Appendix B

TOWARDS NOVEL PHOTORESPONSIVE SURFACES: WETTING ON AZOBENZENE-FUNCTIONALIZED POLY(ETHYLENE GLYCOL)-*BLOCK*-POLY(PROPYLENE SULFIDE) COPOLYMERS

B.1 Introduction

Several groups have demonstrated that the contact angle of water on a surface can change in response to light due to photoresponsive chromophores immobilized on the surface. Two techniques for surface immobilization of chromophores have been investigated: either the formation of self-assembled monolayers (SAMs) of the chromophore[1-5] or formation (by either spin-coating or Langmuir-Blodgett transfer) of a thin film of a hydrophobic polymer with pendant groups bearing the chromophore.[6-9] The change of water contact angle produced by these techniques is modest: for azobenzenes—the most studied photoresponsive chromophore—the largest reported change in advancing contact angle with UV illumination is an 11º decrease with UV illumination.[7] Only Ichimura and coworkers report the change in the receding contact angle for an azobenzene-functionalized surface: 11º increase with UV illumination.[1] A slightly larger change in advancing contact angle was achieved by Sasaki and Shouji, who combined photoresponsive chromophores with surface roughness: irradiation induced a 15º change in advancing contact angle on a malachite green-functionalized surface with nano-scale roughness.[3] In all these examples the change in wettability is due to the change in the dipole moment or net charge of the chromophore alone. No restructuring on a scale larger than the chromophore itself occurs on the surface.

Large restructuring of surface-grafted block copolymers and concomitant large changes in contact angle have been observed, however, in systems where the block copolymer brushes are exposed to a selective solvent for one of the blocks.[10] The topography of the surface depends very much on which block is favored by the solvent. For example, Brittain and coworkers examined brushes consisting of a polystyrene (PS) block proximal to the surface and a poly(methyl methacrylate) (PMMA) block on the distal end of the brush;[11, 12] AFM shows a flat, featureless surface when these brushes are dried from dichloromethane (a selective solvent for the PMMA block) and an irregular, rough "worm-like" structure when exposed to cyclohexane (a selective solvent for the PS block). A gradual change of solvents from dichloromethane to cyclohexane produced a regular nanopattern of bumps; these are hypothesized to be the "pinned micelle" phase predicted by Balazs and coworkers.[13] Additionally, the contact angle of water changes from 75° on the surfaces treated with dichloromethane (a typical contact angle for water on PMMA homopolymer), to 99° on the surfaces treated with cyclohexane (a typical contact angle for water on PS homopolymer), to 120° on the surfaces where dichloromethane was gradually changed to cyclohexane (an increase the authors attribute to the greater surface roughness of the pinned micelles).

Large changes in surface composition and topography—and hence contact angle—are possible because these changes develop from a mobile phase. Such restructuring is not possible in the previously studied photoresponsive surfaces because of the lack of mobility inherent to SAMs or insoluble polymer layers. More dramatic changes in wettability in photoresponsive surfaces may occur if a photoresponsive molecule is coupled to a mobile (water soluble) polymer chain. Illuminating the chromophore might not only induce a change in dipole moment (or net charge) of the chromophore itself, but also change the aggregation state of polymer chains on the surface.

To examine the possibility of photoresponsive, hydrophilic brushes, poly(ethylene glycol) (PEG) is chosen as the water soluble chain because of its ability to prevent non-specific binding of biological materials. Hubbell and coworkers have demonstrated that block copolymers of PEG and poly(propylene sulfide) (PPS) can be synthesized from commercially available PEG in a one-pot process using an anionic polymerization that is insensitive to protic contaminants and does not use extreme reaction conditions.[14] These block copolymers form robust brush systems on gold;[15] they are more stable than the analogous PEG brush formed with a thiol. A careful distinction must be made here: the PPS block in these polymers serves only to bind the chains to the surface; it is immobile in water and does not form part of the brush extending away from the surface. This “anchor” is analogous to the insoluble block used to attach polyelectrolyte brushes in the work of Tirrell and coworkers,[16] in contrast to the PS block in the work of Brittain and coworkers above that is mobile in cyclohexane phases.

Rather than a full photoresponsive block, we examine the possibility of using a single azobenzene due to the molecule’s strong tendency to aggregate in aqueous solution (Appendix A). Luckily, the polymerization of PPS developed by Hubbell and coworkers is gentle enough to tolerate many different molecules that might be bound to the PEG; it can be used to attach a PPS block to PEG already functionalized with a chromophore on one end. When adsorbed onto a gold surface, the molecule will form a PEG brush system with photoresponsive molecules on the chain ends.

To produce heterobifunctional PEG with the photoresponsive molecule (azobenzene) on one end and the initiator (thioacetate) on the other for subsequent polymerization of PPS we adopt the method of Behr and coworkers for producing heterobifunctional PEGs from commercially available PEG diols.[17] The key step is to convert a small fraction of PEG-diol to OH-PEG-COOH, and graft these chains to amine functionalized PS beads. The remaining PEG-diol is simply washed away. The free hydroxyl groups on the grafted chains are tossylated, and the chains are cleaved from the beads to produce heterobifunctional OH-PEG-Ts. For our purpose, the tosylate was used to couple azobenzene, and the hydroxyl was then converted to a thioacetate to proceed to grow the PPS block.

