

## EFFECT OF SIZE AND COMPOSITION ON THE PROPERTIES OF RENEWABLE COPOLYMERS

### Required Reading

**Mohrig:** Chapter 22.10 Sources of Confusion and Common Pitfalls – Section: “*Could My Extra NMR Signals Come from a Mixture of Compounds,*” pp. 394-396.

**Manual:** *Calculation of % Composition of a Sample from <sup>1</sup>H NMR Integration*, p. 17-19.

**Question:** How can the physical and mechanical properties of a triblock copolymer, prepared from all renewable starting materials, be tuned using different monomers for the “soft” midblock and varying proportions of the “hard” end block?

**Green Concepts:** Catalytic reagents, renewable feedstocks, biodegradable materials, minimal solvents

### Introduction

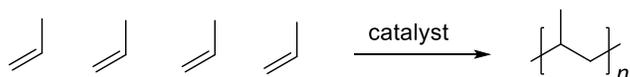
Polymers, the giant chain-like molecules which comprise plastics and rubbers, are amazing and versatile materials. From the shoes we wear, to the personal care products we use, and the cars we drive, these macromolecules permeate nearly every facet of our daily lives. However, some of the characteristics of these materials that make them so desirable for commercial applications - their stability to temperature changes and resistance to corrosion and degradation – are responsible for their continued buildup and harmful effects to our health and the environment. Additionally, these polymers are derived from non-renewable petrochemicals.

To address the future needs of our society, scientists are aggressively researching new alternatives for today’s polymers. Here at the University of Minnesota, the NSF-funded “Center for Sustainable Polymers” has partnered with industry to discover new materials that meet the needs of consumers in an economic way while incorporating the principles of green chemistry and green engineering in their production and life cycle. See <http://www.chem.umn.edu/csp/> for more details.

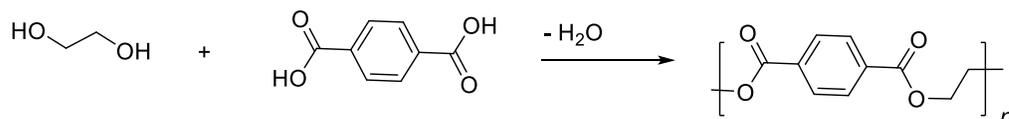
Some basic principles of polymers and plastics will be introduced in the lab lecture and summarized here. Polymers are substances that contain a large number of repeating units called **monomers**. Chemists classify polymers by their method of synthesis. Three general classes of polymers are: a) **addition** or **chain-growth polymers** – most often monomers are alkenes catalyzed to link together in linear or branched chains; b) **condensation** or **step-growth polymers** – a result of bifunctional or polyfunctional materials reacting with the loss of a small molecule; and c) **cross-linked polymers** – large three-dimensional macrostructures with a cross-linked network of addition or condensation polymer chains. See **Figure 1** for examples.

Polymers are also be classified by their thermal properties. **Thermoplastics** can be heated to soften or melt and remolded into other shapes. Non-covalent bonds are broken during heating. These types of polymers, many addition and condensation polymers, can often be recycled as long as degradation has not occurred. In contrast, **thermoset plastics** are cross-linked polymers that when heated continue to harden and additional heating will only result in decomposition. Thermoset plastics are generally stronger than thermoplastics and cannot be recycled. The stability of thermosets has resulted in broad application for durable goods such as insulating foams, car parts, shoe soles, flooring, electrical insulation, epoxy resins, and more.

