Inkjet Printing of Self-Assembled Hydrogels for Bionic Devices

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Abstract

Inkjet printing was used to deposit alternating 100 nm layers of anionic and cationic polymers in order to form self-assembled ionic complexes on flat and fabric substrates. The layers formed are characterized by elemental analysis, microscopy and solubility. As initially deposited, layers are soluble but form insoluble complexes when they are heated and annealed. This approach has been applied to polypeptides, polymer dyes, polymers with nanoparticulate pigments, and hydrogels.

Introduction

In the well-known process of ionic self-assembly, sequential dipping of a substrate into dilute solutions of cationic and anionic polymers builds up a multi-layer structure [1, 2]. This work describes extending this layer-by-layer system to 100 nm layers deposited by two-color inkjet printing. We show that the layers are soluble as deposited but become insoluble on annealing after which the counter-ions can be washed out. This process may be similar to that occurring in many biological self-assembly processes where cells express soluble polymers that subsequently assemble into insoluble structural materials such as tendon, cellulose and insect cuticle [3].

Ionic self-assembly has been studied in great detail for many systems [2]. Polymer-polymer assembly may occur between completely ionized polymeric cations and anions, such as polydiallyldimethylamine hydrochloride and sodium polystyrenesulfonate or between partly ionized polymers such as salts of polyethyleneimine and polyacrylic acid. In addition charged nanoparticles can be used in place of some or all of the species [4]. It is not completely clear whether there is some layering in ionic complexes formed by sequential dipping but one would expect that it might depend on the polymer molecular weights and the processing conditions. To some extent the study of these systems is limited by the lack of a good spectroscopic signature of the ionic complex. Recent studies have determined diffusion coefficients for the components of these layers [5, 6].

Similar polymeric complexes cannot readily be made in bulk but larger scale structures are also formed by dripping a solution of one polymer into the other to form a capsule [7]. There has not been much characterization of these structures but one would assume there is a concentration gradient through the thick wall of the capsule.

In this paper we describe inkjet printing of self-assembling polymers, polymer-nanoparticle combinations and reactive pairs of polymers to form insoluble solids on flat and fabric substrates.

Experimental methods

Inkjet printing

Custom-made inkjet printing systems were used with a conventional commercial cartridge mounted on a robotic system that allows many printing passes over a single line or area. The cartridge was driven by a pulse generator at rates up to 1kHz over a table moving at up to 1cm/sec. Either two single-color cartridges were exchanged at each pass or a color cartridge was cut open and foam-filled pieces of Tygon tube were fitted over the filters in each reservoir. The typical droplet size from such cartridges is 15 pL, corresponding to a 30 micron drop diameter.

Ink formulation

Inks were formulated within the constraints of the cartridge and process. Printable inks are limited to a viscosity of a few centipoise. Polymer solutions need to be of low concentration, low molecular weight or the solvent adjusted to limit chain expansion. Low surface tension may lead to dripping, which can be corrected by applying a negative pressure of a few psi to the cartridge. Suspended particles must be small enough to not settle over a period of about one hour. The commercial cartridges that we use are attacked by good solvents but most alcohols and alkanes can be used in addition to aqueous. Some fraction of low-boiling solvent (<100ºC) is needed to generate a bubble to fire the drop.

Dye inks were a 1% solution of Poly-R478, (Poly(vinylaminesulfonate)backbone with an attached anthrapyridone chromophore) (Sigma Aldrich) and a 1% solution of poly(diallyldimethylammonium chloride), (MW 100,000-200,000) (Sigma Aldrich). Pigment inks were suspensions of CAB-O-JET 300 Black, filtered to 0.5 micron particle size and

CAB-O-JET 260M Magenta, filtered to 0.5 micron particle size plus 1% polystyrenesulfonate-co-maleic anhydride (MW-70,000) (Alfa Aesar) as dispersant. Fabric substrates were cotton from Test Fabrics (West Pittiston, PA), bleached mercerized cotton twill.

