THE GLASSY STATE:
DETERMINATION OF THE GLASS TRANSITION OF POLYSTYRENE USING
DIFFERENTIAL SCANNING CALORIMETRY

Objective:

The objectives of this experiment are:

1. to measure the glass transition temperature of polystyrene of known number average molecular weights using differential scanning calorimetry.

2. to determine the dependence of the glass transition temperature as a function of the average molecular weight.

Text Reference:


Introduction:

The nature of the physical state or morphology of solid polymers differ significantly from typical, low molecular weight compounds. Most polymers simultaneously exhibit sharp features typical of three-dimensionally ordered, crystalline solids and the diffuse characteristics of highly viscous liquids. The terms crystalline and amorphous are used to describe the ordered and unordered polymer domains, respectively. Differing degrees of crystalline behavior are exhibited by different polymers. Some polymers are highly crystalline, some may be either amorphous or crystalline depending on the conditions of crystallization and some are completely amorphous.

The exact nature of polymer crystallinity is open to interpretation. The fringed-micelle theory considers polymers to consist of small, ordered crystalline regions interspersed in a unordered, amorphous matrix. The folded-chain lamella (thin platelets) theory describes the polymer molecules as folding back and forth on themselves in an accordionlike manner in the process of crystallization. Less than 100% crystallinity is attributed to defects in the chain-folding process, such as imperfect folds, packing irregularities, chain entanglements, loose chain ends or occluded impurities.
Polymeric materials are characterized by two types of transition temperatures: the crystalline melting temperature $T_m$ and the glass transition temperature $T_g$. The crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample, whereas, the glass transition temperature is the temperature at which the amorphous domains of a polymer take on the characteristics of the glassy state. At sufficiently low temperatures, all polymers assume the characteristics of glasses, including hardness, stiffness and brittleness. A material in the glassy state exhibits a low volume coefficient of expansion. This low coefficient occurs as the result of a change in slope of the curve of volume vs. temperature at the glass-transition temperature, $T_g$.

The amorphous regions in partially crystalline polymers, such as polystyrene, can assume a glassy state, where to a first approximation, $T_g$ is independent of the degree of crystallinity. However, with increasing amorphous content, the size of the phenomena associated with $T_g$ decreases. Therefore, $T_g$ is sometimes difficult to detect in highly crystalline polymers. The glass transition is considered to involve defect regions within or at the boundaries of the lamellae.

The glass-transition temperature can be detected in a variety of experiments. These experiments can be classified as either dealing with the bulk properties of the polymer and those measuring the nature and degrees of molecular motion. Although the measurement of the volume expansion coefficient is perhaps the most common way of estimating $T_g$, the marked change in the heat content can also be used to determine $T_g$.

In this experiment the glass-transition temperature, $T_g$, will be determined for a set of known number average molecular weight polystyrenes samples. The $T_g$ of polystyrene is given by the relationship,

$$T_g = A - B/M_n$$

where, $A$ and $B$ are constants and $M_n$ is the number average molecular weight. Therefore, a plot of the $T_g$ of a series of polystyrene samples of known $M_n$ vs $1/M_n$ will permit a determination of the constants $A$ and $B$ for polystyrene.

**Experimental:**

Prepare 7-10 mg samples of the polystyrenes of known average molecular weight. A TA will demonstrate the proper technique for preparation and encapsulation of samples and for loading of the DSC furnace. **CAUTION!! FAILURE TO PROPERLY PREPARE SAMPLES AND LOAD THE SAMPLE IN THE DSC CAN RESULT IN DAMAGE TO THE INSTRUMENT.!!!**
Use the following procedure to acquire data:

1. From the Main Menu, select Set Up and Run, F2.

2. Select, Recall Method, F2 and using the mouse click on "PTest" followed by Recall File, F8.

3. Select, Modify Parameter on the Set Up and Run menu to enter your own information concerning Sample ID, Comment, Operator ID, File Name and Sample Weight. In all cases type in each modifications and press Enter to change the entry. Select Exit to end.

4. Prior to the start of the run, press F11, Go to temperature, and enter 50°C. Wait a few minutes for the system to attain this temperature and to stabilize. Both the temperature and the heat flow are displayed as well as an "X" on the y-axis.

5. To start the run, select Start Run, F8, on the Set Up and Run menu. The analyzer will run according to the parameters in the method, and the curve will be drawn in the graphics window of the screen as the data is collected. [In this experiment, the temperature will initially by ramped from ambient to 270°C at a rate of 40°C/min, then cooled back to ambient at a rate of 50°C/min and finally ramped up to 150°C at a rate of 20°C/min.]

6. To stop a run in progress, select Stop Run, F7, in the displayed menu. Press Enter to continue.

Use the following procedure to analyze data:

1. To select the segment you wish to analyze, first de-select the highlighted segment using the mouse and highlight the desired segment. Select Display Segments, F1. To change the display limits, select Optimize Data, F5, followed by Rescale, F2. Use the Type in X Limits and Type in Y Limits function keys and type in the limits. Pressing Rescale, F2, after entering the limits will rescale the display. Select Exit, F1,(twice) to return to the Run menu.

2. Select Select Calc, F6, followed by Tg/Step, F3; two X-shaped cursors will appear at the first and last points displayed on the screen. The X and Y positions of the cursors will also be displayed above the screen, and a new menu will be displayed.

3. Move the mouse pointer to select the left limit and left-click. Move the mouse pointer to select the right limit and right-click.
4. Select **Calculate**, F2; two lines appear on the screen tangent to the curve. Adjust the tangent lines using the cursor keys. The currently selected tangent line appears white and has a small box at one end. This is the anchor point from which the lines move. Use the up \( \uparrow \) or down \( \downarrow \) cursor keys to move the other end of the line to the desired location (tangent to the curve). Use the right \( \rightarrow \) and left \( \leftarrow \) cursor keys to increase or decrease the size of the up or down steps. Press the **Home** key to select the other line. Use the up \( \uparrow \) or down \( \downarrow \) cursor keys to move the end of this line to the desired location (tangent to the curve).

5. Select **Calculate**, F2, again or press the **Enter** key. The calculation is automatically performed and the curve with the calculated results is displayed on the screen. Obtain a print out of the display by pressing the **Print Scrn** key.

6. Using the **Exit** keys, (F1, twice) return to the **Set Up and Run** menu.

Repeat the collection and analysis procedures for all the samples.

**Reporting the Results:**

Make a plot of the glass transition temperatures, \( T_g \), for the various polystyrene standards vs. \( 1/M_n \). From this plot, determine the coefficients \( A \) and \( B \) for polystyrene in equation 1. At what temperature would you predict the glass transition in polystyrene of infinite molecular weight?