The Effect of a Substituent on the Glass Transition Temperature (T_g) of Polymers

Alisa Sment
Dr. Krystyna R. Brzezinska
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Polymers

- Polymer: Macromolecules built up by the linking together of much smaller molecules in large numbers.
- The small molecules (-M-) that link together to form polymer molecules are called monomers.

$$n\ M \longrightarrow -(M)_n-\ldots$$

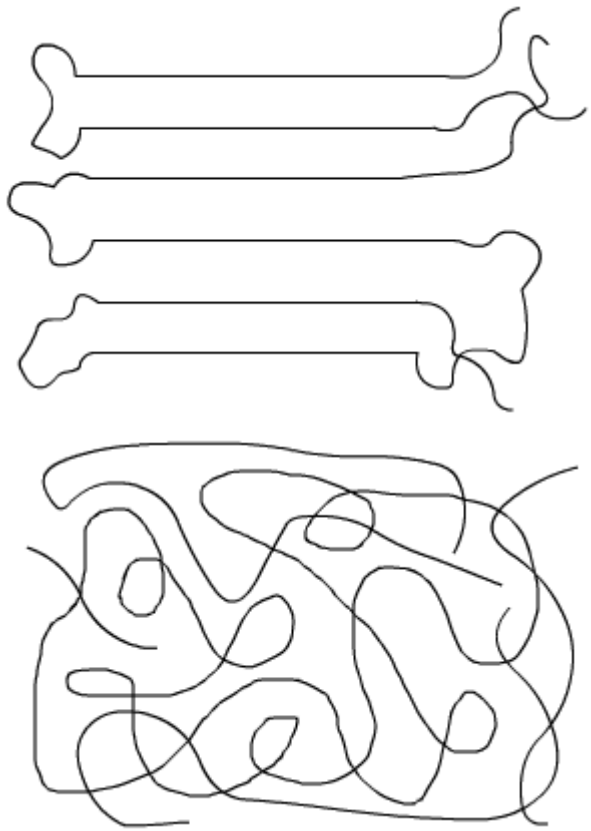
n monomers ⟶ polymer

Polymers

- Natural polymers- carbohydrates, proteins, fibers-wool-silk, rubber, natural resin…
- Synthetic polymers- plastics, fibers, rubbers, adhesives, and coatings have come on the scene as the result of a continual search for man-made substances that can perform better or can be produced at a lower cost than natural materials.

Classification of Polymers

- Crystalline materials have their molecules arranged in repeating patterns.
- Amorphous materials, have their molecules arranged randomly and in large chains that twist and turn around one another.

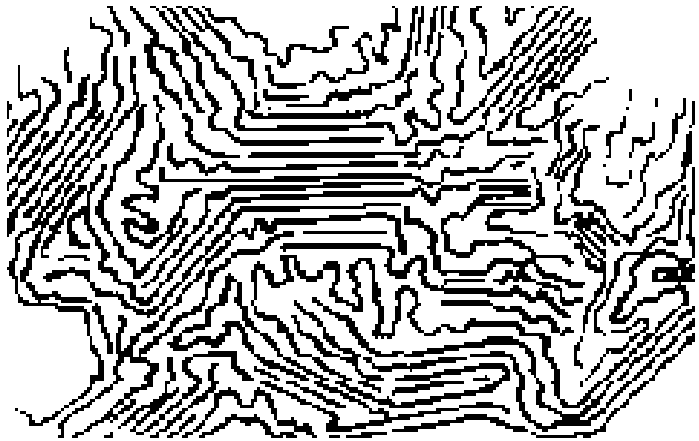


Polymers can be characterized by a melting temperature (T_m) and a glass transition temperature (T_g).

- The T_m is the melting temperature of the crystalline domains of a polymer sample.
- The T_g is the temperature at which the amorphous domains of a polymer take on the characteristic properties of brittleness, stiffness, and rigidity.

