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Polymers: Essential Background and Definitions

Instructor Support Document

How to Use this Document

This document accompanies a set of slides produced by the ACS PolyEd initiative. It is meant to provide deeper explanation of the concepts and content found on these slides, supporting their use in the classroom. For each slide, we suggest how to walk students through the slide to promote learning, then we include background information that will assist you, the instructor, in teaching the material. This document is not intended for dissemination to students, but rather to bring you, the instructor, "up to speed" on this polymer content. You can choose what background information is relevant to your students and course, it is not necessary to include all background information in all teaching contexts. A glossary of new jargon is included at the start of this document, and a list of helpful references is included at the end.

The Slides

This set of slides has been broken into five groups. All five of the modules may be used together, or a single set can be dropped into a lesson plan as appropriate.

Slides 3-6: These slides are a fundamental introduction to polymers as a concept. It is recommended that you start with this module, regardless of further intended learning outcomes, as it lays a groundwork of important vocabulary terms and highlights the differences between small molecules and macromolecules.

Slides 7-8: These slides introduce how to describe and determine polymer molecular weight.

Slides 9-11: These slides provide an overview of physical properties unique to polymers.

Slides 12-13: This slide describes how polymer chains can take on different shapes and bonding structures, called "topologies", which can affect their physical properties.

Slides 14-18: These slides cover everyday polymer topics, intended to establish the relevance of polymer chemistry to students' everyday lives.

Introduction to Polymers (slides 3-6)

Slide 3:

Student walkthrough: Introduce the small molecule and its properties. One by one, contrast these with the properties of the three polymer examples (structure, size, etc.). There are also important contrasts between each of the polymer examples (natural vs. synthetic, number of possible repeat units, material properties). The key student takeaways should be that 1) Polymers are large molecules made from repeating units, and 2) Polymers may have many different structures with many different properties.

Background information: We begin by highlighting the differences between small molecules, which are already familiar to students, to macromolecules, which are not. One small molecule (aspirin) and three common polymers are included on this slide.

Aspirin, as a small molecule, has a definitive structure and molecular weight. Every single molecule of aspirin in the world has the same chemical formula, the same chemical structure, and (discounting isotope effects) the same molecular weight. It is a crystalline solid under standard conditions, and readily dissolves in a variety of solvents.

The polymers are a different story. The three examples on this slide are very different materials, though they are all polymeric in nature. The molecule structures of each are displayed to the right of their photos. The next slide provides detail on how to name polymers and draw their structures.

Styrofoam is made from polystyrene, a polymer with a backbone consisting of a saturated hydrocarbon backbone with a pendant phenyl ring on every other carbon. Polystyrene is a brittle, glassy material that softens at approximately 100 °C. It is rigid and transparent, making it suitable for a variety of products including disposable glassware and cutlery, insulating Styrofoam, and petri dishes and culture flasks that students may have worked with in their lab courses. Polystyrene is a synthetic polymer, made from petroleum sources.

Natural rubber is polyisoprene, which has a backbone containing both saturated and unsaturated hydrocarbons. Depending on how the rubber was made, it may take on three different repeat unit structures. Overall, this leads to a material that is soft and elastic. Rubber will remain rubbery down to nearly -100 °C, below which it will become rigid and glassy like polystyrene. Polyisoprene may be harvested from the rubber plant, or it may be synthetically produced.

Polypeptides are natural polymers, also known as “proteins”. Structural polypeptides can be found in skin, nails, hair, and muscles, while enzymes are carefully folded proteins that carry out many of the vital tasks of life. While polystyrene and polyisoprene have a single or very small number of possible repeat unit structures, peptides are made from many different amino acids, and can therefore take on many different structures. They all share the amide bond in the backbone.

Slide 4:

Student walkthrough: Begin with the structure at the top, introducing poly(vinyl chloride). Explain the naming and structure drawing rules for polymers.

Background: This slide delves deeper into polymer molecular structure. The structure at top is a portion of a poly(vinyl chloride) chain. It possesses a hydrocarbon backbone with a dangling chlorine on every other carbon. This polymer is used for plastic pipes, house siding, shower curtains, and soft tubing. A polymer’s structure is represented by drawing its *repeat unit*, the structure that repeats along the chain, within parentheses. The “*n*” subscript is used when a particular molecular need not be implied, but a number may be used as appropriate if the number of repeats is known. Polymers are generally named by placing the prefix “poly” in front of the name of the monomer from which they are derived. For additional information on naming polymers according to IUPAC rules, please see the reference at the end of this document.

Slide 5:

Student walkthrough: Polymers can be separated into two broad classes, as defined here. These classes are made by different types of reaction mechanisms from different types of monomers. Contrast vinyl vs. condensation polymers.

