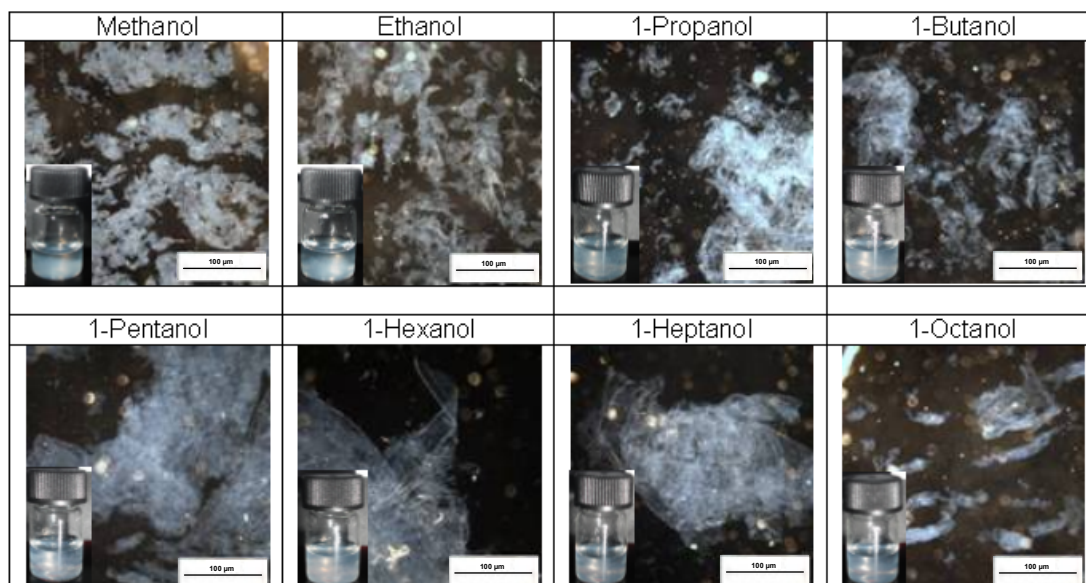
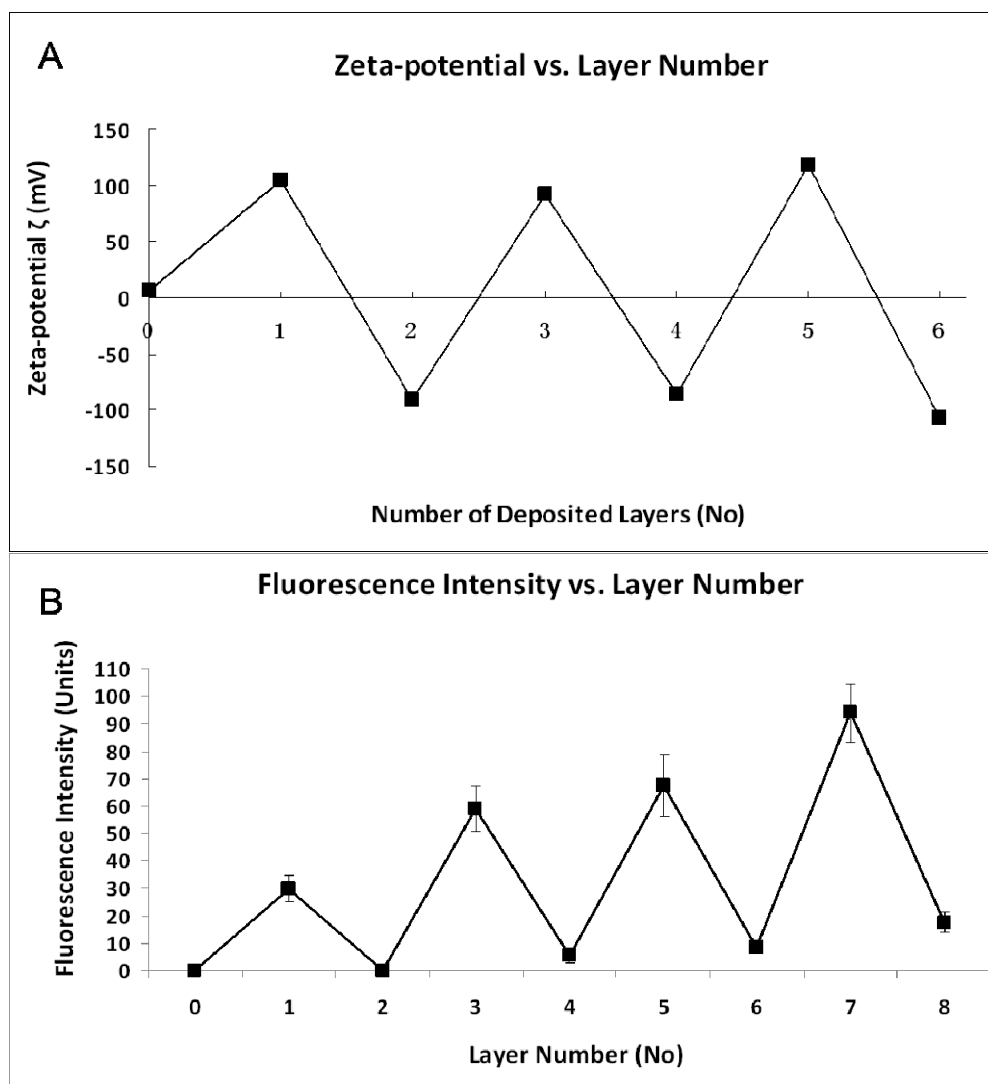


