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PAPER

Inkjet printing of self-assembling polyelectrolyte hydrogels

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Inkjet printing of alternate layers of anionic and cationic polyelectrolytes allows organized gels to form with structures similar to those made by layer-by-layer dipping methods but very much faster. Structures of gels formed using slow and fast inkjet printing systems are compared using elemental analysis, swelling and diffusion kinetics as characterization methods. After printing and washing, most sodium or chloride counter-ions are lost from the gel, leaving only the polymer complex. The swelling properties of the printed and washed gel depend on the deposition rate and on the ratio of the two polymers as originally printed.

Introduction

There are many current and potential applications for hydrogels in biological research and in medical systems. The range of applications would be much expanded if gels could be made with better mechanical properties and easier processing methods.¹ Most synthetic gels are chemically cross-linked, while in most biological gels the polymer chains linked by ionic or hydrogen bonding. One family of gels that has been little explored is the ionically bonded polyelectrolyte complexes. Simple mixing of aqueous solutions of cationic and anionic polyelectrolytes results in a messy precipitate with an unknown structural arrangement. Hydrogel capsules can be formed by polyelectrolyte complexation by dripping solutions of one polymer into a polymer solution of opposite charge. This sets up relatively large scale concentration gradients across the capsule wall, so that the structures are probably very non-uniform.^{2,3} Since the IR spectra of the polymers do not change when the complex forms, these ionic complexes lack a simple spectroscopic signature,⁴ so that it is not possible to characterize the structures without elaborate labeling techniques, such as attaching heavy metals, dyes or fluorophores to the chains. As a result there has been very little characterization of the structure or properties of these polymer complexes in bulk.

Polyelectrolyte complex materials can also be formed by sequentially dipping and washing a glass slide in dilute solutions of cationic and anionic polymers. Such layer-by-layer self-assembly of oppositely charged polymers has been studied for

15 years since the early work of Decher.^{5,6} The resulting complexes have many interesting properties, but are limited to thin films by the slow fabrication process which adds 1–2 nm in thickness per 20 minute cycle of dipping and washing. It is possible to make thicker films using robotic equipment running for long periods, but this still limits the film thickness to a few μm .⁷ Various other methods such as spraying⁸ and spin coating⁹ have been used to speed up the process, but these are mainly aimed at improving the mass transport of each component from solution to deposited layers.

It is also possible to develop more organized structures by mixing weaker polyelectrolytes, such as carboxylates and amines, rather than fully ionized polymers such as sulfonates and quaternary amines. By careful control of pH and using lower molecular weights the process can occur slowly and in a more organized fashion, as demonstrated for extruded gel threads¹⁰ and for polypeptides^{11,12}

Inkjet printing deposits drops with a diameter of 10–50 μm . For dilute solutions printed slowly on a flat surface, these drops will dry to a pancake of about 100 nm thickness in a few seconds. By alternately printing anionic and cationic solutions from a two-color cartridge, a multi-layer stack of polymer can be formed and will diffuse to form the ionic complex. Inkjet printing can thus build films 100 times faster than dipping and offers a promising route to forming self-assembled polyelectrolyte complex gels in bulk. The underlying reasoning is that the timescale for diffusional mixing is proportional to the square of the distance. For example, the time required for a polymer with a diffusion coefficient of about $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ to diffuse through a layer with thickness of 100 nm is about a second. Thus, if we can deposit a multilayer stack of layers each about 100 nm thick, good mixing should occur. This approach has also been used to print metal films by alternate deposition of metal salts and reducing agents.¹³

Previous work has demonstrated that the insoluble complexes do indeed form on inkjet printing both strongly ionized polymers

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and more weakly ionized polypeptides on glass surfaces and on textiles.¹⁴ Two tools were primarily used to study these materials, successive washing was used to determine the extent of solubility after different annealing treatments and elemental analysis was used to establish that the films were free of inorganic counterions and therefore must have formed the complex.

Since inkjet printing initially results in 100 nm or thicker zones of each polymer, it is quite possible that the structure does not anneal all the way to a uniform layer of complex. There has been much study and discussion of the composition and uniformity of films formed by the LBL process.^{15–18} It seems reasonable that two strong, fully ionized, polyelectrolytes should form layers with matched numbers of positive and negative charges and expel the counter ions. With weaker electrolytes, the degree of ionization of the polymers will depend on the pH of the dipping solutions and the proportion of the two polymers in the final films will then depend on these pH's and on the dipping time in relation to the ionization kinetics. These dependencies mean that the structures formed by the LBL process should be similar to those made by inkjet but there will be important differences.

This paper studies the swelling and transport properties of the films formed from strong polyelectrolytes with varying ratios of the two components on two differing printing systems. With the "slow" printing system each polymer layer is about 100 nm thick and there is a time of several minutes between layers, allowing the polymers to complex during printing. "Fast" printing deposits more concentrated solutions so that the individual layers, when dry, are about 10 μm thick and the time between layers is a few seconds. The swelling properties of the gels are found to depend on the processing speed. Once the gels are printed and washed it might be expected that an excess of either polymer would be removed and the final composition would always be 1 : 1 on a cation : anion basis. Swelling properties can be used to explore whether the gel structure is independent of the initial printing composition.

Experimental

Ink preparation for slow inkjet printer

For slow printing, 2% w/v aqueous solutions of poly(sodium 4-styrene sulfonate) (PSS) with average molecular weight (M_w) $\sim 70\,000\text{ g mol}^{-1}$ (Alrich, USA) and poly(diallyldimethylammonium chloride) (PDDA) with $M_w < 100\,000\text{ g mol}^{-1}$ (Aldrich, USA) were prepared by dilution with Milli-Q water (18.2 M Ω cm) from as-received PSS (powder form) and PDDA (40% w/v), respectively. To help printing jet stability, up to 1.2% w/v ethylene glycol (humectant) and 0.8% w/v Triton X-100 (surfactant) were added. The final polymer concentration for both PDDA and PSS in the ink solutions before printing was 1.0% w/v. Solutions were filtered with a 0.5 μm filter before loading them in cartridges.

