

# INTRINSIC VISCOSITY OF POLY(METHYL ACRYLATE)

NOTE: *Your sample of poly(methyl acrylate) [PMA] should be dissolved in toluene at least one day before you intend to perform this experiment. Be sure that the volumetric flask and the PMA are very dry (dry in vac oven if necessary) since traces of water will inhibit dissolution and will give a cloudy mixture. To prepare your PMA stock solution, place 0.50 g (measured on an analytical balance to the nearest tenth of a milligram) of the PMA prepared in a previous lab in a 100 mL volumetric flask. Fill the volumetric flask approximately two-thirds full with toluene (not filtered) and place it on a wrist shaker until the PMA is completely dissolved.*

## MATERIALS

- Cannon-Fenske viscometers. An appropriate bore size for the capillary will give a  $t_0$  of slightly greater than 100 seconds for toluene at 30°C.
- Reagent-grade toluene
- sintered glass funnels and vacuum filter flasks
- 50 mL burets
- 100 mL volumetric flask
- timers (0.1 sec)
- constant temperature bath at 30.0°C  $\pm$  <0.1°
- assorted general glassware (beakers and flasks)

## GENERAL

1. Cleanliness and a particulate-free environment are the most important factors in doing reliable viscometry. *Viscometers must be clean* (if necessary, fill with filtered "No-chromix" and let stand, then rinse repeatedly with filtered water, then filtered acetone, and dry covered in an oven) *and all solvents must be*

*filtered through a sintered glass fritted funnel before being introduced into the viscometer. (To remove particles before filling with filtered solvent, rinse all receiving vessels with several milliliters of filtered solvent and discard the washings.)*

2. All time readings for a given solution should be performed until *three consecutive readings* agree within  $\pm 0.1$  seconds. If you are having difficulties with fluctuations in time, this is most probably due to particulates that are present in the viscometer (another possibility is bath temperature fluctuations). If this is the case, the viscometer should be thoroughly cleaned, rinsed with filtered solvents, and dried (see #1).
3. Do viscosity determinations in a constant temperature bath set at  $30.0^{\circ}\text{C}$ . If measurements are done during two different periods, use the *same* thermometer (or a calibrated thermometer) to insure that the bath temperatures are the same during both determinations.
4. When the viscometer is not in use, the openings in the clean viscometer should be covered with filter paper held in place with rubber bands or copper wire to avoid the introduction of particulates. This is particularly important because particulates may get trapped in the narrow capillary of the viscometer which will effectively ruin it.

## **EXPERIMENTAL**

### **Determination of $t_0$ :**

1. Obtain a Cannon-Fenske viscometer and write down its code number (use the same viscometer for all determinations on a particular sample). Examine the viscometer for impurities and clean it if necessary (see Step 1 in the "General" section above).
2. (*NOTE: This section of the procedure may be omitted if your instructor specifies the volume that should be used in all runs, e.g., 7.0 mL.*) Determine the volume that must be used for all solutions introduced into the viscometer. This is done by inverting the viscometer and placing the narrower end in a beaker of filtered toluene. Apply suction to the other arm and draw the solvent into the viscometer to a point beyond the capillary but before the U-bend. Maintain the solution level by placing a finger over the open end of the viscometer. Remove the viscometer from the solvent and, while still in the inverted position, adjust the liquid level to the upper line on the viscometer (after the capillary but before the two bulbs) by altering the finger pressure on the open end. Drain the contents of the viscometer into a 10 mL graduated cylinder containing exactly one mL of toluene. *The volume of solvent drained from the*

*viscometer is the volume that should be used in all subsequent determinations (be sure to subtract the original one mL in the graduated cylinder).* Using the same volume for all determinations avoids the need for correction factors.

3. Determine  $t_0$  (the efflux time of pure solvent) for toluene at 30.0°C. Average three readings that agree within  $\pm 0.1$  sec. Apply pressure with a rubber bulb on the wider arm of the viscometer to push solvent into the upper bulb of the viscometer. Start the timer when the meniscus of the solvent passes the line located between the bulbs and stop the timer when the solvent meniscus passes the lower line located at the bottom of the lower bulb.

### **Determination of the viscosity of PMA:**

1. When the PMA has completely dissolved, add toluene to the mark on the volumetric flask and agitate vigorously. Filter the solution through a sintered glass funnel (it is best to apply pressure to the *top* of the sintered glass funnel to avoid evaporation of the solvent during filtration).
2. Determine the efflux time of the 0.5 g/dL solution. Use the same volume and technique as described above (NOTE: To avoid dilution effects, add about 4 mL of the filtered PMA solution to the viscometer, draw the solution into the capillary and let it drain, and then remove the solution from the viscometer. Then introduce the proper volume of this solution and determine the efflux times.) Do until three readings agree within  $\pm 0.1$  sec.
3. Calculate the amount of solvent and stock solution (0.5 g/dL) which should be added to the viscometer to give the proper volume of the following concentrations (the proper volume was determined above in part 2 of the "Determination of  $t_0$ " section):

0.5, 0.35, 0.2, 0.1 g/dL

It may be convenient to fill a buret with the filtered stock solution and another buret with filtered toluene (be sure to rinse the burets with the filtered solutions before filling). Then introduce the necessary volumes directly into the viscometer and mix well by swirling the viscometer vigorously and drawing the solution into the capillary several times (you may wish to mix each solution twice, once as a rinse between concentrations). Determine the efflux times of these solutions.

3. Plot the data to obtain the intrinsic viscosity,  $[\eta]$ . Use this value to calculate the viscosity-average molecular weight of the PMA sample (the Mark-Houwink parameters ( $[\eta] = KM_V^a$ ) for PMA in toluene at 30°C are  $K = 7.79 \times 10^{-5}$  dL/g and  $a = 0.697$ ). From  $M_V$ , calculate the degree of polymerization (DP).