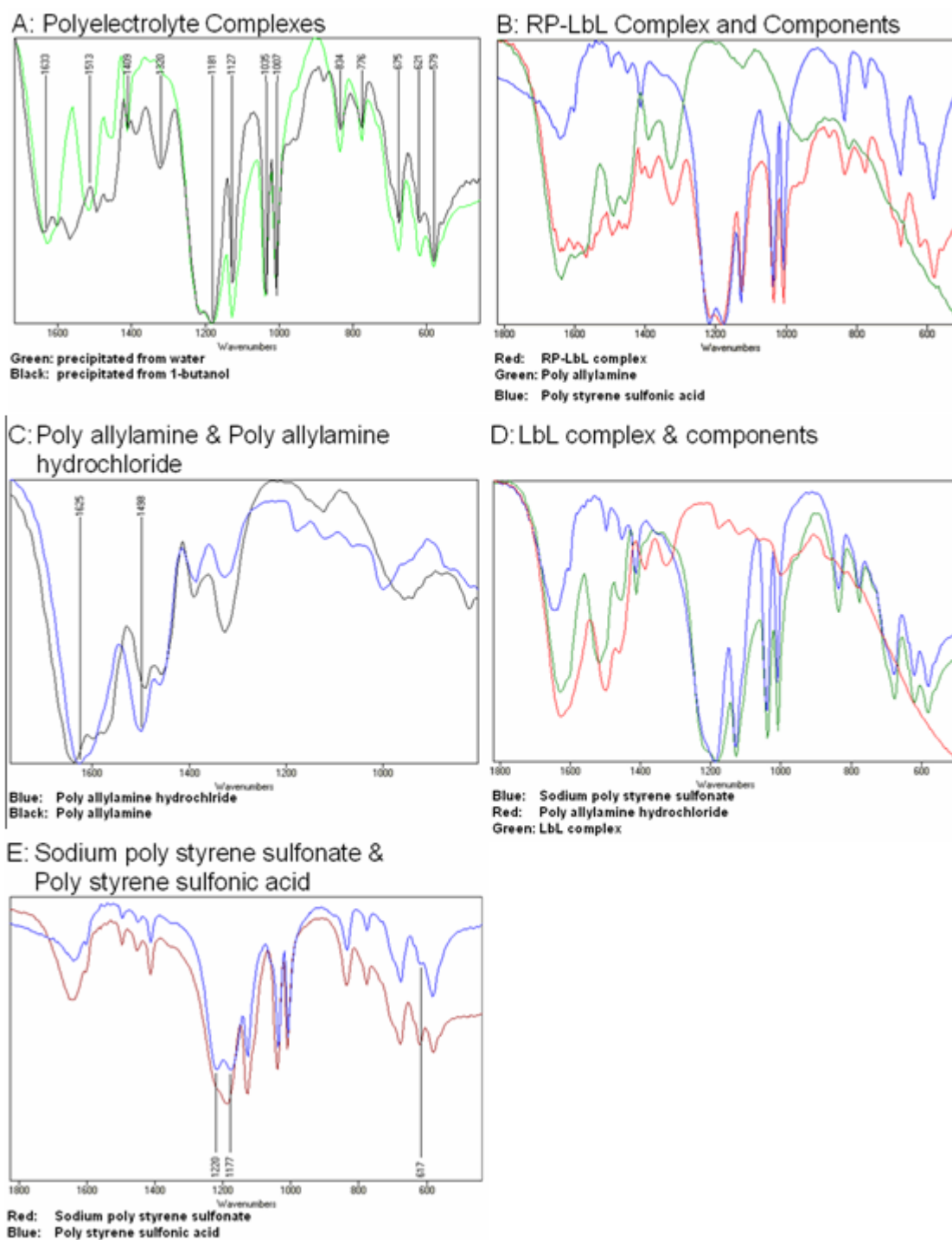
Supporting Information



Supplemental Figure 1: Demonstration of polyelectrolyte complex formation ability. After mixing solutions of PA and PSS separately dissolved in the respective alcohol, increasing turbidity of the mixture and precipitation of the insoluble polyelectrolyte complex was observed.



Supplemental Figure 2. Alternating zeta-potential as a function of layer number indicates stepwise absorption of polymer layer that exhibit opposite charges (A). Increasing fluorescence intensity with every deposition of fluorescent labeled polymer (Polyallylamine-FITC) indicates subsequent increase of deposited polymer (B).