Ink preparation for fast inkjet printer

For fast printing, a PSS solution was prepared at 30% w/v by dissolving poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (Sigma, $M_w \approx 20\,000\text{ g mol}^{-1}$) in Milli-Q water. PDDA was prepared at 20% w/v by dilution with Milli-Q water (18.2 M Ω cm) of the as-received 35% w/v solution. To all

materials 1–2% w/v Triton X-405 (poly(ethylene glycol *p*-(1,1,3,3-tetramethylbutyl)-phenyl ether, Sigma) and 1–2% w/v ethylene glycol (EG, Sigma) were added as surfactant and humectant, respectively. To allow easy monitoring of the deposition, the solutions were colored by adding dyes. PSS was colored with <1% polypyrrole (doped 5 wt% solution in water, Sigma) suspension, and PDDA with food dyes. The resulting polymer concentrations for PDDA and PSS are 17.5% w/v and 23% w/v, respectively. These inks gave apparent viscosities between 7 and 24 cP (Fungilab viscometer), the recommended range for good jetting.

Slow inkjet printer

A dual head IIS 56 printing unit (Imtech, USA) was used to control modified HP-C6602A bubble jet cartridges. Glass slides were used as a printing substrate heated with an SFG-205 heater (Omega, CT) coupled with a temperature controller. The assembly consisted of a stepper motor driven bi-slide stage (Velmex, NY). Printing frequencies, stage speed and surface temperature were adjusted such that each deposited layer dries up before the following one is printed. Printing frequencies and substrate surface temperature ranged respectively from 150 to 450 drops per second and 30 to 60 $^{\circ}\text{C}$. The frequencies at which each of the solutions was printed were selected to reach a target anion/cation ratio in the deposited mixture.

Fast inkjet printer

Fast deposition of hydrogels was carried out using a custom-built inkjet printer. This printer consisted of two piezo inkjet engineered Xaar 126 printheads, with 126 nozzles each spaced 137 μm apart, jetting 80 pL drops at up to 5200 Hz. Each printhead has a print-width of 17.2 mm. Proprietary software and drive electronics connected to the printheads are driven by an ordinary PC. A servo-actuated linear slide with 500 mm travel was used to drive a substrate-table back and forth underneath the printheads. This table operates at 0.5 m s^{-1} , meaning that each layer only takes a few seconds to deposit. The linear substrate-table was fitted with an optical encoder used to control deposition. The encoder delivers (RS422) differential signals to the drive electronics to precisely control the jetting of the drops.

The substrate holder could support substrates up to 297 \times 210 mm^2 in area. The optimal distance between the printheads' nozzle plates and the substrate (throw distance) is 1 mm, although up to 3 mm delivers acceptable print quality.

Fluids (inks) were supplied to the printhead *via* a tube of 3 mm internal diameter and 300 mm length, which is connected to a 50 ml syringe open to atmosphere (reservoir). Important for good printing is the meniscus level of the ink at the nozzle orifice. The negative pressure at the nozzle plate is typically between -1 and -3.5 kPa . For pressures outside this range ink either seeps out the nozzles covering the nozzle plate and inhibiting jetting or it is drawn back into the reservoir, starving the nozzle firing chambers of ink. Varying the height of the reservoir alters the negative pressure, compensating for variations in ink properties to achieve a good meniscus level.

Gels were printed onto glass or onto cellulose acetate membrane sheets (Millipore, 0.45 μm pore size). The membrane

rapidly removes water from the solutions during fast printing and so results in a more uniform deposit. Typically a square of area $17 \times 17 \text{ mm}^2$ was printed on each microscope slide, this size corresponding to the width of the printhead. In order to print the $17 \times 17 \text{ mm}^2$ squares, monochrome bitmaps were prepared in MS Paint at $126 \times 126 \text{ pixels}^2$ per bitmap. Bitmaps were opened with the drive electronics' software. Each pixel corresponds to a drop being ejected (black being on and white off). Manipulation of the bitmaps is a simple way of producing patterns, pictures and text or of controlling the ratios of each material deposited.

Energy dispersive spectroscopy analysis

Slow printed samples were printed onto copper tape placed on $22 \times 22 \text{ mm}^2$ glass slides to prevent interfering signals from the substrate. They were analyzed with a JSM-5510 scanning electron microscope (JEOL, Japan) equipped with energy dispersive spectroscopy, EDS (Oxford Instruments, Model # 6587, MA), coupled with the microanalysis INCA suite (version 4.02 issue 13). The system was operated at 8 kV excitation voltage. The examined areas sampled were approximately 3 mm^2 . Acquisition rates were maintained at 30 to 40% dead time and the total spectrum count per site was at minimum 300 000. The EDS patterns were recorded on INCA 3.00 software and were digitized for analysis. Atomic percentages of sulfur (S), sodium (Na), and chlorine (Cl) were then collected. Average values were calculated based on $n = 5$ samples. Samples were analyzed after printing and before washing, after the first wash, and after the second wash. Samples were washed in DI water overnight then dried at 60°C for about 15 min before EDS analysis.

Weight loss and profilometry

The thicknesses of the gel on the substrate of inkjet printed materials were measured using a contact profilometer (Veeco Dektak 150 with a $12.5 \mu\text{m}$ tip). All samples were conditioned for at least 24 hours at 23°C and 50% relative humidity prior to analysis.