After describing preparation of the materials, we proceed to describe their adlayers on gold and the advancing and receding contact angles observed with and without UV irradiation. Sadly, we find that a single azobenzene group only slightly changed wetting behavior relative to control without chromophore; not surprisingly, the state of the azobenzene (*cis* versus *trans*) has no discernable effect.

B.2 Experimental

PEG-bl-PPS Synthesis. All reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. The synthesis followed published procedures,[14] using a higher molecular weight of PEG. Of the two routes used to synthesize the thioacetate, the tosylation method was chosen rather than the radical addition to the allyl ether. This was done looking foreward to the ultimate goal of polymerizing PPS blocks on PEG chains which have already been reacted on one terminus with azobenzenes. The radical addition of thioacetic acid requires refluxing the PEG in toluene. Due to the side reaction of azobenzenes with methyl-substituted aromatics,[18] this refluxing in toluene would destroy any azobenzenes present on the PEG. PEG thioacetate was purified on a Sephadex LH-20 column with methanol as the solvent.

Synthesis of α-4-Phenylazophenol-ω-thioacetate-poly(ethylene glycol) (Az-PEG2000-S-Ac). The first part of the synthesis was based on the PEG modification procedure developed by Behr and coworkers[17] (Scheme 1). Aminomethylated polystyrene (100-200 mesh, 0.90 mmol/g substitution) was purchased from NovaBiochem (Laufelfingen, Switzerland). A reaction vessel made in the Caltech glass shop was used for the reaction and filtering of the beads. This round bottom flask featured a glass frit and pipette tip set 90 degrees from the bottom so that after reacting, the vessel could be rotated to allow filtering of the beads. The vessel allowed stirring by means of a magnetic stir bar rather than by the bubbling of nitrogen used in commercially available glassware designed for solid-state synthesis.

For brevity, the complete synthesis will not be detailed, only the points that differ from Behr's process. For the initial step, 50 g of dry PEG_{2000} diol were reacted with the 1.23 g of diglycolic anhydride in 80 mL of dichloromethane, 20 mL of THF, and 1.44 mL of pyridine. 1.98 g of beads were added after forming the NHS ester. The PEG was cleaved from the bead after the tosylation was complete. After the solvent was evaporated, reaction with the azobenzene and purification was accomplished as detailed above for Az-PEG_{2000}-Az (Appendix A). The mass of Az-PEG_{2000}-OH collected was 1.60g. To reduce labor, the substitution of the tosyl group with the azobenzene was also attempted while the PEG-tosylate was still attached to the bead. This strategy resulted, however, in loss of all the polymer. Perhaps the base (cesium carbonate) needed to catalyze the substitution of the tosylate with the azobenzene is responsible for the cleavage of the ester link between the polymer and the bead.

When adding the tosyl group to the opposite end of the polymer, it was necessary to use milder conditions than those reported above (Appendix A) for forming the PEG tosylate in order to prevent degradation of the azobenzene. For 1.4004 g of Az-PEG_{2000}-OH, 2.5 g tosyl chloride was used. The flask was stirred in an ice bath, and then 1.96 ml TEA was added to the reaction flask. The flask was stirred on ice for 15 minutes, and then allowed to warm to room temperature. The reaction was continued for 1.5 additional hours. HPLC showed 84% of the polymer was heterobifunctionalized with azobenzene on one end and a tosyl group on the other. The thioacetate group was added according to the published procedure.[14] The resulting polymer had azobenzene on one end and thioacetate on the other (Az-PEG_{2000}-S-Ac) and was used for synthesis of the copolymer.

Azobenzene-Functionalized PEG-bl-PPS Synthesis. The Az-PEG_{2000}-S-Ac was used for synthesis of azobenzene-functionalized diblock (Az-PEG-PPS) and triblock (Az-PEG-PPS-PEG) copolymers. For the diblock, 0.6513 g of Az-PEG_{2000}-S-Ac, 9 ml THF, 0.333 ml of 0.5 *M* sodium methoxide in methanol, 0.263 ml propylene sulfide, and 0.0927 g iodoacetamide were used. For the triblock, 0.28 g of Az-PEG_{2000}-S-Ac, 7 ml THF, 0.259 ml of 0.5 *M* sodium methoxide in methanol, 0.194 ml propylene sulfide, and

0.513 ml PEG monoacrylate were used. After purification, 1.5 g of the diblock and 2.7 g of the triblock were collected.

Polymer Characterization. Nuclear magnetic resonance (NMR) proton spectra were collected on a 300 MHz Varian spectrometer equipped with an automated sampler using 32 scans and a 2 second delay time. Gel permeation chromatography (GPC) was performed using THF (flow rate = 0.9 μL min^{-1}), a Waters 410 differential refractometer, and two Polymer Laboratories 30 cm long PLgel 10 mL analytical columns connected in series (calibrated with polystyrene standards).

