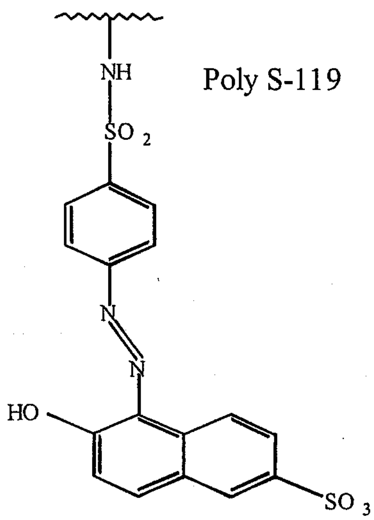
Experiment 15: Traditional and Nontraditional Approaches to Polymer Processing
Experiment for the Last Week of Lab

Aim : To introduce a range of traditional and non-traditional processing techniques, and illustrate issues involved in processing of polymeric materials. This is a short one to two day mini-lab meant to allow loose experimentation with polymer materials. If you wish to try something different, do so with permission from the TA – but describe what you did in the assigned work.

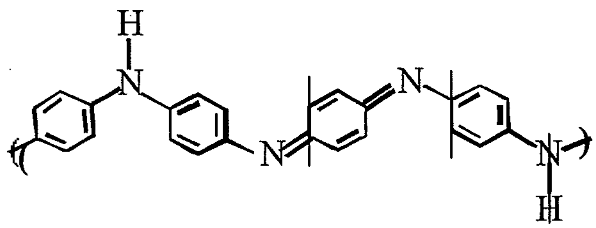
1) Polymer Ultrathin Films: Layer-by-Layer Adsorption of Polyelectrolytes

Ultrathin polymer films can be built up by adsorbing polymers from very dilute solutions onto a substrate. If the substrate is charged (e.g. negatively charged), and immersed in a dilute solution of polyelectrolyte of the opposite charge (e.g. a polycation), the polymer will adsorb until the surface charge is reversed, and electrostatic repulsion prevents further adsorption. The thickness of the adsorbed film can range from 5 to 100 Å, depending on the pH and ionic strength of the conditions used. The polymer film may then be rinsed thoroughly with clean deionized water, and immersed in a solution of polyanion. Polyanion will adsorb to the positively charged polycation film, until, once again the surface charge is reversed. By continuing to alternate the adsorption of charged polyions, composite films are created. This technique can be used to incorporate functional materials within molecularly scaled layers in a polymer thin film. Such materials have potential applications in electro-optical, magnetic, sensor and biomaterials applications. The functionality of the films can be varied by incorporating new charged polymers with different functional groups into the multilayer structures. This technique was first introduced in 1990-91 by Gero Decher at University of Mainz, Germany; since that time, the area of polymer multilayer thin films has grown at incredible rates due to the ease of formation and the low cost of processing these films.

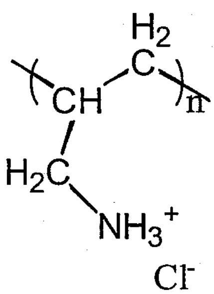
In this case, we will build up films of polyaniline (PANi), a conducting polymer which is positively charged at low pH, and sulfonated polystyrene (SPS). Polyaniline is a deeply colored green polymer. A second system involves a polymer, termed "Poly S-119", which is a polymer with azobenzene side groups which has nonlinear optical properties and is also a strong red chromophore. This polyanion can be alternated in layers with poly allyl amine hydrochloride (PAH) (a polycation at low pH). The structures of all materials are shown below:

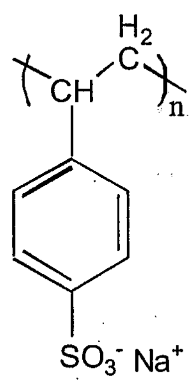


Poly S-119



PANi





PAH SPS

i) The PANi/SPS multilayers will be adsorbed onto glass slides. Plain glass slides should be rinsed thoroughly with ethanol,followed by deionized water, and should then be dipped into a solution of the polycation PAH for 10 minutes, to obtain an initial positively charged surface. Following this step, the entire glass slide can be dipped, first in SPS, then PANi, to begin adsorbing multiple layers of PANi/SPS multilayers as described below in step iv.

ii) The P-S119/PAH multilayers will be built up on gold surfaces (these will be silicon wafers coated with a thin layer of gold. Each group will be given a section of Si/gold wafer. We will experiment with adsorption on a chemically patterned surface of alternating carboxylic acid groups (COOH) with water soluble oligoethyleneoxide groups (EG). The charged COOH regions act as a region that encourages multilayer deposition, while the neutral EG regions have a low interfacial tension in water which discourages polyion deposition. You will stamp a small section of your gold wafer with an acid functionalized molecule to form a monolayer, then adsorb the second EG monolayer with a quick dip in the

EG solution. The TA will assist each group in the stamping process. Once this has been done the entire gold/Si piece is used to adsorb PAH, followed by the alternation of S-119/PAH multiple layers (see below - step iv).

iii) Each group should obtain a 30-50 ml quantity of each of the four polyion solutions above in a small glass vial

iv) Dip your glass slide into the SPS solution and allow it to adsorb for 3 minutes. Rinse thoroughly with DI water , then immerse in PANi solution for 3 minutes. Rinse thoroughly and repeat. Go up to 2 bilayers, 4 bilayers, and 8 bilayers, observing any change in color or intensity with number of layers by placing on a white sheet of paper and making observations. Create more bilayers if time allows. The same should be done for the P-S119/PAH system.

v) For the S119/PAH systems, observe whether the bilayer systems are preferentially adsorbed on one or the other surface by looking at the edges of the film or the blank stamped area. Is a pattern (diffraction grating) present on visual inspection after deposition of several layers?

vi) Stamping a polymer atop another polymer. Adsorb a top layer of SPS to one of your slides with SPS/PANi multilayers (adsorb this last layer for a full ten minutes). Try directly stamping a positively charged polymer – polydiallyldimethylammonium chloride (PDAC) from a dilute water/ethanol solution that the TA will provide for you. Ink the stamp with a cotton swab, allow solvent to dry, and apply the stamp immediately to the multilayer for 60 seconds. Remove stamp, and apply "hoff" test to see if pattern appears upon wetting/dewetting of vapor. This stamping works through the application of a plus charged polymer to a negatively charged surface - only a single monolayer of 30 to 40 Å is obtained.

Short Assignment for Part 1 (on a separate sheet of paper):

a) For each of your two systems, did you see an increase in color intensity with number of layers? Describe your results.

b) What would happen if you increased the pH of the solution to much larger values? Would you expect a difference in the amount of material adsorbed at high versus low pH? Why or why not?

c) Were you able to see a pattern on your SAMs patterned surface modified substrate? Why or why not?