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Multi-Material Inkjet Printing of Self-Assembling and Reacting Coatings

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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 also to epoxy adhesives.

Keywords: Inkjet printing, self-assembly, polymeric dyes, printed adhesives

1 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.

2 Experimental

2.1 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.

2.2 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

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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 ($<100°C$) 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 $45 \pm 4°C$ 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.

2.3 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:

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

2.4 Microscopy

A JSM-5510 scanning electron microscope (SEM) (JEOL, Tokyo, Japan) equipped with an Oxford INCA (Oxford instruments, Concord, MA) energy dispersive X-ray spectroscopy (EDS) unit, was used to determine the elemental composition of our printed layer-by-layer self assemblies. Light and confocal images were captured using a Nikon Eclipse L200 light microscope equipped with a HS200A confocal unit (Hyphenated systems Inc., Burlingame, CA).

2.5 Sample Annealing Treatments

Printed polypeptide structures were annealed at $90 \pm 2°C$ for 24 h. Deionized water was sprayed repeatedly onto annealed samples to wash out non-assembled components. Samples were then immersed in water bath for 15 min, then dried at room temperature prior to examination. The polypeptide samples used for EDS analysis were printed onto copper tape placed on 22 mm × 22 mm glass slides.

3 Results and Discussion

3.1 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 alternately with cationic PDDA. After printing the polymer dye alone the fabric was red but lost its color on rinsing. After printing the anionic dye and cationic polymer in alternate passes, the printed area retains its color after rinsing and a granular precipitate can be seen on the fibers (Fig. 1).

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
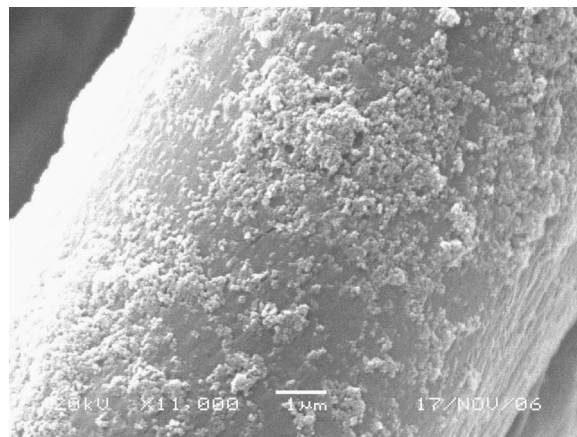
Fig. 1. Anionic polymer (Poly R-478) and cationic polymer (PDDA) printed onto cotton substrate sequentially. The complex appears as clumps on the fiber surface.

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

on the solubility of the complex by following the loss of color upon rinsing. Figure 2 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 h progressively increases the resistance of the dye complex to rinsing.

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 1 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, (Fig. 3). As seen from this figure, 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.

