# 3.014 MATERIALS LABORATORY
## γ2 Module
## Fall 2005

# GLASS TRANSITIONS
# in POLY(METHACRYLATES)

## OBJECTIVE:

•       To determine the glass transition temperature of various methacrylate polymers, using differential scanning calorimetry (DSC).

## WHAT IS GLASS TRANSITION? [1,2,3,4]

•       A thermal property, characteristic of amorphous and semi-crystalline polymers.

*       Identified by a characteristic temperature, $T_g$ (the glass transition temperature), representing a transition of the polymer, from a "rubbery" or "leathery state" to a "glassy state".

*       Represents a change in the mechanical behavior of a polymer.

Below the $T_g$, a polymer is stiff, hard and brittle, and above the $T_g$, a polymer is pliable, soft, and tough.
Changes in the elastic modulus.

•       Manifestation of the changes in the mobility of the polymer chains.

Above $T_g$, the long-range motion (i.e., the segmental motion) of the polymer chains is increased. e.g, chain bending, bond rotation about the segment ends. (Increase in the kinetic energy of the molecules).

Below $T_g$, the chain mobility is suppressed.

Note: Polymer chains lack long-range translational motion.

•       Represents changes in the thermodynamic properties of a polymer.
  •       Heat capacity changes
  •       Entropy changes

- A second order transition.

  Involves a change in the heat capacity at $T_g$.  No latent heat involved, as in the case of melting, which is a first order transition (discontinuous change in the heat capacity at the phase transition temperature).

- $T_g$ can vary over a wide range of temperatures ( $< - 100\ °C$  to $> 100\ °C$ ) for various polymers.

Some factors affecting Tg

- Polymer structure (structural rigidity/ chain mobility)
  Intermolecular forces (secondary forces of polymer chains)
  Chemical composition
  Molecular weight

- Experimental factors –
  Processing
  The rate of heating / cooling
  Thermal history

# EXPERIMENTAL TASKS:

- Determine the glass transition temperatures of various poly(methacrylate) samples from the Heat Flow vs. Temperature measurement, using Differential Scanning Calorimetry (DSC).

- Verify the dependence of $T_g$ on the
  polymer structure
  heating rate
  thermal history

- Determine the specific heat capacity of selected polymer samples in the "glassy" state and in the "polymeric" state.

# MATERIALS:
From Scientific Polymer Product Inc.

Poly(methyl methacrylate), PMMA,  plexiglas / lucite
Poly(ethyl methacrylate)
Poly(n-propyl methacrylate)
Poly(n-butyl methacrylate)
Poly(n-hexyl methacrylate)
Poly(cyclo-hexyl methacrylate)

Methacrylates [2,3] are a series of polymers that belong to the class of addition or vinyl polymers, having the characteristic feature of a carbon – carbon double bond (C = C) in their monomers. Their structure is represented by a $CH_2 = C - CH_3$ group [Note: CH3 -> methyl], attached to a carbonyl functional group as shown below. Hence, they are esters.

H                                        CH₃

C ══ C

HꞰ                            CꞰ══    OꞰ

OꞰ

RꞰ
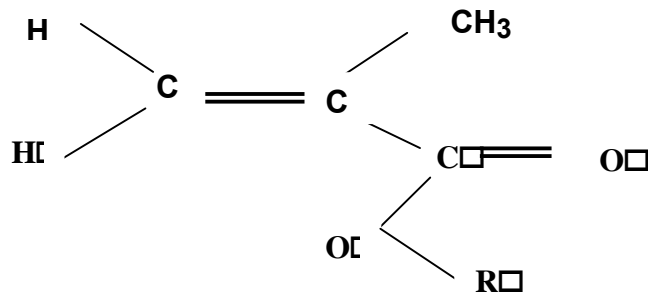
A series of methacrylates can be generated by substituting R with representative functional groups, for e.g., R = $CH_3$, in methyl (methacrylate), R = $CH_3CH_2$ in ethyl (methacrylate) etc.
Polymerization of the methacrylate monomers yields poly(methacrylates)

e.g., polymerization of methyl methacrylate yields poly(methyl methacrylate)