Background: Two of the most common classes of polymers are vinyl polymers and condensation polymers.

Vinyl polymers are made from monomers that have an alkene. This alkene is transformed into two carbon-carbon bonds by a handful of mechanisms (radical or ionic). These are called *chain growth* mechanisms because the active chain end is where new monomers are added to the chain. Vinyl polymers are chain growth materials. This family of materials includes polystyrene, poly(vinyl chloride), poly(methyl methacrylate), and much more.

Condensation polymers are made from condensation reactions, for example producing esters from acids and alcohols or amides from acids and amines. These reactions release a small molecule byproduct as part of the reaction, which must be carefully removed to drive these polymerizations to the high conversion needed for useful, high molecular weights. Condensation polymers include polyesters, polyamides, polycarbonates, polyurethanes, and a number of other materials. These are called *step growth* mechanisms because, rather than adding monomers to an active chain end, these polymerizations progress by condensing monomer pairs in to dimers, then dimers into trimers and tetramers, and so on until, gradually, high molecular weight is achieved.

This distinction between classes becomes much more important when discussing polymer synthesis as part of organic chemistry coursework.

Slide 6:

Student walkthrough: This slide contrasts the behavior of small molecules with that of polymers. Begin in the "small molecule box" by describing how small, light molecules have high molecular velocities and diffuse quickly through solution. Moving to the upper right corner, monomers (which are small molecules) may be polymerized into polymers, creating a long chain that results in a heavier, slower molecule. This is further illustrated by the lower left figure, depicting schemes of ethylene monomer (a gas) vs. polyethylene (a solid) and styrene monomer (a liquid) vs. polystyrene (a solid). Other important consequences of polymer size are listed as bullet points.

Background: The simplest difference between small molecules and macromolecules is their size, as implied by the terminology. Small molecules are generally no heavier then a few hundred grams per mole, which makes them nimble. Gas molecules bounce around inside their containers and diffuse readily. Liquid molecules engage in vibrant, diffusive, Brownian motion, allowing them to flow even in a condensed phase. Some small molecules possess chemical features that let us use them as monomers. Through polymerization, we convert these individual small monomers into long polymer chains.

In general, a molecular weight of about 10,000 g/mol must be reached for the product to properly behave like a polymer. For reference, you would need to string together about 100 styrene molecules to make a polystyrene chain this heavy. Because the repeat units are now bound to many others in the polymer, the mobility of the structure is greatly reduced. This reduced mobility expresses itself as the polymer having a greater solidity than the monomer, as seen in the lower left representation. The ethylene monomer is a gas, but polyethylene is a dependable solid. Similarly, styrene is a volatile liquid, but polystyrene is a glassy plastic. A useful analogy to use with students is that monomers and small molecules are like ants, small and highly mobile, while polymers are like caterpillars, slower because they must inch along due to their length.

This reduced mobility is also responsible for how long it takes polymers to dissolve in a solvent (a week or more!) and how slowly polymers diffuse through a liquid. Finally, the slow polymer chains are similarly slow to respond to deformation, like stretching or compression. They can even get kinetically frozen in a new shape, but still "remember" a previous one because the chains are so slow to relax and take on new arrangements. If this isn't handled properly, it can make molded plastic parts break more easily.

Slide 7:

Student walkthrough: Describe the molecular weight of small molecules, then contrast this with the molecular weight of macromolecules/polymers.

Background: A small molecule, like aspirin, has a defined chemical formula and a defined molecular weight. Polymers, on the other hand, can be any length desired, requiring a few new concepts to express their molecular weight properly. Because the physical properties of polymers can vary based on just how long the chains are, it is important to designate the molecular weight as well as the repeat unit of any given polymer sample. Adding a further layer of complexity, not all chains within the same sample are the same length. The most common terms we use to describe this distribution of chain lengths are introduced on the following slide.

Slide 8:

Student walkthrough: The figure in the upper-left quadrant is a sample of polymer chains. Their differing lengths reflect the real-world composition of polymer materials. Introduce students to M_N and M_W, contrasting these two averages. If time permits, work through or have the students work through, the calculation of these two values based on the information given in the figure. The answers are posted on the slide. Lastly, introduce the concept of dispersity (Đ), the ratio of M_w over M_N, as a short-hand for describing how broadness of the chain length distribution. The 1.07 value for the sample on the slide is actually quite narrow, comparable to some of our most controlled polymerization methods.

Background: Most polymer samples possess a Gaussian-like distribution of molecular weights. Capturing the average size of the chains as well as the spread of this distribution is important for understanding how the sample will behave both chemically and as a material. Different types of synthetic methods can also let us control how long the chains get and how wide the distribution is, a topic that will be covered in more detail in advanced modules. For now, there are three important definitions that students should know.

