Chapter 2 Homework: Characterization of Polymers

Due:

Available Points: 50

1. **Describe Size Exclusion Chromatography. (4 points)**

Polymer Solution is pumped through a column of closely packed porous polystyrene gel. Gels chosen must be compatible with solvent and cannot interact w/ the polymer. As a result, cross-linked polystyrene is used to avoid interactions. Large molecules in solution pass through column first as the small molecules need to pass through each of the pours of the gels. This separates the molecules based on their size, having the largest → smallest pass through the SEC column.

2. **Describe osmotic pressure. (3 points)**

Polymer solution is separated by pure solvent via a semi-permeable membrane which is permeable by the solvent only (not the polymer). A chemical potential driving force pushes the solution until hydrostatic pressure is high enough (equilibrium is reached).

3. **List 2 advantages and 2 disadvantages of osmotic pressure. (4 points)**

This experiment gives absolute molecular weight at a relatively cheap price, with a simple measurement method. This process takes a long time to reach equilibrium, and it is rare to have a true semi-permeable membrane.

4. **What are the three advantages of FT-IR? Briefly describe each advantage. (6 points)**

(i) Jacquinot's Advantage: FT-IR does not use dispersive elements used in reg-lar IR, so there is a much higher energy throughput
Energy throughput

(ii) Connes Advantage: FT-IR uses an interferometer with mirror movement controlled by lasers, leading to higher frequency accuracy (.01 cm^{-1} vs. 1 cm^{-1})
Frequency accuracy

(iii) Fellgett's Advantage: Collected data points contain information on entire frequency range. Many data points are collected for unique information collection. This allows a more wide range analysis compared to individual
Multiplex

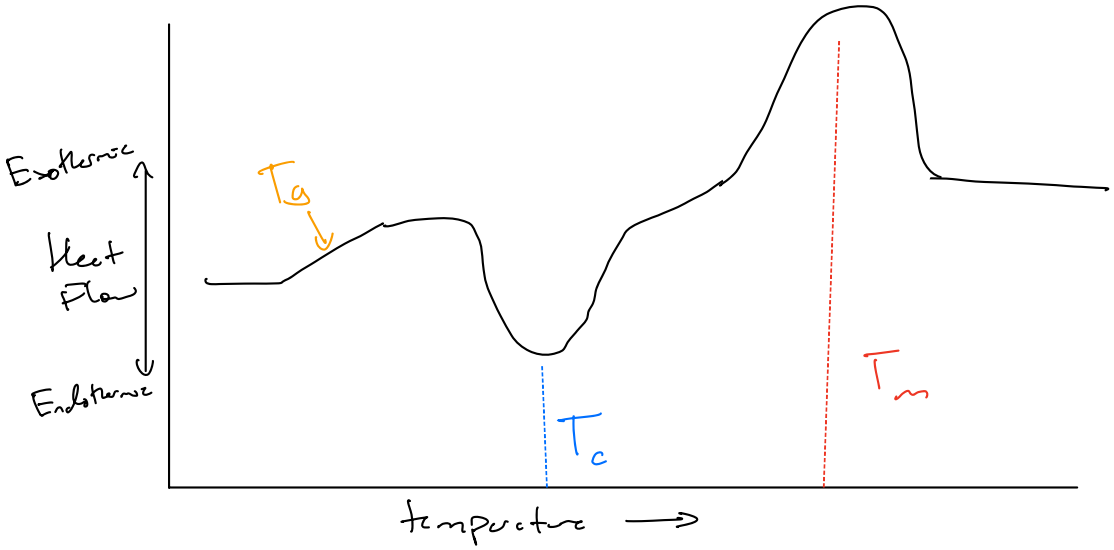
5. **Which two characterization techniques can be used to determine T_g? (2 points)**

Differential Scanning Calorimetry (DSC), and Dynamic Mechanical Analysis (DMA) are often used to determine T_g, with DSC being less accurate.

