Preparation of Polymeric Nanoparticles – [PP]

(Sreela Ramesh, Havlůjová Tereza,Miroslav Šoóš)

1. Introduction

Monodisperse polymer particles have numerous applications including paint formulation, coatings, finishes, chromatographic columns, photonic crystals, and biomedical devices. The preparation of submicron particles has been a topic of interest in academic and industrial settings. Several methods are available for synthesizing such particles such as suspension, dispersion or emulsion polymerization. However, emulsion polymerization is presently the predominant process for the commercial polymerizations of vinyl acetate, chloroprene, various acrylate copolymers as well as copolymers of butadiene with styrene and acrylonitrile. It is also used for methacrylates, vinyl chloride, acrylamide, and some fluorinated ethylenes. In an emulsion polymerization system as depicted in Figure 1, the surfactant is dissolved in the water continuous phase until the **critical micelle concentration (CMC)** is reached. The interior of the micelle provides the site necessary for polymerization. The monomer, which is representing an oil phase and is insoluble in the water continuous phase, is added and the mixture is stirred to make the emulsion. Initiation takes place when a radical formed by the decomposition of an initiator migrates into a micelle and reacts with a monomer molecule. The formed monomer radical propagates in the presence of other monomer molecules to form a polymer chain with two monomer units. This process continues until two polymer chains composed of *i* and *j* monomer units and containing radicals do not meet each other and terminate to form a polymer chain with length *i*+*j*. Due to very low solubility of the polymer in continuous water phase but good solubility of monomer in the formed polymer, formed particles are monomer-swollen up to the point of complete conversion of monomer into polymer. Typical examples of water-soluble initiators, commonly used in industrial praxis, are potassium peroxide or ammonium persulfate.

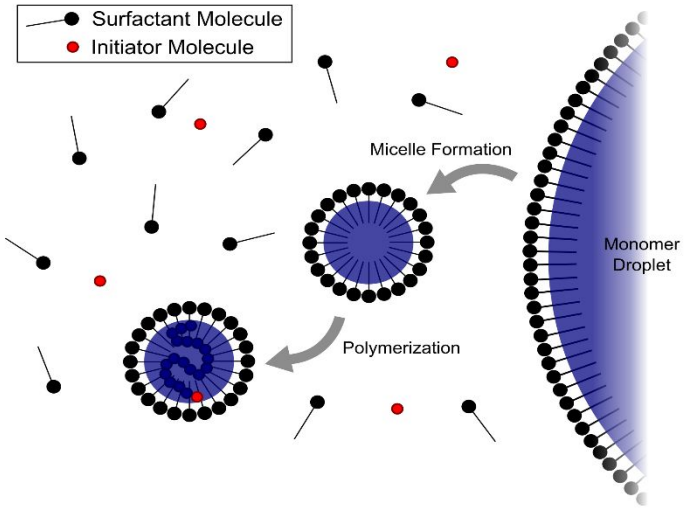

Fig. 1: Scheme of emulsion polymerization

2. Theory

The important parameters that have been reported to influence the product of emulsion polymerization systems include the concentration of monomers, surfactant and initiator as well as reaction temperature. The higher the temperature of polymerization, the higher the rate of the polymerization reaction. High concentrations of surfactant yield small sizes of particles. The quality of the water used in emulsion polymerization is also important since the presence of foreign ions in high amounts can interfere with the initiation process as well as the action of the emulsifier. Deionized water should be used always to avoid such problems.

Emulsion polymerization confers several advantages. It is relatively inexpensive and easy to control. The product of emulsion polymerization is called **latex** and can be used as obtained without further separations. Typical applications are acrylic paints. Due to the low viscosity of emulsion systems, thermal and mass transfer problems are less significant compared to bulk polymerizations. Compared to other methods, emulsion polymerization occurs at the fastest polymerization rate and yields the highest molecular weight polymers. The degree and rate of polymerization are determined by the number of polymer particles:

$$DP = k_p N\,[M]/\rho \tag{1}$$

$$R_p = 10^3 N\ \tilde{n}\ k_p N\,[M]/N_A \tag{2}$$

where k_p is the propagation rate constant, N is the number of particles per milliliter (typically 10^{14}), $[M]$ is the monomer concentration, ρ is the rate of radical production, ñ is the average number of radicals per micelle and N_A is the Avogadro's number. The only disadvantage comes in systems where the surfactant is undesirable in the final product, and cleaning of the latex of the surfactant can be very difficult if not impossible.

