Teacher's Guide

Exploring Surface Energy of Polymers by Contact Angle Estimation

Grade Level: High school

Subject area(s): Chemistry (Honors or AP)

Time required: (2) 50 minute classes

Learning objectives: Through experiment and observation understand hydrophobic and hydrophilic properties of materials and the relationship to contact angle to various polymers.

Summary: Students will qualitatively and quantitatively estimate contact angles of polymers and compare their surface energy. They will use a variety of polymer sheets onto which they will place drops of water. After observing the shape of the drop, they will take digital photographs of the drop, print the images, and measure the contact angle with a protractor. Measurement of the contact angle is fundamental data for determining the degree of wetting when a liquid such as water and solids such as polymers and block copolymers (BCP) interact. Wetting plays an important role in nanofluids, self-cleaning surfaces, electro-wetting and in several industrial processes.

Lesson Background: If a droplet spreads and wets a large area of a surface, then the contact angle is less than 90 degrees and that surface is considered hydrophilic, or water-loving from the Greek words for water, *hydro*, and love, *philos*. If the droplet forms a sphere or round ball that barely touches the surface the contact angle is more than 90 degrees, and the surface is hydrophobic, or water-fearing.

Properties of surfaces and interfaces are due to opposing intermolecular interaction forces across the surface or interface. Some substances such as hydrogels, clean glass, and metal oxides are hydrophilic. They usually have ionic, hydrogen bonding, and polar forces and high energy surfaces in air but form low energy interfaces with water. Polymers such as polyethylene and Teflon are hydrophobic. They are characterized by high dispersion forces and low or zero polar forces. Such polymers have low energy surface in air and form high energy interfaces with water. Polar groups orient away from the surface in air and toward the more polar phase in order to minimize surface energy.

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The image below summarizes polar and non polar interactions and energy levels:

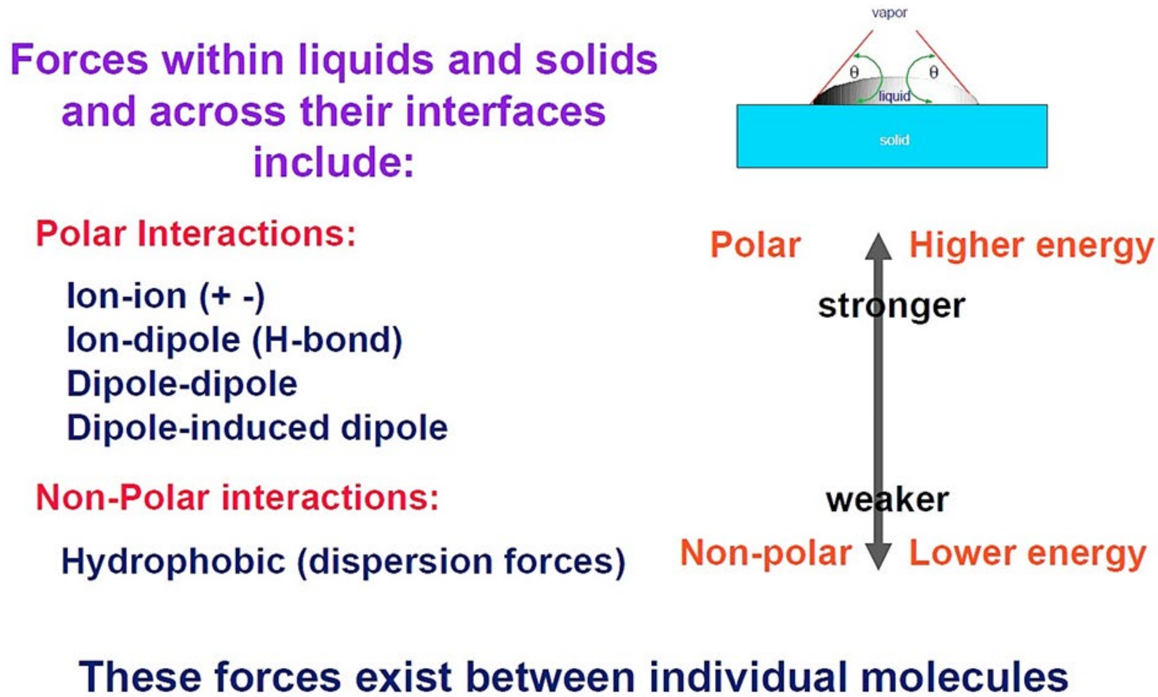

Image Reproduced with Permission from Prof Allan S. Hoffman hoffman@aa.washington.edu alh@u.washington.edu

- Examples of high energy groups include polar, H-bonding, ionized, hydrophilic groups such as hydroxides, amidogen, and carboxylic acids

- Examples of low energy groups include non-polar, hydrophobic groups such as: hydrocarbons, silicones and fluorocarbons.