Deposition of Polymer on Gold Surfaces. Gold surfaces were both produced in the Caltech Micro/Nano Fabrication Laboratory and purchased from Structure Probe, Inc. (West Chester, PA). Two techniques were used for the deposition of block copolymers on gold. The first technique was adopted from Hubbell and coworkers:[15] the gold surface was placed in a 1 mg mL^{-1} solution of the polymer in methanol for 30 minutes. The surfaces were subsequently rinsed with solvent before use. Alternatively, a concentrated solution of the polymer (24 wt% polymer in THF) was placed dropwise on the surface. The surface was then annealed in vacuum over overnight at 45ºC. The surface was then placed in a large excess of dichloromethane for one hour before use to remove any polymer not bound to the gold surface. A Digital Instruments (Goleta, CA) MultiMode scanning probe microscope was used in non-contact mode to collect all AFM images of the gold surfaces with and without the polymer adlayers.

Irradiation. Surfaces were illuminated with UV light using an Oriel Instruments (Stratford, CT) arc lamp equipped with a 500 W Hg-Xe lamp. An Oriel liquid filter was used to remove IR light; water was circulated through the liquid filter cooling jacket using an aquarium pump. To isolate UV light, a high pass filter (Schott WG 320) and a band pass filter (Hoya U 360) were used, both purchased from Edmunds (Barrington, NJ). These colored filters were submerged in water in a home made filter holder to prevent overheating. All samples were irradiated for 1 minute immediately before wetting experiments were performed.

Contact Angle Measurement. Contact angle measurements were performed inside a homemade environmental chamber equipped with quartz windows for taking photographs. All images were taken with an EOS Digital Rebel XT from Canon (Lake Success, NY) equipped with a Canon MP-E 65mm F2.8 1-5x macro lens. To provide lighting, a bank of LEDs was mounted behind the sample holder. Contact angles and drop diameter were measured using ImageJ (public domain, National Institutes of Health). The protocol used to measure wetting on the polymer surfaces began by placing a 2 μL aliquot of water on the surface. A photograph of the drop was taken, and a second 2 μL aliquot was then added to the first. This was repeated until five aliquots were added and the total drop volume was 20 μL. At this point water was then removed from the drop 2 μL at a time, and a photograph of the drop was taken after each removal.

B.3 Results

PEG-bl-PPS Synthesis. Although the NMR showed all the expected peaks, the GPC trace showed a bimodal distribution (Figure 1). PPS is known to dimerize if exposed to air;[14] therefore, the presence of disulfides was tested. Triphenyl phospine was added to the polymer in DCM and reacted for 0.5 hours. Iodoacetamide was then added and stirred overnight. After precipitating the polymer, the IR spectrum was measured and compared to the spectrum of the polymer before the triphenylphosphene/iodoacetamide treatment. The ratio of the amide absorbance at 1683 cm^{-1} with the methylene peak at 1450 cm^{-1} was found to increase 25% after the disulfide test. This is consistent with the GPC trace: the smaller peak (formed when two diblocks dimerize) is of higher molecular weight than the large peak. From the NMR the molecular weight of the PPS block was estimated to be 4.2 kDa.

Azobenzeze-Functionalized PEG-bl-PPS Synthesis. NMR of Az-PEG-PPS and Az-PEG-PPS-PEG confirm the presence of azobenzenes, PEG and PPS (Figures 2 and 3). The GPC traces of both polymers show a trimodal distribution. Besides the peak resulting from dimmerization that also occurred in the diblocks without azobenzenes, the third peak is hypothesized to result from PEG_{2000} with thioacetate groups on both ends. These molecules occur because the synthesis of Az-PEG_{2000}-OH is not perfect, and PEG that lacks azobenzenes at this point gains initiators at both ends during the subsequent steps. The resulting polymer would be a PPS-PEG-PPS triblock. Using NMR to estimate molecular weight, the diblock sample contained 1.2 kDa PPS, and the triblock sample contained 2.0 kDa PPS.

Formation of polymer adlayers. Two methods to form polymer adlayers on gold were investigated to find the technique that would give the densest grafting of the copolymer. While the advancing contact angle of the layers formed by the two methods were indistinguishable, the receding contact angles of the surfaces formed by the annealing method were 15º lower than those surfaces formed by adsorbing polymer from methanol. Since the hydrophilic components of the surface are responsible for the receding contact angle, this lower contact angle was taken to be characteristic of a high density of PEG on the surface. A difference in topography between the two adlayers was also observed in AFM images (Figure 4): the feature size on the surfaces produced from absorption was on the order of 10 nm, and the feature size on the surfaces produced from annealing was on the order of 100 nm. The decreased receding contact angle and the increased feature size in the AFM images were taken to indicate an increased deposition of copolymer on the surface, and the surfaces used for wetting experiments were produced using the annealing method.