3. Aims of the work

a) To synthesize monodisperse PMMA nanoparticles with controlled sizes.
b) To characterize the properties of the obtained nanoparticles
c) To conduct the synthesis of PMMA NPs using varied amounts of surfactant and different flow rates and compare their effect on latex properties.

3.1. Pre-lab preparation

Read the laboratory protocol carefully to understand the safety measures, what the laboratory is about and the basic principles of the method (emulsion polymerization).

Based on the information given in the experimental procedure, fill the table below with the amount of monomer, initiator etc. that you will need for the experiment (this should be done at the beginning of the lab).

4. Experimental procedure

4.1. Materials

Chemicals: Potassium persulfate (KPS)
Sodium dodecyl sulfate (SDS, Mw= 288.372 g/mol)
Methyl methacrylate (MMA)
Distilled water

4.2. Description of the Setup

The experimental apparatus is shown in Figure 2. The polymerization is carried out in a three-neck round bottom flask (3) equipped with reflux condenser (2) which is cooled by a recirculation of water to ensure no material loss by evaporation. The bubbler (1) is used to ensure the presence of inert gas atmosphere (in our case nitrogen) throughout the polymerization. The reaction solution is heated using a metallic heating bowl (4) placed on a magnetic stirrer/heating plate (5).

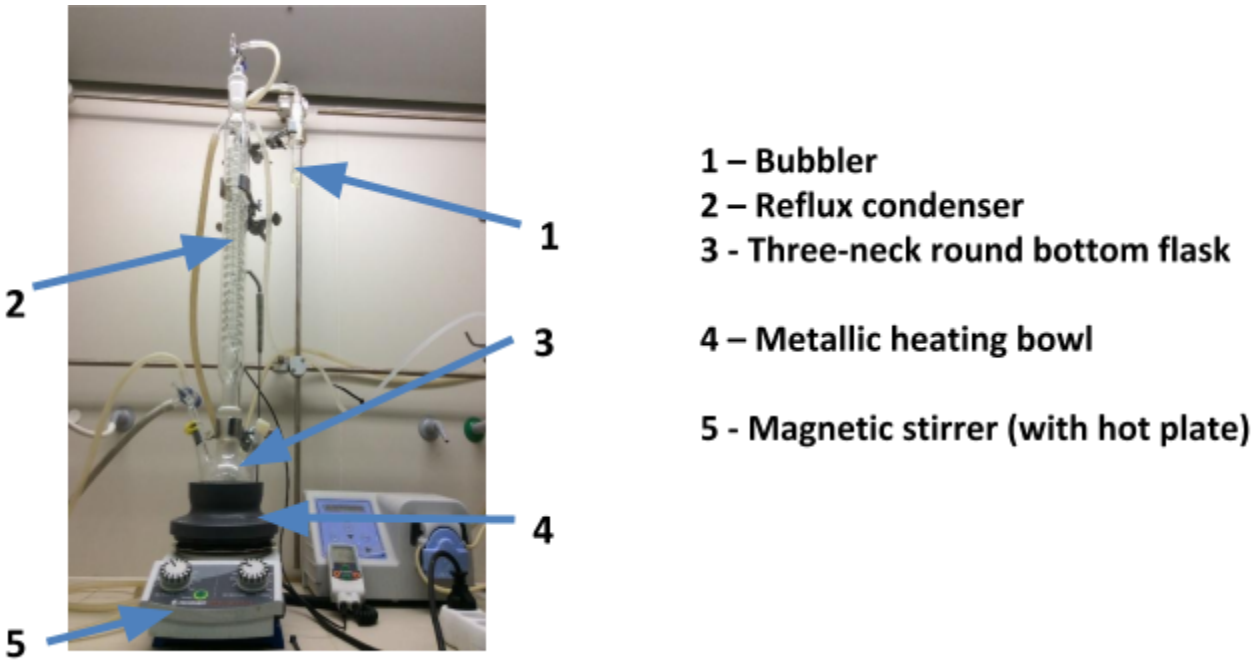

Fig. 2: Setup for emulsion polymerization of styrene

5. Work Procedure

Preparation of 10 wt.% monodisperse poly (methyl methacrylate) (PMMA) nanoparticles by radical emulsion polymerization *(Total volume of 75 mL, ratio of monomer to SDS will be given at the beginning of lab)*