M_n is the *number-average molecular weight*, an average that is weighted towards the most common chain length. It is calculated by summing the mole fraction or number fraction of a given molecular weight multiplied by that weight, as shown in the formula. A mass of polymer can be converted to moles stoichiometrically using its molecular weight like any other molecule. The M_N value tends to be more useful for stoichiometric calculations involving polymers. It can be empirically determined by NMR, if there are endgroup protons that are distinct from the repeat unit.

M_w is the *mass-average molecular weight*, an average that is weighted towards the heaviest chains. As such, it is always larger than the M_N. It is calculated by multiplying a fraction's molecular mass by its mass fraction, rather than the number fraction. M_w has a more pronounced effect on the material properties of the polymer, such as stiffness.

Lastly, *dispersity (Đ)*, is the ratio of M_W/M_N, expressing the breadth of the chain length distribution. The larger this value, the more variety there is in chain length. The DNA and proteins in our cells are almost always *monodisperse*, meaning they have Đ=1.00. All their chains are the exact same length. This is almost universally untrue of other polymers. Polymers grown by chain growth mechanisms (see previous slides) may have Đ ranging from 1-10. Condensation polymers, on the other hand, ideally have a dispersity of 2.0. It is possible to control both molecular weight and dispersity by employing a variety of *living polymerization* methods, which are discussed in more advanced modules.

Slide 9:

Student walkthrough: Begin with the small molecule behavior box. This describes the familiar behavior of small molecule crystalline solids. Contrast this to the polymer figure on the right, representing the configuration of polymer chains within a polymer sample. Point out the presence of both well-ordered crystalline domains and disordered amorphous domains. Higher crystallinity usually improves mechanical properties (stiffness, robustness) and causes light scattering that makes the plastic opaque. Some polymers are very poorly crystalline or entirely amorphous, making them glassy and visually transparent. A useful image for helping students understand light scattering and opacity is asking them to imagine a large salt crystal vs. a spoonful of table salt.

Background: Another key feature of polymers is that they are not entirely crystalline in the solid state. Instead, polymers may be semicrystalline. Small crystallites of ordered polymer are in a sea of disordered, but still solid, polymer. This disordered material is referred to as *amorphous*. The proportion of crystalline to amorphous material depends on the identity of the polymer and exactly how that polymer was processed (for example, how quickly it was cooled from the melt or whether a nucleating agent was added to encourage crystallite growth). Polymers with simple, highly regular structures generally have higher % crystallinity (for example: polyethylene, polypropylene, or Nylon-6,6). Branching, long side chains, and low molecular weight all suppress crystallinity. Some polymers are even fully amorphous in the solid state (for example: poly(methyl methacrylate) and polystyrene).

The crystallites have melting points, just like small molecule crystals, and each polymer has its own particular T_m for the crystalline portion. The amorphous portion has its own thermal transition, the glass transition, which will be further discussed on the following slide.

Crystallinity has two major effects. More crystalline content provides mechanical reinforcement, resulting in harder, stiffer polymers. Crystallites also scatter light, which results in more crystalline polymers appearing visually opaque. Fully amorphous polymers are visually transparent.

Slide 10:

Student walkthrough: Begin by reminding students of the melting phase transition, which is a familiar feature of small molecules. Remind students that polymers possess an amorphous solid phase, in addition to the crystalline portion. Introduce the concept of the glass transition temperature, using the figure at bottom left. The table includes the T_g of some common polymer materials, giving students intuitive data to understand how this phase transition affects the properties of the material.

Background: Most small molecules have only one type of solid phase available to them: a well-ordered crystal. However, polymers are only semicrystalline, at best. The rest of the solid material in a chunk of plastic is “amorphous”. It is kinetically frozen in the solid state (no chains are moving), but it doesn’t have any overall order. This is similar to window glass.

Because polymers have two possible solid states, they also have two different solid-phase thermal transitions. Polymer crystallites and small molecules both have melting temperatures, the temperature at which the solid crystal becomes a liquid. The glass transition, however, is unique to polymers, and applies to the amorphous portion of the solid. Below the Tg, the chains are kinetically frozen in place, resulting in brittle, glassy material properties. If the polymer is heated above the Tg, the chains “unfreeze” and become more mobile. They do not actually melt, but they become flexible rather than frozen. In this state, the polymer shows rubber-like properties like decreased stiffness, increased stretchability, and bounciness.