Removal of material during washing was also determined by weight loss, comparing thoroughly dried samples with the base weight of the glass slide substrate.

Dye diffusion

Diffusion of dye from printed samples was determined by color loss. In order to prevent puddling of the polymers during fast printing, polymers and dyes were printed onto cellulose acetate membrane (Millipore). The membrane has a negative surface charge and does not bind the anionic dye. After printing and various washing treatments samples were scanned on a conventional flat bed scanner (Hewlett Packard 3500c) with a "no color correction" setting. The resulting high resolution (1200 dpi) image.tif file contained 8-bit color data in the red, green and blue channels. These data were analyzed using the Kubelka–Munk equation for each of the three channels:

$$K/S = (1 - R)^2/2R, \quad (1)$$

where K/S is a composite parameter for color strength, combining absorbance and scattering, and R is the reflectance of the incident light.¹⁹

The relationship between K/S and amount of material deposited was tested by printing conventional cyan ink onto photopaper for up to 20 cycles. The printed areas were imaged in the same way using the scanner and K/S plotted against the number of print cycles (Fig. 1). The resulting responses for the three channels were linear up to K/S values of 4 (above which the data became scattered). The straight line fits of these data intersected the x -axis at about $1/2$ cycle, which is attribute to partial uptake of ink (during the first cycle) by the photopaper. This provides the justification for using KM analysis to monitor dye loss from our films.

Results

Slow printing

Printing PDDA and PSS layers at 200 drops per second from a single nozzle onto glass results in a dry film of polymer forming, whereas at twice this printing speed a pool of liquid builds up. This has been observed previously during inkjet printing of a PSS stabilised conducting polymer.²⁰ On subsequent washing single polymer films of either PDDA or PSS are immediately removed while the combined polymers form an insoluble layer as shown in Fig. 2.

As shown in Fig. 3a, the films of the combined polymers show about 20% weight loss on washing in water. In some cases, 2% surfactant (Triton X-100) and humectant (ethylene glycol) are added during the printing to reduce the tendency of the nozzles to block. The larger weight loss observed for the inks with additives after the initial wash corresponds to the fraction of the total weight of the printed mix represented by the surfactant and humectant. After the first wash, subsequent weight losses are quite small, showing that the polyelectrolyte complex is stable.

Elemental analysis of the layers after printing and washing overnight (Table 1) shows no counter-ions remain in the film at levels higher than 0.1 atomic% after 2 washing cycles. The sulfur content reflects the PSS content only and should be about 4% in a complexed material with a 1 : 1 PSS : PDDA ion ratio. As

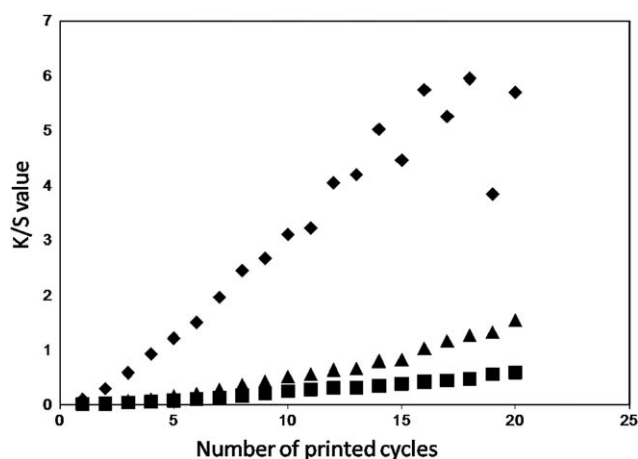


Fig. 1 Kubelka–Munk analysis of inkjet printed cyan blocks on photopaper versus printing cycles. Diamonds, triangles and squares represent the red, green and blue channels of the scanned image.

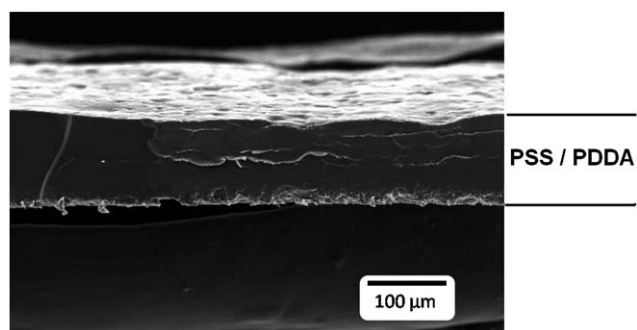


Fig. 2 Scanning electron microscopy image of a film (thickness $117 \pm 13 \mu\text{m}$) prepared by 335 cycles of PDDA and PSS alternately inkjet printed onto glass at an ion ratio of 1 cation (PDDA) to 0.67 anions (PSS) and washed 4 times with Milli-Q water.

expected, the initial PSS content of the 1 : 1 ion ratio sample is higher compared to that in the complex with a 1 : 2 ion ratio. After washing both complexed materials approach very similar PSS content values, implying an excess of PDDA over PSS in the final complex. Most of the counter-ions are washed out, but a slight residue of chloride remains in the high PSS–PDDA ion ratio sample.

Further evidence for progressive loss of excess polymer is shown in Fig. 3b where the degree of swelling in water is determined after various numbers of wash cycles. The additives are removed during the first cycle and so have little effect. Complexed materials with a non-ideal ion stoichiometry (ionic ratio $\neq 1 : 1$) show a progressive reduction in the water swelling capacity with successive overnight washing cycles, apparently as excess of either polymer is removed. Even after 6 cycles there are still swelling differences between the compositions, with those closest to the ideal ion stoichiometry swelling least. For example, complexed materials with ionic ratio 1 : 1 exhibit 150% swelling, whereas materials with ionic ratio 0.22 : 1 show a significantly larger amount of swelling (590%).

