

## **Experiment 13: Bead (suspension) polymerization of MMA and of DVB.**

**Aim:** (a) To study the polymerization of MMA in water solutions of polyvinyl alcohol at different stirring speeds and to measure the diameter of the PMMA beads thus formed using a dial micrometer and an optical microscope.

(b) To study various stages of the polymerization of divinyl benzene (DVB), which is a tetrafunctional monomer (forms cross-linked network) in octane, forming porous PDVB beads, and to measure the diameter of these beads using a dial micrometer and an optical microscope.

### **Materials and Apparatus:**

Polyvinyl alcohol (1% solution in water – to be made ahead of time)

MMA monomer (will use 2 batches of 35 ml each)

DVB (commercial: 55% divinyl benzene plus 45% ethyl vinyl benzene – difunctional, aka “ethylstyrene”)

Isooctane (or n-octane)

benzoyl peroxide

dimethyl paratoluidine

glass slides

pipettes (2ml accurate)

rubber suction bulbs

round bottom flasks *or* Erlenmeyer flasks (250 ml)

Erlenmeyer flask (50 ml)

Beaker (200 ml)

Buchner funnel

Side arm vacuum Erlenmeyer for filtration (250-500 ml)

water induced vacuum set up

filter paper (at least 9 cm diameter)

Stirring bars

Stirrer/mag. stir plate

Thermometer or thermocouple/thermistor

dial micrometer

optical microscope (in TA room)

fiber optic lamp

### **Brief Background:**

Polymers in the form of beads having diameters ranging from 10 microns to several millimeters are used in roadway reflector tapes, in ion exchange resins, and as packing in chromatography columns. For each intended use, the mean diameter and range must be controlled (Exercise: Why should size be controlled for the applications listed above?). The experiments suggested below are intended to give you a sense of how diameter can be controlled, as well as to allow you to judge when polymerization is complete.

The first part of this experiment involves the redox initiation of MMA suspended in the form of droplets in an aqueous solution to form PMMA beads. The dispersed organic phase consists of the monomer and the initiators while the aqueous continuous phase consists of water and poly(vinyl alcohol), PVA. Two key parameters in this process are a) fluid mechanics and b) "fortification" of the organic-water interface. (Exercise: How do these parameters play a role and what should be done to get suitable results? See the Rempp and Merrill excerpt for the answer). You shall be studying both these variables. The reaction kinetics is likely to follow the same general rules as homogeneous bulk free radical polymerization as studied in experiment 1. (Exercise: Why will the reaction kinetics follow the same general trend as in bulk polymerization? If you were to do an exact calculation of temperature change that you will observe, is there a difference between the two systems that may have to be accounted for? hint: what about the heat capacity in this case?)

The second part of the experiment involves the polymerization of divinyl benzene (DVB) by suspension polymerization. The organic phase consists of the monomer DVB (65%) and ethyl vinyl benzene (EVB) (35%) and initiator BP dissolved in a non-reactive solvent (octane) while the aqueous phase consists of water and PVA. As polymerization proceeds, cross-linked networks of poly(divinylbenzene) are formed. PDVB is however not soluble in isoctane (although the monomer is) and hence, phase separation occurs. Consequently, we are left with tiny spheres of PDVB with trapped in locked-in pores containing octane. The final pore volume depends upon the volume of octane used relative to the volume of DVB used.

$$\text{Percent porosity} = \frac{\text{volume octane} \times 100}{(\text{volume octane} + \text{volume DVB})} \quad (1)$$

Porous PDVB beads (such as these) are used in gel permeation chromatography columns (GPC). For GPC, it is essential to create internal porosity in beads, the dimensions of the pores being of the order of magnitude of the effective diameters of the polymer molecules (as isolated random coils) being separated.

Free radical polymerization of MMA to PMMA:

See readings for experiment 10, especially pages 260-263 from Rempp and Merrill, "Polymer Synthesis", Ch 12. Reactions kinetics should be similar to that discussed in experiment 1. See also the handout from Rempp and Merrill, "Polymer Synthesis", pp111-112, and consider what might be the main difference between using a co-monomer and not doing so when polymerizing DVB. What purpose does the co-monomer serve?

