

Chem Educ. Author manuscript; available in PMC 2012 May 1.

Published in final edited form as:

J Chem Educ. 2011 May 1; 88(5): 615–618. doi:10.1021/ed100358n.

Lithography of Polymer Nanostructures on Glass for Teaching Polymer Chemistry and Physics

Adi Sahar-Halbanya, Jennifer M. Vancea,*, and Charles Michael Draina,b

^aDepartment of Chemistry and Biochemistry, Hunter College of the City University of New York, New York, New York, New York 10065, United States

^bThe Rockefeller University, New York, New York 10065, United States

Abstract

As nanolithography becomes increasingly important in technology and daily life, a variety of inexpensive and creative methods toward communicating the concepts underpinning these processes in the classroom are necessary. An experiment is described that uses simple CD-Rs, C-clamps, an oven, and a freezer to provide concrete examples and insights into the chemistry and principles of nanolithography. The experiment also has flexibility, making it suitable for a range of classroom levels from high school to more advanced labs in college. Because CD-Rs are composed of grooves of polycarbonate, the experiment provides a basis for discussions and exploration into the chemistry and physics of polymers on the nanoscale.

Keywords

High School/ Introductory Chemistry; First-Year Undergraduate/General; Upper-Division Undergraduate; Laboratory Instruction; Analytical Chemistry; Polymer Chemistry; Hands-On Learning / Manipulatives; Atomic Spectroscopy; Nanotechnology; Surface Science

Nanomaterials generally have at least one dimension less than about 100 nm and have many current applications such as light-emitting devices and potential applications such as nanomedicine.1 New and useful properties emerge in nanostructures because at these dimensions, electronic and material properties can be different when compared to the bulk materials or molecules. Also, miniaturization of devices requires micro- to nanoscale patterns on surfaces, and these are formed by a variety of lithographic processes that in many ways correspond to those used by artists to make etchings, blue prints, stamps, and lithographs.2⁻⁶ In addition to circuitry, nanolithography provides potential access to fabricating sensors, identification tags, optical devices, and molecular electronics. With this expanding utility of polymer nanostructures, entry points into discussing nanoscale polymer science are increasingly desirable. In addition, as nanolithography becomes increasingly important and pervasive in industry and society, inexpensive and creative ways of communicating the fundamental science underpinning this technology in the classroom becomes more important and attractive.7

We developed a college and high school-level polymer nanoscience laboratory designed to teach concepts in polymer chemistry and physics, surface chemistry, and nanotechology based on our recently reported method for the transfer of polymer patterns to ceramic

^{*} jennifermvance@gmail.com .

surfaces.2 In this laboratory experience, nanopatterns of carbonate polymers from inexpensive writable compact disks (CD-R) can be printed onto microscope glass slides using a C-clamp, a glassware oven, and a freezer. Pieces of the CD-R function as the stamps to print an array of lines that are ca. 900 nm wide, many millimeters to centimeters long, and ca. 15 nm deep when pressed against a glass substrate with a simple C-Clamp and heated to well below the glass transition temperature of the polycarbonate. The results are immediately visible and seen as a rainbow diffraction pattern on the glass substrate. A demonstration video is available on the Web.8

Experimental Overview

Introductory Lecture

The introduction of polymers, polymer chemistry, and polymer properties serves as the foundation of the lecture. Concepts such as glass transition temperature, intermolecular interactions between polymer chains, and the interactions of molecules with surfaces in relation to nanolithography provide the foundation of chemical knowledge that enables students to understand the experiment and the procedures.

Polymer Stamps

The ~1.2 mm thick grooved polycarbonate of the CD-R with dimensions described above serves as the stamp.7 The polycarbonate layer is exposed upon removing a thin layer of photosensitive organic dye such as nickel phthalocyanine; a nanometer-thick metal layer such as aluminum or gold; and a protective lacquer coating (see supporting information).

Printing on the Glass Substrate

With heat and pressure, the prepared CD-R stamp leaves a pattern of polycarbonate lines on the surface of the glass substrate. Polycarbonates are also used in many applications from eyeglass lenses to bulletproof windows. Any polymer or plastic consists of many repeating molecular units that are connected in long chains. Polycarbonate consists of repeating units of bisphenol A and a carbonate functional group (Figure 1).9

The glass transition temperature, $T_{\rm g}$, of a plastic is the temperature at which the plastic is not fully melted, but the polymer chains are able to begin moving past one another. The $T_{\rm g}$ for polycarbonate is 150 °C. The physics and physical properties of ultra-thin films of polymers are more complicated compared to the bulk polymer.10 One model for polymer thin-film physics is the three-layer model, which has been found to be especially useful to describe the patterns of polymer observed in this experiment (Figure 2).11 Because of strong interactions between the polymer molecules and the surface, the ~15 nm of polymer in contact with the glass surface (referred to as a dead layer) is less mobile than the bulk polymer. Because the dead layer interactions with the glass surface are often stronger than with the bulk polymer, compression, heating to reach equilibrium, and separating the stamp from the substrate results in cohesive failure at the bulk polymer–dead layer interface and 15 to 20 nm of polymer remaining on the substrate. Considering the method, the fidelity is remarkable; however, the lines tend to degrade over a few days. The primary reason for the lines delaminating from the support is that the glass and polymer surface preparation are adequate for the experiment, but need to be cleaner and dry to ensure long-term adhesion.