The degree of swelling of the gels by water and by salt solutions should decrease as the polymeric ions become paired and there are fewer stretches of uncomplexed polyanion or polycation. Fig. 3c shows the degree of swelling in water and in saline solutions, after extensive washing, for films printed with different ratios of anionic to cationic polymer. In these films the swelling in saline solution is much less than in distilled water. It can be seen that the degree of swelling is higher with excess of either cationic or anionic polymer, presumably reflecting higher contents of free ions. All the samples were opaque white after swelling in water but clear after swelling in saline solutions, with the opacity being more evident in the samples with ion stoichiometry close to 1 : 1. The differences in the amount of swelling in water vs. saline solution may be attributed to the screening of the charges along the polyelectrolyte chains.

Fast printing

For most practical purposes, it would be desirable to print these self-assembled films as rapidly as possible, but the washing studies above already suggest that the film structure changes with time due to slow complexation kinetics and that this affects composition changes during washing as excess or uncomplexed polymer is

removed. To investigate this, PSS–PDDA films were printed at much higher speed using a custom-build inkjet printer consisting of two Xaar printheads mounted on a moving platform each depositing droplets through 126 nozzles at 1 kHz. The polymer concentrations giving reliable jetting could be much higher than in the “slow” system, *i.e.* 17.5% w/v for PDDA and 23% w/v for PSS. Unlike slow printing, the material deposited using the fast printer first remains in solution state prior to gelation.

Gels were fabricated by sequential deposition of $17 \times 17 \text{ mm}^2$ squares of PDDA and PSS, each overlapping by 10 mm in a single print layer thereby leaving a 7 mm zone of pure PSS or pure PDDA on either side (Fig. 4a). This overlapping procedure was repeated for 2, 4, 8, 16, 32, and 64 layers. The PSS : PDDA ink ratios as determined by the pixel density of the bitmap files were 50 : 50, 66 : 33, 33 : 66, 75 : 25, 25 : 75, 100 : 100, corresponding to PSS : PDDA ion ratios of 2 : 1, 3.9 : 1, 1 : 1, 5.9 : 1, 0.65 : 1 and 4 : 2, respectively. In all cases the overlapped area has formed a gel where the two materials overlapped (see Fig. 4b) whereas the areas of either polymer alone remained liquid and were subsequently washed away. Fig. 4c and d show a thick section of the final gel.

The thicknesses of these films as printed were determined by profilometry. The thickness increased proportionally to the number of layers printed (Fig. 5a). Due to the changing drop ratio and the fact that the PSS solution was twice as concentrated as the PDDA, differing amounts of polymer are deposited for each sample but the final thickness of each film was proportional to the total weight of polymer deposited. Thus, the sample with PSS : PDDA ink ratio 75 : 25 is thicker than that with a ratio of 25 : 75, see Fig. 5a. Based on the numbers of 80 pl drops deposited and the solution concentrations, the film thicknesses correspond to that expected for a polymer with a density of about 0.9 g cm^{-3} , suggesting that the gels are not highly swollen in air.

The thicknesses shown in Fig. 5a represent the printed gel thickness in equilibrium with atmospheric conditions. Fig. 5b shows that after the gels are washed there is a substantial reduction in thickness. One would also expect salts and any impurities to be lost, as well as any polymer that is not bonded into the gel network. It would be expected that the greater losses would be when one or the other polymer is in excess.

The loss of material on washing can also be followed by profilometry of the wet gels, which reflects both the polymer loss and the swelling tendency of the remaining gel (Fig. 6a). The total loss is a minimum at the ideal ion ratio 1 : 1 and increases for other ratios. Fig. 6b shows that the films remaining after washing are not identical. The degree of swelling in water increases with original PSS content even though much of the excess PSS is apparently removed on washing.

A further set of samples were printed at a nominal 1 : 1 ion ratio of PSS to PDDA. This gel lost about 50% of their weight on washing. On swelling from dry in saline, the weight increased by $1000 \pm 200\%$, on redrying and reswelling in water, the gain was only $200 \pm 20\%$. This is in contrast to the slow-printed samples where weight gain in saline was less than in water.

Solute diffusion

As a further characterization of these rapidly printed films, we studied loss of the pH indicating anionic dye, bromocresol green