HꞰ                            CH₃

C══ C

HꞰ                            CꞰ══    O

OꞰ

CH₃
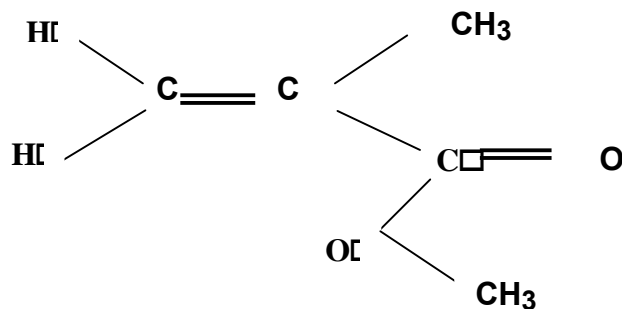
<u>Methyl methacrylate</u>
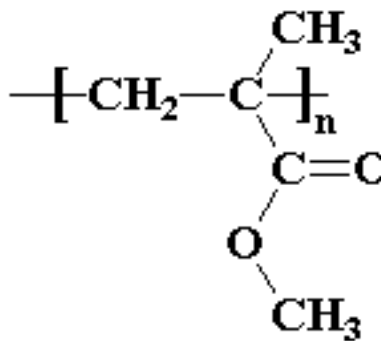
Poly(methyl methacrylate)

[The above Structure adopted from reference 3]

**EXPERIMENTAL TECHNIQUE**:

DIFFERENTIAL SCANNING CALORIMETRY [DSC] – TA INSTRUMENTS – MODEL Q100
- TA Instruments Q-series Manual on DSC[5]
- "Experimental Evaluation Of Procedures For Heat Capacity Measurements By Differential Scanning Calorimetry", K.L.RamKumar, M.K.Saxena, and S. B. Deb, Journal of Thermal Analysis and Calorimetry, vol. 66 (2001) 387-397]

DSC  is a thermal analysis technique useful for measuring thermal and thermodynamic properties of materials  such as, the specific heat, melting and boiling points, glass transitions in amorphous/semi-crystalline materials, heats of fusion, reaction kinetics etc.  The technique measures the temperature and the heat flow (in desired units, mW, W/g etc.) corresponding to the thermal performance of  materials, both as a function of time, and temperature.

The TA Instruments DSC is a "HEAT FLUX" type system where the differential heat flux between a reference (e.g., sealed empty Aluminum pan) and a sample (encapsulated in a similar pan) is measured.  The reference and the sample pans are placed  on  separate, but identical stages on a thermoelectric sensor platform surrounded by a furnace.  As  the temperature of the furnace is changed (usually by heating at a linear rate), heat is transferred to the sample and reference through the thermoelectric platform.  The heat flow difference between the sample and the reference  is  then measured by measuring the temperature difference between them using thermocouples attached to the respective stages.

The DSC provides qualitative and quantitative information on endothermic / heat absorption (e.g., melting) , exothermic / heat releasing (e.g., solidification or fusion) processes of materials.  These processes display sharp deviation from the steady state thermal profile, and exhibit peaks and valleys  in a DSC thermogram (Heat flow  vs.

Temperature profile).  The latent heat of melting or fusion can  then be obtained from the area enclosed within the peak or valley.  The glass transition is characterized by a steady change in the slope of the heat flow vs. temperature profile,  with a corresponding change in the heat capacity of the material.

Some factors that may affect the DSC measurements are :
*   Sample positioning on the DSC  stage
     (variations in baseline)
*   Structure and mass of the sample
     (proper thermal contact )
*   Heating rate
     (Trade-off between sample  attaining thermal equilibrium and  data acquisition times.  A fast heating rate may minimize the data acquisition time compromising salient features of the material property)


## SAMPLE PREPARATION  FOR DIFFERENTIAL SCANNING CALORIMETRY [DSC] MEASUREMENTS:

Weigh 10 - 20 mg of the polymer and  spread it uniformly in a  NORMAL aluminum DSC pan to ensure proper thermal contact.  Crimp the pan with the lid.

For samples dissolved in a solvent, place a few drops of the solution in a weighed normal DSC pan, and heat it on a hot plate until the solvent is completely evaporated.  Cool the pan and record the mass of the polymer sample.


## EXPERIMENTAL PROCEDURE:

### $T_g$ MEASUREMENTS:

1.    Obtain a baseline (zero line) thermal profile (Heat Flow vs. Temperature) with **empty**, identical (equal mass) aluminum pans placed on the reference and the sample stages, respectively.

      The aluminum pan on the reference pan must be **crimped**.
      The pan on the sample stage is left uncrimped for later use.

      The baseline scan corrects for any asymmetry of the system.

      * Ideally, an independent  baseline profile  must be obtained for each sample using the same pan in which it will be placed.  However, in the present study, only one  baseline scan will be performed for all samples, assuming identical mass or volume for all the pans (select pans and lids of similar masses).

**Leave the pan on the reference stage undisturbed for the remaining measurements.**

**Scan conditions:**
Temperature range: - 50 C to 150 C
Scan rate: 20 ˚C / min

2a.    Obtain thermal profiles for the poly(methacrylate) sample series in the desired temperature range at the same scan rate, **20˚C/min**.