Just like each small molecule substance has its own Tm, each type of polymer has its own T_g. The T_g is strongly affected by the structure of the polymer, and even by the way we choose to measure it. Things that can increase T_g, and therefore make a polymer glassier, include stiff structures in the backbone like aromatic rings and strong interactions between chains like hydrogen bonding. Polystyrene has a T_g of about 100 °C, meaning that it is glassy at room temperature. Silicone rubber, on the other hand, has a T_g of about -100 °C, and is therefore rubbery at room temperature.

The T_m and T_g of a particular polymer may be close together, or they may be very far apart. Polyethylene is an excellent example of this. Polyethylene crystals possess T_m between 110 and 130 °C, depending on their size, but a T_g of -90 °C. At room temperature, the rubbery amorphous polyethylene is reinforced by the rigid crystallites, yielding a material that is overall tough and useful.

Slide 11:

Student walkthrough: If it can be arranged, this slide strongly benefits from being accompanied by a hands-on demo or visual aid handled by the instructor. Silly putty, glue slime, or cornstarch/water slurry are all appropriate options.

Begin by discussing solid and liquid behavior with students. An ice cube (solid) shatters when struck by a hammer, but the same amount of liquid water flows or splashes around it. A crystal of sugar maintains its shape, but molten sugar can be poured into molds. When you melt a crystalline solid, it undergoes a transition from solid-like to liquid-like behavior with no practical overlap.

Polymers are different; they can display solid-like and liquid-like behavior at the same time. Demonstrate this by bouncing the silly putty, then slowly stretching it. Compare very fast stretching (it will break like a solid) to letting it flow through your fingers or spread across a table top. A bowl of ice-water will let you chill the silly putty, making it stiffer and glassier, while a bowl of very hot water will soften it.

Background: Much of what we love about polymers as a material derives from the fact that they simultaneously display solid-like and liquid-like responses to mechanical stress. Ideal liquids and solids consist of a surprisingly tiny portion of the materials we handle every day. Ideal fluids always have the same viscosity, or thickness, no matter how fast you force them to flow. Ideal solids behave like perfect rubber bands; after being stretched or compressed, they return exactly to their previous shape. A classic example of an ideal fluid is air, while the classic ideal solid is a crystal.

Polymers blur the line between these two paradigms, behaving more liquid-like or more solid-like depending on exactly how the deformation is taking place. A ball of silly putty is an excellent visual aid or hands-on manipulative for students to grasp this concept. Silly putty is made of poly(dimethyl siloxane), a common polymer. Because polymer chains have reduced mobility, time-scale is one of the factors that controls the material response. If the polymer is deformed quickly (for example, bouncing silly putty on the table), the chains have no time to react and flow, and therefore the material behaves more like a solid. On the other hand, if you deform the polymer slowly (for example, slowly stretching a silly putty rope), the chains have time to relax and reorganize themselves in response, permitting the material to flow in a more liquid-like manner.

Temperature changes also affect viscoelastic behavior. If you chill the material, the chains possess even less mobility, increasing the solid-like character of its behavior. At high temperatures, the chains are more mobile, enabling greater liquid-like response. Low temperatures and short time-scales enforce solid-like properties, while high temperatures and long time-scales allow liquid-like properties.

Slide 12:

Student walkthrough: Up until now, we have discussed linear polymers. Introduce the other topologies, and encourage students to think about how these different types of structure might affect the ability of chains to diffuse, entangle, and interact with solvent.

Background: Because polymers are long chemical chains, akin to pieces of string, they can, like string, take on a number of different shapes called “topologies”. Polymer topology can include branch points, rings, and crosslinks. The topology of the polymer has a significant effect on its material properties because it changes the ability of the polymer to entangle with other chains and interact with solvent molecules. An area of intense interest in synthetic polymer chemistry is devising routes to build specific topologies.

A *linear* topology is a simple polymer chain. It does not branch or loop. This type of topology is the most prone to entanglement. Entangled chains cannot move freely past one another, so large amounts of entanglement lead to stiffer materials. Longer chains promote greater entanglement. Linear chains can also interact the most strongly with a favorable solvent. These polymer-solvent interactions slow down the flow of the solvent, giving linear polymers the biggest effect on solution viscosity.

If you connect the ends of a single chain together, you obtain a *cyclic* topology. The extension of the polymer through space is now constrained by being a loop, reducing its tendency to entangle with other cyclic polymers. If you compare a linear and a cyclic polymer of equal molecular weights, the cyclic polymer will be a softer material due to this lack of entanglement. It also cannot interact with solvent as effectively, so it will not increase solution viscosity as strongly as a linear chain.

