THE UNIVERSITY OF TEXAS AT AUSTIN
DEPARTMENT OF CHEMICAL ENGINEERING
CHE 395E

MEASUREMENT OF THE VISCOSITY AVERAGE MOLECULAR WEIGHT OF POLYSTYRENE

I.Object

Viscosity average molecular weights of the polystyrene materials made previously are to be determined by measurement of their dilute solution viscosities.

II. References

l. McCaffery, E. M., "Laboratory Preparation for Macromolecular Chemistry", McGraw-Hill (1970).

2. Flory, P. J., "The Principles of Polymer Chemistry", Cornell University Press (1953), pages 308-315.

3. Billmeyer, F. W., Jr., "Textbook of Polymer Science", 2nd Edition, J. Wiley (1971).

4. Shroff, R. N., J. Appl. Poly. Sci.,!, 1547 (1965).

5. Handbook of Chemistry and Physics, 24th Edition or equivalent.

III. Equipment and Supplies

l. Glass constant temperature bath set at 25°C.

2. Cannon-Fenske number 100 viscometer

3. Stopwatch

4. Crystal polystyrene solution

5. Benzene

6. Analytical Balance

7. Pyncnometer

IV. Preliminary Considerations

A. The relationship between fluid viscosity and density and its efflux time from a capillary viscometer such as the Cannon- Fenske is often written as

$$\eta = A\rho t - \frac{B\rho}{t} \quad \text{or} \quad \frac{\eta}{\rho t} = A - \frac{B}{t^2} \qquad (1)$$

Where

η = fluid viscosity
ρ = fluid density
t = efflux time
A, B = constants (functions of fluid and viscometer)

B. Two corrections must be made to the Hagen-Poiseville equation for laminar flow through a capillary tube in order to make the equation suitable for viscometry.

I. The Couette correction arises because of the abrupt change of flow lines at either end of the capillary and is made by assuming a hypothetical increase in capillary length equal to nxr, where r is the capillary radius.

2. The second, a kinetic energy term, corrects for the fact that a portion of the total energy arising from the fact that a portion of the total energy arising from the pressure difference at either end of the capillary is expected to impart kinetic energy to the efflux. The correction is given by:

$$P_{KE} = \frac{m\rho v^2}{\pi^2 r^4 t^2} \qquad (2)$$

where m is a constant equal approximately to one, ρ the fluid density, r the capillary radius, and t the efflux time for volume of liquid, v, to pass through the capillary.

3. Determine the form of the calibration constants A and B from the information above, noting that the pressure $P = \rho gh$, where h is the height between the two surfaces in the U tube of the viscometer.

C. The viscosity average molecular weight, $\bar{M}_v$, can be determined from the intrinsic viscosity, $[\eta]$ by the expression:

$$[\eta] = K' \bar{M}_v^a \qquad (3)$$

Where,

$$[\eta] = \lim_{c \to 0} (\frac{\eta_{sp}}{c}) \qquad (4)$$

$$\eta_{sp} = \eta_R - 1 \qquad (5)$$

$$\eta_R = \frac{\eta_{solution}}{\eta_{solvent}} \qquad (6)$$

c = polymer concentration, g/100 ml solvent

K', a = constants

Determine from the references supplied, values of K' and a for use with polystyrene in benzene at 25 °C.

D. There are numerous points of technique required to obtain accurate viscosity measurements. A good review of these may be seen in McCaffery (1). A brief summary of the main points is presented below:

  l. The viscometer and all glassware in contact with the polymer solutions should be very carefully cleaned with hot chromic acid prior to use and should be protected from atmospheric contaminants after cleaning.

  2. Check the constant temperature bath to be sure that it is operating properly.

  3. When used the viscometer should be aligned vertically since tilting the viscometer to any other angle will reduce the head and increase the efflux time.