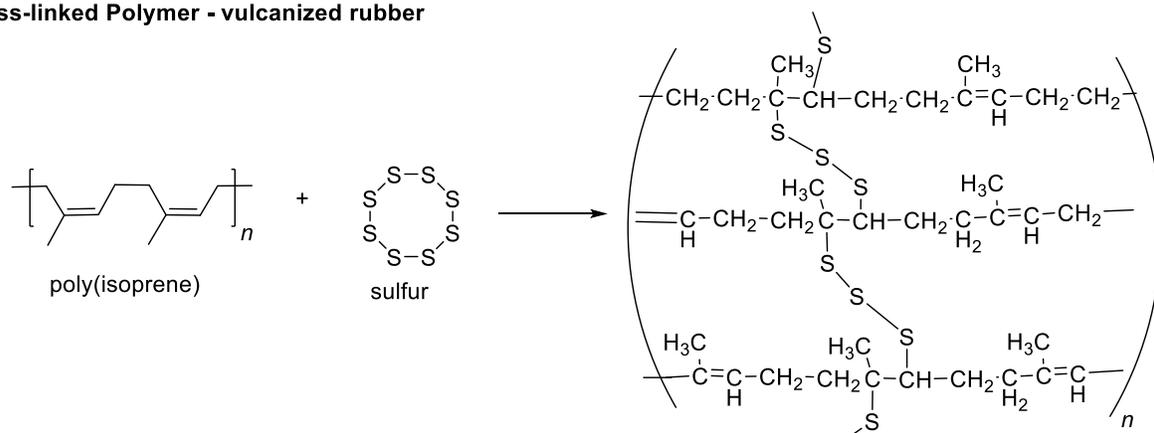
### Addition Polymer - polypropylene



### Condensation Polymer - poly(ethylene terephthalate) PETE



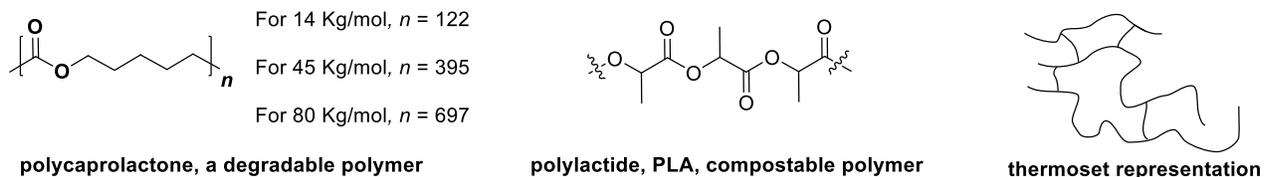
### Cross-linked Polymer - vulcanized rubber



**Figure 1: Examples of polymers classified by synthesis**

### Representing Polymer Structures

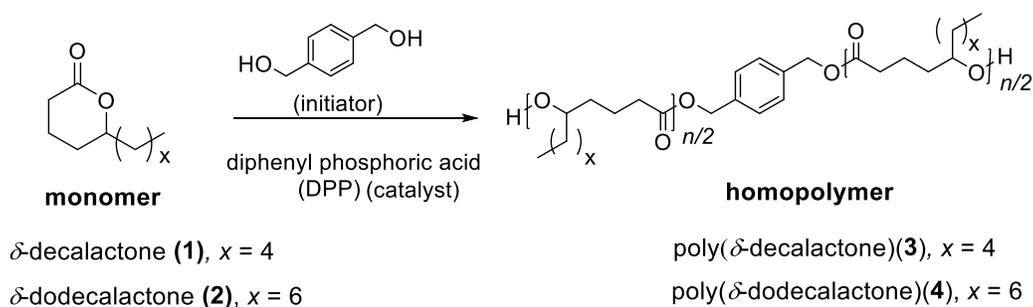
In contrast to the small molecules that have been used all semester with molecular masses in the g/mol, it is impossible to draw polymer structures with extremely large molecular masses in the kg/mol. Therefore, polymers are represented by drawing their repeating units in parentheses or brackets, with the subscript,  $n$ , indicating the number of repeating units. If a generic structure is drawn, a squiggle line is used to denote continuation of the chains (see **Figure 2**). In the case of thermosets which are extremely complex, schematic figures are used to represent the overall macromolecular structure.



**Figure 2: Polymer representations**

## Synthesis of Renewable Triblock Polymers

In this experiment, two naturally occurring lactones,  $\delta$ -decalactone (**1**) and  $\delta$ -dodecalactone (**2**), will be used as renewable monomers for the synthesis of polyesters. They are both commercially available from flavors and fragrances suppliers because of their tropical odor and taste ( $\delta$ -decalactone is characterized by a creamy coconut smell,<sup>1</sup>  $\delta$ -dodecalactone has a creamy peach fragrance<sup>2</sup>). These lactones have been shown to undergo ring-opening transesterification reactions under acidic catalytic conditions as illustrated in Scheme 1.<sup>3,4</sup> As is common in these types of polymerizations, an alcohol initiator is used to begin the ring-opening process. In this procedure, the diol, 1,4-benzenedimethanol, serves as the initiator to grow linear polymer chains outwards from both sides. Recognize that the initiator contributes very little to the overall polymer characteristics, because the number of repeating units,  $n$ , is large, resulting in polymers with molecular weights (described as number average molecular weight,  $M_n$ ) in the kilogram per mole range. Note that the difference between  $\delta$ -decalactone (**1**) and  $\delta$ -dodecalactone (**2**) is the length of the side chain which can change the properties of the corresponding copolymer; for example consider the different properties and uses for polyethylene and polypropylene.