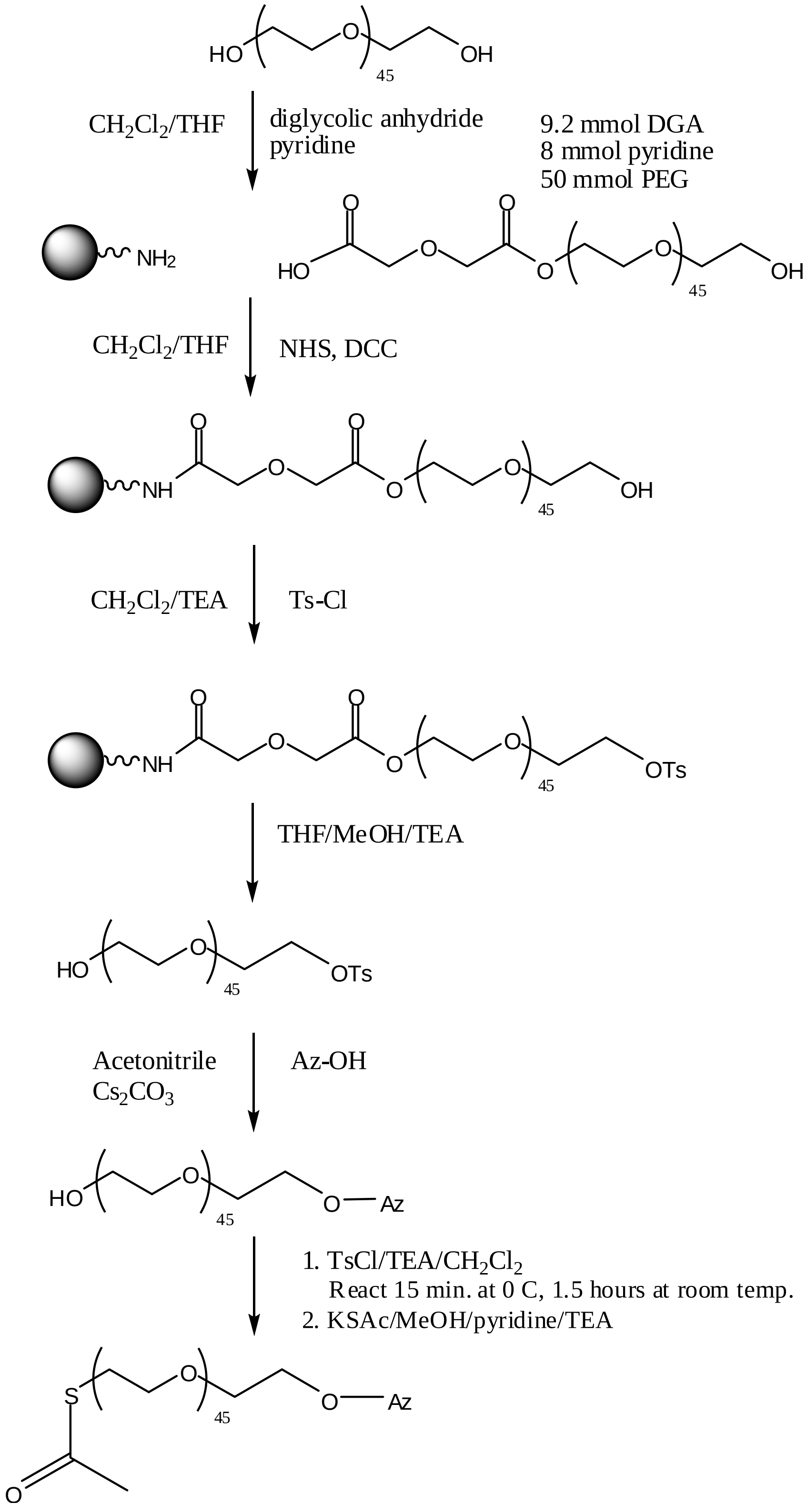
Contact angle measurements. All three surfaces show significant contact angle hysteresis: advancing contact angles range from 59º to 66º for all three surfaces, while the receding contact angles are all less than 40º. The advancing contact angles of water on all three copolymer surfaces are indistinguishable within the uncertainty of the experiments. Also, the contact angles were indistinguishable between a copolymer surface after UV illumination and a copolymer surface without UV illumination.

B.4 Discussion and Conclusion

Polymer adsorption proved to be a convenient way to immobilize azobenzenes on a surface. Unlike SAMs based on thiols or reactive silanes, the functionalized copolymers could be stored for an extended period without degradation and showed no sensitivity to air or water. Even the unintentional formation of dimers does not prevent the formation of end-capped PEG brushes on the surface. The contamination by block copolymers without azobenzenes (those formed from PEG chains with thioacetates on both termini) is detrimental, and could possibly be prevented by an alternative synthesis that begins with a commercially available heterobifunctional PEG.

Subsequent work (chapter X) has shown that hydrophobic groups can be expected to be at the polymer/air interface in a dry layer with mixed composition. Since the azobenzenes can be expected to be near the surface, the lack of photoresponsiveness could indicate too few responsive groups are present compared to the mass of polymer. This might be remedied by functionalization of PEG with a group containing multiple azobenzenes. Also, the concentration of azobenzenes at the polymer/air interface might be tuned by the length of the non-functionalized block in the Az-PEG-PPS-PEG triblock. In such bimodal systems, the chain ends of the longer brushes are predicted to be localized near the outside of the brush system[19] (as opposed to being buried in the interior of the brush system, as occurs in a monodisperse brush system). Since wetting is especially sensitive to the outermost molecular levels, trapping chromophores on this outside edge might give the highest probability of manipulating wettability with light. It is possible that increasing the length of the smaller PEG chain in the triblock copolymer could force the azobenzene functionalized chain ends nearer to the surface.