      **Place each crimped pan containing the weighed amounts of sample on the sample stage.**

2b.    Obtain thermal profiles for the selected poly(methacrylate) sample in the desired temperature range as a function of heating rate,
5 ˚ C / min
10˚C / min
20˚C / min

3.    Subtract the baseline data from the sample data, prior to analysis.
[Remember to change the Heat Flow (y-axis) units to mW, before subtracting the data, to ensure identical units for the sample and baseline profiles]

## SPECIFIC HEAT MEASUREMENTS:

The guidelines for heat capacity measurements provided by TA Instruments (**see handout**)[5] will be followed.

These guidelines are based on ASTM Method, D3947 – 80. [6]
(with modifications* due to time constraints)

1.    Obtain a baseline (zero line) thermal profile (Heat Flow vs. Temperature) with empty, identical (equal mass) aluminum pans placed on the reference and the sample stages, respectively.

      The aluminum pan on the reference pan must be **crimped**.
The pan on the sample stage is left uncrimped for later use.

      The baseline scan corrects for any asymmetry of the system.

      * Ideally, an independent baseline profile must be obtained for each sample using the same pan in which it will be placed. However, in the present study,

only one  baseline scan will be performed for all samples, assuming identical mass or volume for all the pans (select pans and lids of similar masses).

**Leave the pan on the reference stage undisturbed for the remaining measurements.**

**SCAN CONDITIONS:**
Heating rate: 20°C / min
Temperature range: Sample dependent

2.    Obtain a thermal profile with a calibration standard (e.g. Sapphire) using the same scan conditions as in step 1.
Provides a calibration factor that translates the measured Heat Flow units (in mW) to Heat Capacity units (J/g°C).

**Place the crimped  pan containing the calibration standard (sapphire, mass = 25.68 mg) on the sample stage.**

3.    Obtain thermal profiles for the selected poly(methacrylate) samples using same scan conditions as in steps 1 and 2.

**Place each crimped pan containing the weighed amounts of sample on the sample stage.**

4.    Subtract the baseline data from the sample and the sapphire data, prior to analysis.
[Remember to change the Heat Flow (y-axis) units to mW,   before subtracting the data,  to ensure identical units for the sample and baseline profiles]


# ANALYSIS:

**Tg MEASUREMENTS:**

1.    Use the Universal Analysis software of  the DSC and the "GLASS TRANSITION" routine to determine from the thermal profile,  the $T_g$ for each  polymer sample.

2.    How does $T_g$ vary for the poly(methacrylates)? Plot a graph of  $T_g$ vs. the # of Carbon atoms in the functional group R for the n-series methacrylates.
[See the structure in page 3]

From the graph, estimate the $T_g$ for poly(n-pentyl methacrylate)
Present the structural formula for each polymer

3.    How does $T_g$ vary for the n-hexyl methacrylate and cyclo-hexyl methacrylate?
Display the thermal profiles for the polymers on the same plot.

Present the structural differences in these polymers.

4.    Comment on the affect of heating rate on the Tg measurement. Recommend your choice of the heating rate for future measurements.

**SPECIFIC HEAT MEASUREMENT:**
[see hand out: Quantitative Analysis – TA Instruments] [5]


1.    Calculate the specific heat ($C_p$) of the selected polymer samples @ a temperature below Tg and a temperature above Tg


$$C_p \text{ (sample)} = \frac{C_p \text{ (sapphire)} \times m \text{ (sapphire)} \times \Delta H \text{ (sample)}}{\Delta H \text{ (sapphire)} \times m \text{ (sample)}}$$

Where,

$\Delta H$ is the heat flow (in mW) at a given temperature, obtained from the baseline subtracted plot of Heat Flow (mW) vs. Temperature for each sample, and for sapphire.

m is the mass of each sample, and sapphire, in mg

Note:
•    The table in the hand-out [5] provides the $C_p$ (sapphire) values as a function of temperature. Estimate the Cp values at the desired temperature.

•    The known $C_p$ (sapphire) values at a given temperature, translates the measured Heat Flow (in units of mW) to Heat Capacity units (J / g ˚C).

•    The above equation is obtained by writing the equation for Cp, given in step 5 of reference 1, explicitly for the sample, and sapphire, and dividing the two equations.

**REFERENCES:**

1.      "POLYMERS, Structure and Bulk Properties", by Patrick Meares,
        D. Van Nostrand Company, London, 1965.

2.      Principles of polymerization", by George Odin, John Wiley and Sons, New York,
        $3^{rd}$ edition, 1991

3.      http://www.psrc.usm.edu/macrog/tg.htm

4.      Thermal Characterization of Polymeric Materials, edited by Edith A. Turi,  Press,
        1981

5.      "Guidelines for Quantitative Studies – Heat Capacity Experiments"
        TA Instruments Manual DSC 2920, 4-15.

6.      D3947- 80.  Annual Book of ASTM Standards, Part 25, ASTM, Philadelphia, PA
        (1980)