

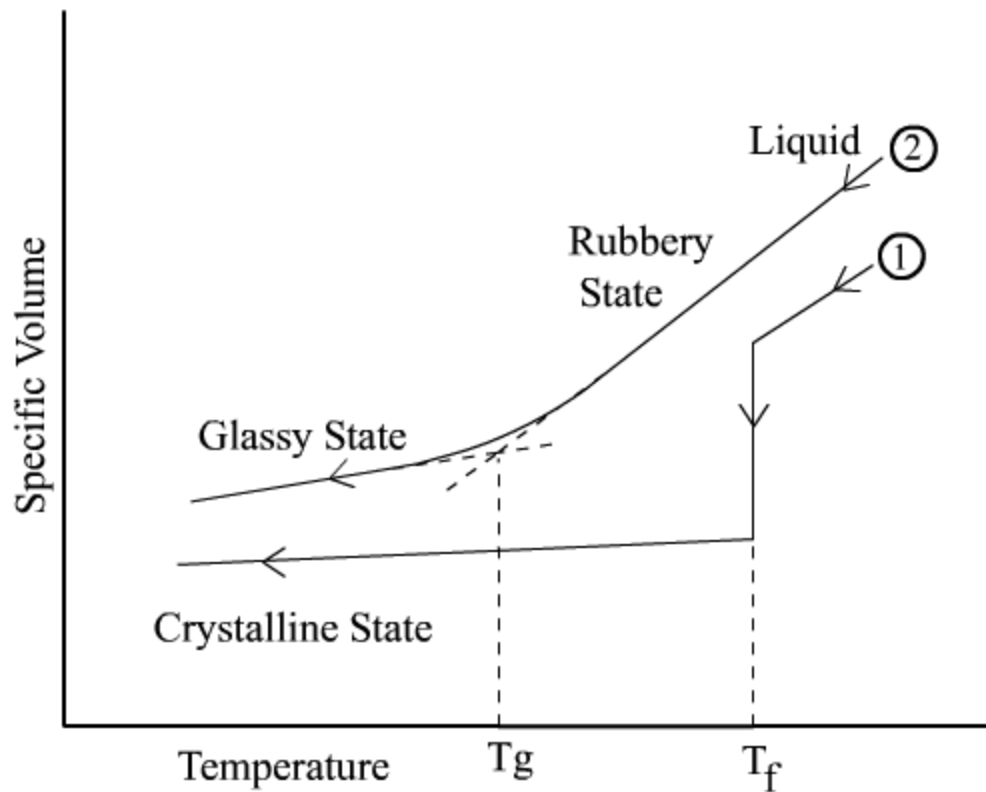
Thermal Properties of Polymers

Polymer Glass Transition

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature, T_g . As the temperature of a polymer drops below T_g , it behaves in an increasingly brittle manner. As the temperature rises above the T_g , the polymer becomes more rubber-like. Thus, knowledge of T_g is essential in the selection of materials for various applications. In general, values of T_g well below room temperature define the domain of elastomers and values above room temperature define rigid, structural polymers.