Polymer Structure

- Whether a polymer sample exhibits both thermal transitions or only one depends on its morphology. Completely amor-phous polymers show only a T_g. Crystalline polymer shows only a T_m. Semicrystalline polymers exhibit both.



Mechanical properties of a polymer

- Amorphous polymer - below T_g a polymer becomes a hard, rigid glass. Above T_g it becomes soft, rubbery, and flexible and can be shaped.

- Crystalline polymer- above the T_m crystals melt and the polymer flows. Crystalline polymers are stiffer, stronger, harder than amorphous polymers.

Industry

- Crystalline polymers: *__Fiber__-nylon-clothing *__Flexible plastic__-Polyethylene-packing supplies, seat covers.
- Amorphous polymers: *__Rigid plastic__-polystyrene-eyeglass lenses-housing for appliances *__Elastomer__-tires-rubber bands.

Differential Scanning Calorimetry (DSC)

- Thermal analysis technique can determine:

- 1.The glass transition temperature T_g
- 2. The melting temperature T_m

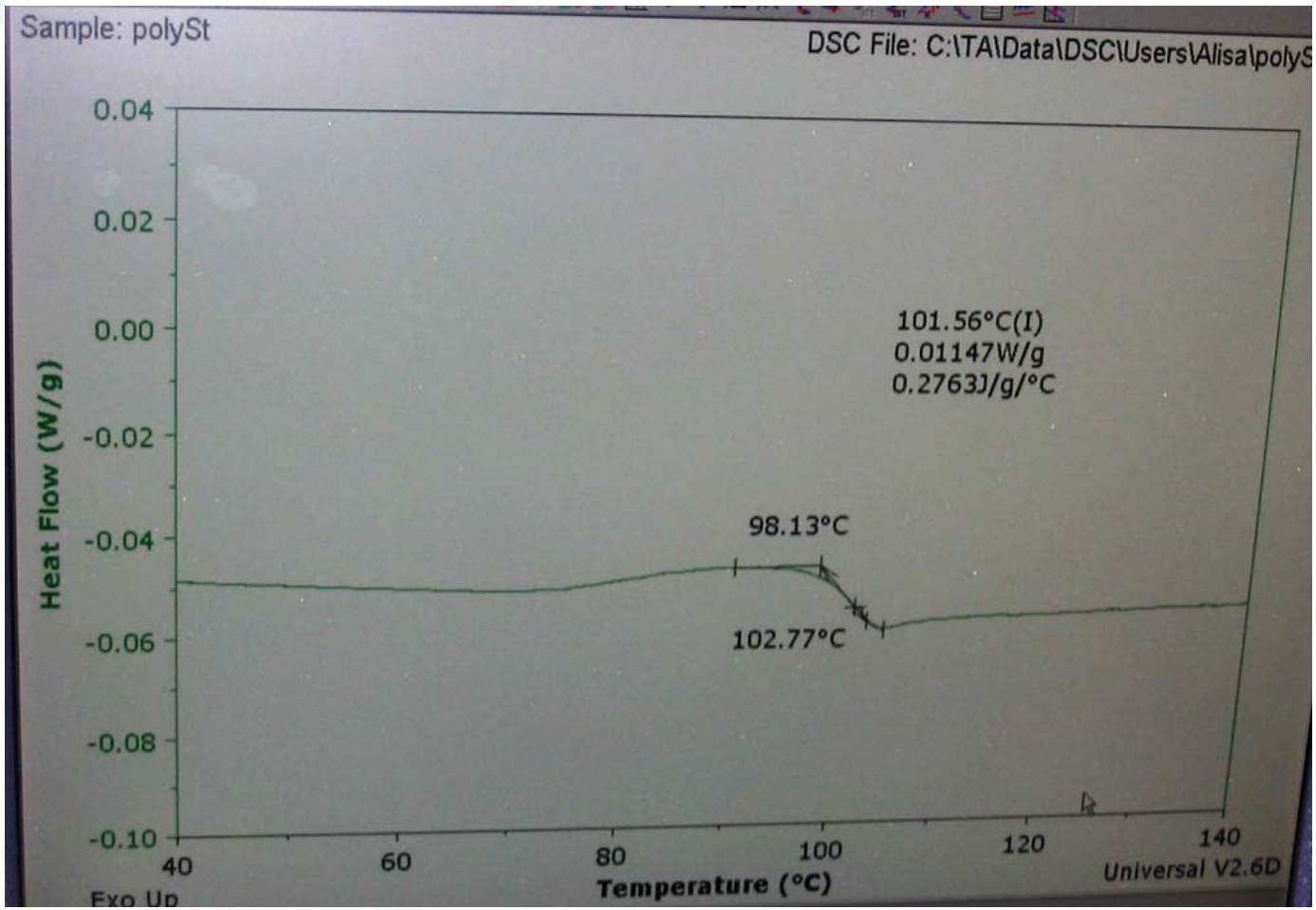
Differential Scanning Calorimetry (DSC)

