Microcontact Printing of Thiols

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Purpose:

Polydimethylsiloxane (PDMS) is cured to produce an optically transparent polymer that is able to reproduce surface features of objects it comes into contact with. During the curing process, a quarter is used to create an image in the PDMS. This image is inked with 1-octadecanethiol, and used as a stamp on a silver surface. The thiol molecules are deposited on the surface of the silver, which transfers the image of the quarter, which is readily visible when it is exposed to water vapor.

Learning Objectives:

1. Assess the effects of altering the thiol on the characteristics of the monolayer produced.

2. Identify if a polymer was formed though an addition or condensation reaction.

3. Explain the process of microcontact printing in their own words.

Introduction:

A polymer is a substance that is composed of long chains of repeating smaller molecular units (called monomers) that are covalently bonded to one another. They can be homogeneous (made up of only one type of molecule) but many consist of mixtures of two or more different molecules, and they tend to have high molecular weights associated with them. Polymers can be made through condensation or addition reactions. Condensation polymers form when a covalent bond is made between two molecules with the loss of some small molecule. Addition polymers are when two molecules covalently bond to one another, and retain all the origin atoms in the starting molecules. Polymers are versatile and are used commonly in our everyday lives. Examples of polymers include plastics, fibers like rayon and nylon, and rubber.

Polydimethylsiloxane (PDMS) is a silicone-based polymer, with monomer units $[SiO(CH_3)_2]$. One method of preparing PDMS is by reacting dimethylchlorosilane with water, which produces PDMS and hydrogen chloride gas:

$$[Si(CH_3)_2Cl_2] + H_2O \rightarrow [Si(CH_3)_2O]_n + 2\ HCl$$

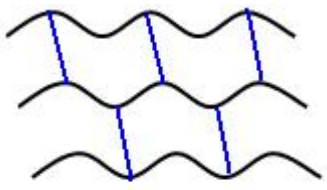

Fig. 1

PDMS is optically transparent, non-toxic and rather viscous at room temperature. As with other polymers, PDMS can be cross-linked with various substances to change its physical properties through a process called curing. Cross-linking involves adding a substance that will bond is such a way as to link two polymer chains together (Figure 1). When a polymer is crossed-linked, the individual linear chains loose their

ability to move about as freely as before, causing the material to become more rigid in structure.

In this experiment, PDMS is cured through an organometallic cross-linking reaction, which in turn hardens the PDMS to form a transparent, flexible solid. If during the hardening process the PDMS comes into contact with an object, it will replicate the image of whatever it comes into contact with, forming a stamp. This stamp can be "inked" or coated with a substance to form a monolayer on the surface, which can then be used to transfer the image of the stamp onto another surface through a process called mircocontact printing. Microcontact printing is a nanoscale interaction between the stamp and a substance that results in the transfer of ink molecules in the image of the stamp onto the surface of the other substance.

Typically, thiols are used to ink the stamp and transfer images onto metal surfaces. Thiols (RSH) have a unique and very strong attraction to metal surfaces, and will organize in a monolayer when it comes into contact with metal, such as gold or silver. The sulfur head of the thiol covalently attaches to the metal surface in an orderly fashion with the "tail" portion pointing away (Figure 2). These self-assembled monolayers can serve various functions, which are dependent on the specific functional group that makes up the "tail" of the thiol molecule. The tail portion can vary greatly, and the properties of the self-assembled monolayers can be altered to suit a particular purpose by changing the functional group of the tail.

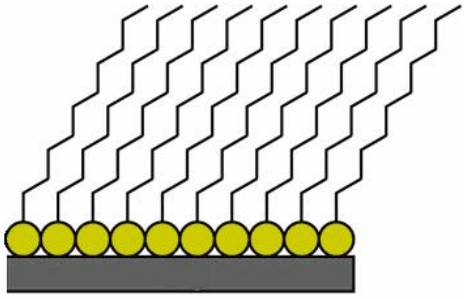

Fig. 2

Materials:

0.5 M glucose
0.8 M potassium hydroxide (KOH)
0.1 M silver nitrate ($AgNO_3$)
6 M nitric acid (HNO_3)
15 M ammonium hydroxide (NH_4OH)
1 - 10 x 10 cm glass plate
1 - large crystallizing dish
1 – small crystallizing dish
1- large weighboat
ethanol
PDMS base
curing agent
aluminum foil
wooden stick
razor trimmer
spoonula
forceps
quarter

Procedure:

