

# Polymerized Crystalline Colloidal Arrays Photonic Cosmetic Contact Lenses

V.L. Alexeev<sup>\*</sup>, G.G. Cano<sup>\*</sup>, S.A. Asher<sup>\*\*</sup>

<sup>\*</sup>Glucose Sensing Technologies, 1343 Beulah Road, Pittsburgh, PA 15235, USA,

[valexeev@earthlink.net](mailto:valexeev@earthlink.net), [ggcano@earthlink.net](mailto:ggcano@earthlink.net)

<sup>\*\*</sup>University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260, USA,

[asher@pitt.edu](mailto:asher@pitt.edu)

## ABSTRACT

We demonstrate the feasibility of making contact lenses from polymerized crystalline colloidal array materials to produce lenses with beautiful sparkling colors. We utilize poly[HEMA-(ethyleneglycol)200dimethacrylate] hydrogel with a crystalline colloidal array (CCA) embedded in it. The CCA material is composed of mesoscopic spheres of polystyrene latex particles dispersed in water. These particles self assemble in an aqueous medium to form a three-dimensional array that efficiently Bragg diffracts visible light producing colors from blue to red as determined by its interparticle spacing. The monodisperse spherical particles have diameters between 106 to 170 nm. The CCA structure is well preserved within the poly(HEMA) hydrogel giving the contact lens models beautiful sparkling violet, blue, blue-greenish, green and yellow colors, all without the use of dyes.

## INTRODUCTION

Colored contact lenses are becoming very popular. According to Cassel [1] approximately 25 million people are interested in colored cosmetic lenses. This represents a huge market for growth in the contact lens industry. There is also a demand for contact lenses which can filter out certain wavelengths of visible light. This may be beneficial for sport enthusiasts providing them with better visual perception of small objects like tennis and golf balls.

In the work here we demonstrate an original approach to fabricate lens models made of CCA incorporated in a polymer hydrogel. These materials were pioneered by Asher et al. [2] and are called polymerized crystalline colloidal arrays (PCCAs). They were widely utilized for fabrication of materials to sense different analytes such as cations [3], glucose [4], creatinine [5] etc.

These sensing materials utilize a mesoscopically periodic array of polystyrene latex particles polymerized within hydrogels. This array diffracts light in the visible spectral region, due to the periodic spacing of an embedded crystalline colloidal array.

The colloidal particles used are monodisperse in size, and possess numerous (>1000) strong acid surface groups. The ionization of these groups in water causes strong electrostatic repulsions between particles.

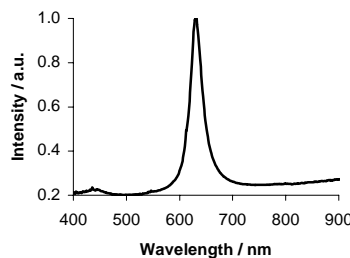
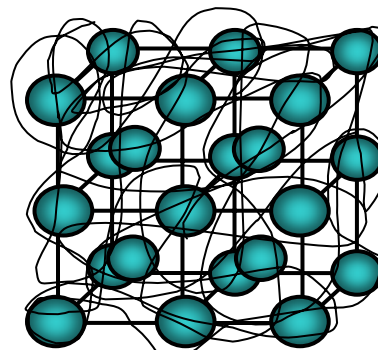


Figure 1: PCCAs are fabricated by dissolving a CCA in polymerizable monomers and polymerizing them to form a crosslinked hydrogel network (top). The hydrogel preserves the crystalline order of the array and diffracts visible light (bottom), which gives a sparkling and bright diffraction to the material. Each sphere in this figure represents a polyanionic colloidal particle.

CCAs self-assemble into an array due to electrostatic repulsion between colloidal particles in low ionic strength aqueous solutions. At high

concentrations ( $\sim 10^{13}$  particles/mL) the colloidal particles are forced to self-assemble into either a face centered cubic array or a body centered cubic array in order to minimize the electrostatic interaction.

The array lattice constant may be many times the particle diameter. Thus, the lattice constant can be easily fabricated to have a spacing that diffracts light in the visible spectral region [6]. The CCA efficiently diffracts all light meeting the Bragg condition. This efficient diffraction motivated the development of these CCA materials for optical devices such as filters and optical switchers [6-8]. In addition, this diffraction is responsible for a beautiful sparkling color of these materials. The diffraction closely follows Bragg's law; the diffracted wavelength (in air),  $\lambda_0$ , depends on the lattice spacing,  $d$ , and the refractive index of the system,  $n$ :

$$\lambda_0 = 2nd \sin \theta$$

where  $\theta$  is the Bragg glancing angle.

