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Abstract

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. The synthetic polyelectrolytes reported here can be compared with biological polyelectrolytes reported earlier by us.

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Self-Assembled Gels from Biological and Synthetic Polyelectrolytes.

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ABSTRACT

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. The synthetic polyelectrolytes reported here can be compared with biological polyelectrolytes reported earlier by us.

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 are 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 film thickness to a few μm ⁷. Various other methods such as spraying [8] and spin coating [9] 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 threads [10] 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} cm^2/s 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 papers have demonstrated that the insoluble complexes do indeed form on inkjet printing both strongly ionized polymers 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 positive and negative charges and expel the counter ions [19].



Figure 1: Scanning electron microscopy image of a film prepared by 50 cycles of PDPA and PSS alternately inkjet printed onto glass and washed. Remaining film of complex is about 50 μm thick.

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. The results on the strong synthetic polyelectrolytes reported here can be compared with those on the weaker polyelectrolytes, poly-L-lysine and polyglutamic acid reported earlier [14].

Results

Slow printing

Printing PDDA and PSS layers at 200 drops per minute 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. 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 figure 1.

As shown in figure 2A, 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. Since the polyelectrolytes are present in low concentrations in the inks used in the slow printing system, the weight loss on the first two washes then corresponds to about that fraction of the total weight of the printed mix represented by the surfactant and humectant, i.e. ~60%. 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 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 figure 2B 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 degree of swelling in water 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.

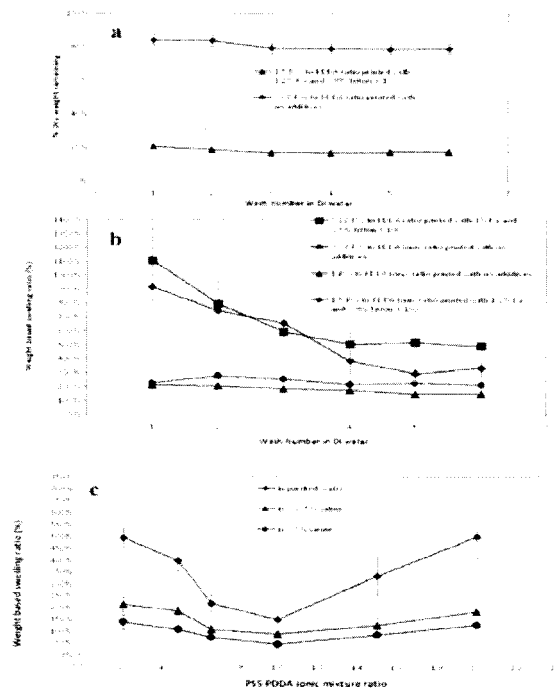


Figure 2: A: Weight loss of printed films with numbers of wash cycles in DI water. B: Swelling of films by DI water through sequential overnight washing cycles. C: Swelling of twice-washed films in water and salt solutions.

Table 1: EDS atomic % of sulfur, sodium and chloride in films as printed and after washing

	At.% S	Std Dev	At.% Na	Std Dev	At.% Cl	Std Dev
1:1 PSS:PDPA ion ratio						
As printed	3.27	0.33	1.63	0.43	2.02	0.38
1 st wash	2.13	0.22	0.15	0.10	0.15	0.05
2 nd Wash	1.97	0.21	0	0.02	0	0.03
1:2 PSS:PDPA ion ratio						
As printed	2.14	0.20	2.38	1.13	4.30	0.82
1 st wash	1.86	0.08	0.15	0.06	0.86	0.55
2 nd wash	1.69	0.18	0	0.04	0.10	0.06

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. Figure 2C 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. These samples were opaque white after swelling in water but clear after swelling in saline solutions. 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 x 17 mm² 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 (Figure 3A). 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 2:2, respectively. In all cases the overlapped area has formed a gel where the two materials overlapped (see Figure 3B) whereas the areas of either polymer alone remained liquid and were subsequently washed away. Figure 3C and D shows a thick section of the final gel.

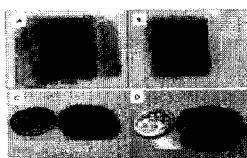


Figure 3: Photographs of printed PSS-PDDA gels. A) Freshly printed 17x17 mm² square of PSS (right) and an offset 17x17 mm² square of PDDA (left) overlapping by 10 mm. (B) Gel after mild washing, showing that only the gel from the overlapped area remains. C) A PDDA/PSS gel of 256 layers 2 days after printing, and (D) taken 1 week after printing. Scale is Australian 5 cent coin (diameter = 1.9 cm).

DISCUSSION

Thick layers self-assembled polymer gels can be formed by inkjet printing other pairs of anionic and cationic polymers. The structure and properties of the final layers do depend on the kinetics of deposition and on the ratio of the two components. By layering the two polymer solutions on the micron scale, inkjet printing allows these complexes to be formed much more rapidly than by the dipping approach to ionic self-assembly. The necessary interdiffusion can take place on this micron scale but would be too slow to allow uniform complex formation by conventional mixing methods.

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