The polypeptide inks were formulated similarly. Poly-L-lysine hydrobromide, poly-L-glutamic acid sodium salt (Sigma-Aldrich Inc., St Louis, MO) and sodium chloride were used to prepare two 0.25% w/v water-based ink solutions with 0.25% w/v sodium chloride in deionized water. The stage surface temperature was maintained at 45 ± 4°C to speed up the water evaporation from printed lines. Lines were printed onto glass microscope cover slips

For the adhesive inks, polyethyleneglycol diglycidylether (PEGDGE, MW 526) and polyethyleneimine (PEI, MW 10,000) (Sigma-Aldrich) were used. The epoxy ink was a 48 % aqueous PEGDGE solution, equivalent to 3 mol epoxide per liter of solution. 4 % and 8 % aqueous PEI solutions were also prepared.

These two concentrations are equivalent to 1 and 2 mol amine hydrogen per liter of solution. Adhesive layers could be formed by printing pure PEI on one flexible substrate and alternating layers of PEI with excess PEGDGE, to make an epoxy-rich gel, on the other.

Spectroscopy

Reflectance spectra from fabrics were measured on a Macbeth series 1500 Color Measurement System with an integrating sphere. Reflectance is plotted in Kubelka –Munk units based on a relationship between the fractional spectral reflectance (R) of the sample and its absorption (k) and scattering (S) characteristics given by:

$$\frac{k}{s} = \frac{(1-R)^2}{2R}$$

.

Results

Self-assembled polymeric dyes and pigments on fabric

In earlier work it was shown that printed layers of ceramic particles dispersed in an anionic polymer could be fixed against redispersion by printing cationic polymer into the layer [8]. The complex formed between the two polymers is insoluble.

A red anionic polymeric dye (Poly R-478) was printed onto a woven cotton fabric and readily washed off, figure 1. When the red polymer was printed alternately with cationic PDDA, the printed area retains its color after rinsing and a granular precipitate can be seen on the fibers (figure 2).

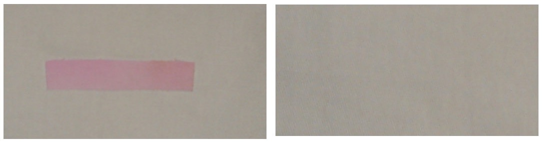


Figure 1: *Cotton twill inkjet printed with Poly-R478 (left) before and (right) after washing.*

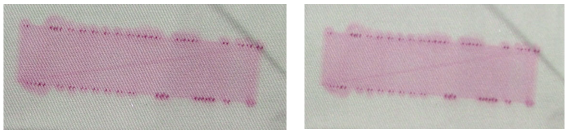


Figure 2: *Cotton twill inkjet printed with Poly-R478 and PDDA (left) before and (right) after washing.*

It would be expected that the extent of complex formation depend on the slow interdiffusion between the polymer layers. Since extent of ionic complexation lacks a clear spectroscopic signature, we monitored the effect of annealing on the solubility of the complex by following the loss of color upon rinsing. Figure 3 shows the color change on rinsing as a function of the time of annealing after printing. It can be seen that annealing up to 12 hours progressively increases the resistance of the dye complex to rinsing.

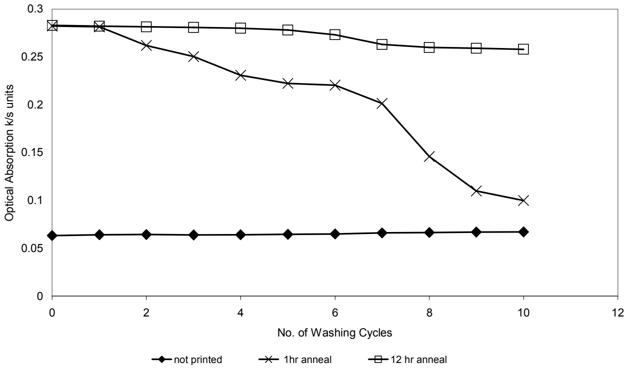


Figure 3: *Effect of annealing time on the resistance to washing of printed anionic polymer (Poly R-478) and cationic polymer (PDDA) sequentially onto cotton substrate.*

