

CHARACTERIZATION OF NOVEL ORGANIC POLYMER MATERIALS FOR THERMOCHEMICAL LITHOGRAPHY

Adam Jakus, Georgia Institute of Technology, Atlanta, Georgia, SURF 2006 Fellow
Faculty Advisor: Dr. Seth Marder Mentor: Dr. Simon Jones

Introduction

With much of the current development of technology being curtailed by size limitations, the ability of the atomic force microscope (AFM) to etch lines and complex patterns only a few nanometers in width has great potential for allowing many technologies to become smaller and more compact without sacrificing reliability and performance. By using a heated AFM tip, it is possible to cause specific regions of a thin film of a compound (organic polymers in this case) to undergo a thermochemical reaction with high resolution. Using molecular recognition chemistry, the patterned regions of the film can potentially react further with a variety of other compounds to produce a desired chemical structure only in the region predefined by the heated AFM tip. Experiments were conducted using methacrylate-based polymers with the following side-chain functionalities: azobenzene, a tetrahydropyran (THP)-carbamate, and a THP-ester. Infrared and UV-vis spectroscopy, TGA, and fluorescence microscopy were used to characterize and analyze these polymers in order to gain a better understanding of their properties and to determine if certain molecular recognition type reactions behave as predicted on a larger scale so that they can later be tested on the nano-scale.

Photoisomerization of the azobenzene structure results in a transition from the more stable *trans*-isomer to the less stable *cis*-isomer. Additionally, this isomerization can be fully reversed by the use of heat. There is potentially a measurable difference in "height" relative to the substrate surface between the two azobenzene isomers. An AFM tip can not only detect the topographical difference between the two isomers but, with a heated tip, can also isomerize (*cis* → *trans*) a pre-specified region of the coated substrate to a precision of a few nanometers. Hence, topographical information can potentially be written using the heated tip at high density.

The THP-carbamate polymer reacts by loss of its protecting group when heated to 170°C, exposing an amine functionality. By creating a region of the polymer defined by the heated AFM tip, the unprotected amine group now has the potential to react with other desired compounds, leaving the rest of the polymer unreacted.

The THP-ester polymer displays highly hydrophobic properties. When heated, a carboxylic acid group is generated, changing the properties of the polymer to hydrophilic, and resulting in a chemical functionality that can be reacted further. We investigated the binding of an oligonucleotide to this acid group, followed by further reaction with its dye-labeled complement to determine whether we could use the heated AFM tip to generate regions that would display molecular recognition properties.

Procedure

Approximately 0.5 mL of a 10%wt azobenzene solution was spin-coated onto a quartz substrate at 500rpm for 5 seconds and then at 1500rpm for 2 minutes. An initial UV-vis spectrum was taken of the sample. The sample underwent photolysis with four 350nm wavelength bulbs for 1 minute intervals up to 5 minutes, and then at 5 minute intervals up to 20 minutes. After each interval, a UV-vis spectrum was taken. Upon reaching a photostationary point, the sample was heated on a hotplate at 20°C intervals starting at 50°C for 30 second intervals until 150°C, then at 60 second intervals until 250°C. A UV-vis spectrum was taken after each interval.

The same spin-coating procedure was followed for the THP-carbamate, although it was spin-coated onto a silicon substrate for IR experiments. Previous TGA results showed that the mass of the THP-carbamate began decreasing at approximately 170°C. To determine the component groups of the carbamate, an initial IR spectrum was taken. The sample was heated at 170°C at 1, 2, 3, and 5 minute intervals. Then the sample was heated at 180°C at 1, 2, and 5 minute intervals. An IR spectrum was taken after each time interval.

The THP-ester was spin-coated onto glass substrates using the same method as the two other polymers except that it was 5.5%wt solution. The polymer underwent photolysis with four 300nm bulbs for 15 minutes in order to cross-link the polymer. The samples were cut into approximately 5mmx5mm sections and several were put on a 150°C hotplate for 15

minutes in order to convert them to the acid form. Both the ester and acid form were used in the following experiments. These experiments used various combinations and concentrations of the following in pH7 0.15 M NaPO₄ buffer: oligonucleotide amine (20 base pairs), EDC as the coupling agent, 2-methoxyethylamine as a spacer g, and the complementary 20 base pair oligonucleotide with a fluorescent dye(Cy3) attached. Samples of both the ester and acid form were each placed in separate eppendorf tubes and different combinations of EDC, amine-oligo, and spacer were added and allowed to react overnight at 0°C. The samples were then cleaned using milliQ water and placed in clean eppendorf tubes. A 2 μM solution of the dye oligonucleotide was added to each sample tube and was heated at 50°C for 30 minutes to allow for hybridization with the amine-oligo to take place. The Samples were once again washed using milliQ water and were then viewed under fluorescent microscope with a rhodamine filter in order to confirm the presence, or lack there of, of the Cy3-labeled complement. Unfortunately, in all cases the polymer was no longer present on the substrate surface and it was later discovered that both the milliQ water as well as the pH7 NaPO₄ destroyed the polymer.

Solvents other than milliQ water and pH7 buffer were investigated and it was found that the organic solvent DMF with 0.2 M NaBr did not destroy the sample, although swelling in the polymer did occur. The previous procedure was then carried out but with 1,3-Di-*tert*-butyl-carbodiimide (TBCDI) as the coupling agent and hexylamine as the spacer. The DMF 0.2M NaBr solution was used to wash the samples in these experiments rather than milliQ water.

Results and Discussion

The *trans*→*cis* reaction of the azobenzene was found to be completely reversible by use of heat, and both isomerization directions could go to completion at least several times without any permanent loss in concentration of either isomer. Kinetics calculations will be carried using the data gathered from UV-vis spectroscopy to determine the rate of both isomerization reactions.

Using IR spectroscopy, the THP-carbamate was found to lose its protecting group and generate an amine when heated to 170°C. When heated to 180°C, the polymer cross-linked with itself and formed an amide group in place of the amine group. Hence, the polymer will only be heated up to 170°C in future experiments.

The THP-ester when used in the acid form with all the DMF NaBr solution components listed in the procedure, has shown promising fluorescent results and contrast (Fig. 1b) as compared to the acid form that has no amine-nvc, to hybridize with the oligonucleotide dye (Fig.1a), possibly indicating that the hybridization between the amine-nvc and oligonucleotide dye was successful. Further tests are necessary to maximize the amount of hybridization that takes place.

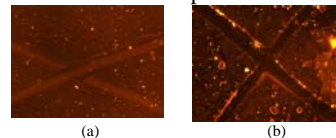


Fig. 1: 10x objective fluorescence images of acid form THP-ester on glass substrate treated with: (a) hexylamine, TBCDI, dye (b) Amine-oligo, hexylamine, TBCDI, dye-oligo ("x" mark denotes area on substrate with no polymer in order to see contrast)

Conclusion

These experiments have so far demonstrated promise for the azobenzene and THP-carbamate polymers to be used for thermochemical lithography. The THP-ester requires more tests to determine if molecular recognition applications on the nano-scale using this system would be feasible. The ability of the AFM to precisely and accurately define a region as thin as a few nanometers through thermochemical reactions combined with the precise nature of molecular recognition chemistry allows for a new and powerful push to develop new technologies and improve old ones by minimizing the space that they consume and allowing for a wide range of versatility of nano-patterned compounds to produce of variety of very useful results.