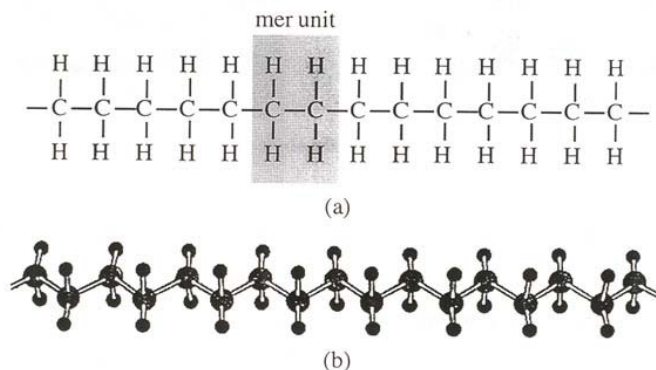


## ESc 22 Lab #9: Temperature Dependence of Stiffness of Polymers

Polymers consist of long molecules composed of smaller, repeating-unit molecules known as “mers”. A single “mer” is called a monomer and the term “polymer” means many, many mer units. Within and between each molecule, the atoms are bound together primarily by strong, covalent bonds. This makes polymeric molecules rather gigantic, “macromolecules”, with long, flexible chains. There is usually a backbone and a chain structure, as shown in the figure of polyethylene:



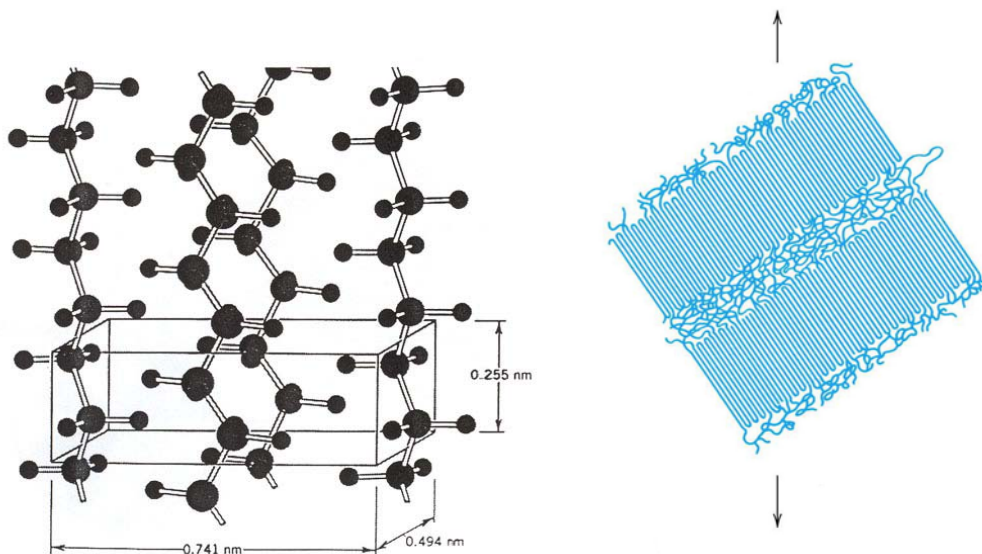
**Figure 1: Schematic representations of polyethylene. (a) The “mer” and chain structure of carbon and hydrogen atoms. (b) A perspective view of the molecule, showing the zigzag backbone structure.**

Polymers can have four different type of molecular structures. They can be linear, branched, crosslinked, or networked. In linear polymers, the mers are joined together end to end in single chains. The long chains are flexible and may be considered as a mass of spaghetti. Extensive van der Waals bonding between the chains exist in these polymers. Branched polymers have side-branch chains that are connected to the main ones. These branches result from side reactions that occur during the synthesis of the polymer. The formation of side branches reduces the chain packing efficiency, resulting in a lowering of the polymer density. In crosslinked polymers, adjacent linear chains are joined to one another at various positions along their lengths. Generally, crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Network polymers are more three-dimensional and therefore tend to be very rigid. The type of molecular structure affects its behavior in relationship to temperature. Polymers that become easier to slide and move upon increase in temperature are called thermoplastics and polymers that become harder to slide and move upon increase in temperature are called thermosets (like epoxies). In general, as the strength of the connections between the chains increase, the thermal and mechanical stability of the material increases. These connections might be intermolecular bonds (van der Waals, dipolar, or H bonds) or covalent crosslinks.



**Figure 2: Schematic illustrations of (a) linear, (b) branched, (c) crosslinked, and (d) network 3-D molecular structures. The circles indicate individual mer units.**

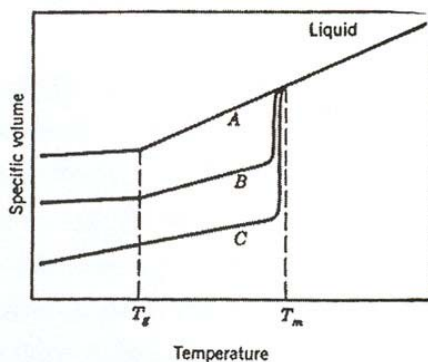
While many polymeric materials are amorphous, some can also exist in a crystalline state. The atomic arrangements in polymers are more complex than in metals, since they involve the configuration of large molecules instead of individual atoms. So polymer crystallinity is the packing of molecular chains so that an ordered molecular array is produced. Yet, crystal structures in these materials can still be specified in terms of unit cells. The unit cell for polyethylene has orthorhombic symmetry.