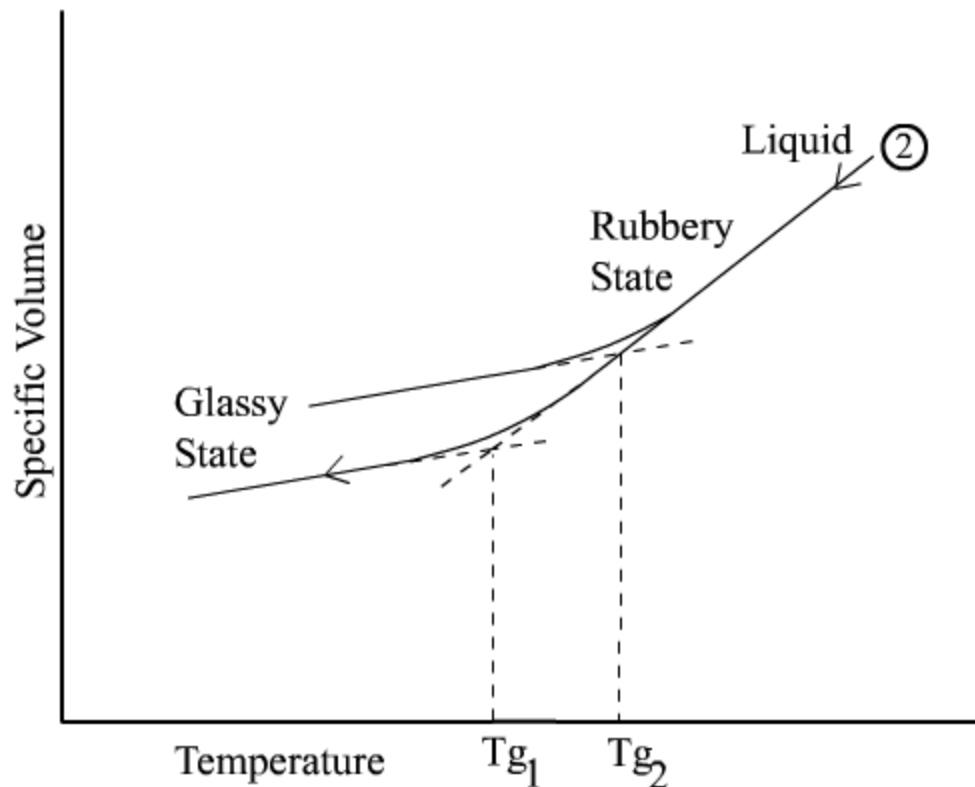
This behavior can be understood in terms of the structure of glassy materials which are formed typically by substances containing long chains, networks of linked atoms or those that possess a complex molecular structure. Normally such materials have a high [viscosity](#) in the liquid state. When rapid cooling occurs to a temperature at which the crystalline state is expected to be the more stable, molecular movement is too sluggish or the geometry too awkward to take up a [crystalline](#) conformation. Therefore the random arrangement characteristic of the liquid persists down to temperatures at which the viscosity is so high that the material is considered to be solid. The term glassy has come to be synonymous with a persistent non-equilibrium state. In fact, a path to the state of lowest energy might not be available.

To become more quantitative about the characterization of the liquid-glass transition phenomenon and T_g , we note that in cooling an amorphous material from the liquid state, there is no abrupt change in volume such as occurs in the case of cooling of a crystalline material through its freezing point, T_f . Instead, at the glass transition temperature, T_g , there is a change in slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value in the rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in the figure below. Note that the intersections of the two straight line segments of curve (2) defines the quantity T_g .



The specific volume measurements shown here, made on an amorphous polymer (2), are carried out in a dilatometer at a slow heating rate. In this apparatus, a sample is placed in a glass bulb and a confining liquid, usually mercury, is introduced into the bulb so that the liquid surrounds the sample and extends partway up a narrow bore glass capillary tube. A capillary tube is used so that relatively small changes in polymer volume caused by changing the temperature produce easily measured changes in the height of the mercury in the capillary.

The determination of T_g for amorphous materials, including polymers as mentioned above, by dilatometric methods (as well as by other methods) are found to be rate dependent. This is schematically illustrated in the figure below, again representing an amorphous polymer, where the higher value, T_{g2} , is obtained with a substantially higher cooling rate than for T_{g1} .



We can understand this rate dependence in terms of intermolecular relaxation processes. Since a glass is not an equilibrium phase, its properties will exhibit a time dependence, or physical aging. The primary portion of the relaxation behavior governing the glass transition in polymers can be related to their tangled chain structure where cooperative molecular motion is required for internal readjustments. At temperatures well above T_g , 10 to 50 repeat units of the polymer backbone are relatively free to move in cooperative thermal motion to provide conformational rearrangement of the backbone. Below T_g , the motion of these individual chains segments becomes frozen with only small scale molecular motion remaining, involving individual or small groups of atoms. Thus a rapid cooling rate or "quench" takes rubbery material into glassy behavior at higher temperatures (higher T_g).

While the dilatometer method is the more precise method of determining the glass transition temperature, it is a rather tedious experimental procedure and measurements of T_g are often made in a differential scanning calorimeter (DSC). In this instrument, the heat flow into or out of a small (10 – 20 mg) sample is measured as the sample is subjected to a programmed linear temperature change. This will be discussed in the next section. There are other methods of measurement such as density, dielectric constant and elastic modulus which are treated in texts on polymers. These methods are, of course, also rate dependent.

T_g and Mechanical Properties

Another important property of polymers, also strongly dependent on their temperatures, is their response to the application of a force, as indicated by two main types of behavior: *elastic* and *plastic*.

Elastic materials will return to their original shape once the force is removed. Plastic materials will not regain their shape. In plastic materials, flow is occurring, much like a highly viscous liquid. Most materials demonstrate a combination of elastic and plastic behavior, showing plastic behavior after the elastic limit has been exceeded.