A. Making foil dish

1. Cut out 3 pieces of aluminum foil squares about 15 x 15 cm long. Place the three layers directly on top of one another, and smooth them out as best as possible.
2. Place the bottom of a 250-mL beaker in the center of the aluminum. Fold the foil around the bottom of the beaker.
3. Remove the beaker, but retain the foil dish

B. Preparing PDMS stamp

1. In a large weigh boat, measure out 8.00 g (nearest 0.01 g) of the sylgard polymer base. It is a viscous liquid, so it is best to wear gloves and to use a spoonula to scoop out small quantities into the weigh boat.
2. Using a pipette, add 0.80 g (nearest 0.01 g) of the curing agent dropwise to the weigh boat. Spread out the drops over the whole surface, not just in one spot so it will be easier to mix.
3. Mix the contents with a wooden stick, using a gentle back and forth motion for about 100 strokes. Try to get the least amount of air bubbles possible.
4. In the foil dish, place a quarter in the center, making sure the bottom of the quarter is lying flat against the foil and the correct side for the stamp is facing upwards.
5. Slowly pour the PDMS solution into the bottom of the foil dish, starting at the center on top of the quarter, letting the polymer spread evenly over the entire surface. Make sure the entire surface of the quarter is completely covered.
6. Place the foil dish into a small crystallizing dish. Place whole apparatus in an oven set at 120°C and heat for 20 minutes.
7. Precede to parts C and D while polymer is curing in the oven.

C. Preparing Active Silver Solution

In the fume hood:

1. Add 10 mL of 0.1 M $AgNO_3$ to 50-mL flask
2. Add 15 M NH_4OH dropwise. A precipitate will initially form. Continue adding drops of NH_4OH until this precipitate is dissolved (~9 drops).
3. Add 5.0 mL of 0.8 M KOH to the flask. Another precipitate will form. Add NH_4OH dropwise until this precipitate dissolves (~7 drops).

D. Preparing silver mirror

1. Obtain and clean a 10 x 10 cm glass plate with water and acetone. Let it air dry.
2. Place 500 µl of 0.5 M glucose in the center of the glass plate as evenly as possible.
3. On top of this, add 1500 µl of the active silver ion solution (this can be done with two 750 µl portions of solution). A grey precipitate will start to form.

4. Release the tip of the micropipetter and use it to stir the two solutions together.
5. Wait five minutes. Carefully bring glass plates to the sink and rinse them off with water followed by acetone. To facilitate drying, use a hot air blower on low heat for about 15 seconds.

Look at the surface of the silver coated mirror, and lift up the glass plate to look underneath. What difference do you observe? Why is this?

E. Inking the PDMS stamp

1. Remove the crystallizing dish from the oven. Take out the foil dish and allow it to cool for about 5 minutes or until it is cool enough to handle.
2. Flatten the foil on the counter, and use a razor trimmer to carefully cut around the edge of the quarter. Lift up the quarter and remove any foil remaining on the bottom of the coin. Gently peel the polymer away from the quarter, trying not to damage the surface of it.
3. Place the stamp impression-side-up on a paper towel.
4. With a pipette, add several drops of the octadecanethiol-ethanol solution to the surface of the stamp, making sure to cover the entire impression.
5. Let the thiol solution sit on the stamp for a minute. Use another pipette and rinse the stamp off with ethanol to remove any excess thiol.
6. Gently move the stamp to a dry portion of the paper towel (keeping the impression side still up), and allow it to completely dry by evaporation (~ 2 minutes).

F. Microcontact printing

1. Place the stamp face down onto the surface of the silver mirror. Place one finger in the center of the stamp, and using your other fingers, apply even but firm pressure to the whole face of the stamp. Keep the stamp as stationary as possible.
2. With one finger still on the stamp to prevent it from moving, use forceps to grab the very edge and lift it straight up to avoid smudging.

Look at the glass plate—did the stamp transfer the image? If so, is it clearly visible?

Look at the stamp—did anything transfer onto the stamp? If so, what is this substance?

3. Inhale deeply and hold your breath for a few seconds. Lift the glass plate up toward your face and exhale on it.

What happens to the image as the water evaporates from the surface? How can this be explained?

G. Clean up

1. Once the experiment is completed, the silver-coated glass plate can be cleaned by submerging it in a large crystallizing dish (or some sort of large glass container) with enough 6 M HNO_3 to cover the surface completely. Wear gloves to remove the plate, and rinse it off with water followed by acetone.
2. The active silver solution can be washed down the sink with plenty of water, as well as any extra glucose, KOH, and $AgNO_3$.

Questions

1. Would you classify PDMS as a condensation or addition polymer? Explain.

2. The silver deposited on the glass plate is whitish in appearance, but if you look at the underside of the plate it looks completely metallic. What could cause this white film on the silver surface?

