122.6 ± 4.7	96.4 ± 9.2	102.7 ± 8.7
5:4 pEDMA/pDVB	37.7 ± 2.4	29.2 ± 2.0	32.7 ± 2.1
5:4 pEDMA/pDVB	233.6 ± 11.3	190.3 ± 10.8	206.7 ± 11.6
pHDMA	122.6 ± 4.7	110.4 ± 3.5	105.2 ± 3.1
pBDMA	122.6 ± 4.7	98.8 ± 4.2	105.7 ± 4.6

Figure 7. Top: SEM image of an 83 nm pEDMA inverse opal prior to filling. Bottom: SEM image of the resulting 103 nm silica opal after filling and removing the pEDMA template.

double replica silica film with the pEDMA template from which it was grown. Images of other silica replicas are shown in Figure S5. Double replication led to lattice expansion, relative to the polymer inverse opal, in all cases except the least contracting rigid pDVB and pHDMA films, in which the final particles were slightly smaller than the original template particles. Some contraction in double replication is expected since the ceramic yield of the sol-gel process is less than 100%, even with multiple filling cycles. However, this cannot be the principal cause of the lattice expansion, because even poorly filled templates expanded. Partially formed hemispherical particles were observed with wider diameters than the polymer pores. This suggests that the lowering of the polymer surface energy

Figure 8. SEM micrographs of (a) top-view 34.8 ± 1.8 nm and 22.8 ± 1.9 nm AB₂-type binary colloidal crystal, (b) 5:4 pEDMA/pDVB inverse polymer opal of part a with 25.8 ± 2.3 nm and 16.5 ± 1.3 nm pores, (c) cross-section of part a, (d) cross-section of part c, (e) SiO₂ opal generated from part b, (f) TiO₂ double replica generated from the polymer inverse opal in part b. All inset images are scaled to the same magnification.

upon pore filling with silica is the primary driver for reexpansion of the lattice.

Water sorption in methacrylate polymers has been reported as a cause of dimensional changes that occur upon polymerization and drying.⁶⁵ Some film cracking/loss did occur in the drying stage from film re-expansion and overlayer growth. Attempts to carbonize the polymer templates to preserve their contracted pore sizes were unsuccessful because of the poor ceramic yield of carbons made from dimethacrylates.

Binary Film Double Replication in Silica and Titania. Polymer inverse opals (5:4 pEDMA/pDVB) prepared from binary silica colloidal crystal films were filled with sol-gel precursors to produce double replicas in silica (Figure 8e) and titania (Figure 8f). The silica opal template was prepared by the same method as described above for single-sized templates. The purpose was to demonstrate replication of a multicomponent opal in the original material (silica), as well as in a different material.

Although titania inverse opals have been studied extensively for their photonic crystal properties, titania AB₂-type binary colloidal crystal films cannot be easily prepared, and we demonstrate here that this is possible on the tens-ofnanometers scale by double replication. Periodic titania assemblies have typically been synthesized as hollow inverse periodic structures through template or nanoparticle codeposition strategies with polymer sphere scaffolds to circumvent the challenge of synthesizing and assembling monodisperse titania spheres directly. There are few examples of ordered assembly of solid TiO₂ nanoparticles by sedimentation or other methods, but only in single-sized assemblies and usually with particles that are >100 nm in diameter.^{8,9,66–70}

Figure 8a-d depicts top and cross-sectional SEM views of an AB₂-type binary colloidal crystal film composed of 34.8 ± 1.8 nm and 22.8 ± 1.9 nm silica particles and their 5:4 pEDMA/ pDVB polymer inverse opal replica. The most distinguishable feature of this binary arrangement is the topside view pattern in Figure 8a of hexagonally arranged larger particles each surrounded by six of the smaller particles. The percent pore contraction was similar to that of other colloidal templates shown in Figures 2 and 3 for this polymer. The larger particles

in the binary template appeared to contract slightly more at $21.6\% \pm 2.8\%$ than the smaller ones at $19.2\% \pm 2.9\%$; however, this difference is within experimental error. The percent lattice contraction was calculated from particle-to-particle distance in repeating features in the cross-section since the top view had lower resolution. When compared to Figure 2 data, these numbers are in line with the general trend of approximately 20% contraction with the 5:4 pEDMA/pDVB polymer.

Titanium dioxide double replica films were prepared by immersing the polymer inverse opal in titanium(IV) isopropoxide (Aldrich, 97%) for 2 h, followed by transfer to 0.1 M HCl and immersion overnight. The film was then dried at 60 °C and the filling process repeated three more times. The final product was calcined at 450 °C to remove the polymer template. Titania infiltration gave areas of incomplete filling, especially in the interior of thicker films, access to which become obstructed as the surface pores tended to fill first. However, titania replication provided a proof of concept of the utility of double replication, as seen in Figure 8f, with the familiar binary patterning and distinguishable particles of different sizes. Infiltration resulted in varying thicknesses of a titania overlayer over most of the film, with the less apparent, finest residues covering regions like that imaged in Figure 8f. As expected from observations with facecentered cubic double replicas, pore expansion also occurred upon silica or titania sol-gel infiltration of binary inverse opals.

CONCLUSIONS

Silica colloidal crystal film templates of sizes ranging from 32.9 to 225.5 nm were infiltrated with several polymers in order to quantify the degree of pore contraction that occurs after a polymer is formed and the original template removed. Supported colloidal crystal films can be replicated, and the resulting inverse opals have smaller dimensions by as much as 32% with pEDMA. Binary colloidal crystal films grown from a mixture of 34.8 and 22.8 nm diameter silica spheres were also replicated, and showed the same degree of lattice contraction while maintaining binary component ordering. The binary inverse opal was infiltrated with oxide sol–gels (silica and titania) to make double replica inorganic opals. There is also the possibility of extending this double replication process to

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other materials that are stable in the polymer removal process (sintering or solvation) such as metals, other inorganic oxides, and semiconductors.

The volumetric contraction that occurs during addition polymerization is well-documented in bulk polymerization, but unusually large changes in lattice spacing, which are substantially reversed upon double replication, were observed with polymer inverse opals. The reversibility of the process suggests that surface energy effects are the primary driver of lattice contraction and re-expansion. Consistent with this idea, the least polar polymer (pHMDA) showed the least contraction and re-expansion, despite its lower elastic modulus, than the most polar polymer (pEDMA). The re-expansion that occurs upon pore filling limits the utility of double replication for making opals with successively smaller lattice dimensions and pore sizes. However, it may be possible in future studies to minimize this effect, e.g., through precursor/solvent selection or cross-linking of the contracted polymer inverse opals prior to filling with the inorganic component.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b12662.

Summary of lattice contraction results for different polymers and template dimensions, and additional figures and physical characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

pEDMA, poly(ethylene glycol dimethacrylate) pDVB, poly(divinylbenzene) pEDMA, poly(1,6-hexanediol dimethacrylate) pBDMA, poly(1,4-butanediol dimethacrylate) TEOS, tetraethyl orthosilicate AFM, atomic force microscopy SEM, scanning electron microscopy

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