

# Robust polymer colloidal crystal photonic bandgap structures

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New polymeric matrices are presented that embed organic colloidal crystalline arrays (CCA's) into mechanically stable photonic bandgap structures. We achieved these new matrices either by dispersing polystyrene CCA's with high molecular weight hydrophilic polymer [poly(ethylene glycol); (PEG)] or through *in situ* polymerization of hydrophilic monomers (acrylamide and acrylate functional PEG variants) about the CCA. CCA-dispersed PEG matrices exhibited strong red opalescence with a narrow peak at 614 nm and were sufficiently rigid to withstand repeated mechanical deformation. Visible photonic bandgaps also were observed from free-standing CCA composites with cross-linked poly(*N,N*-dimethylacrylamide) matrices. The results demonstrate the technological potential for robust organic photonic crystals. © 2000 Optical Society of America

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Spatial periodicities in the dielectric function of an optical material can yield both allowed and forbidden directions in which electromagnetic waves of certain energies may propagate. These photonic bandgap effects arise from coherent interference by multiple scattering when the wavelengths of the electromagnetic waves are comparable with the periodicity scale.<sup>1</sup> Such an optically ordered medium, now commonly called a photonic crystal, permits control over the propagation and characteristics of light passing through it. This control feature has led to international research efforts to develop devices based on photonic crystals, given the global importance of optical and optoelectronic systems. Here we build on previous research in ceramic photonic crystals by Ballato<sup>2</sup> to develop organic analogs based on the self-assembly of monodispersed charged particles in suspension. Such colloidal crystalline arrays (CCA's) are three-dimensionally periodic structures that are spontaneously ordered through electrostatic interactions between the particle's surface charge, coupled with a consequent diffuse counterion cloud, when the CCA's are dispersed in a polar medium. The repulsive interaction between spherical macro ions can be significant over distances greater than 1  $\mu\text{m}$  if the solution is pure and nearly free of ionic species that would collapse the double layer.<sup>3</sup> At high particle concentrations ( $>10^{13}/\text{cm}^3$ ), the significant interparticle repulsion results in the adoption of a minimum-energy colloidal crystal structure. These CCA's can be fabricated to length scales that diffract light and have been employed in active photonic switching and sensory roles.<sup>4</sup>

Unfortunately, most CCA's are liquid-phase-based structures and therefore do not exhibit a high degree of mechanical robustness or stability. For instance, a liquid-phase CCA will undergo transitory disordering

when it is subjected to a mechanical shock, whereas permanent disordering can be induced to incur by the introduction of ionic impurities. Recently, robust network matrices were developed to stabilize the array through *in situ* polymerization of a water-miscible monomer that resulted in a relatively robust polymerized crystalline colloidal array (PCCA).<sup>5</sup> Here we explore alternative matrices with which to extend the number of ways stable PCCA's can be fabricated by focusing on (1) polyethylene glycol (PEG) and (2) polyacrylamide-based variants in both thermoplastic and thermoset forms. Because organic photonic crystals open the door to a myriad of opportunities that arise when the polymeric molecular structure is tailored to impart task-specific optical functionalities (e.g., emission of light and optical nonlinearities), we assert that efforts toward achieving mechanically robust systems are critical endeavors if practical devices are to be commercially realized.

We prepared monodispersed polystyrene particles by using an emulsion polymerization procedure described elsewhere.<sup>6</sup> The resultant particle diameters were measured with a Brookhaven BI-90 dynamic light-scattering apparatus. The particles were dialyzed against deionized water for approximately 30 h at 60 °C and then shaken with a Bio-Rad AG 501-X8 mixed bed ion-exchange resin. We stored the cleaned suspensions in Nalgene bottles to minimize contamination from ionic impurities. Matrix precursors and all other materials (coded 1–4 in Fig. 1, bottom) utilized in this study are all commercially available and were purchased through either Fisher Scientific or the Aldrich Chemical Company and used as received. The CCA composites were injected between quartz or glass plates separated by a 125- $\mu\text{m}$  spacer and then polymerized *in situ* with a Blak-Ray UV lamp (Model B-100A). Extinction spectra were

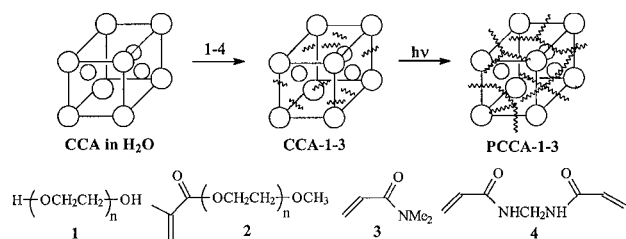


Fig. 1. Top, process schematic for robust matrix formation. Precursors are added to aqueous CCA (denoted CCA- $N$ , where  $N$  is 1, 2, or 3, depending on the precursor). Photoinitiated polymerized composites are denoted PCCA- $N$ . Bottom, structures of precursors 1–3 and cross linker 4.

collected on a Shimadzu UV3101 UV–visible–near-IR spectrophotometer with the incident light normal to the plate surface. Reflectance spectra were obtained with a GreTag MacBeth CE741 UV–visible goniospectrometer.