3. What type of surface does the 1-octadecanethiol produce on the silver in terms of polarity and hydrophobicity? Explain how this surface causes the image of the stamp to become visible when you exhale on the glass plate.

4. 11-Mercaptoundecanoic acid is an eleven carbon thiol with a carboxylic acid grouping at the end of the carbon chain. Predict what would happen to the image of the quarter if the PDMS stamp had been inked with 11-Mercaptoundecanoic acid instead of 1-octadecanethiol.

Pre-lab Preparations: Individual

A. 0.5 M glucose
Measure 0.90 grams of glucose in a 50-mL 14/20 flask and dissolve in 10 mL water

B. 0.8 M KOH
Measure 0.45 grams of KOH in a 50-mL 14/20 flask and dissolve in 10 mL of water

C. 0.1 M $AgNO_3$
Measure 0.17 grams $AgNO_3$ in a 50-mL 14/20 flask and dissolve in 10 mL of water

D. 1-octadecanethiol-ethanol solution
Measure 0.008 g 1-octadecanethiol in a 50-mL 14/20 flask and dissolve in 20 mL ethanol, heating to dissolve the solid if necessary

Pre-lab Preparations: 25 students

A. 0.5 M glucose
Measure 3.6 g of glucose in a 50-mL 14/20 flask and dissolve in 40 mL water

B. 0.8 M KOH
Measure 6.75 g of KOH in a 250-mL 14/20 flask and dissolve in 150 mL of water

C. 0.1 M $AgNO_3$
Measure 5.1 g $AgNO_3$ in a 500-mL 14/20 flask and dissolve in 300 mL of water

D. 1-octadecanethiol-ethanol solution
Measure 0.016 g 1-octadecanethiol in a 50-mL 14/20 flask and dissolve in 40 mL ethanol, heating to dissolve the solid if necessary

Supplies for 10 students

80.0 g of the sylgard polymer base
8.0 g of the curing agent
0.10 L of 0.1 M $AgNO_3$
20.0 mL of 15 M NH_4OH
50.0 mL of 0.8 M KOH
5.0 mL of 0.5 M glucose
0.5 L 6 M HNO_3
10 quarters
10 10 x 10 cm glass plates
10 wooden sticks
1 box of aluminum foil

Suggestion for Placement:

This lab is relatively easy to prepare and complete, and technically could be done with general chemistry students if they were supervised to ensure proper lab technique. The only problem with this is they may not have the background on the different organic molecules used in this lab (polymers and thiols). Organic chemistry lab could easily use this as an experiment, although the only complaint would be that it is much simpler than typical organic lab experiments.

Questions regarding lab:

As is proposed in the *Octadecanethiol Monolayer on Silver* lab, the only question is what characteristics of sulfur allow the thiol to behave in such as way as to produce a monolayer?

Answer Key

1. Would you classify PDMS as a condensation or addition polymer? Explain.

   Condensation because in the reaction shown 1) not all of the original atoms in the two starting materials are present after the formation of the polymer and/or 2) there is the loss of a small molecule (HCl).

2. The silver deposited on the glass plate is whitish in appearance, but if you look at the underside of the plate it looks completely metallic. What could cause this white film on the silver surface?

   The surface of the silver is tarnished; it is exposed to the air and it undergoes oxidation, while the part that is in direct contact with the glass plate is not expose to oxygen and remains in its original form.

3. What type of surface does the 1-octadecanethiol produce on the silver in terms of polarity and hydrophobicity? Explain how this surface causes the image of the stamp to become visible when you exhale on the glass plate.

   The surface is non-polar and hydrophobic since the tail portion of the thiol was an alkyl group. When you exhale on the glass, water vapor from your breath condenses on the surface of the silver. The portions of the silver that have been coated with the thiol will repel water, and cause it to bead up on the surface. This leads to the contrast that allows you to see the stamp as the water vapor is evaporating off the surface of the silver.

4. 11-Mercaptoundecanoic acid is an eleven carbon thiol with a carboxylic acid grouping at the end of the carbon chain. Predict what would happen to the image of the quarter if the PDMS stamp had been inked with 11-Mercaptoundecanoic acid instead of 1-octadecanethiol.

   The carboxylic group at the end of the carbon chain will produce a monolayer that is hydrophilic as oppose to hydrophobic. When you exhale on the silver surface, the water will be attracted to the entire surface, including the part that is coated in the thiol. Because of this, there will be no contrast, and the stamp will not be visible.

Citations

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