Polymerization Processes

MSE 383, Unit 2-1

Joshua U. Otaigbe
Iowa State University
Materials Science & Engineering Dept.

Polymerization Methods

- Bulk
- Solution
- Emulsion
- Suspension
- Heat of reaction must be removed otherwise explosion may occur. (critical problem in bulk)
- Get large surface to volume of reacting monomer in solution, emulsion & suspension

Bulk Polymerization

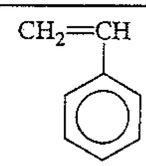
- Reaction is carried out in the absence of solvent, diluent, or other materials
- Useful for epoxy, ethylene, MMA
- Heat removal is critical to avoid formation of explosive compounds

Example of Bulk Polymerization

- free radical (addition) polymerization of ethylene (narrow tubular reactors are used to facilitate heat removal)
- Ethylene gas + Oxygen (trace) @ T=200°C & 1500 atm.

Advantages of Bulk Polymerization

- High yield which depends on reactor volume
- Very high purity product formed
- Adaptable to copolymerization with other compatible comonomers (vinyls)

Monomer	Chemical Structure
Ethylene	$CH_2=CH_2$
Tetrafluoroethylene	$CF_2=CF_2$
Butadiene	$CH_2=CH-CH=CH_2$
Isoprene	$CH_2=\overset{CH_3}{\overset{\vert}{C}}-CH=CH_2$
Chloroprene	$CH_2=\overset{Cl}{\overset{\vert}{C}}-CH=CH_2$
Styrene	
Vinyl chloride	$CH_2=\overset{Cl}{\overset{\vert}{CH}}$
Vinylidine chloride	$CH_2=\underset{Cl}{\underset{\vert}{\overset{Cl}{\overset{\vert}{C}}}}$
Vinyl acetate	$CH_2=\overset{OCOCH_3}{\overset{\vert}{CH}}$
Acrylonitrile	$CH_2=\overset{CN}{\overset{\vert}{CH}}$
Acrylic acid	$CH_2=\overset{COOH}{\overset{\vert}{CH}}$
Methyl methacrylate	$CH_2=\underset{CH_3}{\underset{\vert}{\overset{COOCH_3}{\overset{\vert}{C}}}}$
Methyl acrylate	$CH_2=\overset{COOCH_3}{\overset{\vert}{CH}}$

Solution Polymerization

- Reaction is carried out in the presence of <u>inert</u> solvent & initiator (20% monomer + 80% solvent typical)
- Useful for polystyrene i.e., 20% styrene + 80% Benzene + initiator
- Get temperature rise without solvent. For e.g.:

$$\Delta T = \frac{nQ}{C_p m} = \frac{\left(\frac{m}{0.104\ kg}\right)\left(\frac{70\ kJ}{mol}\right)}{\left(\frac{2.1\ kJ}{kg \cdot K}\right)(m\ kg)} = 320\ K$$

- With solvent, C_p is same: >> large reduction in heat generated

$$\Delta T = \frac{nQ}{C_p m} = \frac{\left(\frac{0.2\ m}{0.104\ kg}\right)\left(\frac{70\ kJ}{mol}\right)}{\left(\frac{2.1\ kJ}{kg \cdot K}\right)(m\ kg)} = 64\ K$$

Advantages of Solution Polymerization

- Very useful for polymers used as solutions (e.g. lacquers, paints)
- Better heat control

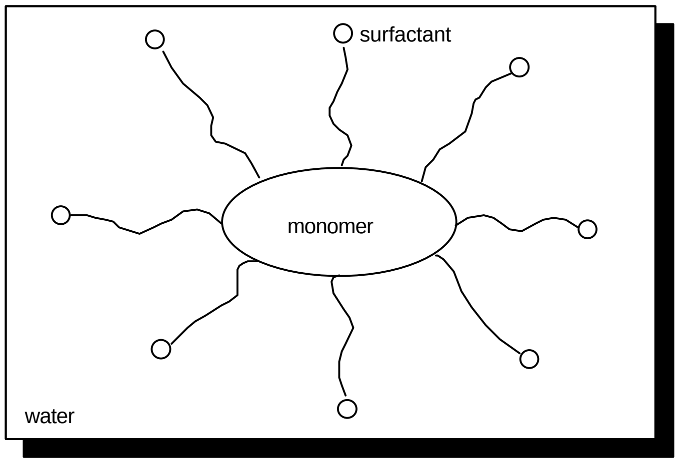
Disadvantages of Solution Polymerization

- Potential toxicity, flammability and environmental pollution (<u>VOC</u>) of solvents
- Polymer product contains solvent impurities
- Yield is significantly lower than in bulk polymerization
- Expensive due to additional solvent costs

Emulsion Polymerization

- Reaction is carried out in monomer
  >> Water emulsion phase (<u>or droplet or Micelle)</u>
  >> More **environmentally safe**

EXPLAIN: hydrophobic monomer + surfactant + water
(e.g., surfactants - soaps, detergents, etc.)

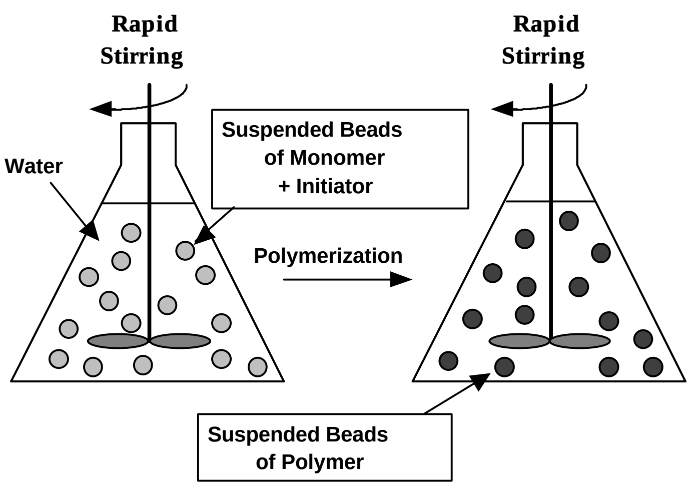


- Reaction occurs in the small droplets (or micelles)
- Role of water is that of a heat sink
- Product is marketed as polymer-water emulsions
  [e.g. water-borne paints, adhesives (white glue), etc.]
- Coagulating agents and/or heating used
  to separate water from polymer
- Surfactant impurity likely in polymer
  >> overhead

Suspension Polymerization

- Reaction is carried out in monomer
- Water dispersions but not stabilized with
  surfactant
- Therefore constant agitation is a must
- Particle size of polymer depends on
  droplet size and rate of agitation
- Relative to emulsion process:
  >> Constant stirring required
  >> Easier separation of water from polymer
  >> No surfactant impurities in polymer

Suspension Polymerization, Cont'd



Schematic representation of suspension polymerization.

Polymerization Processes for Commercial Polymers

Polymer	**Process**
LDPE	Bulk
HDPE	Solution
PP	Solution
PS	Bulk; Suspension
PC	Bulk
PMMA	Bulk; Suspension
PVC	Emulsion; Suspension
PET	Bulk
PA (Nylons)	Bulk
PIsoP	Solution
PCR	Emulsion
SBP	Emulsion
PF	Solution
PTFE	Suspension

End of Lecture