Reagent	Amount [mg]
MMA	
KPS	
H_2O mL	
SDS	

1. Fill a 100 mL three-neck round bottom flask with 60 mL of water and add a magnetic bead. Place the setup on a metallic bowl on a hot plate. The middle opening of the round flask will be equipped with a reflux condenser and the two side openings should be closed with septa. Sparge the water with nitrogen for about 20-30 minutes to strip oxygen from the reaction solution while mixing with a magnetic stirrer at 300 - 500 rpm (adjust accordingly). A thermometer should be inserted through the other septum to monitor the temperature.
2. Heat up to 80 degrees measured on the thermometer inside the flask (usually obtained by setting the temperature on the hot plate to 10 or 15 degrees higher than the desired temperature) and monitor it throughout the reaction. Do not forget to start circulating water in the reflux condenser once heating begins.
3. Add the required concentration of SDS dissolved in 5 mL water to the RB flask and let the mixture stir under nitrogen atmosphere. Adjust the stirring speed.
4. Dissolve 506 mg of KPS in 25 mL water in a standard flask. Sparge this solution with nitrogen for around 15-20 minutes. Do not forget to put an additional needle for letting the gas out.
5. Add the initiator solution of KPS (2,5 mL) into the emulsion using a syringe and needle. Sparging with nitrogen can be stopped after this step.
6. Every group of students will follow either step 6a or step 6b according to instructions:
    a. Start feeding the necessary amount of monomer MMA at the desired rate (will be specified at the beginning of the laboratory session) into the mixture. After feed addition allow the polymerization to run for around 1 hour to complete the conversion.
    b. Add the necessary amount of monomer MMA and allow the polymerization to run for 1 hour.
7. As soon as the monomer addition begins, take out 1 mL of the reaction mixture every 10 - 15 minutes to record the conversion of monomer to polymer, this will be measured by moisture analyzer. Plot a graph at the end of the experiment with the collected data.
8. At the end of the polymerization, stop the heating and remove the nanoparticle solution from the heating bowl to allow it to cool off to room temperature.

9. **FOR SOME GROUPS ONLY:** To measure the critical coagulation concentration, prepare 30 mL of 4M NaCl solution. This stock solution should be prepared at the beginning of the lab as it may take a while to dissolve. Dilute half of the prepared solution with the same amount of water in another beaker. Repeat the dilution for the most recently prepared solution 8 times (until the concentration of the solution is 0.015625 M). Use Pasteur pipette to add a drop of the latex into all the prepared solutions to determine the CCC.
10. After the recovery of polymer latex, all the glassware used for polymerization should be thoroughly cleaned. Please keep in mind that your colleague will use it another time and your bad cleaning can ruin their work!

CHARACTERIZATION: The PMMA nanoparticles will be characterized using Dynamic Light Scattering (DLS) for size, SEM for morphology, DSC (NP powder) for glass transition etc. in another lab session.

6. Evaluation and Report preparation guidelines

A report including a brief description of the experiment with the following sections: Aims, Experimental procedure, Results (could be a picture of how the final latex solution looks, could be pictures from the CCC analysis, conversion rate etc.) should be presented. Content of the protocol should be consulted immediately after your work with the assistant!

7. Precautions and safety information

(i) **Safety first!** Personal protective equipment (lab coats, gloves, goggles, shoes that cover the entire feet: no slippers or sandals allowed) should be worn at all times when in the lab and when handling all chemicals.

(ii) Methyl methacrylate has a strong sharp penetrating odor and weighing should be done using a syringe (assistant will show you how to do this) and in a fume hood to avoid inhalation. Safety information (Source: Sigma Aldrich material safety data sheet) regarding all reagents used in this lab is as follows:

Chemical	Signal word	Symbol		
MMA	Danger (Flammable, acute toxicity, respiratory hazard) May irritate eyes, nose, throat			
PVP	No toxicity data available Safe / low hazard chemical			

Ammonium persulfate	Danger (Oxidizing agent, may intensify fire, may cause skin, eye and respiratory irritation			

In case of contact with any chemical, wash off immediately under running water and notify the assistant. If you are not sure about how to carry out a particular task, or information related to handling chemicals, consult first the assistant before proceeding. **Prevention is better than cure!**

(iii) Before starting the experiment, ensure all glassware are clean, contamination can alter the results of your hard work.

(iv) While heating the solution, ensure all silicon tubings are kept away from the heating bowl to avoid melting.

8. Control questions

1. What is an emulsion? What does “critical micelle concentration” mean? How could this be measured?
2. In simple terms describe the principle of emulsion polymerization.
3. How are the particles stabilized in an emulsion polymerization system? What stabilizer was used in this experiment? Which other types of stabilizers do you know?
4. Why is it necessary to do the degassing step prior to addition of the initiator?
5. What factors control the size of the final latex solution?
6. What are the advantages and disadvantages of emulsion polymerization as compared to other polymerization methods?

Good luck!