**Figure 3: (left) The arrangement of molecular chains in a unit cell of crystalline polyethylene, C-H, (right) schematic of a semicrystalline polymer.**

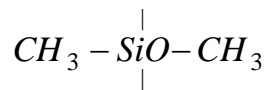
In most cases, polymers are only partially crystalline, having crystalline regions interspersed with amorphous material. The degree of crystallinity may range from completely amorphous to almost entirely crystalline (~95%). The density of a crystalline polymer is greater than its amorphous state, since the chains are more closely packed together in the crystalline state.

The melting temperature  $T_m$  and glass transition temperature  $T_g$  for a polymer are clearly shown in a plot of specific volume versus temperature. For the crystalline material, there is a discontinuous change in specific volume at the melting temperature,  $T_m$ . The curve of the amorphous material is continuous, but upon cooling, it experiences a slight decrease in slope at the glass transition temperature,  $T_g$ . Below  $T_g$ , the material is considered to be amorphous. Above  $T_g$ , it is a rubbery solid and then a viscous liquid. For a semicrystalline polymer, the behavior is between these two extremes. Both  $T_m$  and  $T_g$  are observed, respective of the crystalline and amorphous phases. Therefore, as in a glass, the temperature at which a noncrystalline ceramic or polymer transforms from a supercooled liquid to a rigid glass upon slow cooling is the glass transition,  $T_g$ . The molecules that are virtually frozen in position below  $T_g$  start to “relax” and experience rotational and translational motions above  $T_g$ .



**Figure 4: specific volume vs. temperature, upon cooling from the liquid melt, for totally amorphous (A), semicrystalline (B), and crystalline (C) polymers.**

**Procedure:** In this experiment, we will study the elastic deformation of a crosslinked silicone rubber ball by measuring the rebound height of the ball as a function of temperature. The “mer” from which silicone rubber is built upon is shown in the figure below. The objective is to relate the rebound height of the ball to the temperature dependent elastic moduli and associated modes of deformation.



1. Split up into 2 groups of 3-4 people. Assign a ball-dropper, a time-keeper, two height-watchers, one-ball catcher, one temperature-measurer, and one data-recorder.
2. Take a polymer ball and measure its temperature by inserting the thermocouple into the drilled 1 cm deep hole in the polymer ball. Record its temperature.
3. Put on protective gloves and carefully take a polymer ball that has been immersed and soaked in liquid nitrogen (for at least 10 minutes – ask professor for actual time if you want). Be careful not to drop the ball on the ground or freeze your hand in the liquid N<sub>2</sub>!
4. Acting quickly, insert the thermocouple into the hole of the frozen ball. Let the temperature equilibrate for a few seconds, then read and record the temperature. Have your ball-dropper in position!
5. As soon as possible after the temperature measurement, release the ball from the 6-ft mark and measure the rebound height. Do not let the ball bounce more than once – the ball-**catcher** must be "on the ball" to accomplish this! The ball-**dropper** must be careful to only *release* the ball and not GIVE it a bounce or throw it towards the ground. The height-**watchers** must be attentive and quick.
6. Immediately after the ball is caught, quickly record the temperature and time of recording.
7. Repeat this ball-dropping and temperature-measuring procedure quickly and carefully until the ball warms up to room temperature again. You should have at least 30 data points.
8. In your notebook, roughly plot the rebound height as a function of temperature.
9. Identify any interesting temperature points.
10. Explain the observed trend in rebound height with temperature.

### Questions to Discuss and Answer:

1. What do you think the liquid nitrogen did to the microstructure/polymer bonding of the ball?
2. What do you think is happening to the microstructure and bonding of the silicone as it is slowly warming up to room temperature?
3. Describe the “bounce-ability” or stiffness of your silicone ball. How does bounce-ability relate to Young’s modulus? Did you observe a dependence of Young’s modulus on temperature?
4. What are the causes of stiffness? Are they the same at really low temperatures and at room temperature? Correspond the mode of deformation to the microstructure to the changes in temperature.
5. Define  $T_g$  and  $T_m$  in your own words.
6. Did you observe a  $T_m$  or a  $T_g$  or both?
7. Is this an amorphous, semicrystalline, or crystalline polymer?
8. Be sure to provide a plot of rebound distance vs. temperature and rebound distance vs. time in your lab report and comment and evaluate each plot in the discussion section.
9. Read pages 484-488 in your textbook for further insight into what happened to your silicone ball microstructurally and mechanically upon increase in temperature.