3.2 Inkjet Printed Biopolymers

As with the self-assembling printing of polymeric dyes, solutions of anionic and cationic polypeptides (polyglutamic acid, 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 as shown in Figure 4. 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 (Fig. 4a) shows the glutamate-only line going straight and the lysine-only line going down. Table 2 gives the linewidth of the printed complex. This width increases from 100 to 200 μm as the total number of printed polymer layers increases by ten times. Lines containing PLL only, shown in Figure 5(a), or PGA only, shown in Figure 5(b), comprised two smooth parallel
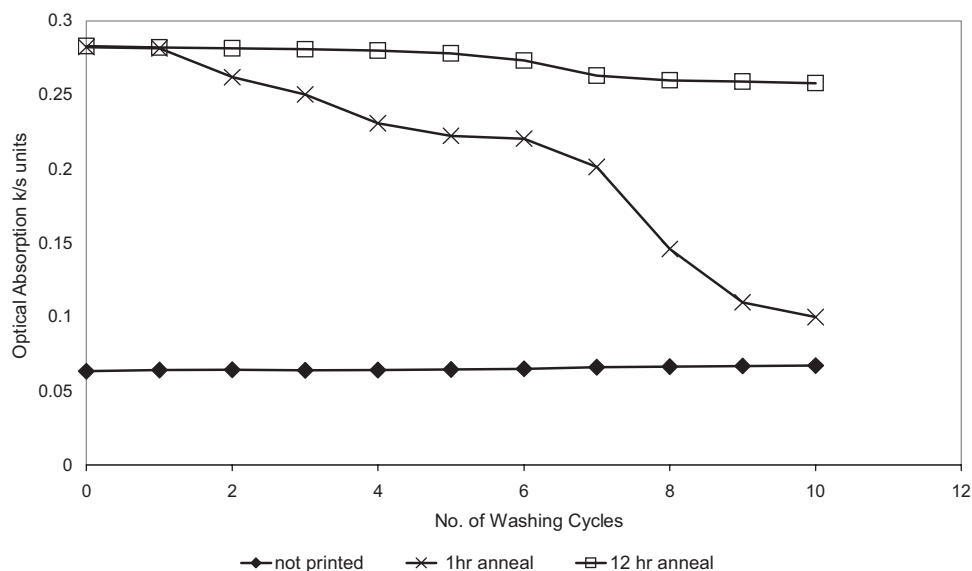
Fig. 2. Effect of annealing time on the resistance to washing of printed anionic polymer (Poly R-478) and cationic polymer (PDDA) sequentially onto cotton substrate.
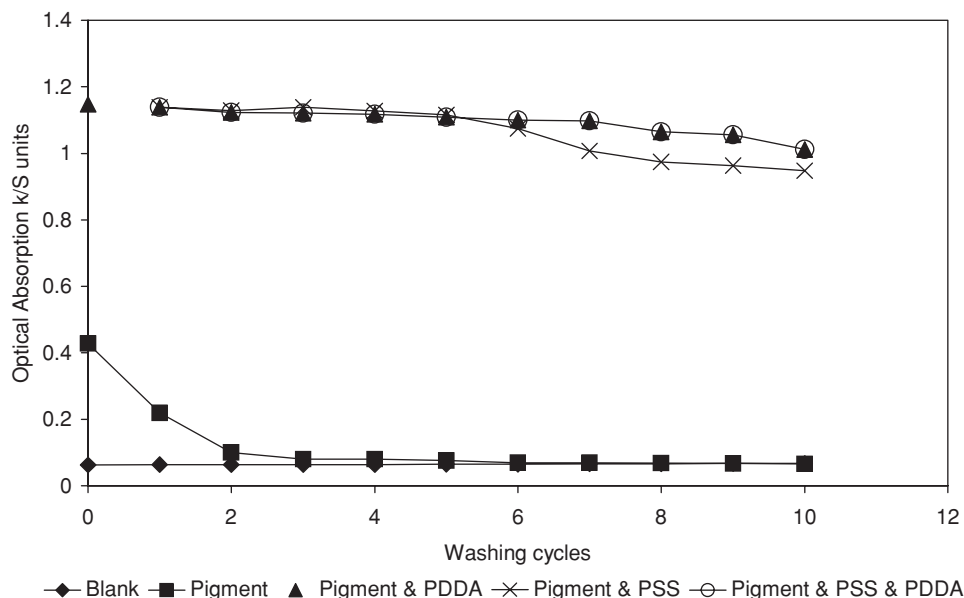
Fig. 3. Washing of cotton fabric printed with pigment and polymer electrolyte binders.

ridges where most of the ink has moved to the edge of the line upon drying. Crystals of the salt present in the printing solution can also be seen. These single-polymer lines readily disappeared after rinsing with deionized water. When the oppositely charged polymer inks PLL and PGA where alternately printed, as shown in Figure 5(c and d), 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 shown in Figure 5(d) where the line consisted of 20 layers of PLL/PGA vs. Figure 5(c) where only 10 layers were printed. As with the polymeric dyes, insoluble complex was formed after annealing for 24 h at 90°C in 60–80% relative humidity, followed by rinsing in deionized water. Both line edges and clumps remained, as shown in Figure 6, 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. As seen from Table 3, 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.

Table 2. Average line width after rinsing of printed PLL/PGA as a function of the number of printed layers

| Number of printed layers	10	20	50	100
Average width (μm) [(i)]	112	162	173	222
Standard deviation (μm) [(i)]	12	18	21	11

(i) Average and standard deviation values are based on N = 5.