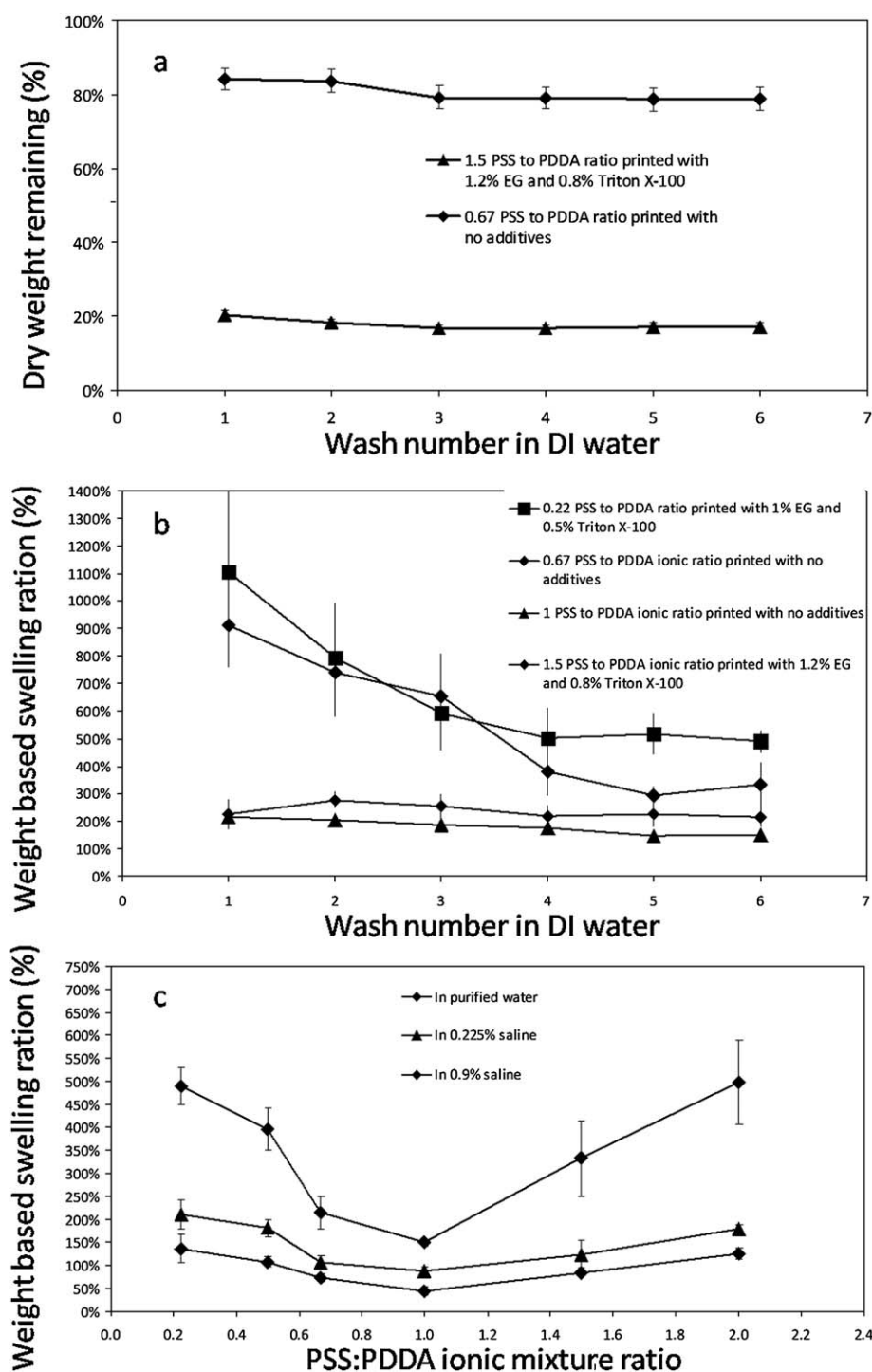


Fig. 3 (a) Weight loss of printed films with numbers of wash cycles in DI water. (b) Swelling of films by DI water through sequential overnight washing cycles. (c) Swelling of twice-washed films in water and salt solutions.

from the film on soaking in water or saline solution. The dye was incorporated into the films at a concentration in the printed ink of 0.1% w/v. Fig. 7a shows samples printed onto glass, where the initial printed layer shows signs of incomplete mixing, with the pH indicator having different colors in different regions, *i.e.* green (low pH) and blue (high pH). After extensive washing, a significant amount of the dye was lost from the polymer complex in some areas, but retained in the high pH (blue) state in other areas (Fig. 7b).

This non-uniform behavior makes it difficult to follow the dye loss process spectroscopically. Therefore, polymer complexes were printed onto cellulose acetate membrane and the loss of color followed using Kubelka–Munk analysis of images taken using reflected light. The validity of this approach has been detailed in the Experimental section, colour strength increases linearly with printed ink density. Fig. 7c and d show that the printed pattern reflects the drop deposition, which is retained after extensive

Table 1 Energy dispersive spectroscopy of sulfur (S), sodium (Na) and chloride (Cl) in films as printed, and after washing

PSS-PDDA ion ratio	Treatment	S atomic%	Na atomic%	Cl atomic%
1 : 1	As prepared	3.27 ± 0.33	1.63 ± 0.43	2.02 ± 0.38
1 : 1	1 st wash	2.13 ± 0.22	0.15 ± 0.10	0.15 ± 0.05
1 : 1	2 nd wash	1.97 ± 0.21	0 ± 0.02	0 ± 0.03
1 : 2	As prepared	2.14 ± 0.20	2.38 ± 1.13	4.30 ± 0.38
1 : 2	1 st wash	1.86 ± 0.08	0.15 ± 0.06	0.86 ± 0.55
1 : 2	2 nd wash	1.69 ± 0.18	0 ± 0.04	0.10 ± 0.06

washing. Using a scan of the whole area to obtain an average reflectivity, the retained color could be plotted in K/S or the colour strength *versus* the washing time. The first washing data point was taken at 30 minutes and a large amount of dye was lost by virtue of not being entrained in the gel. Accordingly the loss data were fitted to loss after 30 minutes and fitted to the expected profile for Fickian diffusion from a thin film.²¹ The expected ratio of dye retained after 30 minutes to dye retained at longer times was calculated iteratively and compared with experiment values. Fig. 7e shows that the loss profile up to about 4 hours fits a diffusion coefficient between 1.5 and $2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, but longer washing resulted in much slower loss of the dye. That is after 1 week the dye can no longer be seen.

Similar studies in distilled water showed no loss after the first 30 minutes wash. Films with a less than stoichiometric amount of PDDA showed more rapid loss to a lower baseline, whereas films with an excess of PDDA showed little loss at all after the first 30 minutes.