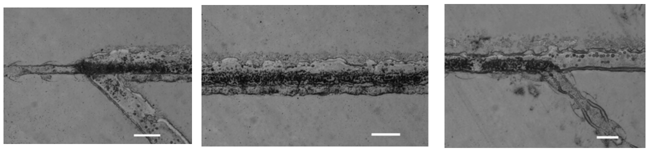
As a second method to demonstrate the formation of the complex, EDS elemental analysis was used to follow the loss of counterions during rinsing. Table I presents data on the observed elemental composition for printing and rinsing of the anionic polymer dye and PDDA. The C and O signals are affected by the underlying cotton but S and N are signals for the two polymers, which remain after rinsing, while the counterions (Na and Cl) are lost on rinsing, showing that an insoluble complex has formed. As also seen from figure 2 there is little loss of the dye on a single washing cycle. Using the same approach nanoparticulate black pigment was printed, as a suspension alternating printing with a solution of cationic polymer, as a suspension with anionic polymer, and as a suspension with anionic polymer alternating with cationic polymer. The particles alone are rapidly washed off the fabric. The particles in anionic polymer were more resistant to washing, while those with cationic polymer, with or without anionic polymer were highly resistant.

Table 1: Elemental Analysis of Poly R-478 and Cationic Polymer (PDDA) printed as 30 alternating layers onto a cotton substrate.

Element	Measured Atomic % in Poly R-478-PDDA complexes on cotton using EDS			
	Printed	Printed, washed	Printed, annealed	Printed, annealed, washed
C	47	47	47	47
O	52	54	53	54
N	1.3	1.3	1.3	1.3
S	0.13	0.14	0.13	0.14
Na	0.6	0.01	0.3	0.01
Cl	0.9	0.02	0.4	0.01

Inkjet printed biopolymers

As with the self-assembling printing of polymeric dyes, solutions of anionic and cationic polypeptides (polyglutamic acid,



(a) (b) (c)

Figure 4. *Over-printing of polyglutamate and polylysine solutions. Light microscope images of (a) left (partially overlapping), (b) middle (fully overlapping), and (c) right (partially overlapping) sections of a printed parallelogram after 5 cycles of printing on glass substrate. No rinsing. (Scale bar = 200μm)*

sodium salt and polylysine hydrobromide) were printed as 10 alternating layers (corresponding to 5 printing cycles) onto glass slide, using two wells of a color cartridge. In the central section the nozzles are in line and superimpose the inks while in the end sections the polymers are separate owing to the offset of nozzles. Thus the left-hand end of the image (figure 4a) shows the glutamate-only line going straight and the lysine-only line going down. The linewidth increases from 100 to 200 µm as the total number of printed polymer layers increases by ten times. Single-polymer lines readily disappeared after rinsing with deionized water. When the oppositely charged polymer inks PLL and PGA where alternately printed, the polymers formed scattered clumps in the middle section of the printed line and rougher ridges along the edges. The density and size of these clumps increased with the number of printed layers. As with the polymeric dyes, insoluble complex was formed after annealing for 24 hours at 90°C in 60-80% relative humidity, followed by rinsing in deionized water. Both line edges and clumps remained, confirming the formation of PLL-PGA water-insoluble complex..

EDS analysis was performed on the layered complex printed onto copper to avoid carbon or oxygen signals from the substrate. Both the added salt from the original buffer and counterions of the polyelectrolytes, namely Na^+, Br^-, and Cl^-, were removed after rinsing, leaving only the polymer chains.

Conclusions

We have shown that inkjet printing of pairs of self-assembling or reactive polymer solutions can lead to formation of insoluble gels by interdiffusion and reaction. The thickness scale of this process is much greater than that of ionic layer-by-layer assembly and patterning is simple. The kinetics of the interdiffusion process appear to be quite slow as would be expected from polymer-polymer diffusion. This approach can be used to print and bind dyes and pigments, to print adhesives and to print biopolymer gels.

Acknowledgements

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Author Biography

Paul Calvert was educated as a materials scientist at Cambridge and MIT and has been on the faculty at the University of Sussex, University of Arizona and UMass Dartmouth. He has worked on polymer crystallization and stabilization, composites and ceramics, biomimetic materials, rapid prototyping and inkjet printing.