Our strategy for stabilizing CCA's in polymeric matrices is illustrated in Fig. 1. Monodispersed polystyrene particles, 159 nm in diameter, were dispersed in ion-exchange-treated deionized water to form the initial CCA mesophase at a particle density of approximately  $6.3 \times 10^{13} \text{ cm}^{-3}$ . Inert water-soluble polyethylene glycol (molecule 1), poly(ethylene glycol)-terminated methylmethacrylate (molecule 2), or  $N,N$ -dimethylacrylamide (molecule 3) was then added with and without a bis-acrylamide cross linker (molecule 4) and a photoinitiator (diethoxyacetophenone) in the presence of the ion-exchange resin. Stable blends (denoted CCA-1–CCA-3) were then characterized by UV–visible spectroscopy and subsequently polymerized by exposure to UV light (for acrylic precursors), which yielded free-standing polymeric photonic composites (denoted PCCA-1–PCCA-3).

**PEG-based matrices (CCA-1 and CCA-2):** Focusing initially on high-molecular-weight forms of PEG to assess the propensity of the CCA's to coexist in the presence of this hydrophilic polymer, we combined polystyrene suspensions with PEG's that had a molecular weight,  $M_n$ , of 10,000 (Fig. 1, molecule 1). Figure 2 presents the extinction spectra of CCA-1 for which the PEG has been incorporated into the CCA suspension at a 40 wt.% level, yielding a particle density of approximately  $4.7 \times 10^{13} \text{ cm}^{-3}$ . At this level of PEG incorporation, the solution blend exhibited a significantly increased viscosity relative to a pure *in aqueo* CCA. This increased viscosity resulted in a reduction of the sensitivity of CCA-1 to minor mechanical disturbances.

The diffraction characteristics of these systems are most accurately predicted through the application of dynamic diffraction theory, although Bragg's law is a reasonable approximation.<sup>7</sup> Using Bragg's law and assuming a (111)-oriented fcc lattice result in a value of  $d_{111} = 224 \text{ nm}$  for the peak in Fig. 2 ( $\lambda = 614 \text{ nm}$ ,  $n = 1.37$ ) and a resultant lattice constant of 388 nm, which corresponds to a nearest-neighbor distance (i.e., spacing between particles at unit cell fractional coordinates 0, 0, 0, and 1/2, 0, 1/2) of 247 nm. Note that this value is 72% larger than a nearest-neighbor

distance based solely on intimate contact of the particles and shows the prominence of double-layer effects in these electrostatically stabilized systems.

Of functionalized PEG-based systems that can be polymerized *in situ* throughout the ordered arrays, poly(ethylene glycol)methyl ether methacrylate (Fig. 1, molecule 2) with  $M_n = 2080$  was added to the CCA suspension along with 2, 2-diethoxyacetophenone as a photoinitiator. The mixture was injected into the glass plate assembly and polymerized by exposure to UV light for 5 min, yielding what is to our knowledge the first example of a CCA–PEG composite. The reflectance spectrum of the CCA-2 blend before and after polymerization exhibited a single diffraction peak. Table 1 lists the corresponding estimated interplanar spacings. A disordered blend did not exhibit any marked diffraction peaks and was relatively uniform in reflectivity with wavelength. Adding a minute amount of sodium hydroxide to the unpolymers ordered blend produced this disordered array. The result was an immediate cessation of iridescence. The peak, which is observed in the unpolymers ordered blend, is still apparent in the polymerized system, although it is altered in position. The origin of the slight shift from  $\sim 620$  to  $\sim 660 \text{ nm}$  on polymerization is unclear, although minor changes in index

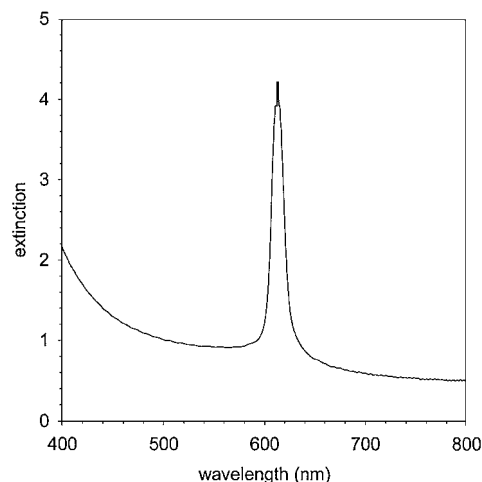


Fig. 2. Red opalescence from CCA-1 that comprises 159-nm-diameter monodispersed polystyrene spheres at a particle density of approximately  $4.7 \times 10^{13} \text{ cm}^{-3}$  blended with 40 wt.% PEG.