Let's start introducing some branch points into our topologies. If you start with a single core and attach multiple polymer arms to it, the result is a *star* morphology. It compacts the polymer into an even smaller space than a cyclic morphology, reducing material stiffness and solution viscosity effects even further. If there are enough arms protruding from the core, it even begins to make sense to think of the star globule as a tiny, solid particle.

We can extend the zero-dimensional star topology into a one-dimensional *graft, comb, or brush* morphology. Instead of a single core point with protruding arms, we now have a core that is itself a linear polymer chain. Each repeat unit of the backbone polymer bears its own pendant polymer chain. These chains extend outwards from the linear core, like a bottle brush. Like star polymers, brush polymers have few chain entanglements and low interaction with solvent. Fascinatingly, they can be used to mirror on a larger length scale similar behaviors individual polymer chains display. Imagine a thin piece of thread vs. a fluffy pipe cleaner, and how they can behave similarly, though on different length scales.

The previous two morphologies are characterized by carefully placed branch points and well-defined polymer arms. A *branched* topology uses a known chemistry or functional group to induce a branch in the chain, but control over where each branch point occurs is less precise. The greater the amount of branching, the fewer entanglements the chain experiences, and the softer it becomes. A useful engineering trick is to blend together a linear polymer and a branched polymer with the same repeat unit. Because the materials are chemically virtually identical, they readily mix with each other to form a stable resin, but the branched additive provides softening that can improve the toughness or moldability of the linear polymer.

As the amount of branching gets very high, we can access the *dendritic* morphology. This morphology is characterized by a well-defined branch point built into every repeat unit of the polymer. It derives its name from the world for "roots", because this morphology resembles the roots of a plant. In the example here, three arms emerge from a core, then each branches into two more arms. If this polymer continued to grow, the next repeat units would each split into two arms, and so on. Like a dense polymer star, dendritic polymers do not tend to entangle or interact with solvent.

If the branching is dense, but not well-defined, it is more appropriate to call it a *network* morphology. These materials are often prepared by adding a special molecule called a "crosslinker" to the polymerization. A crosslinker is a (usually small) molecule that bears two or more polymerizable functional groups, allowing it to polymerize into one chain on one end, and another chain on the other, tying them together in a "crosslink". Inducing crosslinking in a material slows down the chain motion of the polymer, leading to an increase in stiffness. Natural rubber is a good example of the effect of crosslinking. Natural rubber, when it is freshly-harvested, is a liquid mass of linear polyisoprene. After crosslinking by sulfur treatment (vulcanization), the chains become a dense, rubbery mass suitable for a number of applications.

Slide 13:

Student walkthrough: These three examples are all topologies of poly(ethylene), one of the most common polymers. Begin at the far right or far left, and describe how changing the topology changes the ability of the polymer to form crystallites and chain entanglements, and how this affects the physical properties of the plastic. Emphasize that the repeat unit is exactly the same across all three examples to underscore the dramatic influence of chain topology.

Background: Low density polyethylene (LDPE) has multiple branch points at random locations along the polymer backbone. The branching inhibits chain entanglement and crystallite formation, leading to a very soft, visibly transparent material. LDPE is typically use for plastic wrap or for six-pack rings (yokes). High density polyethylene (HDPE) has fewer branch points than LDPE and has large linear segments which lead to chain entanglement and support the growth of some crystallites. This combination of very hard crystallites and entangled amorphous chains make HDPE stiffer and more opaque than LDPE. HDPE is typically used for plastic bottle caps and plastic folding chairs. Ultra molecular weight polyethylene (UHPE) has least amount of branch points when compared to LDPE or HDPE. It is very easy for UHPE to form large, dense crystallites that greatly increase the stiffness of the plastic. These crystallites are surrounded by a strongly entangled amorphous phase that adds robustness. These impressive physical properties include high impact and tensile strength, making UHPE useful for parachute cords and body armor.

Slide 14:

Student walkthrough: Introduce the three polymers to students, and ask them to identify where they use these polymers in their everyday lives. Look carefully at the structures, and identify key differences. Make explicit connections between these repeat unit structures and the physical properties of the polymers.

Background: We use a number of common polymers every day. By examining three polymers in particular, we can see how the repeating unit structure of the polymer can amplify the effects of even small changes to the repeat unit structure. The modification of a hydrogen to a halogen to multiple halogens has tremendous impact upon the material properties.

First, consider poly(ethylene). Polyethylene is a semicrystalline polymer with a T_g of -125 °C and T_m in the range of 110-135 °C. It is extremely tolerate of aqueous solutions and even extremes of pH, because of its nonpolar structure. Softened polyethylene makes up shopping bags, while high-density polyethylene is used for robust bottles and packaging.