More likely, an approach closer to that of tethered block copolymers is probably necessary: a photoresponsive block might prove more useful than a photoresponsive group. Also, pinned micelles have been observed in densely grafted systems generated from surface polymerizations (as opposed to the “mushroom regime” accessible using “grafting-to” techniques such as the one utilized here.) Since polyamides are amenable to ATRP, an alternate system of poly(N,N-dimethylacrylamide) and a vinyl functionalized malachite green monomer was investigated with an eye towards eventually using these monomers to form brushes using a surface polymerization technique (Appendix C). Unfortunately, this system proved to possess both synthetic problems (the Malachite Green monomer was an excellent chain transfer agent) and poor photoresponsiveness outside a limited pH range (it would only work properly at high pH.)



Scheme B.1 Synthesis of Az-PEG-S-Ac. The thioacetate group serves as the initiator for the polymerization of PPS. The sphere with the amine group on the surface represents an amine-functionalized polystyrene bead. Termination of the PPS polymerization with iodoacetamide gives a diblock, and termination of the polymerization with PEG acrylate gives a triblock.

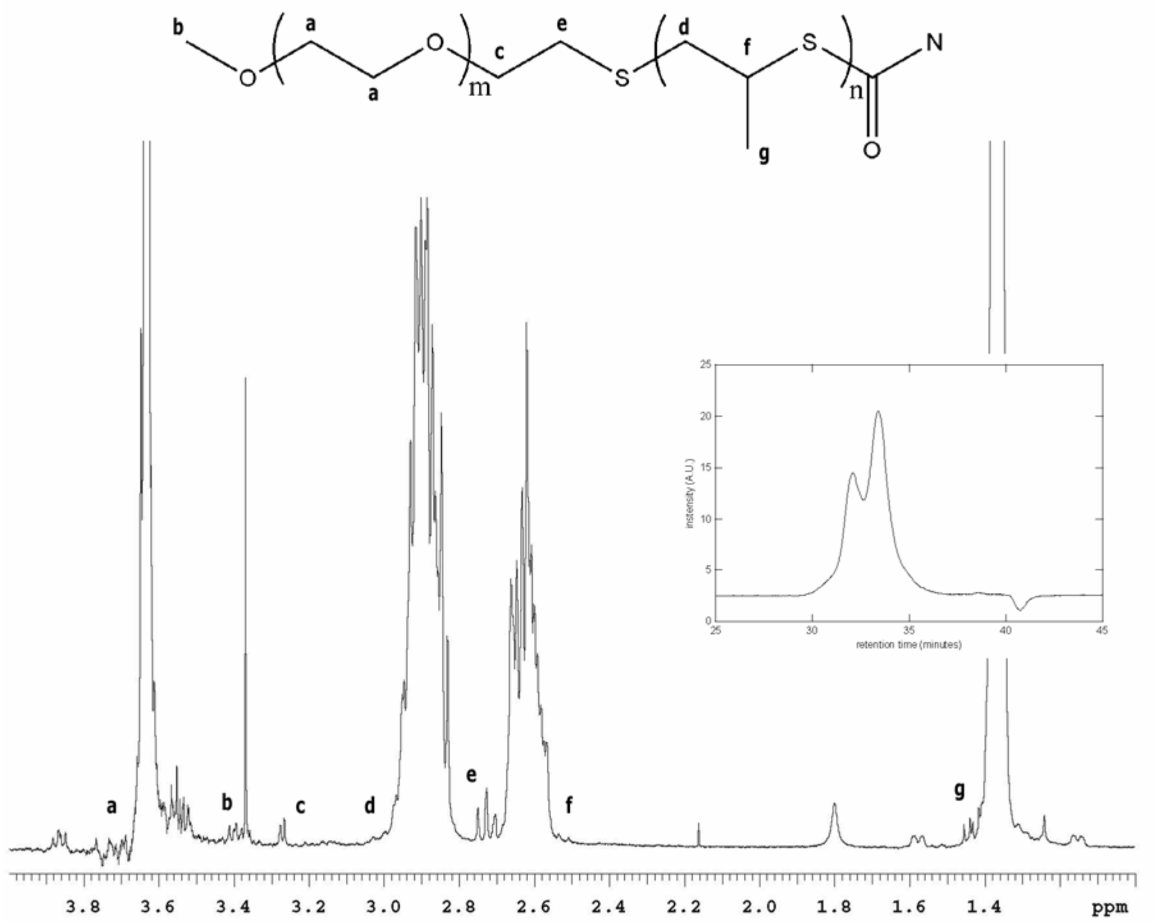


Figure B.1 NMR specta and GPC trace of PEG-PPS copolymer. The value of m is approximately 45, and the value of n is approximately 57.