Experimental Procedure

CD-R Stamp Preparation

A square piece (22 mm \times 22 mm) of the CD-R was cut with scissors to act as the stamp. The stamp was submersed (and held under with a ceramic spatula) in concentrated nitric acid for

3 min to remove the top layers of dye, aluminum, and lacquer. The CD-R stamps were rinsed with tap water for 5 min, washed with nanopurified water, and dried under a stream of argon gas.12 The stamps were then dried overnight in air. The overnight drying step is important because solvent embedded in the polymer matrix can be deleterious to obtaining good results when printing on glass by diminishing adhesion. An alternative method to prepare the stamp using ethanol and water is presented in the supporting information, but the coverage and fidelity of the stamp product is reduced.

Glass Substrate Preparation

A cut microscope slide ($25 \text{ mm} \times 25 \text{ mm}$, Fischer plain microscope slide cut in three pieces) was prepared as the substrate. Glass pieces were soaked in concentrated nitric acid for five min, followed by rinsing with tap water for five min, and washed with nanopure water. The glass pieces were dried under a stream of argon gas and allowed to sit in air overnight to dry. An alternative method soaks the glass in potassium hydroxide, followed by a tap water rinse (see supporting information).

Thermal Contact Transfer: C-Clamp Stamping

Variables such as pressure, temperature, heating time, and cooling time dictate the successful stamping process when using a C-clamp (Figure 3). Students centered the glass substrate on a steel plate (9 cm \times 9 cm \times 6 mm thick)13 and placed the CD-R stamp pattern side down over the glass. A high temperature-stable rubber sheet (2 mm thick \times 5 cm diameter), followed by second steel plate (6 mm thick \times 5 cm diameter) were carefully placed above the CD-R stamp and glass substrate and finally pressed together with the C-clamp. Pressure was applied, by tightening the screw as much as possible and then loosening the clamp half a turn. Using thermal gloves, the students inserted the assembly into the oven at 90–110 °C for 10 min. Immediately afterwards, the assembly was placed into a freezer for 15 min and then allowed to warm to room temperature. The pressure was very slowly released with the C-clamp, allowing the nanolithographed product on the glass to be removed.

Hazards

Concentrated nitric acid is extremely corrosive and should be handled with caution in a fume hood with appropriate protective gear and disposed of properly. Addition of water to acid is also highly exothermic and should never be done during the washing procedure.

Results and Discussion

When viewing a glass slide printed with a pattern of nanoscale lines underneath an intense desk lamp, a rainbow arising from the diffraction of light from the printed pattern is observed. The nanoscale lines of the pattern interact and bend light, so that the different colors are visible to the eye. The causes of the rainbow pattern are discussed elsewhere,14 but arise from both refractive index differences and the pitch of the pattern on the surface being similar to visible light wavelengths. These lithographed patterns are also visible with an optical microscope where focusing on the edge of the slide and then moving in from the side provides the best results (Figure 4). One observes these because of the pattern and because of the horizontal dimensions of the lines (millimeters long by 900 nm wide). Students can observe a diffraction pattern resulting from passing a laser pointer light through the repeating nanopattern printed on the substrate, giving an indication of the geometry and spacing.7

If there are several teaching atomic force microscopes (AFMs) available (see the supporting information), the pattern on the glass substrate can be probed to explore both the

morphology in terms of images and to look at defects in the structures (Figure 5).15 The exact dimensions of the printed lines can be plotted and defects in materials science yield information on the mechanism, in this case of the stamping process. For example, the jagged lines, height differences, and coverage yield information on the polymer layer thicknesses and the adhesive forces between the polymer layers and to the substrate.

This experiment was integrated into an instrumental chemistry laboratory and conducted by six, third-year chemistry and biochemistry majors. The students conducted the experiment from beginning to end and all were able to print and observe the lithographed lines on glass as a rainbow pattern and four out of the six students were able to locate the nanopatterns using an optical microscope and AFM. The students rated the experiment highly in terms of interest and knowledge gained in surface chemistry and polymer properties (see the supporting information). Significant independent exploration by students is possible. Depending on the size of the class and the time allotted to the experiment, several of the key processing variables can be evaluated to correlate with coverage and stability of the lines. Furthermore, students can develop theories on how these parameters affect the physical properties of the polycarbonate polymer (see the supporting information).