If you replace one of the hydrogen atoms in the repeat unit with a chlorine atom, you get poly(vinyl chloride), or PVC. PVC is also a semicrystalline polymer, but has a T_g of 70 °C and a T_m of about 160 °C. This massive shift in thermal properties is the result of several subtle effects. Introducing the chlorine atom adds steric hindrance that overall stiffens the polymer chain, increasing T_g. The C-Cl bond is also polar, adding stabilizing dipole-dipole interactions to its crystalline structure and increasing their melting point. PVC is also more vulnerable to damage from organic solvents than polyethylene, due to its greater ability to form intermolecular interactions with solvent molecules.

Lastly, replace all of the hydrogen in polyethylene with fluorine atoms. This material is poly(tetrafluoroethylene), or Teflon^{TM}. Teflon is the polymer used to make non-stick cookware. Despite possessing strongly polar C-F bonds, the overall symmetry of the molecular structure reduces the molecular dipole, leading to Teflon possessing a rather low T_g of -50 to -70 °C. Its highly regular structure promotes semicrystallinity, with two frequently observed melting points around 330 and 340 °C. This is reinforced by the increased chain stiffness induced by the larger fluorine atoms along the backbone.

Slide 15:

Student walkthrough: Simply introduce these two common-use polymers. Both are amorphous polymers with high T_g (~100 °C). Contrast the different products made with these polymers to emphasize the important role processing has in controlling polymer properties.

Background: There are many polymers that are suitable for a variety of uses, but polystyrene and poly(methyl methacrylate) are two of the multipurpose polymer all-stars. Because they are both fully amorphous polymers with moderate T_g (about 100 °C), these materials are readily melt-processed. Melt processing is a powerful set of techniques that includes injection molding, blow molding, and fiber spinning, allowing a huge variety of films, fibers, cast products, and much more to be made from PS and PMMA.

Polystyrene in particular can be processed with a blowing agent, which causes many bubbles to form that freeze in place as the polystyrene cools, resulting in Styrofoam. This material is an excellent insulator and packing material. A fun experiment is to determine just how much of a Styrofoam peanut's volume is actually polystyrene and how much is just air by dropping packing peanuts in a small amount of acetone. Just 2-3 mL of acetone can fully dissolve dozens of peanuts. A similar experiment can be done with the new starch-based peanuts and water, an experiment safely performed in the classroom.

PMMA is sold under the trade names Lucite and Plexiglass, and is frequently used to make windows, home furnishings, and even shoes and accessories. Because of its high reactivity in polymerization, it is the basis of resin dental fillings. After drilling out the cavity, the dentist fills the tooth with a mixture of methyl methacrylate monomer, crosslinker, and glass particle filler. This mixture also includes a small amount of a compound that releases radicals when it is exposed to UV light. These radicals react with the methyl methacrylate and crosslinker to polymerize the filling in place, repairing the tooth. The acrylate class of molecules derives their name from the word "acrid" due to their unpleasant odor, which anyone who has had a resin filling will recognize.

PMMA can also be used to make hard contact lenses due to is high visible transparency. This results from two factors. First, the polymer is fully amorphous and never develops crystallites that can scatter light and cause opacity. Second, its molecular structure doesn't possess any functional groups that absorb visible light wavelengths.

Slide 16:

Student walkthrough: Here are more examples of everyday polymers. Again, look at the unique features of the repeat unit structures and explain how they give rise to polymer properties. Instructors can ask students to review their shampoo bottles and other bathroom item ingredients list to find uses of polymers.

Background: Polymers are very common ingredients in personal care products like soaps, shampoos, lotions, and cosmetics. They are usually used to change the physical properties of the product to make it feel luxurious or assist with cleansing.

Poly(ethylene oxide), also called PEO or PEG, is a water-soluble polymer used as a thickening agent in shampoos, conditioners, shower gels, and more. The length of the PEO chain used is denoted by a hyphenated number. For instance, PEG-500 is a poly(ethylene oxide) chain that is 500 g/mol. Longer chains have greater thickening power. This polymer is also used in laxative formulations. Its high affinity for water helps water stay in the gut, promoting regularity.

Poly(vinyl alcohol), or PVOH, can also be used as a thickening agent due to its high affinity for water. One notable application of PVOH is in peel-off face masks. You apply a thick gel to your face, made of a concentrated PVOH solution in water. The water dries, leaving behind a pliable polymer film that can be peeled off. It can also be found in Elmer's glue and hair gel.