- We heat our polymer (10-15 mg) in a DSC using two aluminum pans (1. with polymer 2. without polymer).
- Each pan sit on top of a heater. We heat the two pans at a rate of 10 ^{o}C/min.

DSC

- Having extra material means that it will take more heat to keep temperatures of the sample increasing at the same rate as the empty pan.
- By measuring just how much more heat it has to put out is what we measure in a DSC experiment.

DSC plot for Polystyrene

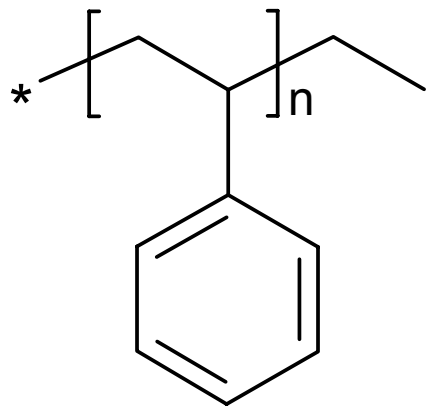


Results

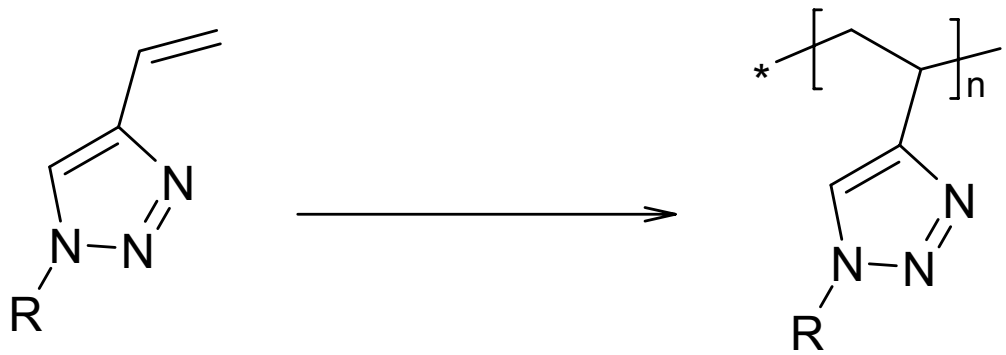
Polystyrene

T_g = 101 °C

Below 101 °C a polymer becomes a hard, rigid glass. Above T_g it becomes soft, rubbery, and flexible and can be shaped