Polymers are capable of forming nanometer-sized patterns with orientations and alignment of chemically distinct blocks. Thin films of diblock copolymers can self-assemble into ordered periodic structures at the molecular scale (~5 to 50 nm). These nanopatterns are formed when block copolymers (BCP) self-assemble when the process of chemical dis-affinity between the blocks driving them apart is balanced by a restorative force from the attractive chemical bonds between the blocks. Such self-assembling BCPs play a very important role in nanoelectronic fabrication.

Oil and water are not miscible at the molecular level. They readily separate into two distinct layers within a short period of time. However, at high temperatures and high pressures, it is possible to form nanometer-scale oil droplets. At these high temperatures and high pressures, oil and water can form emulsions when these tiny oil droplets are dispersed in water. Nano-emulsions have promising applications in both the cosmetic and pharmaceutical industries. Unlike oil and water, BCP are capable of forming a homogeneous solution at the molecular scale. Overtime, the dissolved molecules aggregate to form nanoparticles which separate into

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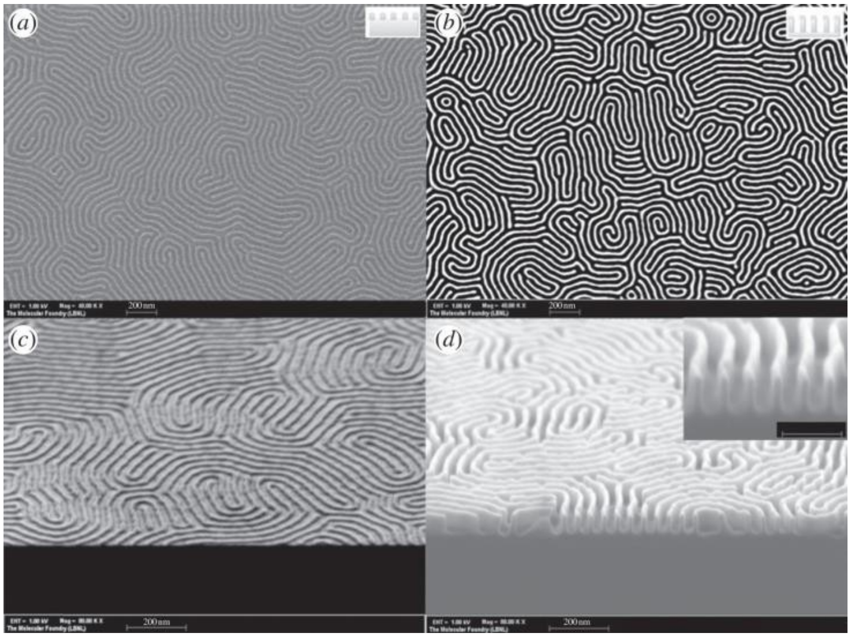
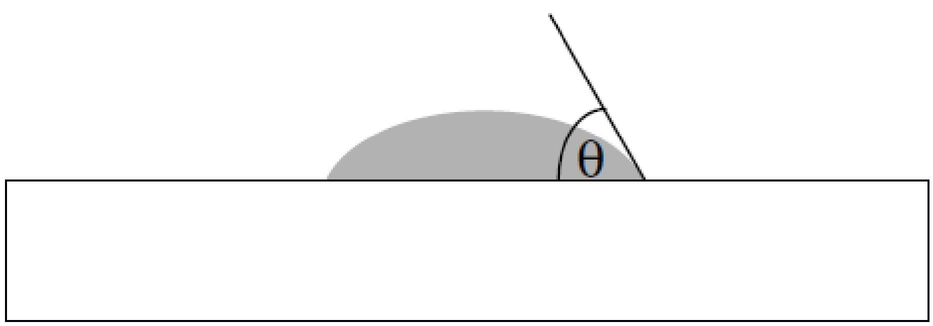
its constituent blocks of polymers.