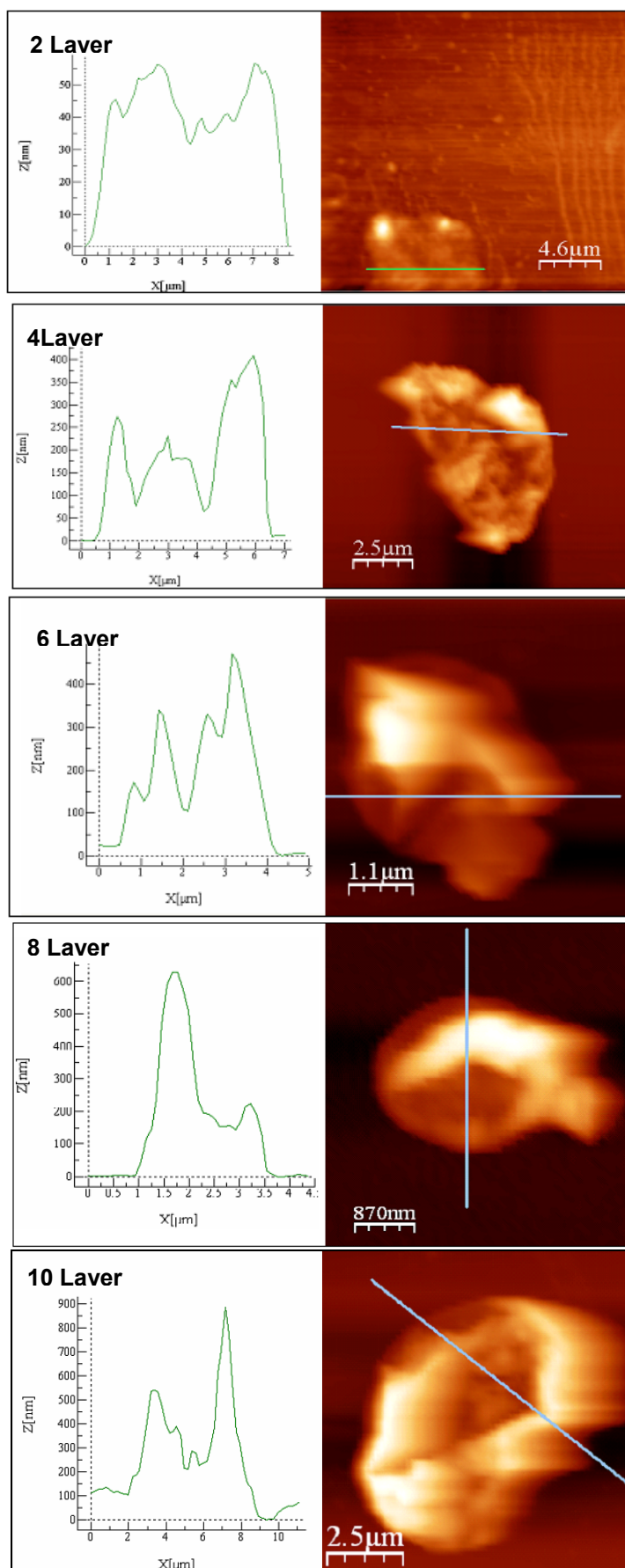


Supplemental Figure 3: IR spectra of polyelectrolyte complexes and their components

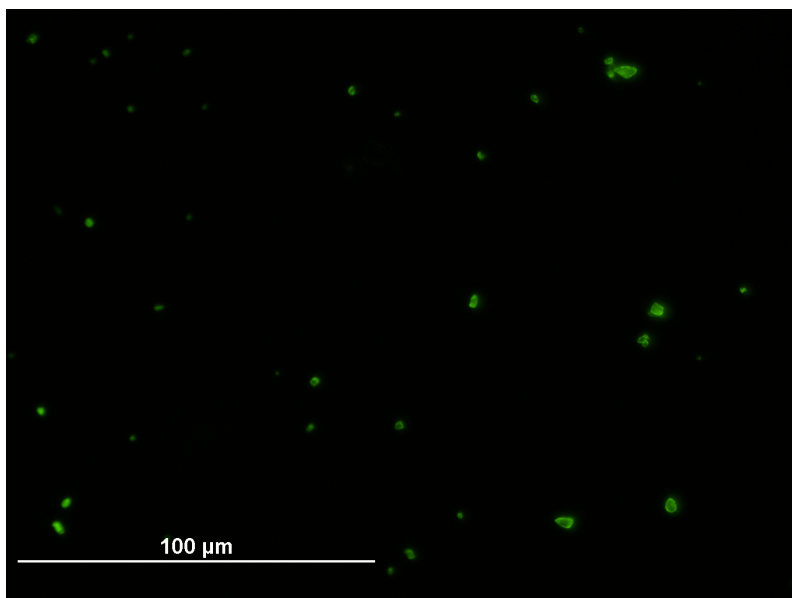
IR spectroscopic investigation:

IR spectra of sulfonic acids often resemble those of sulfonic acid salts due to hydration to hydronium salts under normal working conditions. However, distinct features in IR spectra were observed allowing conclusion of polymer interactions. In summary the components of the spectra for the polyelectrolyte complex assembled in water resembles more those of PA hydrochloride and that of PSS sodium and components of the spectra for the polyelectrolyte complex assembled from 1-butanol resembles more those from PA and PSS. A detailed outline of spectral differences between PSS and PSS sodium PA and PA hydrochloride, PSS/PA complexes assembled from water or 1-butanol can be found in the following. It is remarkable that the spectra of the PSS/PA complex formed in butanol still resemble properties of free polystyrenesulfonic acid even though amine groups are roughly in 2.4 times molar excess. Comparing the spectra from PSS/PA complex assembled from water and Butanol (Spectra A) it can be seen that the spectra for aqueous LBL in the region of 1800 cm^{-1} to 1400 cm^{-1} is similar to that of polyallylamine hydrochloride and that of RP-LbL similar to that of polyallylamine. From Spectra B, it can be seen that the peak at 1500 cm^{-1} becomes more defined upon PSS and PA complex formation in 1-butanol compared to the spectra of the free base polyallylamine, indicating amine-hydro salt formation. Differences between polyallylamine and polyallylamine hydrochloride can be observed at 1630 cm^{-1} and 1500 cm^{-1} which are bend and deformation vibration for free base primary amines and primary ammonium salts, respectively (Spectra C). The bend vibration peak of ammonia salts is significantly more defined for the spectra of the polyelectrolyte complex assembled from water (Spectra C). The peak at 1200 cm^{-1} is sharp for polystyrenesulfonic acid sodium salt but a symmetric shoulder for polystyrenesulfonic acid with maxima at 1220 cm^{-1} and 1177 cm^{-1} . Furthermore the C-S stretch peak at 620 cm^{-1} is more defined for the salt form compared to that of the free acid. Comparing the spectra of both polystyrenesulfonic sodium salt and PSS/PA polyelectrolyte complex from water and polystyrenesulfonic acid and PSS/PA polyelectrolyte complex from butanol in the