Discussion

While polyelectrolyte complexes are familiar in principle, extensive characterization has only been carried out on samples formed by the

LBL method. The slow inkjet method should have much in common with LBL in that the complexation process probably occurs on the scale of a single drop, since the time between deposition of drops is relatively long. In the fast inkjet process material is being added rapidly so the process is closer to rapid mixing followed by slower complexation. The experiments reported here give us some insight into how the structure of the complex depends on the processing method.

Formation kinetics: slow print

During slow inkjet printing the polymers form dry, but water-plasticized layers. These are similar to those produced by the LBL process but each layer is about 100 times thicker. The layers dry as they are printed and then presumably anneal to form complexes slowly after printing. The washing studies agree with this as most of the dry weight (excluding low molecular weight additives) remains after washing.

In studies of LBL films, thin multilayer films (200 nm) were found to anneal, from being initially rough to smooth. The annealing occurred rapidly in concentrated salt solutions and very slowly in water.^{15,22} Estimates of diffusion coefficients for the polymers in these films vary from 10^{-14} to $10^{-17} \text{ cm}^2 \text{ s}^{-1}$.¹⁶

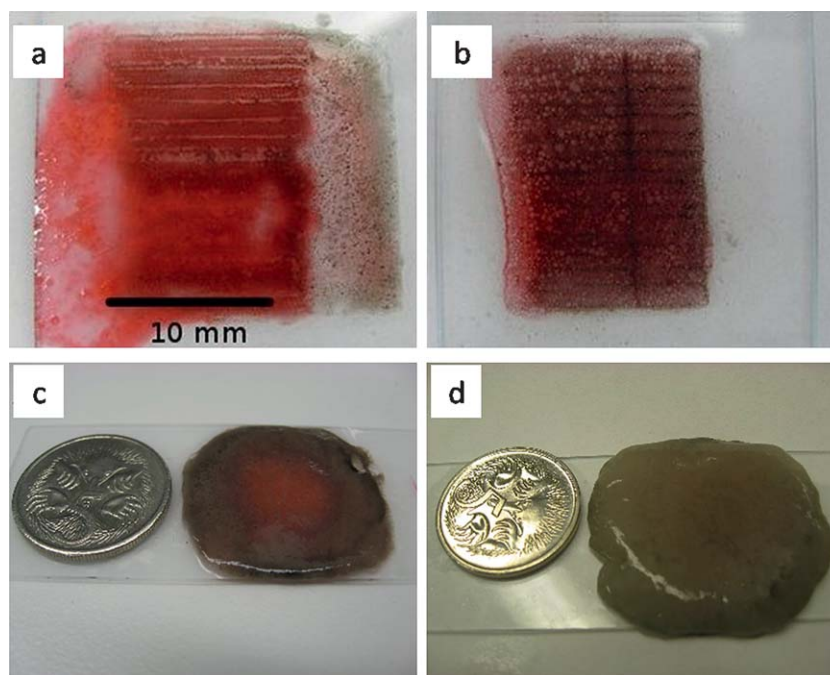


Fig. 4 Photographs of printed PSS-PDDA gels. (a) Freshly printed $17 \times 17 \text{ mm}^2$ square of PSS (blackish) and an offset $17 \times 17 \text{ mm}^2$ square of PDDA (reddish) overlapping by 10 mm. (b) Gel after mild washing, showing that only the gel from the overlapped area remains. (c) A PDDA/PSS gel of 256 layers 2 days after printing, and (d) taken 1 week after printing. Scale is Australian 5 cent coin (diameter = 1.9 cm).