Images from author of lesson. (a) is PS-b-P2VP phase separated. (c) is that same sample with one block etched with a tilted view. (b) is a top down of a siliconfin made from that PS-b-P2VP pattern. (d) is a tilted view of that same sample.

To see a simulation of a block copolymer phase separation in 3-D visit:
https://www.youtube.com/watch?v=cDkJLEq6XEo

Surface energies are important in understanding wetting of materials and adhesion properties. Contact angle is the angle between the surface and a line that is tangent to a drop of liquid on the surface at the point where it intersects the surface.



Schematic Diagram of a Contact Angle

The molecules exposed at the surface are pulled inward by the neighboring polymer molecules creating an internal pressure. As a result, the liquid contracts its surface area to maintain the lowest surface free energy. This intermolecular force to contract the surface is responsible for the shape of liquid droplets.

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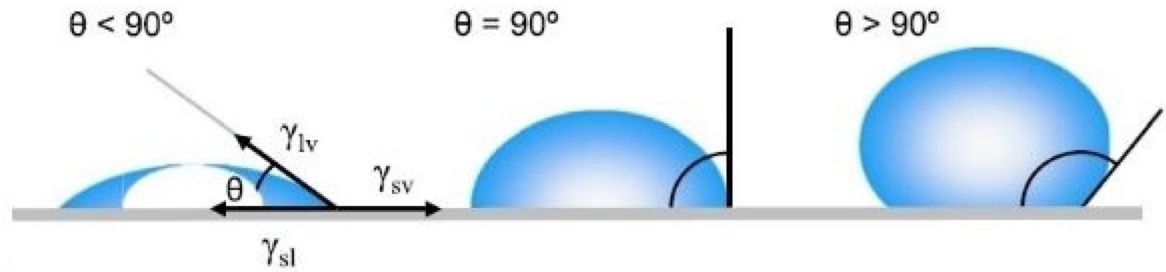
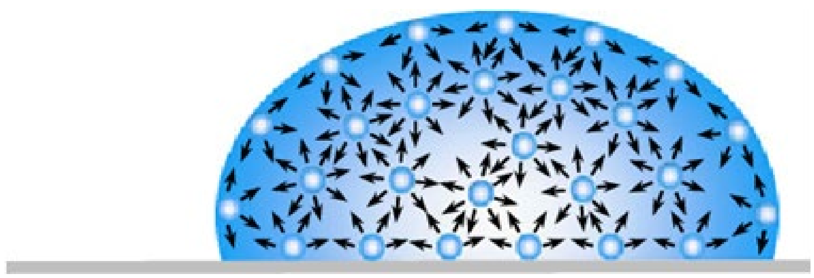


Schematic of contact angles formed by liquid drops on a smooth solid surface



Schematic of surface tension caused by unbalanced forces of liquid molecules at the surface
Images from Yuan, Y. and Lee, T.R. (2013) Contact Angle and Wetting Properties. In: Bracco, and Holst, B., Eds., Surface Science Techniques Springer Series, Surface Sciences, Volume 51, Springer Berlin Heidelberg, Berlin and Heidelberg, 3-34. Open Access: https://www.scirp.org/(S(351jmbntvnsjt1aadkposzje))/reference/ReferencesPapers.aspx?Re

Small contact angles (<90°) correspond to high surface energy and high wettability, while large contact angles (>90°) correspond to low surface energy and low wettability.
Due to the complexity of contact angle phenomena, the experimentally observed contact angle may only be used to qualitatively estimate the surface energy of substrates. This activity assumes that the solid surface is as smooth as possible, and inert to water.

Some Concerns and Considerations in Contact Angle Measurements

- Liquid penetrating surface
- Liquid dissolving the surface
- Contamination of liquid
- Size of drop and effect of gravity
- Evaporation of the liquid
- Limitation to ambient temperature
- Limitation to flat surfaces

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- Surface roughness
- Surface heterogeneity
- Surface group mobility and kinetics
- Limitation to low energy polymers and solids
- Investigator eyeball bias.

Pre-requisite Knowledge: Students have understanding of bonding and intermolecular forces. They also understand common laboratory measuring techniques especially the use of a protractor.