area from 1800 cm^{-1} - 1400 cm^{-1} , it is clear in both cases that the peaks of the polyelectrolyte complex are N-H bend or deformation vibration and not found in polystyrenesulfonic acid or polystyrenesulfonic acid sodium salt (Spectra B and D). Comparing the spectra of polystyrenesulfonic acid and polystyrenesulfonic acid sodium salt, (Spectra E) only a few differences can be seen. When comparing the spectra of PSS/PA polyelectrolyte complex from butanol and PSS/PA polyelectrolyte complex from water, it becomes clear that the peak at 620 cm^{-1} becomes more defined in the spectra of PSS/PA polyelectrolyte complex from butanol compared to the spectra of the polystyrenesulfonic acid but less defined compared to the spectra of sodium polystyrenesulfonate or that of PSS/PA polyelectrolyte complex from water. When comparing the peak at 1200 cm^{-1} it can be seen that the peak has still a slight shoulder form for PSS/PA polyelectrolyte complex from butanol but not in the spectra of PSS/PA complex assembled from water. By taking into account the molar ratio of ammine groups to sulfonic acid groups that was used to precipitate the PSS/PA polyelectrolyte complex.

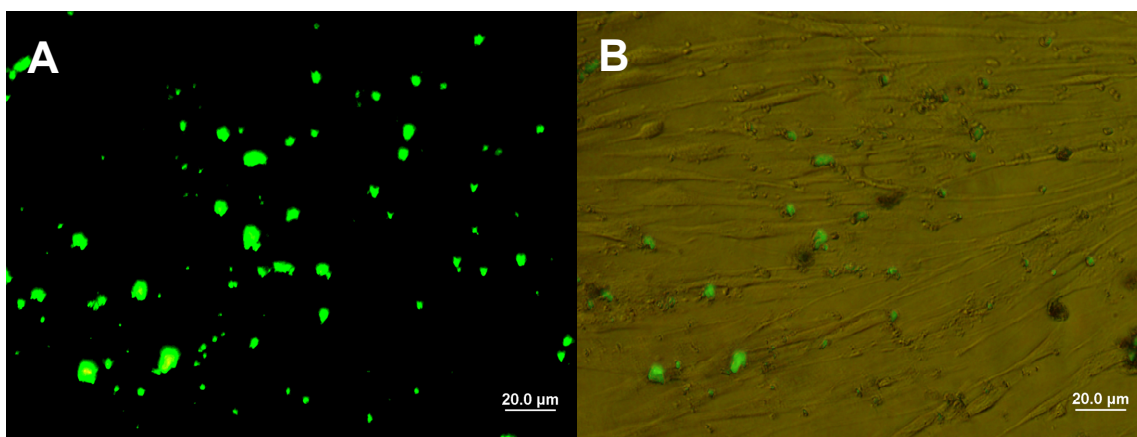


Supplemental Figure 4: Collapsed polyelectrolyte microcapsules, demonstrating layer dependent increase in average thickness in their corresponding cross sections. Images of single capsules are zoom in areas of larger pictures which results in the limited resolution depicted.



Supplemental Figure 5 .

Fluorescent micrograph of $(\text{PA-FITC/PSA})_2\text{PA-FITC}$ microcapsules dispersed in cell culture medium after successfully performed phase transfer protocol. The irregular crystal shape can still be recognized after glucose core dissolution.



Supplemental Figure 6. Fluorescent micrograph showing internalized microcapsules of $(\text{PA-FITC/PSA})_2\text{PA-FITC}$ into IMR 90 fibroblast by quenching extracellular fluorescence with 0.004% w/v Trypan blue solution (A). Overlaid fluorescence and bright field micrographs reveal partial internalization depending on location and size of microcapsules (B).