Polymers

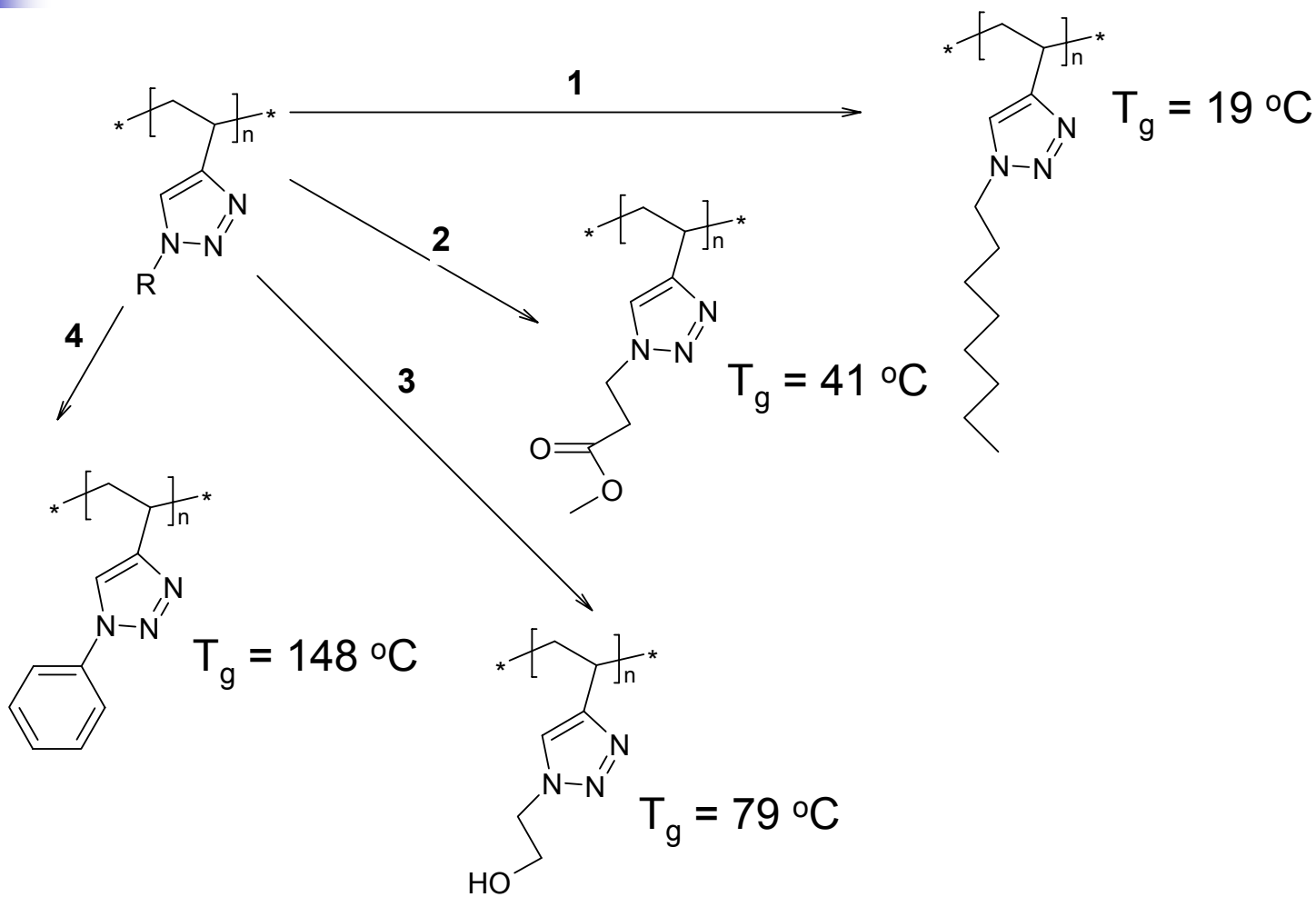


Monomer

Polymer

Dr. Raymond Thibault
Prof. Craig Hawker

Results



Conclusions

- The glass transition temp. (T_g) of a polymer can be modified by substituent -R.
- For bulky side groups-T_g is higher (4).
- For smaller substituents- T_g is lower (1).
- Interaction between substituent and the polymer also can increase T_g (3).
- Changing substituent- T_g we modify mechanical properties of a polymer and how the polymer can be used.