
CHAPTER 3

EMULSION POLYMERIZATION

3.1 INTRODUCTION

In emulsion polymerization two immiscible liquid phases are present, an aqueous continuous phase and a non-aqueous discontinuous phase consisting of monomer and polymer. The initiator is located in the aqueous phase. And the monomer-polymer particles are quite small, of the order of 0.1 μm in diameter.

Emulsion systems allow higher-molecular-weight polymer to be produced at higher rates than do bulk or suspension systems. The soap plays an important role in emulsion polymerization. At the beginning of the reaction it exists in the form of micelles, aggregates of 50-100 soap molecules.

Part of the monomer enters the micelles, but most of it exists as droplets a micrometer or more in diameter. In the ideal case no polymer is formed in the monomer droplets. Polymerization can take place (at a very low rate) in the homogeneous phase in the absence of soap, but this cannot account for the bulk of the polymer formed. At the beginning of the reaction, polymer is formed in the soap micelles; these represent a favorable environment for the free radicals generated in the aqueous phase, because of the relative abundance of monomer and the high surface / volume ratio of the micelles compared to the monomer droplets. As polymer is formed, the micelles grow by the addition of monomer from the aqueous phase (and ultimately from the monomer droplets.)

Soon (2-3% polymerization) the polymer particles much larger than the original micelles and absorb almost all the soap from the aqueous phase. Any micelles not already activated disappear; further polymerization takes place within the polymer particles already formed. The monomer droplets are unstable at this stage; if agitation is stopped, they coalesce into a continuous oil phase containing no polymer. The droplets act as reservoirs of monomer, which is fed to the growing polymer particles by diffusion through the aqueous phase. The polymer particles may contain about 50% monomer up to the point at which the monomer droplets disappear, at 60-80 % polymerization. The rate of polymerization is constant over most of the reaction up to this point, but then falls off as monomer is depleted in the polymer particles. Rate increases soap (and initial micelle) concentration.

3.2 SMITH-EWART KINETICS

In an ideal emulsion system, free radicals are generated in the aqueous phase at a rate of about 10^{13} Per cubic centimeter Per second. There are about 10^{14} -polymer particles Per cubic centimeter. Simple calculation show that termination of the free radicals in the aqueous phase is negligible and that diffusion currents are adequate for the rapid

diffusion of free radicals into the polymer particles- on the average, about one per particle every 10 sec.

It can also be calculated from the known termination rate constants that two free radicals within the same polymer particle would mutually terminate within a few thousands of a second. Therefore each polymer particle must contain most of the time either one or no free radicals.

At any time half of the particles (on the average) contain one free radical, the other half none. The rate of polymerization Per cubic centimeter of emulsion is

$$V_p = k_p [M] N / 2$$

[M]: Monomer concentration

k_p : propagation rate constant

N: the number of polymer particles per cubic centimeter

Since the monomer concentration is approximately constant, the rate depends principally on the number of particles present and not on the rate of generation of radicals.

The degree of polymerization also depends upon the number of particles:

$$X_n = k_p N [M] / \rho$$

ρ : the rate of generation radicals

Unlike v_p , x_n is a function of the rate of free-radical formation. In bulk polymerization rate can be increased only by increasing the rate of initiation; this, however, causes a decrease in the degree of polymerization. In emulsion polymerization the rate may be increased by increasing the number of polymer particles. If the rate of initiation is kept constant, the degree of polymerization increases rather than decreases as the rate rises. Since the number of polymer particles is determined by the number of soap micelles initially present, both rate and molecular weight increase with increasing soap concentration.

The Smith-Ewart kinetics require that

$$\begin{aligned} V_p &\propto N, [I]^{0.4}, [E]^{0.6} \\ N &\propto [I]^{0.4}, [E]^{0.6} \\ x_n &\propto N, [I]^{-0.6}, [E]^{0.6} \end{aligned}$$

[E] is the soap or emulsifier concentration

3.3 EMULSION POLYMERIZATION OF STYRENE

3.3.1 MATERIALS REQUIRED

Styrene, potassium persulphate, soap solution, potassium-aluminum sulfate distilled water.

7.3.2 EXPERIMENTAL PROCEDURE

To a resin kettle equipped with a mechanical stirrer, condenser and nitrogen inlet tube, is added 128.2 g. of distilled water, 71.2 g. of styrene, 31.4 mL of 0.68% potassium persulfate, and 100 mL of 3.56% soap solution (sodium stearate one can use 1 g. of

either sodium dodecyl benzenesulfonate or sodium lauryl sulfate). The system is purged with nitrogen to remove dissolved air. Then the temperature is raised to 50 °C and kept there for 2 hour to afford a 90% conversion of polymer. The polymer is isolated by freezing- thawing or by adding potassium-aluminum solution and boiling the mixture. The polystyrene is filtered, washed with water and methanol and dried in vacuum at 50 °C. The total yield, and the limiting viscosity number (degree of polymerization) of one sample is determined by using

$$[\eta] = k_m \cdot M^\alpha \text{ equation.}$$

k_m and α for polystyrene in benzene at 20 °C are $12.3 \cdot 10^{-3}$ and 0.72 respectively.

REFERENCES

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- 2) Practical Macromolecular Organic Chem. Dietrich Braun, Harald Cherdron and Werner Kern, Vol.2, Harwood Academic Publisher, 1984