**Polymers: Essential Background and Definitions**

Instructor Support Document

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*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. This document is not intended for dissemination to students, but rather to bring you, the instructor, “up to speed” on this polymer content. At the end is a list of helpful references, in case you wish to dig deeper into a subject.

*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.

Slide 12: This slide describes how polymer chains can take on different shapes and bonding structures, called “topologies”, which can affect their physical properties.

Slides 13-17: 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: 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.

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: 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.

Slide 5: 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.

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

Slide 6: 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.

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: 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.

The “n” subscript outside the parenthesis may be replaced with a number of repeat units, if known.

Slide 8: Adding a further layer of complexity, not all chains within the same sample are the same length. 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.

MN 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 MN 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.

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

Lastly, *dispersity (Ɖ)*, is the ratio of MW/MN, 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 Ɖ=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 Ɖ of 1.4-1.6, if the reaction is carried out cleanly. 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: Conventional 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, stretchability, and bounciness.

Just like each small molecule substance has its own Tm, each type of polymer has its own Tg. The Tg is strongly affected by the structure of the polymer. Things that can increase Tg, 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 Tg of about 100 °C, meaning that it is glassy at room temperature. Silicone rubber, on the other hand, has a Tg of about -100 °C, and is therefore rubbery at room temperature.

Slide 10: 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. This important concept is called *time-temperature superposition* and is a powerful design tool when making a polymer for a particular use.

Slide 11: 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 transitions, just like small molecule crystals, and each polymer has its own particular Tm for the crystalline portion. The amorphous portion has its own thermal transition, the glass transition, which has been discussed previously. The Tm and Tg 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 Tm between 110 and 130 °C, depending on their size, but a Tg 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.

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 12: 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.

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.

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 froma 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: 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.

First, consider poly(ethylene). Polyethylene is a semicrystalline polymer with a Tg of -125 °C and Tm 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 Tg of 70 °C and a Tm 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 Tg. 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 TeflonTM. 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 Tg 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 14: 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.

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 15: 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 16: 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 Tg (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 process 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.

PMMA is sold under the trade names Lucite and , 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 17: 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 Tg (80 °C) and crystallinity (Tm 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/#](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).

*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

Introduction to Polymers (3rd ed.) by Robert Young and Peter Lovell