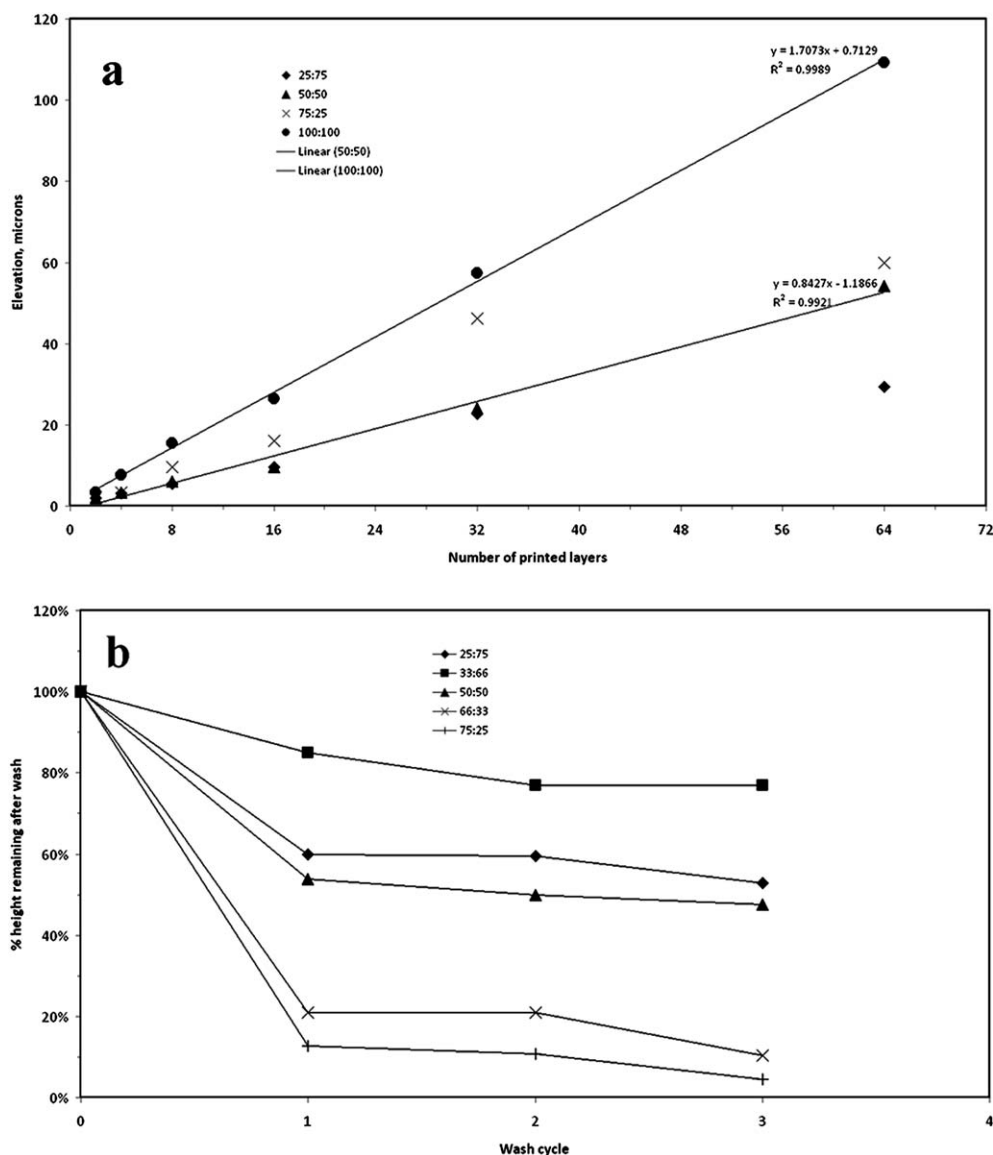


Fig. 5 (a) Thickness of gels as a function of printed layers increases. (b) Thickness remaining after several washing cycles. Ratios (25 : 75 to 100 : 100) refer to weight ratios of PSS to PDDA in the films and to the number of active nozzles. 50 : 50 was printed with half the nozzles active, compared to 100 : 100.

Presumably the polymer diffusion rates will depend on the extent of ion pairing in the gel, on the swelling and on the ionic strength of the swelling solution. In our previous work we found that slow-printed films became less soluble when annealed for 24 hours in moist air at 80 °C. For our slow-printed samples, 80 μm thick with 400 nm per double layer, the calculated diffusion time would be from about 2 hours to 2000 hours. Thus it is reasonable that the complexes continue to anneal for some time after printing.

Formation kinetics: fast print

During fast printing of the two polymers a mixed solution is first formed. Since solutions of dissimilar polymers are usually immiscible, we would expect liquid–liquid phase separation, complex formation and gelation to occur simultaneously. In samples printed on glass (Fig. 7a), large local differences in properties are evident. Subsequent complexation would depend

on the extent of the initial phase separation and so on the details of the printing and drying processes. The weight losses on washing fast-printed samples are much greater than that for slowly printed samples, reflecting the phase separation processes that may interfere with complex formation.

Printing onto paper or membrane modifies this by rapidly removing the excess water during deposition so that the product is quite uniform on the millimetre scale but does show fine-scale structure arising from the actual positioning of the drops, which are placed reproducibly to within 10 μm , Fig. 7c.

Compositional variation

Both the slow and fast printed films show a degree of swelling that depends on printed composition of washed and annealed films. This implies that printing an excess of one polymer does result in a film with an excess of polycations or polyanions. At

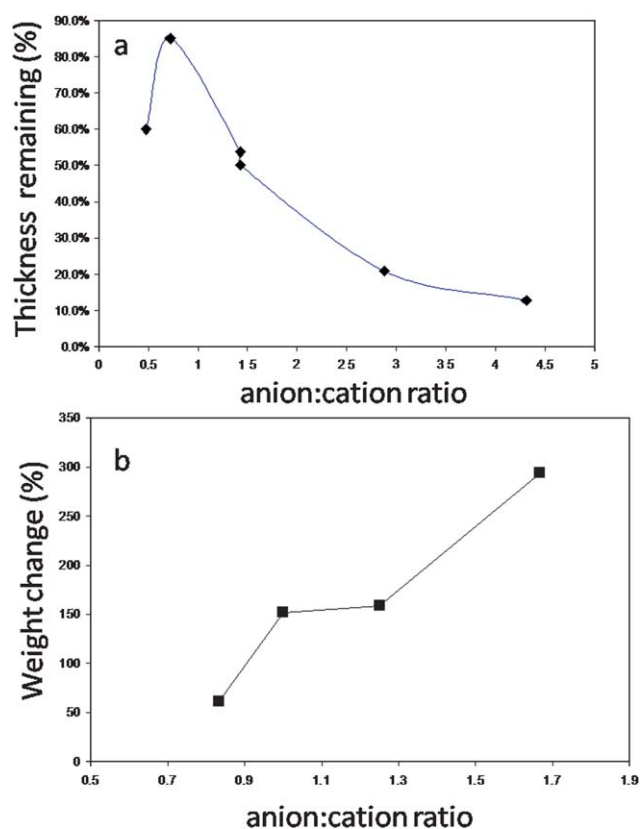


Fig. 6 (a) Thickness remaining after first wash as a function of anion/cation ratio derived from the PSS/PDDA ratio. (b) Weight gain of washed and dried films, with varying anion/cation ratios as printed, on further swelling in water.

the same time it is clear that an excess of PDDA polycation is mainly removed on washing as suggested by the weight loss data in Fig. 3. There is an asymmetry arising from the fact that the molecular weight of the polyanion, PSS, is about $20\,000\text{ g mol}^{-1}$ while that of the PDDA polycation is $100\,000\text{ g mol}^{-1}$. Thus, a gel with an excess of short polyanions is apparently more stable than a gel with an excess of long polycations.