**Scheme 1. Polymerization of  $\delta$ -decalactone or  $\delta$ -dodecalactone**

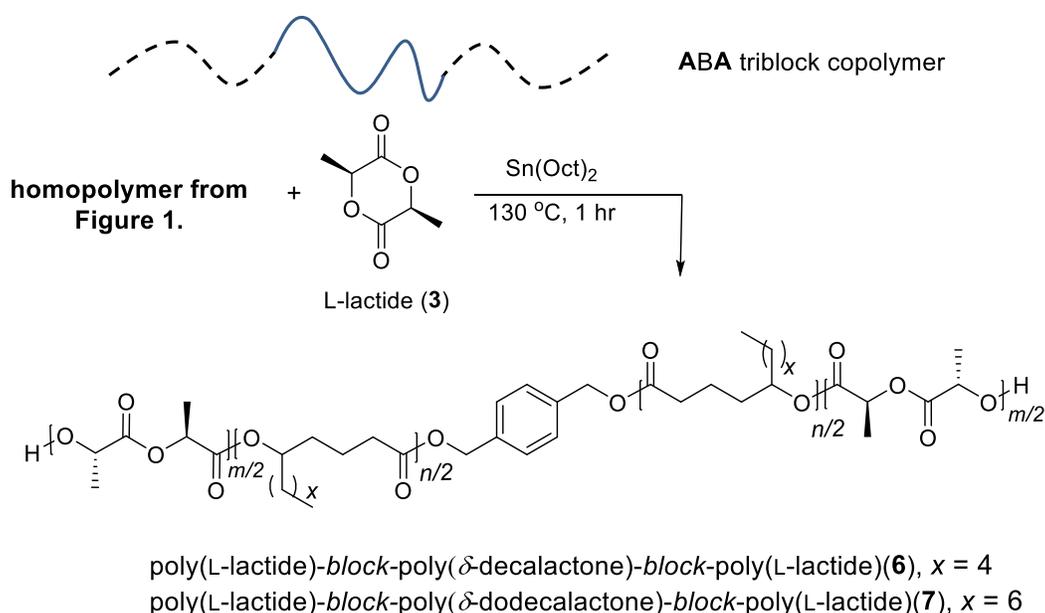
The resulting homopolymers, (**3**) and (**4**), are both viscous liquids with a low softening temperature. These polymers have alcohol functional groups on the end of the polymer chain, meaning they can act as initiators for the polymerization of a second monomer. This polymer extension results in a linear chain with distinct regions or blocks derived from the sequential polymerizations of each of the two different monomers. In this experiment we use L-lactide as the monomer in the second reaction. Because the second block grows out from the ends, the resulting polymer chain contains poly(L-lactide) end blocks, as illustrated in Scheme 2. These types of polymer architectures are called ABA triblock polymers as represented below. One commercial example of an ABA polymer, comprised of polystyrene and polybutadiene blocks, is called Kraton<sup>®</sup> and is used in shoe soles and adhesives. The unique elastomeric properties of many block polymers such as Kraton<sup>®</sup> is a result of the different contributions of each homopolymer unit to the overall block polymer structure.

<sup>1</sup> Delta-decalactone: <http://www.thegoodscentscompany.com/data/rw1013411.html> (accessed March 2, 2014).

<sup>2</sup> Delta-dodecalactone: <http://www.thegoodscentscompany.com/data/rw1013351.html> (accessed March 2, 2014).

<sup>3</sup> Martello, M. T.; Burns, A.; Hillmyer, M. A. *ACS Macro. Lett.* **2012**, *1*, 131-135.

<sup>4</sup> Schneiderman, D. K.; Gilmer, C.; Wentzel, M. T.; Martello, M. T.; Kubo, T.; Wissinger, J. E. *J. Chem. Educ.* **2014**, *91*, p. 131-135.