3.3 Inkjet Printed Adhesives

To explore the possibility of printing adhesives, we printed multiple alternating layers of water-soluble, polymeric epoxies and polymeric amines. The available polyethylene glycol diepoxide is a low molecular weight liquid, too fluid to form a well-defined line. On one surface was printed a line of polymeric epoxy alternating with polyamine at 2/3 mol equivalent of >NH to form a gel with free epoxy groups. On the other surface was printed polyamine equivalent to 1/3 mol of >NH. The surfaces were aligned, put together and allowed to cure. The transparencies have an absorbing coating that helps to retain the adhesive prior to reaction. These two lines formed a bond, while two types of control sample, with two PEI lines or with two PEDGE/PEI lines with excess epoxy, did not show any measurable adhesion strength. Pulling the films apart in a 180° peel strength test gave a peel strength of 1060 +/−300 N/m, shown in Figure 7. Finite element modeling of this system gives a stress in the adhesive layer of about 4 MPa at this fracture load.

### 3.4 Diffusion and Reaction in Inkjet Printing

Previous studies with our printing system have shown that individual dots, lines and layers of a single material can be printed (8, 9). A single drop with a solids content of a few percent from a nozzle of diameter 30–80 microns will dry to form a pancake of about 100nm thickness on the substrate. The diameter of the pancake will normally be determined by the wetting properties of the solution and subsequent drying may leave a flat disc of a "coffee-ring" disc with a raised edge (10). Similarly, the lines with raised edges, as seen in figure 6b, can be attributed to the drying dynamics.

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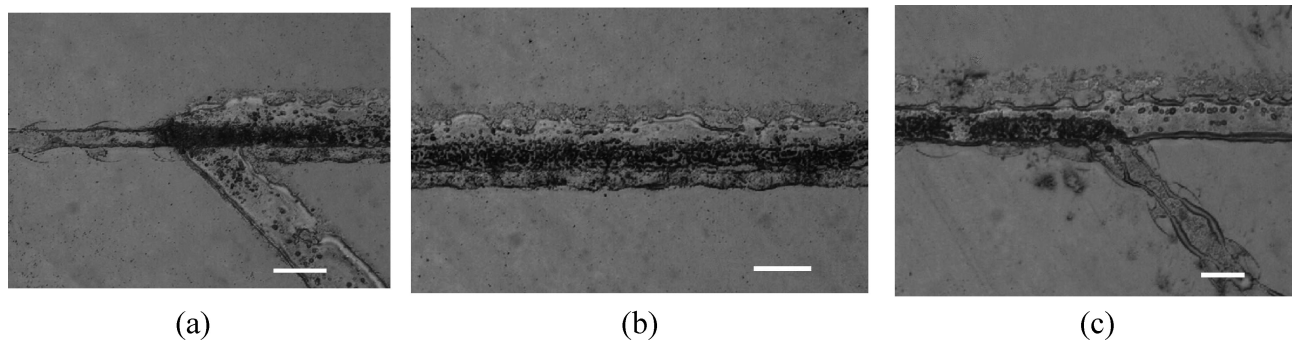
Fig. 4. Over-printing of polyglutamate and polylysine solutions. Light microscope images of (a) left (partially overlapping), (b) middle (fully overlapping), and (c) right (partially overlapping) sections of a printed parallelogram after 5 cycles of printing on glass substrate. No rinsing. (Scale bar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

(a)   (b)

