
CHAPTER 4

SUSPENSION POLYMERIZATION

4.1 INTRODUCTION

Hoffman and Delbruch first developed suspension polymerization in 1909. In suspension polymerization the initiator is soluble in the monomer phase, which is dispersed by comminuting into the dispersion medium (usually water) to form droplets. The solubility of the dispersed monomer (droplet) phase and also the resultant polymer in the dispersion medium are usually low. The volume fraction of the monomer phase is usually within the range 0.1-0.5. Polymerization reactions may be performed at lower monomer volume fractions, but are not usually economically viable. At higher volume fractions, the concentration of continuous phase may be insufficient to fill the space between droplets. Polymerization proceeds in the droplet phase, and in most cases occurs by a free radical mechanism. Suspension polymerization usually requires the addition of small amounts of a stabilizer to hinder coalescence and break-up of droplets during polymerization. The size distribution of the initial emulsion droplets and, hence, also of the polymer beads that are formed, is dependent upon the balance between droplet break-up and droplet coalescence. This is in turn controlled by the type and speed of agitator used, the volume fraction of the monomer phase, and the type and concentration of stabilizer used. If the polymer is soluble in the monomer, a gel is formed within the droplets at low conversion leading to harder spheres at high conversion. If the polymer is insoluble in the monomer solution, precipitation will occur within the droplets, which will result in the formation of opaque, often irregularly shaped particles. If the polymer is partially soluble in the monomer mixture, the composition of the final product can be difficult to predict. Polymer beads find applications in a number of technologies, such as molding plastics. However, their largest application is in chromatographic separation media (as ion exchange resin and as supports for enzyme immobilization). Such applications frequently require large particle surface areas, which necessitates the formation of pores (of the required dimensions) in the bead structure.

The polymer beads may be made porous by the inclusion of an inert diluent (or porogen) to the monomer phase, which may be extracted after polymerization. Other additions to the monomer phase can include UV stabilizers (aromatic ketones and esters), heat stabilizers (ethylene oxide derivatives and inorganic metal salts), molding lubricants and foaming agents (porogens).

4.2 POLYMERIC STABILIZERS

Typical polymeric stabilizers used for oil-in-water suspension polymerization reactions are poly (vinyl alcohol) -co- (vinyl acetate) (formed from the partial hydrolysis (80-90%) of polyvinyl acetate), poly (vinyl-pyrrolidone), salts of acrylic acid polymers, cellulose ethers and natural gums.

Polymeric stabilizers used in inverse suspension polymerization reactions include block copolymers poly (hydroxy-stearic acid) -co-poly ethylene oxide). Surfactants used for oil-in-water suspensions include spans and the anionic emulsifier (sodium

12-butinyloxy-9-octadecenate).

4.3 POLYMERIZATION CONDITIONS AND KINETICS

Extensive studies have shown that, in general, reaction kinetics in suspension polymerization is found to show good agreement with bulk phase kinetics (in absence of any monomer diluent). This observation suggests that in suspension polymerization, the emulsification conditions (agitation conditions, emulsion droplet size and concentration / type of stabilizer) appear to have little effect on reaction kinetics. Moreover, it can be concluded that any mass transfer between two phases in the emulsion does not affect the overall reaction rate. The major challenge in designing a suspension reaction is therefore the formation of a stable emulsion, preferably having a uniform size distribution. The monomer droplets are large enough to contain a large number of free radicals (may be as many as 10^5) and this is why the polymerization in general proceeds with a similar mechanism to that of bulk polymerization, particularly when the polymer is soluble in the monomer.

4.4 EXPERIMENT

Styrene and 1, 4-divinylbenzene (the latter as 50-60% solution in ethyl benzene) are destabilized and distilled.

A three-necked flask, fitted with stirrer (preferably with revolution counter), thermometer, reflux condenser and nitrogen inlet, is evacuated and filled with nitrogen three times. 250 mg of poly (vinyl alcohol) are placed in the flask and dissolved in 150 mL of de-aerated water at 50°C. A freshly prepared solution of 0.25g (1.03 mmol) of dibenzoyl peroxide in 25 mL (0.22 mmol) of styrene and 2 mL (7 mmol) of 1, 4-divinylbenzene is added with constant stirring so as to produce an emulsion of fine droplets of monomer in water. This is heated to 90°C on a water bath while maintaining a constant rate of stirring and passing a gentle stream of nitrogen through the reaction vessel. After about 1 h (about 5% conversion) the cross-linking becomes noticeable (gelation). Stirring is continued for another 7 h at 90° C, the reaction mixture then being allowed to cool to room temperature while stirring. The supernatant liquid is decanted from the beads, which are washed several times with methanol and finally stirred for another 2 h with 200 ml of methanol. The polymer is filtered off and dried overnight in vacuum at 50° C. Yield: practically quantitative.

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