**Table 1. Maximum Reflectance Peak Angles and Wavelengths with Corresponding Estimated Lattice Spacings  $D$  for Organic Photonic Crystals**

Sample	$\theta$ ( $^\circ$ ) <sup>a</sup>	Peak (nm)	$D$ (nm)
CCA-2	55	620	280 <sup>b</sup>
PCCA-2	55	660	298 <sup>b</sup>
CCA-3	67.5	600	237 <sup>c</sup>
PCCA-3	67.5	600	237 <sup>c</sup>
CCA-3	80	620	229 <sup>c</sup>
PCCA-3	80	620	229 <sup>c</sup>

<sup>a</sup>Bragg angle of the incident beam relative to the diffracting plane.

<sup>b</sup>Refractive index of the composite, taken as 1.35.

<sup>c</sup>Refractive index of the composite, taken as 1.37.

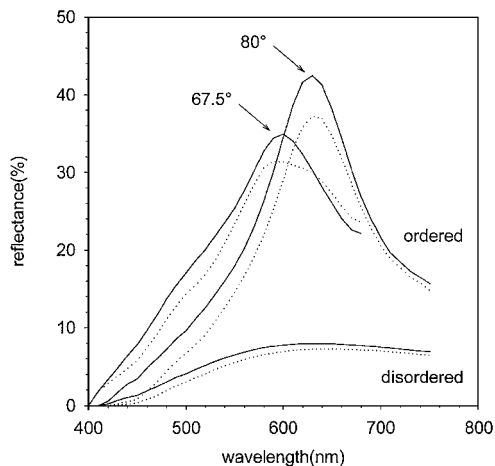


Fig. 3. Reflectance spectra, at Bragg angles of  $80^\circ$  and  $67.5^\circ$ , of CCA-3 (solid curves) that comprise 159-nm-diameter monodisperse polystyrene spheres at a particle density of approximately  $6.3 \times 10^{13} \text{ cm}^{-3}$  and PCCA-3 (dotted curves) following encapsulation with *N, N*-dimethylacrylamide. The corresponding disordered structures are presented at an angle of  $80^\circ$ ; the lower angle is omitted because of a lack of angle dependence for these structures.

contrast and the compressive state of the system could account for the shift.<sup>3</sup> Nonetheless, it is clear that PEG-based variants, which are polymerized *in situ* about the CCA, are successful routes to producing robust PCCA composites, as these samples exhibit sufficient stability to withstand repeated mechanical deformation with retention of CCA order.

**Poly(Acrylamide)-Based Matrices:** Previous research has utilized photoinitiated acrylic monomers in the presence of bis-acrylic monomers as a cross-linking agent to produce PCCA's.<sup>3</sup> Focusing on acrylamide, we introduce monomers that have similar chemical architecture but whose substituent groups are altered. Each approach introduces subtle structural changes, which should be revealed in the CCA stabilization and subsequent PCCA optical performance because the diffractive behavior is sensitive to both the chemical architecture of the matrix (hence refractive index) and the CCA lattice parameters.

Figure 3 presents the reflectance spectra at Bragg angles of  $67.5^\circ$  and  $80^\circ$  of a CCA *N, N*-dimethylacrylamide blend before (CCA-3) and after (PCCA-3) polymerization, as well as a similar nonopalescent disordered system, whereas Table 1 presents the corresponding wavelengths of the peak maxima and the resultant interplanar spacings. These mixtures contain 0.7 wt. % *N, N*-methylenebisacrylamide (Fig. 1, molecule 4) as a cross-linking agent and 2,2-diethoxyacetophenone as the photoinitiator. The reflectance spectra of the ordered and the disordered systems are dramatically

different, whereas the action of encapsulating the CCA with the cross-linked hydrogel does little to alter the diffraction characteristics. The angle dependence of the spectra for the ordered structures is indicative of the effects of coherent scattering, which are not clearly delineated in the disordered system. The increased peak breadth of these ordered systems relative to that of CCA-1 may result from both short- and long-range lattice defects. Such a discussion is beyond the scope of this Letter, and the reader is referred to Ref. 8. In addition, PCCA-3 was sufficiently robust to withstand being removed from the glass plates without loss of opalescence. However, continued exposure to the air resulted in dehydration of the matrix and eventually brought the film to a nonopalescent state as the CCA destabilized. The development of variant materials that are not so sensitive to dehydration continues.

Alternative matrices that extend the routes by which mechanically stable colloidal crystalline photonic bandgap structures can be embedded with organic polymers have been successfully developed. Two methodologies have been explored: (1) blending of the CCA with a high-molecular-weight hydrophilic polymer and (2) *in situ* polymerization of hydrophilic monomers to both thermoplastic and thermoset polymer matrices with dispersed ordered arrays. To this end we have focused on polyethylene glycol (PEG) and polyacrylamide-based variants, which are shown to exhibit a higher degree of mechanical stability in their polymerized composite form (PCCA) than does the CCA while they maintain visible diffractive characteristics. The results demonstrate the potential for robust photonic bandgap structures made from polymeric systems.

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