Percent porosity:

Consider the case of PDVB beads. Immediately after polymerization, the beads consist of polymer PDVB and octane trapped in the pores. Let the total wet mass of each bead be  $M_w$ . After drying these beads, the octane escapes and one is left with just the polymer. Let the dry mass of each bead be  $M_d$ . Let the density of octane and the polymer be  $\rho_s$  and  $\rho_p$ . Then percent porosity is given as:

$$\begin{aligned}\text{Percent porosity} &= \frac{\text{Volume of pores} \times 100}{(\text{Volume of pores} + \text{Volume of the polymer})} \\ &= \frac{(M_w - M_d)/\rho_s \times 100}{(M_w - M_d)/\rho_s + M_d/\rho_p}\end{aligned}\tag{2}$$

### **Precautions:**

1. Use vinyl gloves.
2. Handle MMA and DVB in the hood.

### **Procedure:**

#### A. Controlling the diameter of PMMA beads and extent of polymerization:

1. Set up a 250 ml round bottom flask (a “flat bottom” Erlenmeyer may be used in place of the round bottom) provided with a football shaped stirring bar, mounted on a magnetic stir plate. Insulate the sides of the flask with glass wool. **You will not be heating the flask in this experiment.** You will be measuring temperature increases in the fluid phase as the reaction progresses. Note – proceed with one trial at a time!

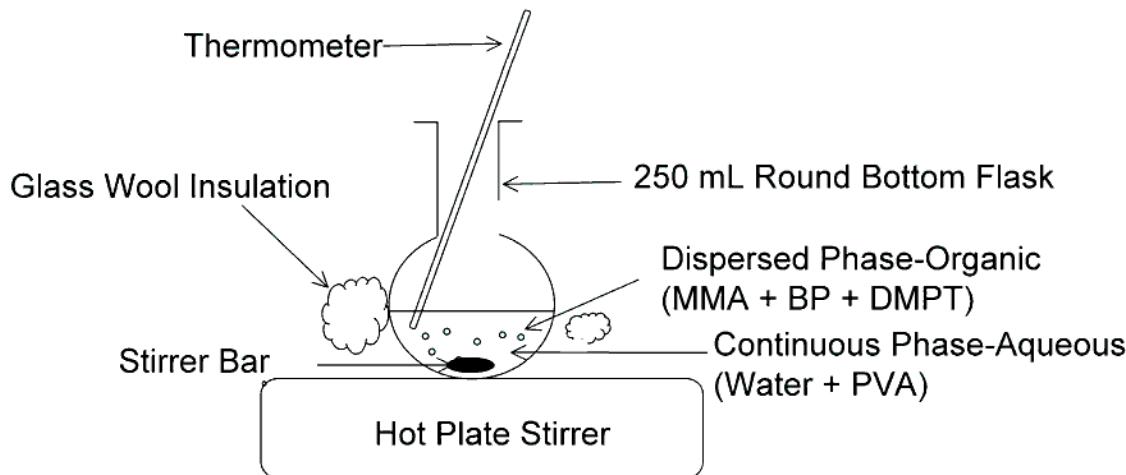


Figure: Experimental set up for part A

2. Fill the flask with about 120 ml of the water solution of polyvinyl alcohol, at room temperature, as specified in the below table. Set the stirrer bar to rotate also as specified in the table.

Table: Conditions

Trial #	Water phase	Stirring
1	1% PV Alcohol	Slowly without vortex.
2	1% PV Alcohol	Fast with vortex.

3. Next you will prepare a solution of monomer plus initiator. In a 50 ml Erlenmeyer flask place 35 ml of methyl methacrylate monomer. Add with stirring 1.8 g benzoyl

peroxide (grind BP before adding), and stir until dissolved. Then add 0.75 ml of dimethyl paratoluidine, stir very briefly, then pour into the 250 ml flask. Adjust the stirrer bar speed so that it creates a vortex. Introduce a thermometer at an angle so that it is clear of the stirring bar.

4. Maintaining a well-insulated flask, record the temperature vs. time, until the temperature ceases to rise; at this point, let the reaction proceed another 15 min. Throughout the polymerization - every 15 minutes - withdraw about 2 ml of suspension using the wide end of a disposable pipette. Place the suspension on ordinary filter paper and absorb the water. Back up the filter paper with paper towels. Record what you have left on the filter, e.g., oily drops, sticky drops, soft beads, hard beads.

5. After the reaction is complete, empty the contents of the flask, approximately 120 + 35 ml, into a 200 ml beaker. Retrieve the stirring bar. Rinse the flask with tap water to rinse out any remaining beads. Move on to trial #2 using the same set of instructions.

6. Regardless of whether the beads are fine or coarse, and whether or not they readily settle under gravity, retrieve them by filtration through a Buchner funnel under water aspirator vacuum using filter paper. Transfer beads into pre-weighed weighing dish. Put in 80°C air oven for 30 minutes. Reweigh. Is all mass recovered with respect to initial weight of the monomer (density = 0.85)?