(c)   (d)
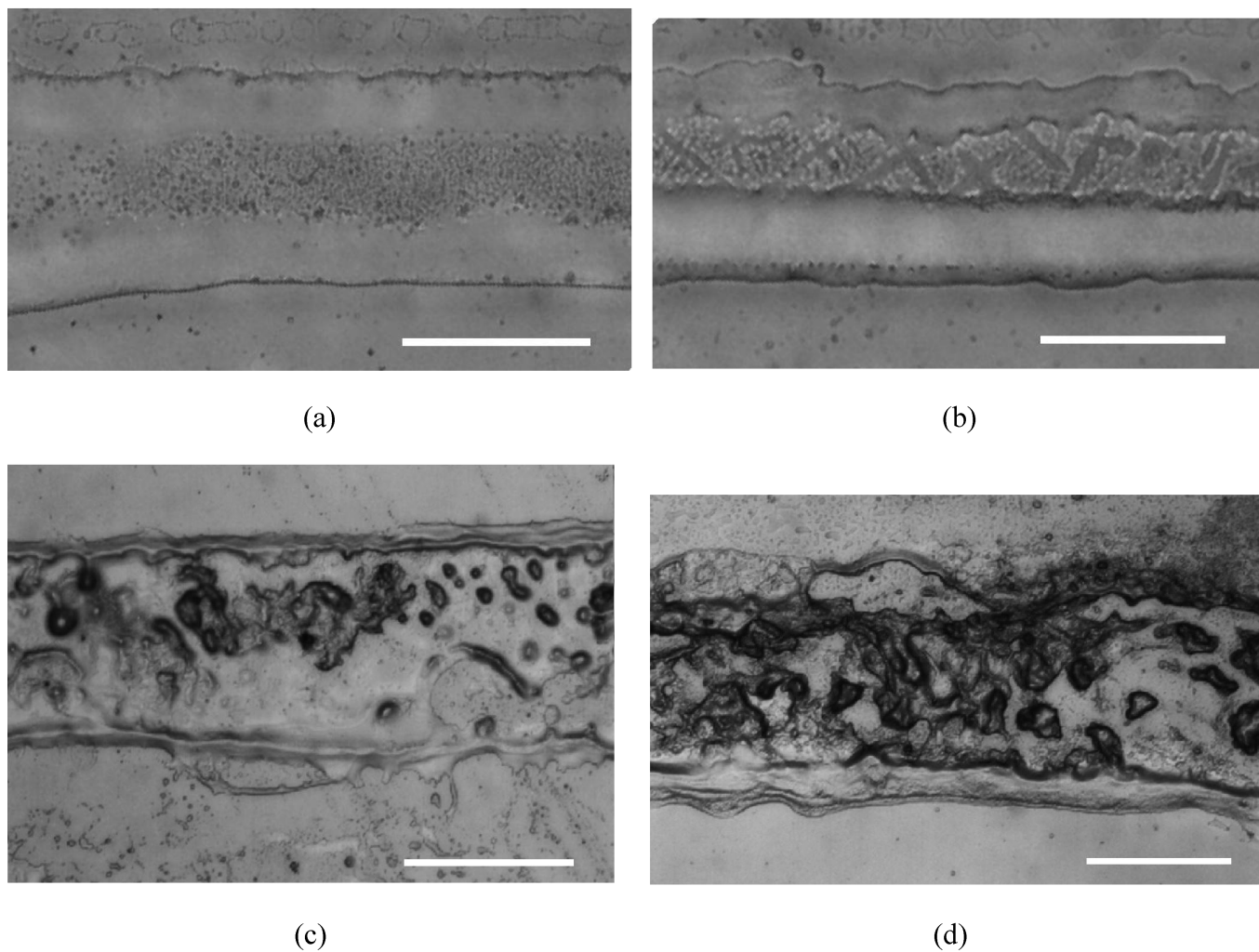
Fig. 5. Light microscope images of printed lines annealed overnight at 90C annealing, and not rinsed: (a) 10 layers of PGA; (b) 10 layers of PLL; (c) 10 