Poly(dimethyl siloxane), or PDMS, is part of a different class of polymer. All of the other polymers we've discussed so far are hydrocarbons. Their backbones are made mostly of carbon and hydrogen, sometimes with added oxygen or nitrogen. Siloxane polymers have backbones made of alternating silicon and oxygen bonds. The longer bond lengths of Si-O bonds give these polymers a high degree of flexibility, making these extraordinarily soft materials. Siloxanes are popular additives to skin lotions and hair products because they offer long-lasting moisturizing.

Slide 17:

Student walkthrough: Polymers that make the fibers in our textiles share some features that lead to strong fiber formation. Help students identify the regular structures, that promote crystallinity, and the amide/ester functional groups that can hydrogen-bond or dipole-dipole interact between chains, helping to hold them together and strengthening the fiber.

Background: All of our fabrics are made from polymers, whether natural or synthetic. Many fiber polymers are condensation polymers, which contain functional groups within the backbone such as esters or amides. Appropriate fiber polymers show high tensile strength and resistance to heat and solvents. You wouldn't want your sweater to shrink in the wash or dissolve in water!

Polyamides are an important class of fiber polymers. The amide groups in the backbone can form a powerful hydrogen bonding network that helps hold chains together and promote the formation of robust fibers. The R groups between the amides are what control the ultimate properties of the material. Natural polyamides include silk and wool. These fibers readily take up a variety of dyes and are warm and comfortable.

Polyesters are largely synthetic materials. The most common polyester is poly(ethylene terephthalate), and is used to make both plastic bottles and textiles.

Cotton and Rayon are both fibers made of cellulose, the major structural polymer in plants. Cellulose is a carbohydrate polymer, with the individual sugar units held together with acetal linkages. It forms a dense network of hydrogen bonds between the different alcohols on the sugars, giving these fibers toughness, insolubility, and high dye uptake. Cotton is the natural fiber, combed and washed before being twisted into fibers for weaving. It is soft and breathable, and possesses a matte texture resulting from the natural cellulose fibrils in its structure.

Rayon is chemically identical to cotton cellulose, but has been treated with the viscose process to result in a smooth, shiny fiber. Natural cellulose is profoundly insoluble in nearly all solvents, but treatment with strong aqueous base and carbon disulfide converts the cellulose alcohols to xanthate groups, allowing the chains to dissolve. This viscous solution is spun into a bath that reacts with the xanthates, converting them back to alcohols, and precipitating the new fiber out of the solution. This dissolution and reformation of the fibrils cause Rayon fibers to be shiny and smooth, while still possessing the breathability and dyeability of natural cotton.

Slide 18:

Student walkthrough: Ask students what types of items they use that are marked with recycling symbols, and ask them to guess what the numbers mean. As you discuss each example, explain how the polymer is recycled, and what products it is made into after the recycling process. This is also a good opportunity to make connections to global stewardship, the principles of green chemistry, and other expanded topics.

Background: One of the greatest strengths of polymer materials is their ability to be recycled. The recycling symbols found on items like bottles and packaging tell you not just what type of polymer it is, but also how easily this material is recycled into useful products.

Recycling number 1 is poly(ethylene terephthalate), the workhorse polyester. PET can be hydrolyzed back to its monomers (terepthalic acid and ethylene glycol) as part of the recycling process. It's amorphous nature and reasonable processing temperatures also make it readily refashioned into new products. One of these products is synthetic fleece for warm clothing. PET is a popular material for drink bottles and packaging of all kinds. Recycled, it is often made into various types of textiles, from clothing to furniture to carpet.

Recycling number 2 is high density polyethylene (HDPE), and 4 is low density polyethylene (LDPE). While both are made from polymerized ethylene, their marked different in properties arises from the topology of the chains. To make HDPE, early transition metal catalysts are used that produce long, linear polymer chains. These highly regular chains readily pack into a crystal lattice, leading to HDPE to be full of reinforcing crystallites that make it suitable for molded parts, reusable bottles, and engineering applications. LDPE is made with late transition metal catalysts that generate highly branched polymers. These branched structures don't pack neatly, and the suppressed crystallinity yields a soft, flexible plastic suitable for sheeting and bags. Despite sharing the same repeat unit, it is important to keep these two recycling streams separate to avoid blending their properties.

Recycling number 3 is poly(vinyl chloride). PVC can be used as-synthesized for piping, molded parts, and building siding due to its relatively high T_g (80 °C) and crystallinity (T_m 100-260 °C), but it can also be blended with small molecule *plasticizers* that interrupt crystal packing and increase chain flexibility. Plasticized PVC is used in sheeting, garments, and flexible tubing. The semicrystalline PVC is recyclable, the plasticized is not.

Recycling number 5 is polypropylene, another semicrystalline polymer. It is used to make jugs, molded parts, and packaging.

Recycling number 6 is polystyrene, an amorphous, glassy polymer that can be used for disposable cutlery, food containers, cups, and more.