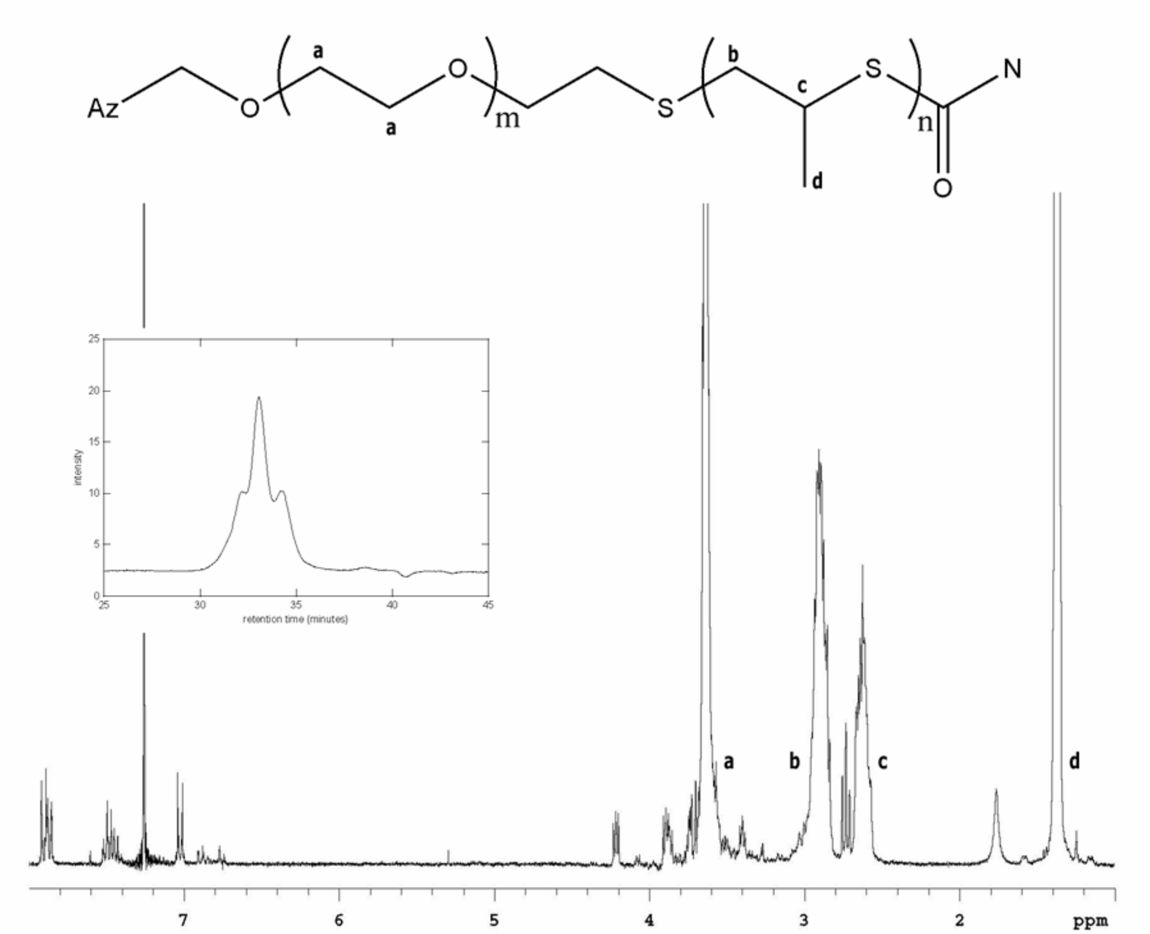


Figure B.2 NMR spectrum and GPC trace of Az-PEG-PPS copolymer. The number of PEG monomers (m) is approximately 45, and the number of PPS monomers (n) is approximately 16.