### Scheme 2. Addition of L-lactide as the end block for the triblock copolymer

The L-Lactide monomer (3) is derived from plants such as corn and sugarcane. Poly(lactide) (PLA) is the most prevalent eco-friendly biopolymer on the market today. All of the compostable cups and dining ware on campus is made from PLA. Because the PLLA homopolymer (poly(L-lactide)) is very brittle and stiff, incorporation of PLLA segments as the ends block to the soft  $\delta$ -lactone midblock adds strength and rigidity to the material. The PLLA-*block*-poly( $\delta$ -decalactone)-*block*-PLLA, (6), and PLLA-*block*-poly( $\delta$ -dodecalactone)-*block*-PLLA (7) triblock polymers, are both *thermoplastics*, that is, they can be molded by heating above the melting temperature of the hard poly(L-lactide) blocks.

Each section will prepare a combination of four different triblock polymers by combining poly( $\delta$ -decalactone) or poly( $\delta$ -dodecalactone) with varying weight percent of poly(L-lactide) incorporation as detailed in Table 1. These triblock polymers will be compared to determine how each combination of lactone derived block and polylactide block influences properties such as flexibility, clarity, tackiness, or other observable properties.

**Table 1: Triblock Polymer Reagent Quantities**

Polymer	<sup>a</sup> Midblock	Day 1 Reagents					Day 2 Reagents	
		<sup>b</sup> PLLA (wt.%)	<sup>c</sup> DDL (mL)	<sup>d</sup> DDDL (mL)	<sup>e</sup> BDM (g)	<sup>f</sup> DPP (g)	L-Lactide (g)	<sup>g</sup> Catalyst (mL)
<b>A</b>	PDDL	35	2.40	-	0.015	0.063	1.23	0.76
<b>B</b>	PDDL	45	2.05	-	0.013	0.054	1.59	0.71
<b>C</b>	PDDDL	35	-	2.45	0.013	0.055	1.24	0.68
<b>D</b>	PDDDL	45	-	2.05	0.011	0.046	1.58	0.63

<sup>a</sup>PDDL = Poly( $\delta$ -decalactone), PDDDL = poly( $\delta$ -dodecalactone), <sup>b</sup>PLLA = poly(L-lactide) <sup>c</sup>DDL =  $\delta$ -decalactone, <sup>d</sup>DDDL =  $\delta$ -dodecalactone, <sup>e</sup>BDM = 1,4-benzenedimethanol initiator, <sup>f</sup>DPP = diphenyl phosphate, <sup>g</sup>0.4 M tin(II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>) in toluene

### Experimental Procedure:

**Hazards:** Ethyl acetate, methanol, and toluene are flammable. L-Lactide,  $\delta$ -decalactone,  $\delta$ -dodecalactone, 1,4-benzenedimethanol, and tin(II) 2-ethylhexanoate are potential irritants. Chloroform-*d* is an inhalation hazard and suspected carcinogen.  $\delta$ -Decalactone is reported to have an odor threshold detection limit in water of 100 parts per billion and has a persistent aroma. Therefore, it should be handled in a hood with gloves at all times. The product should be handled with gloves in the event that residual  $\delta$ -decalactone monomer remains. Diphenyl phosphoric acid has no known hazards.

### **Day 1. Synthesis of homopolymer - poly( $\delta$ -decalactone) or poly( $\delta$ -dodecalactone)**

Place a glass vial (6 dram with cap, 23 x 85 mm) with a micro-stir bar in a beaker on a balance. Close all of the doors and tare the balance to zero. Open the door and add precisely the quantity,  $\pm 1$  mg, of benzene dimethanol of your assigned triblock copolymer. Close the door and record the exact mass you used since the amount of initiator has a large effect on the number of repeat units of the copolymer. Clamp the vial in the hood on a stirrer hotplate with cap nearby. Carefully, add either the  $\delta$ -decalactone or  $\delta$ -dodecalactone monomer via syringe and cap quickly. Stir until the initiator is dissolved. When ready to add the catalyst, weigh the designated mass ( $\pm 5$  mg) of diphenylphosphoric acid (also called diphenyl phosphate). The exact quantity of the catalyst is less crucial so it is not necessary to spend too much time trying to get the target mass. What is important is to break up any chunks and make a fine powder of the DPP. This can be accomplished by carefully folding the weigh paper containing the DPP in half and gently crushing the solid with the pestle. Add the catalyst and cap the vial tightly. Stir until all solids are dissolved (30 minutes to 1 hour).

Place the vial in a beaker in your drawer until the next laboratory period. Remember to record all observations before and after the polymerization. Calculate the theoretical molecular weight of the polymer based on quantities of the initiator and monomer used.