layers of alternately printed PLL and PGA; and (d) 20 layers of alternately printed PLL and PGA (scale bars: 100 μm).
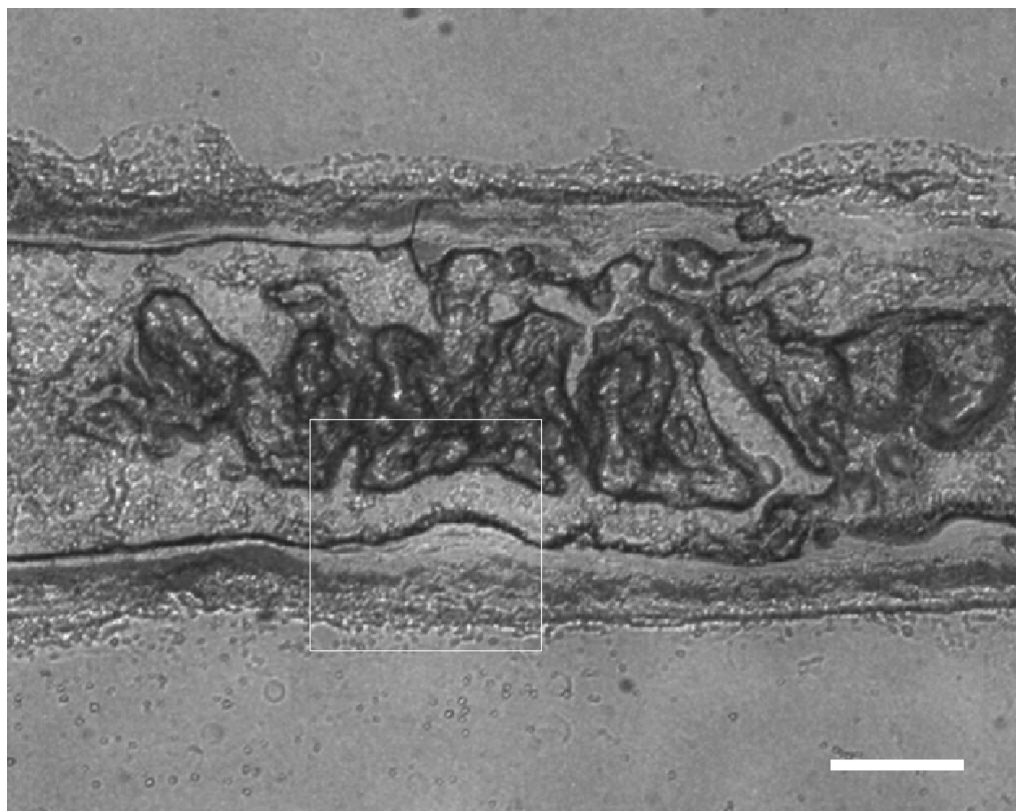
(a)
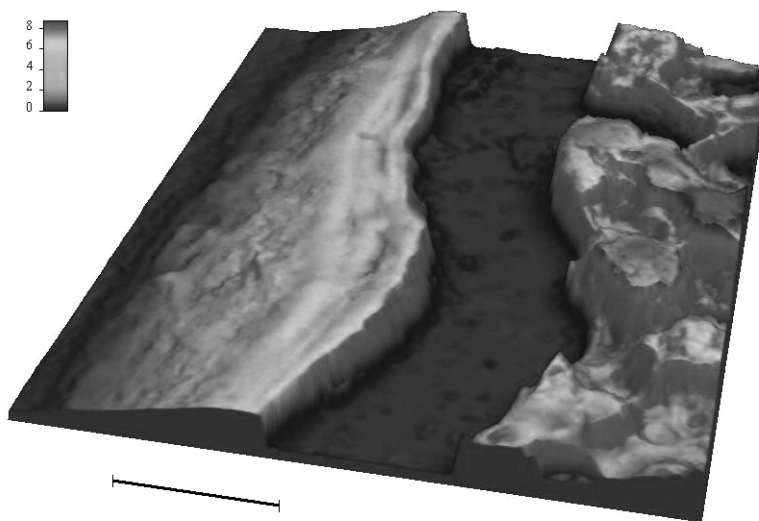
(b)