An excess of either polymer would result in a gel that has some residual counterions. Continued annealing and washing of this gel should allow further complexation and release of the counterions as is shown in Table 1 where there is a large excess of chloride after the first washing but not after the second. At this stage our analytical methods do not give us enough sensitivity to detect small concentrations of retained ions below about 1%.

Our results are consistent with the concept that gels with excess of either polymer do swell more. Even though much of the excess is apparently lost, the remaining unpaired ions seem to be enough to affect the swelling properties of the gel dramatically. On the slowly printed samples, the swelling is greater in water, which would be expected for a fully complemented gel, whereas the fast printed samples swell more in saline solution, reflecting a higher level of unpaired charge on the polymers.

Release kinetics

Diffusion of dyes into and out of LBL films have been measured, with a half-time of about 10 minutes for a 300 nm film.²³ The

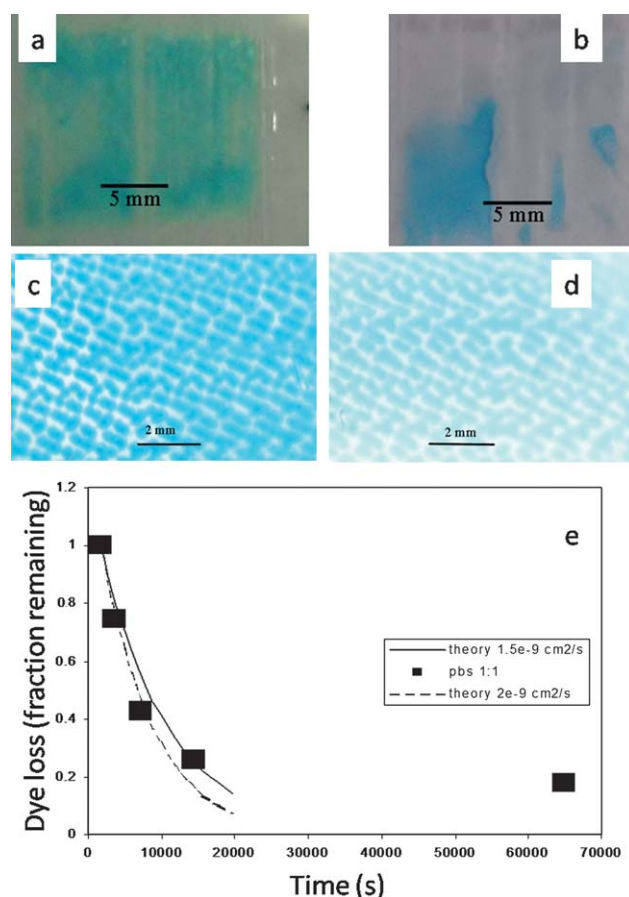


Fig. 7 Photographs of printed bromocresol green dye on a glass substrate. (a) Immediately after printing and (b) after washing in water for 1 week. (c) PSS : PDDA gel with ion ratio 1 : 1 containing bromocresol green printed on cellulose acetate membrane immediately after printing and (d) after washing for 18 hours in PBS. (e) Loss of dye from printed films (squares) using KM analysis compared with theoretical predictions of calculated loss assuming diffusion coefficients of $1.5 \times 10^{-9}\text{ cm}^2\text{ s}^{-1}$ (solid line) and $2.0 \times 10^{-9}\text{ cm}^2\text{ s}^{-1}$ (dotted line).

great variability in loss from fast printed films on glass (Fig. 7b) shows that there are larger variations in gel structure that lead to significant changes in diffusion rates. As shown by studies of surfactant interaction with polyelectrolytes²⁴ there is also the possibility of anionic bromocresol green binding to the PDDA and so being slowly released from regions where PDDA is in excess. Our parallel studies on the release of crystal violet, a cationic dye, from the gels printed on glass showed, after an initial burst loss on the first wash, no detectable release over 2 days (data not shown). Likewise, the diffusion kinetics from samples printed onto cellulose acetate membrane measured in Fig. 7 of $1\text{--}2 \times 10^{-9}\text{ cm}^2\text{ s}^{-1}$ are much slower than would be expected for a swollen gel, where the diffusion coefficient should be a fraction of the diffusion coefficient in water, which is about $10^{-6}\text{ cm}^2\text{ s}^{-1}$ for molecules of this size. Values for the diffusion coefficient of similar drug molecules in gels at about 50% water are $1\text{--}2 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$.^{25,26} It is well known that ionic gels will bind dyes and other small molecules of opposite charge.²⁷ We thus conclude that loss of charged dyes from these gels is slower than simple diffusion in gels and should be treated as a combination of ionic binding and diffusion. Films with higher levels of

polycations or polyanions showed slower or faster diffusion of dye with higher or lower retention levels, suggesting that a complete model would include a reversible binding equilibrium and diffusion. The dye studied here and many drug molecules would be expected to interact with the gel both through ion pairing and through hydrophobic interaction with the polymer chain. As a result, the binding constant may be larger than those that would be predicted on the basis of simple Coulombic interactions.

Conclusions

The ionic gels described here have not previously been well understood because of the lack of a versatile method for preparing them. Inkjet printing allows the mixing process and composition to be controlled while preparing gels several millimetres thick. These gels can be regarded as a partial model for the highly anionic gels that make up the extra-cellular matrix and the matrix of tissues such as cartilage, which are held together by a combination of ionic interactions, hydrogen bonding and hydrophobic interactions between soluble components and with collagen microfibers.

We have shown that the structure and properties of these gels depend on the ratio of the cationic and anionic component and on the processing method as it affects the degree of complexation between the two polymers. It is clear that a wide range of properties would be accessible by also varying molecular weights, hydrophobicity, hydrogen bonding and block copolymer structure in these self-assembling gels.

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