### **Day 2. Addition of L-Lactide end blocks**

Record the appearance of the polymer from Day 1.

Prepare a sandbath in a 50 mL heating mantle and place it on a stirrer hotplate resting on a ringstand (note, the hotplate will be used only for stirring, NOT heating). Attach a thermometer to the ringstand and place it in the sandbath. Plug the heating mantle into a variac (be sure not to plug it into a regular outlet) and set the variac to ca. 30-40 to begin heating. When the temperature reaches approximately 92-94 °C (the melting point of L-lactide), dig a well in the sandbath using a metal scoopula large enough for the vial and submerge the vial so that the level of the contents is below the level of the sand. Add the designated quantity of L-lactide through a glass funnel and stir. An opaque, white gel should form in 1-2 minutes as the L-lactide melts. Once the L-lactide is melted and stirred in, add the 0.2 M tin(II) 2-ethylhexanoate ( $\text{Sn}(\text{Oct})_2$ ) in toluene and stir. Continue to heat the sand bath until it reaches 130 °C and begin timing the reaction. Monitor the temperature throughout the experiment so the sand does not become too hot (above 140 °C). Either use mechanical stirring or the metal spatula to be sure mixing continues and two layers do not form. Lightly place the cap on the vial and heat at 130 °C for 50 minutes. As the new copolymer is formed, the solution may thicken.

When 10 minutes remain, begin to warm 20 mL of ethyl acetate on a hot plate (setting 4). Record the reaction time and remove the vial from the heat. Allow to cool for NO MORE than 1-2 minutes since the polymer will begin to solidify to an opaque solid and will make the next step difficult. Slowly add the warmed ethyl acetate in small portions while stirring vigorously with a glass stir rod to dissolve the solid pieces of polymer. The solution will remain opaque during this process. Use the minimal amount of ethyl acetate necessary. Pour the dissolved polymer slowly into 40 mL of methanol, which has been cooled in an ice bath, while stirring. The polymer most likely will be a flocculent white powder material. If a solid forms, continue with workup A. If no precipitate forms, go to workup B.

**Workup A for solid.** Allow the polymer to settle. Either the solution can be decanted from the polymer or a quick gravity filtration can be applied to isolate the polymeric material before vacuum filtration. Note, that direct vacuum filtration of the poly( $\delta$ -decalactone) is not recommended without a filtration trap to avoid the odor from remaining monomer from entering the house vacuum line. Vacuum filter the triblock polymer on a Buchner funnel, breaking up any chunks with the thin metal spatula, and dry for 10 minutes. Continue below.\*

**Workup B if no solid formed.** If no precipitate formed, leave the polymer in an ice bath for 10 minutes undisturbed. Decant off the methanol and scrape the viscous polymer into the pre-weighed aluminum tin. Continue below.\*

\*Weigh a small aluminum weigh boat. Transfer the white polymer material to the aluminum boat on a hot plate and heat (setting of 3.5-4.0 and increase if necessary) to remove excess solvent, and melt. Use your wooden or metal test tube holder to handle the aluminum tin (not your fingers). Samples with a large amount of L-lactide incorporation and high yield may be slow to anneal. In these cases, place a second aluminum boat or aluminum foil tent over the top to heat more uniformly and decrease the annealing time required. Record any change in appearance of the polymer during this process. If the polymer begins to evolve smoke at any time, remove it from the heat. When it appears that all or most of the solvent bubbles have been removed and a uniform polymer is formed, remove from the hotplate and cool to room temperature.

Determine the mass of the polymer isolated and calculate the % yield. Prepare a  $^1\text{H}$  NMR sample by dissolving 20 mg of the triblock polymer in the appropriate amount of  $\text{CDCl}_3$ . Alternatively or in addition, an IR spectrum may be requested by your instructor. Place the annealed polymer in a beaker in your drawer for further curing.