  4. The viscometer should be filled in a manner to ensure that the volume of solution employed will remain constant for each determination and will require a minimum number of corrections. This is done in the following way:

    a. Invert the viscometer and insert the narrower of the two arms in a small beaker of water.

    b. Apply suction to the other arm and draw liquid into the viscometer to a point beyond the capillary tube but before the U bend.

    c. Place finger over the lip of the tube containing the liquid and remove the viscometer from the beaker.

    d. Adjust the liquid level in the viscometer to the fiducial mark (between the two bulbs) by varying the finger pressure against the lip.

    e. Return viscometer to its upright position. Transfer the contents to a 10 ml graduated cylinder already containing exactly l ml of water. The ideal quantity of liquid to be used in subsequent viscosity measurements can be estimated from the difference in volume measured in the graduate. Before attempting to make an efflux time measurement, the viscometer should.be filled from a 10 ml burette or graduated pipette with precisely the same quantity of liquid for each measurement; the quantity of liquid chosen should approximate, to the nearest milliliter, the predetermined ideal volume.

  5. After the liquid has traversed the capillary tube of the viscometer it can be returned to a position above the upper fiducial mark by applying a slight positive

pressure of air to the larger viscometer arm with a rubber bulb. Suction should be avoided since it promotes volatilization of the solvent.

6. A typical efflux-time measurement is made (after liquid has been forced into the reservoir beyond the upper fiducial mark on the viscometer) by permitting the fluid to flow freely under its own hydrokinetic head. A stopwatch should be started at the point where the liquid meniscus just passes the upper fiducial mark and should be stopped when the meniscus passes the lower fiducial mark. All meniscus observations should be made at eye level to minimize parallax errors. A precision of 0.2% should be realized in a series of 5 consecutive efflux time measurements provided thermal equilibrium has been obtained.

7. Between runs the viscometer should be rinsed with a small portion of the new solution, forcing the liquid up into the fiducial bulb and upper reservoir. Several minutes should be allowed after the liquid has run out of the viscometer for proper drainage prior to introducing the new solution.

8. Efflux times of the order 100-200 seconds are preferred in order to minimize the viscometer corrections.

V. Preliminary Work – Period 1

I. Clean viscometers in chromic acid solution and rinse them successively with water, distilled water, and acetone. The cleaned viscometers may be dried in the oven.

2. Prepare polymer solutions for use in the next period as follows:

   a. Weigh out approximately 0.2 g of each of the polymer fraction! prepared earlier and of the crystal polystyrene.

   b. Transfer each sample quantitatively into a 100 ml volumetric flask filled about half way with benzene.

   c. Do not add the remaining solvent until the next period so as to avoid volume of mixing problems or the possibility of gel formation in the neck of the flask.

   d. Label and set aside the volumetric flasks until next period.

3. Calibrate the viscometer with pure benzene by measuring the efflux times at 25.0°C. A precision of 0.2% should be realized in a series of 5 consecutive efflux-time measurements. If the measurements are not reproducible there is a good chance that the viscometer is dirty. Step 1 should be repeated if this is the case.

4. Calculate the constants A and B in equation (1).

5. When not in use, the viscometer should be dried and its open ends covered. Store the viscometer until the next period so that it remains clean.

VI. Experimental Procedure – Period 2

I. Add remaining benzene to the samples prepared in period 1 so that the concentrations are all precisely known. Swirl the contents of each volumetric flask until optical striations disappear and the solutions are well mixed.

2. Recheck benzene calibration by determining efflux times per procedure of Period 1. Check bath temperature to make sure that it corresponds to that used in period 1. Ask your instructor to adjust bath if necessary. Reclean viscometer, if necessary.

3. Prepare 20 ml samples of polystyrene in benzene at 0.1 and 0.05 g/100 ml concentration levels for each of the four samples by dilution of the .2 g/100 ml samples prepared in step I. Do this dilution by dispensing the solution and solvents with separate pipettes.

   a. Take care not to waste any of the solutions since the entire amount will be needed for the viscosity determination and for the required viscometer rinsing.

   b. Solutions should be stored in sealed containers prior to use.

4. Measure efflux times for the 12 different solutions {(.2,.1, and .05 g/100 ml) x 4 samples} at 25ºC following the techniques outlined in IV. Determine the density of each solution at 25ºC by use of the pyncnometer and analytical balance. This can be done with the same solution used in the viscometer.

VII. Report

I. What viscosity average molecular weights were obtained for the three fractions. Do your Which fraction has the highest molecular weight? Why?

2. Are the molecular weights determined for the fractions consistent with that obtained for the crystal polystyrene?

3. What relationship, if any, is there between the viscosity average molecular weight determined by dilute solution behavior and the melt viscosity molecular weight dependence of a polymer?