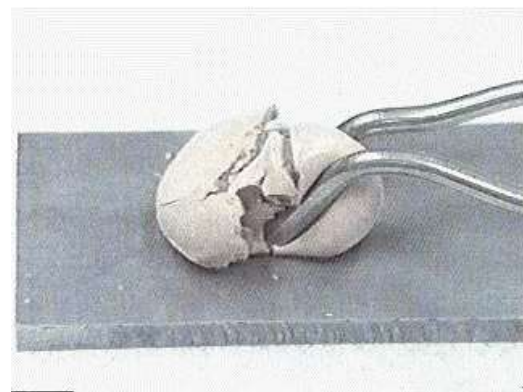
Glass is one of the few completely elastic materials while it is below its T_g . It will remain elastic until it reaches its breaking point. The T_g of glass occurs between 510 and 560 degrees C, meaning that it will always be a brittle solid at room temperature. In comparison, polyvinyl chloride (PVC) has a T_g of 83 degrees C, making it good, for example, for cold water pipes, but unsuitable for hot water. PVC also will always be a brittle solid at room temperature.

Adding a small amount of [*plasticizer*](#) to PVC can lower the T_g to -40 degrees C. This addition renders the PVC a soft, flexible material at room temperature, ideal for applications such as garden hoses. A plasticized PVC hose can, however, become stiff and brittle in winter. In this case, as in any other, the relation of the T_g to the ambient temperature is what determines the choice of a given material in a particular application.

A striking example of the rate dependence of these viscoelastic properties is furnished by Silly Putty. Slowly pulling on two parts of the Silly Putty stretches it apart until it very slowly separates. Placing the Silly Putty on a table and hitting it with a hammer will shatter it.



Slowly Deformed



Rapidly Deformed

Photos courtesy of Geon Corp.

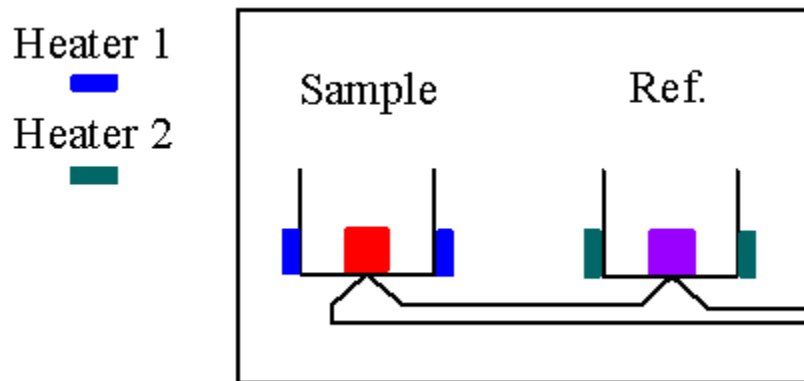
The above images are representative of the behavior of a material above and below its glass transition temperature. The image on the (left) is Silly Putty that has been slowly stretched. The image on the (right) is Silly Putty which has been hit with a hammer. The speed of the hammer raised the rate of the application of the force and in turn raised the T_g . This caused the Silly Putty to react as if it were below its T_g and to shatter. Even though both reactions took place at the same ambient temperature, one reaction appeared to be above the effective T_g and the other appeared to be below.

Our focus has been on amorphous polymers in the preceding discussion but we have hardly touched on their mechanical properties. A further complication arises in dealing with general polymers from their semi-crystalline morphology in which amorphous regions and crystalline regions are intermingled. This gives rise to a mixed behavior depending on the percent crystallinity and on their

temperature, relative to T_g of the amorphous regions. You are referred to texts on polymer science for basic discussion of these topic but the inhomogeneity of the material and its characteristics presents interesting analytical challenges.

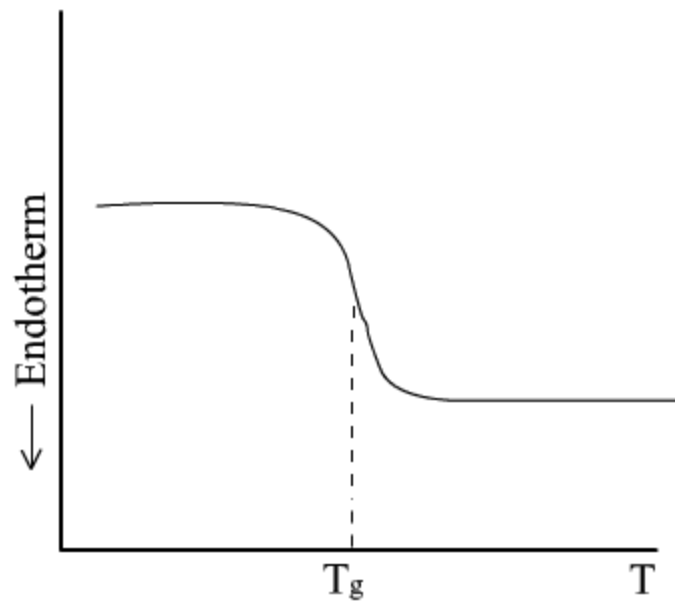
Differential Scanning Calorimetry

In differential scanning calorimetry (DSC), the thermal properties of a sample are compared against a standard reference material which has no transition in the temperature range of interest, such as powdered alumina. Each is contained in a small holder within an adiabatic enclosure as illustrated below.