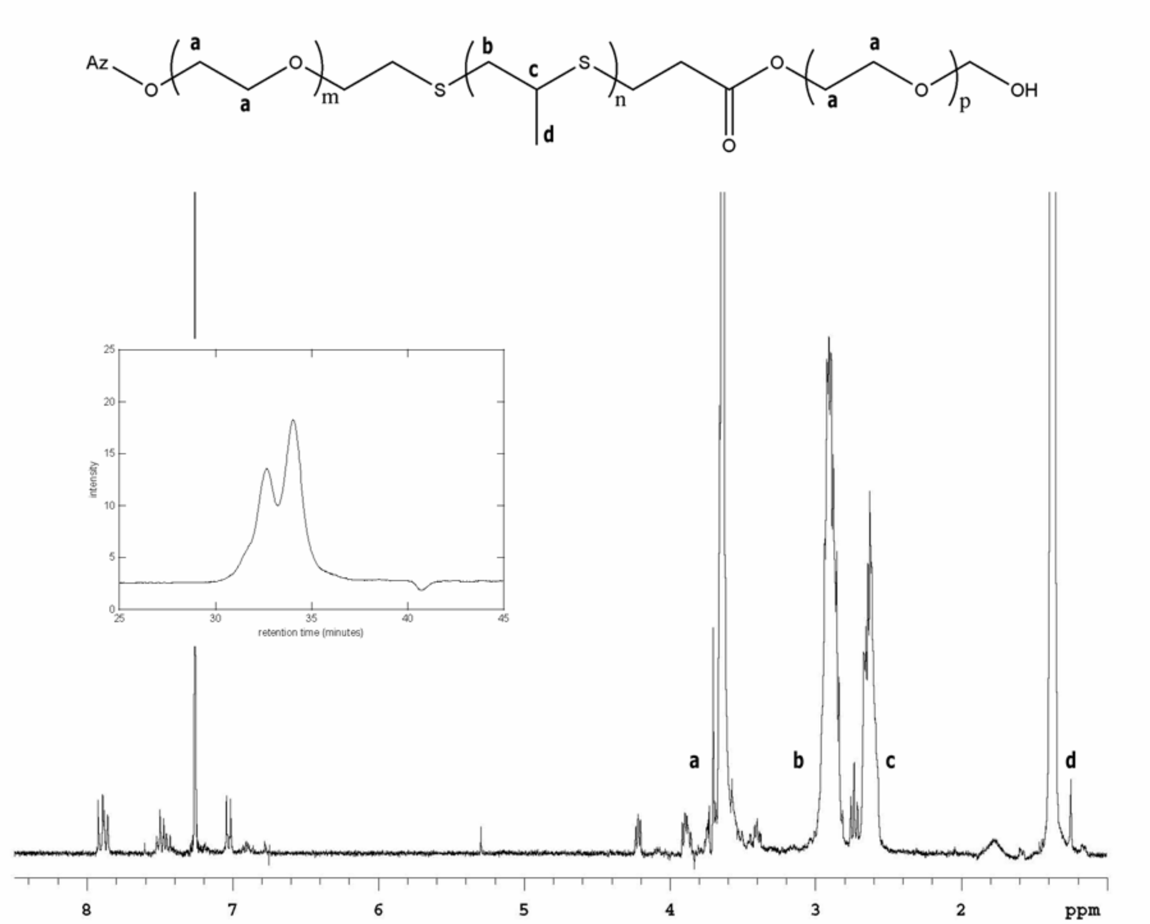


Figure B.3 NMR spectra and GPC trace of azobenzene-functionalized Az-PEG-PPS-PEG copolymer. From the NMR, m approximately equals 45, n approximately equals 27, and p approximately equals 9.