Materials:

- Sheets of films of cut into 5cm x 5cm squares:
  - Polystyrene
  - Polymethyl methacrylate (PMMA)
  - Polyethylene
  - Polyvinyl chloride (PVC)
  - aluminum (these may be in the form of sheets or films)
- protractors
- droppers/pipets
- water
- USB or cellphone camera
  - Images need to be able to be printed in class
- Printer

Suggested Polymer Sample Sources:

1. Hardware Stores such as Home Depot and Lowes
2. US Plastics: http://www.usplastic.com/catalog/
   - Item # 43331 .030" Thick High Impact Styrene Sheet 40" X 72"
   - Item # 48701 1" x 10" x 10" PVC Sheet
   - Item # 42600 1/32" x 24" x 48" Polypropylene Sheet Item # 44234 Acrylic Sheet 12" x 48" x 5/64" (.080) Thick Item # 44092.001 x 40" x 100' Clear Polyester Film
3. Interstate Plastics cuts to order: https://www.interstateplastics.com/plastics_sheet_rod_tube

Safety Information: Teacher and students should adhere to regular laboratory safety rules and wear disposable safety gloves at all times while handling substrate samples.

Vocabulary and Definitions: Review the meaning of the following terms before beginning the lab.

1. *Surface Energy*: the disruption of intermolecular bonds that occurs when a surface is created. It can be defined as the work per unit area done by the force that creates the new surface.

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2. Surface energies range from high to low. The molecular force of attraction between unlike materials determines their adhesion. Surface energies range from high to low with the strength of attraction dependent on the surface energy of the substrate. High surface energy means a strong molecular attraction, while low surface energy means weaker attractive forces.
3. *Surface Tension*: the tendency of liquid surfaces to shrink into the minimum surface area possible. At liquid–air interfaces, surface tension results from the greater attraction of liquid molecules to each other (due to cohesion) than to the molecules in the air (due to adhesion). (https://en.wikipedia.org/wiki/Surface_tension)
4. *Hydrophobic Polymer*: hydrophobic materials are resistant to water and a hydrophobic polymer will only dissolve in oil-based substances. Hydrophobic molecules are non-polar.
5. *Hydrophilic Polymer*: polymers which get absorbed or dissolved in water. Hydrophilic molecules are polar and ionic.
6. *Cohesive Energy Density*: The cohesive energy density is the amount of energy needed to completely remove unit volume of molecules from their neighbors to infinite separation (https://en.wikipedia.org/wiki/Hildebrand_solubility_parameter). It is the potential energy of a liquid divided by its volume and is associated with the forces that keep the molecules close together in a condensed state.
7. *Solubility*: the ability of a substance to be dissolved, such as salt in water. It is the property of a solid, liquid or gaseous chemical substance called solute to dissolve in a solid, liquid or gaseous solvent. (https://en.wikipedia.org/wiki/Solubility)
8. *Solubility parameter*: It is a numerical value that indicates the relative solvency behavior of a specific solvent. The value is obtained from the cohesive energy density of the solvent.
9. *Interaction Energy*: the contribution to the total energy caused by an interaction between objects. It is the energy when two objects interact.
10. *Polymer*: materials made of long, repeating chains of molecules. It is a chemical compound or mixture of compounds that have been created by the combining of two or more molecules to form larger molecules that contain repeating structural units.
11. *Copolymer*: polymer derived from more than one species of monomer
12. *Block copolymer*: a copolymer formed when the two monomers group together and form blocks of repeating units. The blocks will be arranged in a linear fashion.
13. *Diblock copolymer*: A diblock copolymer is a polymer consisting of two types of monomers, A and B. The monomers are arranged such that there is a chain of each monomer, and those two chains are grafted together to form a single copolymer chain. (https://web.mit.edu/8.334/www/grades/projects/projects10/AlexanderPapageorge/Page6.html)
14. *Microphase separation*: a phenomenon generated by block copolymers composed of incompatible chemical components, where they tend to spontaneously form phase-separated structures with microscopic length scales due to intramolecular phase separation in bulk or in concentrated solutions. (https://link.springer.com/referenceworkentry/10.1007%2F978-3-642-36199-9_149-1)

Advance Preparation: The teacher can cut the polymer sheets into squares (5cm x 5cm) of have students do this. Wear gloves to prevent oils from hands contaminating the surfaces. Assemble droppers, water, and protractors for students to gather for activity.