Multiple Choice. Choose the answer that is <u>NOT</u> true for each technique. (6 points)

6. Dynamic mechanical spectroscopy (DMA)
    a. It can measure viscosity
    b. It is a thermomechanical technique
    c. It measures viscoelastic properties
    d. It can measure the strength of a solid polymer
7. Size exclusion chromatography (SEC)
    a. It uses a porous polystyrene gel
    b. The molecular size is separated based on the chemical interaction
    c. The larger molecules come out of the column earlier than the small ones
    d. It is a relative molecular weight measurement technique
8. Thermogravimetric analysis (TGA)
    a. Heat flux relative to the reference material is measured
    b. Weight loss as a function of the temperature forms the basis for the thermogram
    c. Char yield is one of the important quantities measured
    d. Crystallization, melting, and T_g are the quantity that cannot be measured
9. Differential scanning calorimetry (DSC)
    a. It is a technique that can study thermal events such as liquid crystalline transitions
    b. Crystallization and melting show an endothermic peak whereas T_g shows an exothermic peak
    c. Only a few mg of sample is sufficient for the measurement
    d. Conversion of a thermosetting polymer, such as epoxy, can be studied
10. Nuclear magnetic resonance spectroscopy (NMR)
    a. ^{1}H NMR has much higher sensitivity than ^{13}C NMR in part due to the near 100% of the natural abundance of the ^{1}H atoms
    b. NMR is one of the most useful techniques to identify the number of components in an unknown sample
    c. The sensitivity of the technique increases as the strength of the main magnet used increases
    d. NMR, IR and elemental analysis are the three typical methods that are most frequently used for molecular structural identification
11. Fourier transform infrared spectroscopy (FT-IR)
    a. Infrared radiation absorbed corresponds to the vibrational energy level
    b. The energy source emits a single frequency radiation like a laser
    c. FT-IR provides higher signal-to-noise ratio than the traditional dispersive IR instruments
    d. Conne's and Fellgets' advantages are a few of the unique advantages of FT-IR

12. Draw a DSC thermogram from a semi-crystalline material. Label T_g, T_m, and T_c. Don't forget your axis labels. (4 points)



13. Choose an appropriate characterization technique from the list below that matches the situation. (8 points)

- Size exclusion chromatography (SEC)
- Nuclear magnetic resonance (NMR)
- Dynamic mechanical spectroscopy (DMA)
- Thermogravimetric analysis (TGA)
- Fourier Transform Infrared spectroscopy (FT-IR)
- Differential scanning calorimetry (DSC)
- Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS)

a. Detection of a natural polymer that was produced in different locations of the world. It is known that the isotope ratio of those locations are different and the natural polymer incorporate those isotopes. Mass differences MALDI-TOF MS

b. Studying the effect of quenching on the degree of crystallinity change DSC

c. Verifying if a polymer is a cross-linked material or a high molecular weight thermoplastic Prove thermoset properties DMA

d. Studying if a carbonyl containing polymer is hydrogen bonding to a hydroxyl containing polymer chemical composition analysis FT-IR

e. Determining if an unknown polymer is a polymer blend of homopolymers derived from monomer X and Y or a copolymer consisting of the comonomers XY SEC
Separates based on size

f. Investigating the tacticity ratio of a polymer to see if the polymer is isotactic rich or syndiotactic rich NMR Analyzes structure directly

g. To compare which polymer is more fire-safe TGA Thermal Stability

h. Gelation point upon polymerization of a benzoxazine resin DMA G' and G'' Crossing point

14. Fill in the blanks in the following paragraph with the correct characterization technique using the abbreviations from Problem 13. (5 points)

I have just synthesized a benzoxazine monomer in the laboratory. I first used NMR to confirm the monomer structure because it is the most precise way to determine the structure of my compound. To confirm that polymerization took place, I used FT-IR multiple times for different temperatures to see when the oxazine ring stretch disappeared. When this stretch disappears the polymer is formed. I used TGA and looked at the char yield to learn more about the fire retardant properties of the polymer. To study the mechanical properties, DMA was used to figure and the Tg and crosslinking density of the polymer were measured. I used the Tan δ peak to record the Tg. Lastly, I want to know the molecular weight distribution (Mn, Mw, Mz) of my polymer so SEC was used.

True or False (3 points)

Doesn't have to be empty

15. DSC detects heat flux differences between an empty sample pan and a pan with a sample. The advantage of DSC is the ability to measure thermal properties with a very limited amount (mg) of the sample. False

16. NMR is ideal in determining detailed chemical structures of liquid samples. Using the chemical shift concept, one can readily determine the chemical structure of the component in the unknown sample. NMR can also be used to study molecular mobility using relaxation times such as T_1 and T_2 relaxation. True

17. DMA is a technique used to measure rheological properties. Tan δ is often used as a useful method to determine the T_g of a polymer. However, a more precise definition of the T_g uses G'' rather than tan δ. G'' is more rigorous True

18. Draw a DMA spectra for a cross-linked material. Label G', G", and tan δ. Don't forget your axis labels. (5 points)