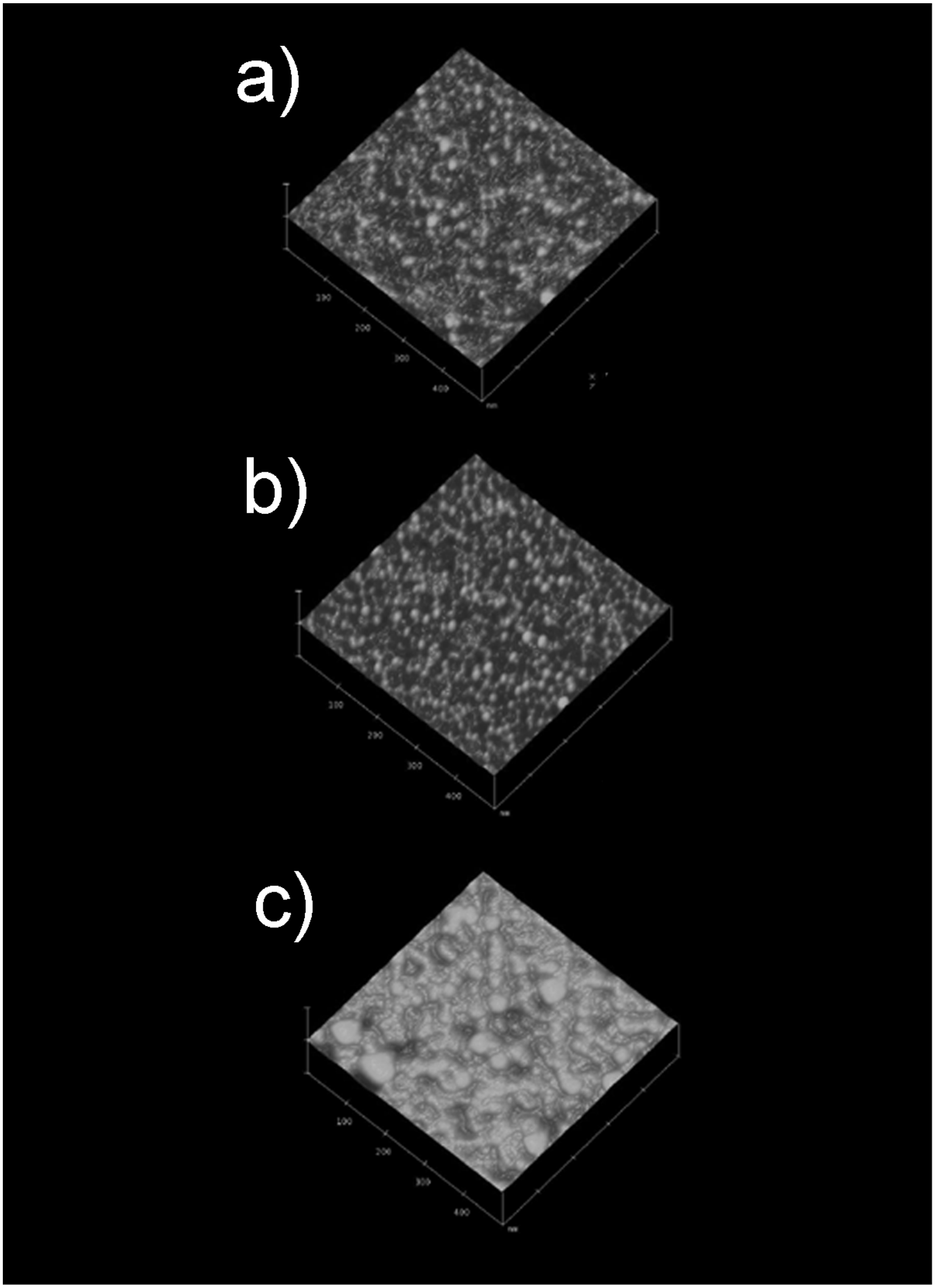


Figure B.4 AFM images of bare gold and gold surfaces functionalized with a PEG-PPS adlayer. Bare gold (a) shows an RMS roughness of .943 nm. Polymer adlayers are created with two different protocols: the surface is either (b) dipped in an ethanol solution of the copolymer (RMS roughness = 1.115 nm) or (c) the surface was annealed at 45 ºC overnight in vacuum with a layer of copolymer deposited from TFH solution (RMS roughness = 1.299 nm).

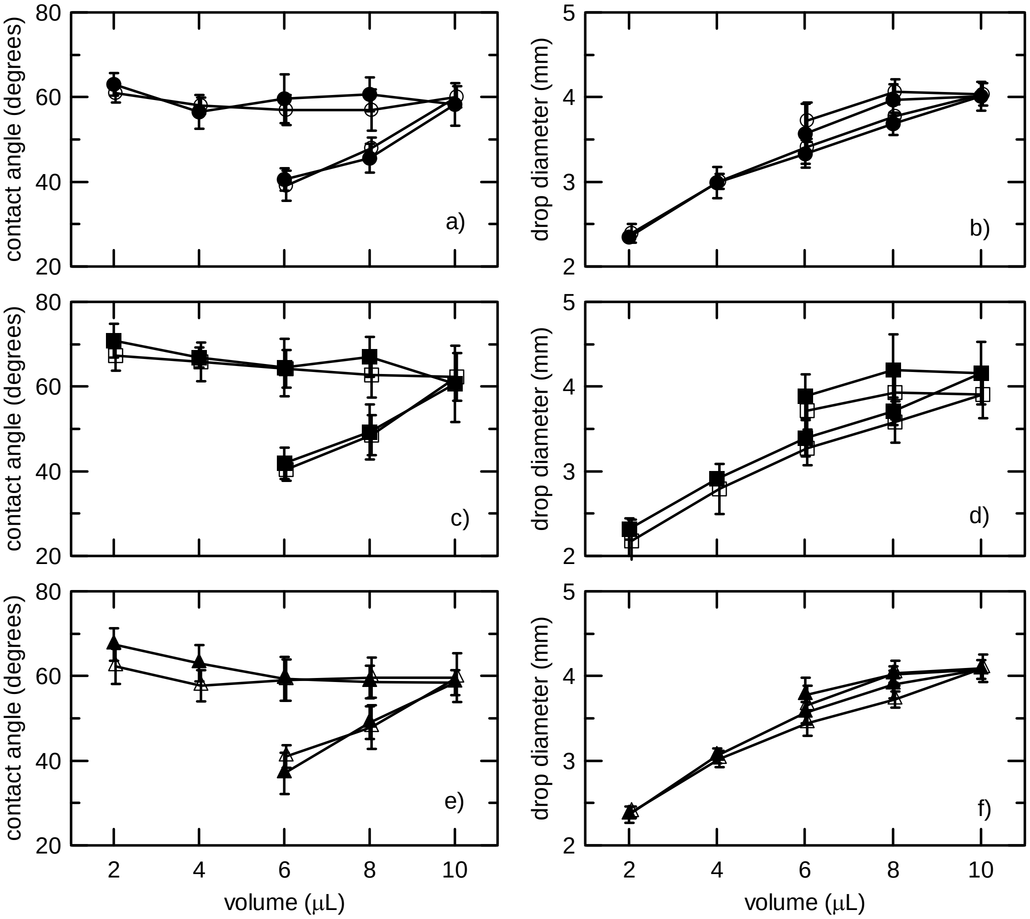


Figure B.5 Contact angle (left) and drop diameters (right) measured during successive additions or subtractions of the volume of a water drop on a given surface: Az-PEG-PPS (a,b), Az-PEG-PPS-PEG, (c,d) and PEG-PPS (e,f). Open symbols indicate surfaces exposed to 1 minute of UV illumination prior to the experiment; closed symbols indicate surfaces not irradiated with UV light. Each reported contact angle is the average of eight contact angle measurements, and each drop diameter is the average of four measurements. Error bars are one standard deviation.

B.6 References

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