Summary

As the fabrication of nanostructures becomes increasingly pervasive in everyday technologies and in science, inexpensive and accessible teaching methods for the classroom will be needed. Utilizing common CD-R pieces, microscope slides, and C-clamps, together with immediate and clear visible results, provides an accessible laboratory experience that illustrates the roles of surface and polymer chemistry in nanolithography.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Science Foundation (NSF, CHE-0847997 to C.M.D.); Hunter College science infrastructure is supported by the NSF, the National Institutes of Health (including RCMI, G12-RR-03037), and CUNY.

References

- 1. Ozin, GA.; Arsenault, AC.; Cademartiri, L. Nanochemistry: A Chemical Approach to Nanomaterials. 2nd ed.. Royal Society of Chemistry; London: 2009.
- 2. Helt JM, Drain CM, Bazzan G. J. Am. Chem. Soc. 2006; 128:9371–9377. [PubMed: 16848472]
- 3. Menard E, Meitl MA, Sun Y, Park J-U, Shir DJ-L, Nam Y-S, Jeon S, Rogers JA. Chem. Rev. 2007; 107:1117–1160. [PubMed: 17428024]
- 4. Ahn SH, Guo LJ. ACS Nano. 2009; 3:2304–2310. [PubMed: 19702323]
- 5. Khang D-Y, Lee HH. Langmuir. 2008; 24:5459–5463. [PubMed: 18412377]
- 6. Moran IW, Briseno AL, Loser S, Carter KR. Chem. Mater. 2008; 20:4595–4601.
- 7. Meenakshi V, Babyan Y, Odom TW. J. Chem. Educ. 2007; 84:1795–1798.
- 8. YouTube Video of the Experiment. [accessed Feb 2011]. http://www.youtube.com/watch?v=hO80TzL5-vs&feature=youtube_gdata
- 9. Abrams CF, Site LD, Kremer K. Phys. Rev. E. 2003; 67:021807.
- Cross GLW, O'Connell BS, Pethica JB, Rowland H, King WP. Rev. Scientific Instr. 2008; 79:1– 13.
- 11. Fukao K, Miyamoto Y. Phys. Rev. E. 2000; 61:1743-1754.

12. Distilled water, nitrogen gas, or purified air can be used. Both the substrate and the CD stamp can be prepared beforehand depending on the level of the students.

- 13. [accessed Feb 2011]. Steel plates are available for purchase at http://www.wagnercompanies.com for close to \$2 a piece
- 14. Planinšič G, Corona A, Slisko J. Phys. Teacher. 2008; 46:329–333. G.
- Zhong C-J, Han L, Maye MM, Luo J, Kariuki NN, Jones WE Jr. J. Chem. Educ. 2003; 80:194– 198.
- 16. Bazzan, G. Ph.D. dissertation. Graduate Center of the City University of New York; 2008.

bisphenol A carbonate

Figure 1. Polycarbonate is made of repeating units of bisphenol A and a carbonate functional group.

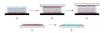


Figure 2.

Schematic representations of the three-layer model used to describe the behavior of thin polymer films at interfaces. (A) Substrate-supported thin film representing the CD stamp before compression against the glass substrate in the C-clamp: red: *dead layer* where the polymer chain mobility is strongly diminished by interactions with the substrate; gray: *bulk-like* layer where the polymer chains have mobilities described by the bulk properties; light blue: *liquid-like* layer, at the polymer–air interface, has polymer chains with greater mobility; and dark blue: interfaces between these layers where the polymer separates in the stamping process. (B) Film confined between the glass substrate (white rectangle) and CD during the stamping process. (C) Glass substrate is removed from C-clamp, along with the polymer dead layer. (D) The printed, dead layer, becomes a liquid layer (E), upon exposure to air. Illustration adapted from ref 16.



Figure 3. C-clamp setup: from bottom: (i) 9 cm \times 9 cm steel plate, (ii) glass slide, (iii) delaminated CD-R placed facedown over the glass, (iv) high temperature-resistant rubber layer, and (v) 6 mm \times 5 cm diameter steel plate.

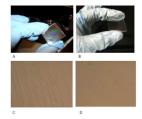


Figure 4.

(A) Rainbow diffraction pattern on a stamped glass sample. (B) Image of the pre-printed glass substrate. (C) Optical image of CD-R stamp. (D) Optical image of lines printed on glass. Both optical images were taken through 40x microscope objective seen through a CCD camera with 2x magnification.

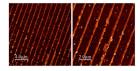


Figure 5.AFM characterization of a student's nanolithography product from a CD stamped onto glass; root-squared-mean roughness (RMS) feature height is about 15 nm. An Asylum Research AFM was used, but the feature size and periodicity are well within the capabilities of most teaching AFMs.