Suggested Teaching Strategies: Before beginning the lesson, you may want to have students read about polymers and contact angles. The resource section has links to information on these two topics.

Directions for the Activity: Found in Student Guide with answers below. Contact angles can be accurately measured using such instruments as a contact angle goniometer. This instrument and others are usually very expensive and therefore not available at the high school level. For this reason, the activity uses a rudimentary manual measurement approach. The students will follow the steps outlined in the Student Guide to determine the contact angle of water drops on different polymer surfaces. Samples should include both hydrophobic and hydrophilic polymers. Hydrophilic polymers contain polar or charged functional groups, rendering them soluble in water. Hydrophobic polymers have non-polar chemical groups and low energy monomer functionality. The Sigma-Aldrich Chemical Catalog is a good reference source to use in determining which polymer sample is hydrophobic (https://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=16372120) or hydrophilic (https://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=16372116).

Resources:

- Contact Angle Measurements Using the Drop Shape Method by Roger P. Woodward www.firsttenangstroms.com/pdfdocs/CAPaper.pdf
- Contact Angles of Polymer Solutions on Anodized Aluminum Oxide Templates and their Effect on Nanostructure Morphology by Rebecca Lynn Byberg and Sahag Voskian http://www.wpi.edu/Pubs/E-project/Available/E-project-042811- 111428/unrestricted/IQP_-Sahag_Voskian,_Rebecca_Byberg.pdf
- NanoLeap Lessons on surfaces: http://teachers.egfi-k12.org/curriculum-nanotechnology-lesson-plans/
- Contact Angles at Chemistry LibreTexts®: https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/States_of_Matter/Properties_of_Liquids/Contact_Angles
- Wetting and Contact Angle: https://www.teachengineering.org/lessons/view/duk_surfacetensionunit_less3
- Investigating Contact Angle: https://www.teachengineering.org/activities/view/duk_surfacetensionunit_act3
- Everyday Polymers: https://www.teachengineering.org/lessons/view/csu_polymer_lesson01

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- What is a Polymer from Live Science: https://www.livescience.com/60682-polymers.html
- What are Polymers from Science News for Students: https://www.sciencenewsforstudents.org/article/explainer-what-are-polymers

Next Generation Science Standards:

- HS-PS1-3: Plan and conduct an investigation to gather evidence to compare the structure of substances at the bulk scale to infer the strength of electrical forces between particles.
- HS-PS2-3: Apply science and engineering ideas to design, evaluate, and refine a device that minimizes the force on a macroscopic object during a collision.
- HS-PS2-6: Communicate scientific and technical information about why the molecular-level structure is important in the functioning of designed materials
- HS-PS3-2: Develop and use models to illustrate that energy at the macroscopic scale can be accounted for as a combination of energy associated with the motion of particles (objects) and energy associated with the relative positions of particles (objects).

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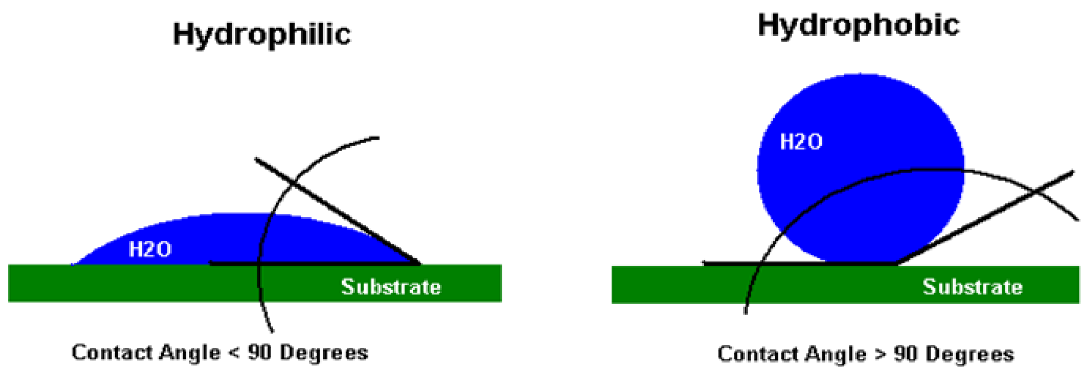
Student worksheet with answers in red

Exploring Surface Energy of Polymers by Contact Angle Estimation

Introduction: A liquid has a tendency to form a bead or a sheet on solid surfaces depending on the properties of the surface and the liquid. Properties of surfaces and interfaces are due to opposing intermolecular interaction forces across the surface or interface. The interaction between the surface and liquid can be described as either hydrophilic ("water loving") or hydrophobic ("water hating"). These characteristics can be attributed to the surface energy between the solid substrate and the liquid.