Recycling number 7 is a catch-all for other polymers that may be recyclable. This can cover some polyurethanes, polycarbonates, polyacrylates, and more.

Useful References

Websites

ACS Division of Polymer Chemistry (POLY) - http://www.polyacs.org/Home

Their education section contains a large number of resources at all education levels.

ACS Division of Polymer Materials: Science and Engineering - https://pmsedivision.org/#

The "Teaching Polymers" section (under "Resources") provides a more multidisciplinary set of resources for polymer education.

LearnChemistry from the Royal Society of Chemistry - http://www.rsc.org/Learn-Chemistry

Find a number of premade teaching modules for various settings (lab, lecture, etc.) and education levels (K-12, secondary).

A Brief Introduction to Polymer Nomenclature (IUPAC) - http://iupac.org/publications/pac/pdf/2012/pdf/8410x2167.pdf

Books

Introduction to Polymer Chemistry by Charles E. Carraher, Jr. Currently in the 4th edition from CRC press.

Contemporary Polymer Chemistry by Harry R. Allcock, Frederick W. Lampe, and James E. Mark.

Principles of Polymerization (4th ed.) by George Odian

Glossary

Amorphous: The non-crystalline or disordered portion of the polymer mass

Backbone: The principal chain of a polymer, in which is defined the repeat unit

Branched polymer: A polymer possessing one or more points at which the chain extends; distinct from a polymer that possesses pendant groups from the backbone

Chain-growth mechanism: A type of polymerization in which new monomers are added to an activated, propagating chain end; at any time during polymerization, the reaction mixture consists of rapidly growing chains and unreacted monomer

Condensation polymer: A polymer prepared by a chemical reaction between two functional groups, releasing a small molecule byproduct for each backbone bond formed

Conformation: Different shapes of the polymer chain obtained through rotation of the polymer bonds

Crosslinking/crosslinker: A molecule with two or more polymerizable groups, resulting in the linking of two or more growing chains during polymerization; results in increased material stiffness and decreased crystallinity

Crystallite: A small region of crystallized polymer within the polymer mass

Cyclic Polymer: A polymer in which the backbone has been linked into a large ring

Dendrimer/dendritic polymer: A highly branched polymer, may even include one or more branch points per repeat unit

Dispersity (Đ): The ratio of M_W to M_N for a polymer sample; an expression of the breadth of the molecular weight distribution in the sample

Elastic behavior: The solid-like behavior of a polymer mass, encompassing the storage and later release of accumulated stress; this behavior is not usually associated with permanent shape changes

Glass transition temperature: The temperature below which the polymer behaves as a glass, and above which it behaves like a rubber. The transition is a result of increased local, but not total, mobility of the chain.

Graft polymer: A structure in which a linear backbone possesses macromolecular side chains; a structure in which each repeat unit of the backbone itself contains a macromolecular side chain

Linear polymer: A polymer structure with a single backbone chain and no branch points

Living mechanism: A polymerization reaction with suppressed chain termination

Macromolecule: A large molecule consisting of linked repeating subunits; may also be a polymer

Melting temperature: The temperature at which polymer crystallites transition from solid to liquid state

Molecular weight: The mass of a polymer chain, expressed in various units including g/mol

Network polymer

Number-average molecular weight (M_N): The average molecular weight of polymer chains in the sample, weighted by number of chains that possess a given weight

Pendant group: Side groups bound to the polymer backbone that are 1) consistently repeating in the repeat unit, and 2) not large enough to be considered branch points or macromolecular themselves

Polymer: A large molecule consisting of covalently linked repeating subunits; created from monomers

Repeat unit: The simplest repeating structure in the polymer backbone

Semicrystalline/semicrystallinity: The property of polymers that accounts for their ability to only partially crystallize in the solid state

Star Polymer: A topology resulting from three or more macromolecular chains originating from a single, small core structure

Step-growth mechanism: A polymerization mechanism in which polymerizable groups on any monomers or oligomers may react to grow the chain; unreacted monomer disappears very early in the polymerization and high molecular-weight polymer is only obtained after nearly full conversion

Topology: The arrangement of the polymer resulting from branching, grafting, and other structure considerations

Vinyl polymer: A polymer derived from the polymerization of an alkene-containing monomer

Viscoelasticity: The combination of fluid-like and solid-like material behavior of a polymer mass

Viscous behavior: The fluid-like behavior of a polymer, expressed as various types of flow that dissipate accumulated stress; this behavior is frequently associated with permanent shape changes

Weigh-average molecular weight: The average molecular weight of polymer chains in the sample, weighted by the mass fraction of chains within the sample