The optical properties of these materials motivated us to fabricate contact lens models which may be utilized for cosmetic lens application.

## EXPERIMENTAL

Monodisperse, highly charged polystyrene particles were synthesized by the emulsion polymerization described elsewhere [9].

We used styrene and divinylbenzene supplied by Sigma-Aldrich. Divinylbenzene was cleaned from inhibitor with aluminum oxide column. We also utilized COPS-1 (Sigma-Aldrich), which is 3-allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt, to introduce the charged groups to polystyrene particles. As a surfactant we utilized Aerosol MA-80-1, which is sodium dihexyl sulfosuccinate in mixture of isopropanol and water. We utilized the recipe described in [9] and varied the concentration of the surfactant. Lower surfactant concentration allows for the formation of fewer micelles resulting in larger particles. After the synthesis the dispersion of polystyrene particles was filtered through boiled glass wool and was dialyzed (Spectra/Pore Cellulose Ester Dialysis Membranes, 1,000,000 MWCO) against distilled water for 14 days. Ion-exchange resin (Bio Rad mixed bed; AG501-X8) was added to the dispersions to remove the rest of ionic impurities. At this point polystyrene spheres self

assemble in a brightly iridescent CCA dispersion (Figure 2).

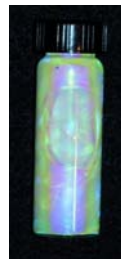


Figure 2. Photograph of polystyrene latex CCA in aqueous medium. The colloidal particles self assemble in a three dimensional crystalline colloidal array structure, which Bragg diffracts visible light. This gives rise to the bright iridescent color of the CCA.

The particle size diameter was determined from quasi-elastic light scattering (Brookhaven Zeta 90Plus) and transmission electron microscopy (Zeiss EM 902A). We utilized the particles with diameter of 106 to 170 nm.

The PCCA contact lens models were synthesized by UV free radical polymerization. We utilized 2-HEMA (ophthalmic grade, > 99.5 %) and poly(ethylene glycol) 200 dimethacrylate (PEG 200 DMA) supplied by Polysciences. Right before polymerization they were cleaned with aluminum oxide to remove inhibitor. We used 2,2-diethoxyacetophenone (DEAP, Acros Organics) as initiator. Colloidal dispersions were mixed before polymerization with 30 wt% of diethyleneglycol co-solvent (Acros Organics). A typical recipe for making green contact lens materials is 0.6 g of HEMA and 0.006 g of PEG 200 DMA and 2 g of colloid with particle size of 170 nm. We used 0.05 g of 10 wt% DEAP in dimethylsulfoxide as a UV initiator. To make prototypes with different color across the visible spectrum range we mainly varied the size of the colloid particles.

## RESULTS

Figure 3 shows photographs of the PCCA hydrogel flat sheets. We are able to fabricate hydrogels with violet, blue, greenish-blue, green, yellow and red colors. The colors are bright and sparkling. Figure 4 demonstrates a contact lens prototype made of PCCA. The central part is made of transparent hydrogel for better visual perception. These materials can be used in contact

lenses to enhance or change the natural iris color. In addition, lenses can be made in such embodiment that they will effectively diffract

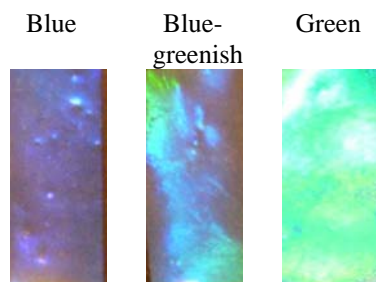


Figure 3. Photographs of flat sheets of PCCA material made of poly(HEMA) hydrogel. The CCAs incorporated in the hydrogels diffract visible light. This diffraction is responsible for a bright sparkling coloration of the hydrogels.



Figure 4. Photograph of the blue cosmetic lens prototype made of PCCA with the central transparent part. The prototype is placed on the artificial eye ball.

visible light of different wavelengths. Thus, such cosmetic lenses will combine the cosmetic effect with the light filtering.

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