7. Bead diameter estimation:

a) Using the dial micrometer: Zero the dial micrometer. Then place a layer of beads on the platform. Measure the diameter of the largest bead that happens to be under the micrometer foot-plate.

b) Using the binocular microscope: Place your sample of beads (a very small sample) on a glass slide. Adjust to move slide under objective. Illuminate from above with fiber optic lamp. With luck, you will see a multi-line calibration scale in the field of vision. Place some 200 micron PMMA beads on your slide and calibrate the scale. (How many divisions do you count in moving across the diameter of a bead?) Then try to estimate the diameters of the beads in your sample: the smallest, the largest, and (approximately) the most populous.

B. Polymerization of DVB:

1. Prepare the organic phase by dissolving 8 ml of isoctane in 30 ml of DVB. Then add 1.8 g of benzoyl peroxide and allow to dissolve. (Exercise: What is the expected percent porosity?)

2. The aqueous phase is a solution of 1% polyvinyl alcohol in water. Heat this to 80 C. Place 100 ml in a 250 ml round bottom flask that is immersed in a water bath (or use a flat bottomed 50 ml Erlenmeyer flask). Place flask on hot plate/stirrer.
3. When the temperature reaches 80 C, pour in the organic phase (38 ml) with the stirring bar moving just fast enough to create a vortex. Allow the temperature to get back up to 80°C after addition of your monomer, then turn off the hot plate. . Monitor and record temperature vs. time for the fluid phase (the temperature should rise to 90 to 95 °C as the polymerization goes to completion).
4. Every 15 minutes withdraw about 2 ml of suspension using the wide end of a disposable pipette. Plate in on ordinary filter paper and absorb the water. Back up the filter paper with paper towels. Record what you have left on the filter, e.g., oily drops, stick drops, soft beads, hard beads. Also record any temperature variation.
5. When you have hard beads, stop the reaction and cool the contents. Then collect the beads by filtration through a Buchner funnel. Wash the beads on the funnel with 200 ml of warm water, then dry by drawing air through the funnel.
6. Roughly weigh the beads, and compare with mass charged to the vessel. Place bead in vacuum over at 80 C. Re-weigh next lab period and report final yield. Thus estimate porosity.
7. Use methods described in part A to measure the bead diameters.

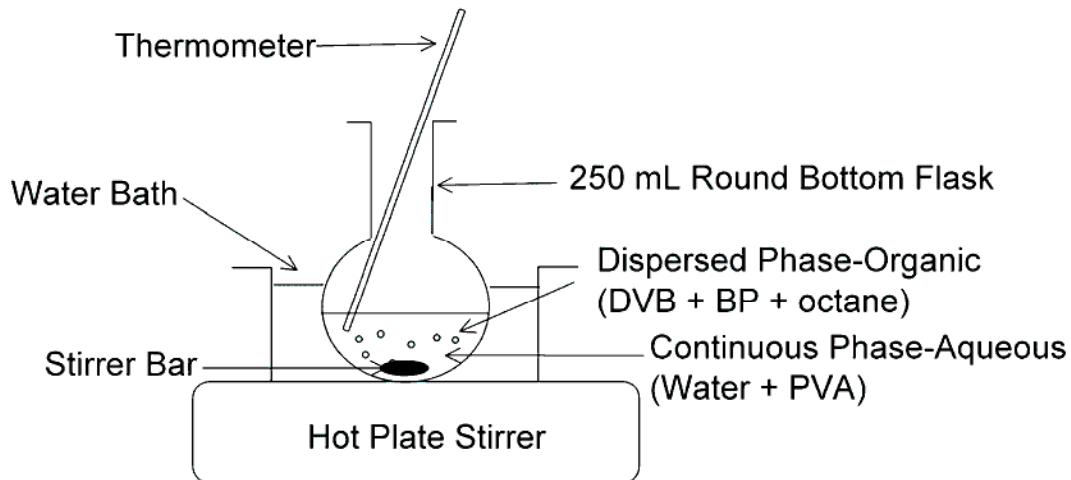


Figure: Experimental setup for Part B

#### **Observations and Calculations:**

1. Part A:
  - 1) Time vs. temperature measurements.
  - 2) Tabulate for each trial-bead sizes and measurement method used.

2. Part B:
- 1) Time vs. temperature measurements.
  - 2) Qualitative observations on PDVB beads at different times.
  - 3) Percent porosity - expected vs. experimental.
  - 4) Size measurements.

**Discussion:**

1. Use a heat balance to analyze the time vs. temperature data. Recall you have the mass of water (about 120 g) and the organic mass (about 30 g). You can use “engineering estimates” of parameters like heat capacities.
2. Discuss other results in light of the background provided to you in this handout. Address the anticipated and calculated porosities found, the reasons for mass loss, if any, etc.