Fig. 6. Images of poly-L-lysine/poly-L-glutamic acid printed line made of 20 layers of each solution, annealed at 90°C overnight, and rinsed. (a) Light microscopy, scalebar 50 μm; (b) Confocal image of the area delimited by the white square in Figure 6(a) (gray scale in μm, scale bar: 25 μm).

From Table 3 it appears that the salt concentration after printing is lower than expected. This may reflect the salt and water actually wetting out beyond the boundaries of the polymer lines.

The drying time for a single inkjet drop is a few seconds so that mixing of the polymer solutions is limited and the dried structure is layered on the scale of about 100nm. As-printed lines on flat surfaces are soluble but become insoluble after

Table 3. Theoretical vs. experimental elemental composition of layer-by-layer printed PLL and PGA inks: (NANW) no annealing and no washing, (ANW) annealed but not washed, and (AW) annealed and washed

Atomic compos-ition	NANW		ANW		AW	
	Theory	Expt [*]	Theory	Expt[*]	Theory	Expt[*]
C	19.0	41.8 ± 1.5	19.0	39.6 ± 3.4	54.4	45.8 ± 2.6
O	10.1	16.5 ± 1.4	10.1	19.6 ± 3.3	28.9	33.2 ± 1.9
N	5.8	9.3 ± 1.0	5.8	8.6 ± 1.8	16.6	20.5 ± 1.1
Br	9.8	12.8 ± 1.3	9.8	12.9 ± 2.8	0.00	0.1 ± 0.1
Na	24.1	15.8 ± 1.5	24.1	14.8 ± 1.8	0.00	0.0 ± 0.1
Cl	31.1	3.8 ± 0.9	31.1	4.5 ± 1.0	0.00	0.3 ± 0.1

(*) Figures are presented as average ± standard deviation based on 8 experimental values. All samples used in EDS analysis were formed from 50 printing cycles.

extended annealing. Studies of the interdiffusion of polymer electrolytes show diffusion coefficients of the order of 10^{-14} cm^2/sec (5, 6) which leads to interdiffusion times of hours for layers of this thickness. Thus, we would expect full complex formation to occur over a timescale of several hours, as shown by the annealing experiments on polymeric dyes. At this point, we are not certain at what point the irregular clumps of complex form and whether these clumps are fully structured before annealing.

On porous surfaces, the distribution of the two self-assembling polymers can be more complex. The deposition of inkjet drops onto fabrics has been modeled as a capillary flow of fluid between bundles of fibers plus loss of fluid by absorption into the fibers (11). The resulting distribution of the two inks may be sequential in channels rather than layered.
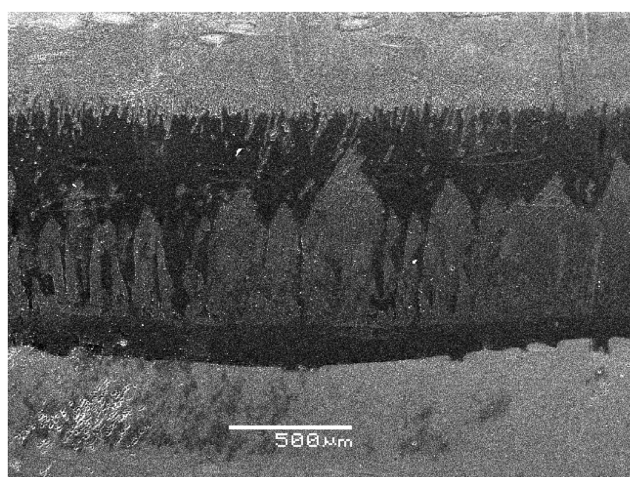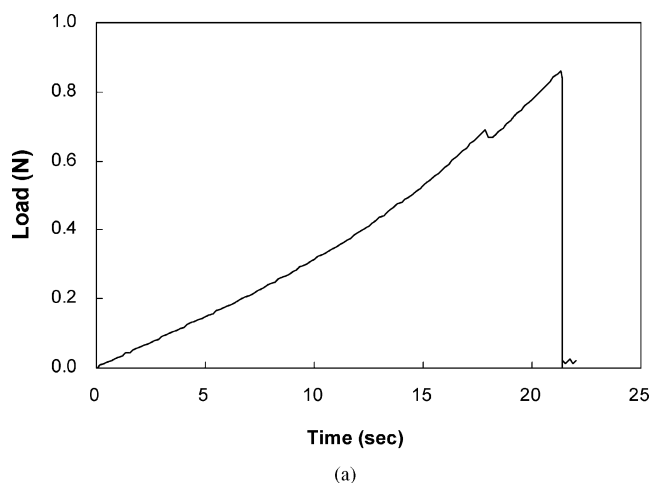
4 Conclusions

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.

(a)

(b)

Fig. 7. (a) Load-extension curve for peeling printed adhesive films, (b) Surface of debonded films.

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