Both hydrophilic and hydrophobic surfaces have important applications in all types of engineering: chemical, automotive, nautical, industrial and civil. For example, applying a hydrophilic anti-fog coating to glass causes any condensation to form into a thin, even layer of water instead of droplets, so the glass remains transparent, while adding hydrophobic rain-repellent glass treatments to windshields causes water to bead and roll off the windshield surface to improve visibility and enhance safety. Hydrophobic surfaces are also important in protecting surfaces from water damage and stains.

In this activity, you will explore the concepts of wetting and contact angle. You will distinguish between hydrophobic and hydrophilic surfaces. You will examine the contact angle of water on different polymer films or sheets and relate your measured contact angles to the surface energy of water and the polymer substrate. Finally, you will predict whether the water substrate interaction can be described as hydrophilic or hydrophobic. In addition, the class will discuss the intermolecular forces that may be prevalent at the nano-scale level, the wettability, and possible engineering and technological applications of your polymer samples based on your observations and measurements. Below is a schematic of contact angles for hydrophilic and hydrophobic surfaces.



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Safety: Safety gloves and goggles should be worn when working with laboratory chemicals and polymer sheets

Materials:

- Sheets of films of cut into 5cm x 5cm squares:
  - Polystyrene
  - Polymethyl methacrylate (PMMA)
  - Polyethylene
  - Polyvinyl chloride (PVC)
  - aluminum (these maybe in the form of sheets or films)
- protractors
- droppers/pipets
- water
- USB or cellphone camera
  - Images need to be able to be printed in class
- Printer

Activity:

1. Cut polymer films and aluminum into 5 cm x 5 cm squares.
2. Place the 5 cm x 5 cm piece of polymer on a flat surface.
3. Use a pipet to place 3 drops of water on the center of the surface of the 5 cm x 5 cm pieces.
4. After about 30 seconds, observe and describe the shape of the drop.
5. Take a digital photograph of the drop from the side. Make sure that the camera is level with the surface of the sheet. (see images in Appendix)
6. Repeat steps 2- 5 for all of the samples.
7. Print a copy of the images and measure the contact angle with a protractor.
8. Record the results.
9. Repeat steps 2-7 to confirm your results.

Record your observations:

Polymer	Test 1	Test 2	Average Contact Angle
	Measured Contact Angle	Measured Contact Angle	
PMMA			
PS			
PS			
PVA			
Aluminum (non polymer)			

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Analyze your results:

1. Describe the shape and estimate the size of the drops in terms of diameter, height or volume.
Description may include spherical, round, crescent shaped or flat drops. Size estimates will vary.

2. Did you have a control group?
Yes. The aluminum foil/sheet was the control. This provided an avenue to compare the contact angle of a commonly used household metal to the contact angle of polymers.

3. Do your observations leave you with any more questions? Do they enable you to make more predictions? If so, what are they?
The more spherical the bubble, the more likely the solid is to be hydrophobic and the more flat drop, the more likely it is to be hydrophilic.

4. Classify the polymer samples you used as hydrophobic or hydrophilic Answers may vary depending of polymer samples used.
Example:

Hydrophobic	Hydrophilic
Polystyrene	Polyethylenimine
Polyvinyl acetate	Polyvinylalcohol
Polypropylene	Poly methyl methacrylate
Teflon	Polyacrylic acid
Nylon 6,6	Polyhydroeyehtyl ethacrylate
Polyvinyl chloride	Polyethylenine

Draw Conclusions:

1. Based on your results, do you feel that you can predict the type of forces and interaction in a polymer sample at the nanometer level? Explain your answer.

Yes. The polymers that exhibited very large contact angles have low surface energy: non-polar groups and are hydrophobic. Those that exhibited low contact angles have high surface energy: polar, H-bonding, ionized and hydrophilic.

2. How could the size of the contact angle be used to predict if two polymers in a block copolymer can undergo phase separation?
The smaller the contact angle the larger the interaction between the BCP and the more difficult it is to achieve phase separation.

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