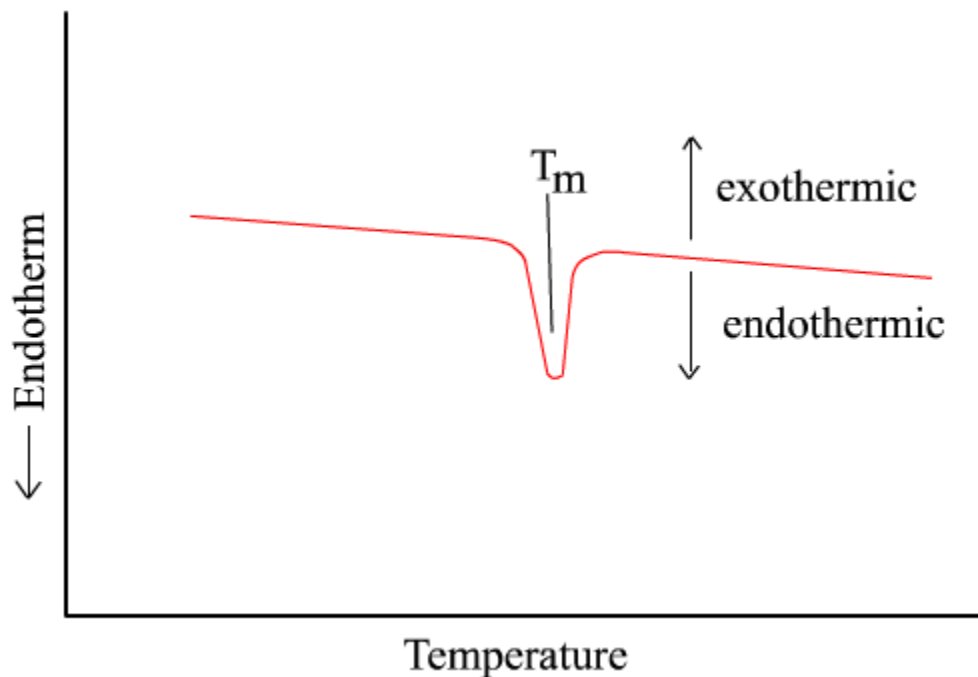
The temperature of each holder is monitored by a thermocouple and heat can be supplied electrically to each holder to keep the temperature of the two equal. A plot of the difference in energy supplied to the sample against the average temperature, as the latter is slowly increased through one or more thermal transitions of the sample yields important information about the transition, such as latent heat or a relatively abrupt change in heat capacity.

The glass transition process is illustrated in the figure below for a glassy polymer which does not crystallize and is being slowly heated from below T_g .



Here, the drop marked T_g at its midpoint represents the increase in energy supplied to the sample to maintain it at the same temperature as the reference material, due to the relatively rapid increase in the heat capacity of the sample as its temperature is raised through T_g . The addition of heat energy corresponds to this endothermal direction.

A melting process is also illustrated below for the case of a highly crystalline polymer which is slowly heated through its melting temperature:



Again, as the melting temperature is reached, an endothermal peak appears because heat must be

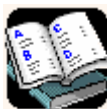
preferentially added to the sample to continue this essentially constant temperature process. The peak breadth is primarily related to the size and degree of perfection of the polymer crystals.

Note that if the process were reversed so that the sample were being cooled from the melt, the plot would be inverted. In that case, as both are being cooled by ambient conditions, even less heat would need to be supplied to the sample than to the reference material, in order that crystals can form. This corresponds to an exothermal process.

Use of the DSC will be illustrated again in the section on liquid crystals in connection with the identification of their phase transitions. An interesting exercise for the reader would be to predict the general form of a DSC plot for a semicrystalline polymer which has been rapidly quenched from the melt to a temperature below T_g . In the DSC plot, assume the temperature is slowly increased from this value below T_g to a value well above, thus allowing for significant increases in the chain mobility as temperatures above T_g are reached so that some crystallization can begin, well before the melting point is reached.



Polymer
Morphology



Applications of
Polymers