### **Mechanical Property Testing**

On the day that the polymers will be tested, attempt to remove the polymer from the aluminum tin using a spatula to loosen the sides and/or by peeling away the aluminum boat. If a disk did not form, see if the material can be rolled into a ball or gathered on a wooden stick. Each lab section should design a method appropriate for testing the polymers isolated. Be creative and consider the properties observed. An example of a flexibility test would be to clamp the polymer to a ring stand. Use a paper clip to hang a weight, such as the cork ring. Use a protractor to measure the degree of bending and record. Compare the physical and mechanical properties of all of the synthesized polymers within your lab section (e.g. odor, color, flexible, stiff, sticky, brittle, opaque, etc.) and carefully record all data for discussion in your worksheet or laboratory report. Was a difference observed between the triblock polymers prepared from poly( $\delta$ -decalactone) versus poly( $\delta$ -dodecalactone)? Was a trend observed for the different target poly(L-lactide) content in one or both series? Did the calculated average number molecular weights (more accurately molecular mass) and poly(L-lactide) composition from the  $^1\text{H}$  NMRs agree with the theoretical values expected?



### **Waste Disposal**

The polymer filtrate (containing mostly methanol and ethyl acetate) should be disposed of in the **ORGANIC SOLVENT HAZARDOUS WASTE**. The vial and all glassware that come in contact with the polymers should be rinsed immediately with acetone into the **ORGANIC SOLVENT HAZARDOUS WASTE**. The aluminum tins can be placed in the green trash cans. Please save your products until directions are received from your TA.

### Calculation of Theoretical $M_n$ (Number Average Molar Mass)

The  $M_n$  is described as the total molecular weight of all the polymer chains in a sample divided by the number of polymer chains. Additionally, it is assumed that all of the monomer(s) used is divided evenly between the moles of initiator so that the number of repeat units,  $n$ , can be calculated as follows:

$$\# \text{monomer repeat unit per polymer} = \frac{\text{mol monomer}}{\text{mol initiator}}$$

The theoretical  $M_n$  can then be calculated using the molecular mass of the initiator, 1,4-benzenedimethanol, plus the number of repeat units of monomer(s) times the molecular mass of the monomer(s).

**Table 2: Common Terms Used to Describe Polymers and Copolymers**

Symbol	Term	Definition
$M_n$	<b>number average molar weight (mass)</b>	The total molecular weight of all the chains in the polymer sample divided by the number of polymer chains in the sample
$M_w$ ( $M_n$ is now recommended)	<b>weight (mass) average molecular mass</b>	A weighted average that takes into account the weight fraction of each chain. Since heavier chains are given more weight in averaging, $M_w > M_n$ unless the sample is made up of chains that are all exactly the same length
$\bar{D}$ (PDI)	<b>Dispersity</b> (formerly polydispersity)	A measure of the distribution of polymer chains in a sample. $\bar{D} = M_w/M_n \geq 1$ , The larger the dispersity the greater the variation in chain length. A uniform polymer has a dispersity close to 1.
$T_m$	<b>melting temperature</b>	Temperature, upon heating, where the crystalline domains of a semi-crystalline polymer transition from an ordered solid to an amorphous liquid. For a semi-crystalline polymer $T_m > T_g$
$T_g$	<b>glass transition temperature</b>	Temperature, upon heating, where the amorphous domains of a polymer transition from an amorphous solid to an amorphous liquid and softening is observed
$T_c$	<b>ceiling temperature</b>	The temperature at which a monomer at a specified concentration will not polymerize. That is the rates of depolymerization and polymerization are equal.
	<b>chain-growth polymerization</b>	A type of polymerization where monomers add to the propagating site of a growing polymer chain one at a time.
	<b>living polymerization</b>	A specific type of chain-growth polymerization in which a polymer chain grows without the ability to terminate. In addition the polymerization must also occur without chain transfer; that is, the propagating species remain on the polymer chain and does not get transferred to monomer or solvent.
	<b>ring-opening polymerization</b>	A specific form of chain growth polymerization where cyclic monomers are opened as they add to propagating polymer. The driving force for ROP is usually, but not always the release of monomer ring strain.
	<b>amorphous regions of a polymer</b>	Regions of a polymer where chains are randomly arranged in space and have weak intermolecular interactions

	<b>crystalline</b> regions of a polymer	Ordered regions of a polymer where strong intermolecular interactions exist (crystallites). Examples of interactions are van der Waals or hydrogen bonding.
	<b>thermoplastic</b>	A class of material that can become pliable or moldable above a specific temperature and returns to a solid upon cooling.
	<b>elastomer</b>	Polymeric material that can be deformed to large strains and recover from this strain (a rubbery material that is stretchy).
TPE	<b>thermoplastic elastomer</b>	Mixture of polymers (copolymer) with both thermoplastic and elastomer properties (elastic materials that can be molded)