

## Leading Contribution

### Suspension, emulsion, and dispersion polymerization: A methodological survey

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*Abstract:* A methodological description of heterogeneous polymerization processes, including suspension, emulsion, dispersion, and precipitation polymerization is presented. The discussion focuses on the initial state of the polymerization mixture, mechanism of particle formation, and the shape and size of polymer particles produced in different heterogeneous polymerization systems. The dependence of particle size and morphology on manufacturing parameters such as emulsifier, stabilizer, reactor design, and stirring speed is discussed. Special topics, including emulsifier-free (soapless) emulsion polymerization, seeded polymerization, and the formation of core-shell particles are also briefly covered.

*Key words:* Heterogeneous polymerization; suspension polymerization; emulsion polymerization; dispersion polymerization; precipitation polymerization; particle formation; particle size; core-shell particles

#### Introduction

Details and progress of suspension, emulsion, and dispersion polymerizations are regularly reviewed in specialist polymer publications. However, a concise treatment of the subject of heterogeneous polymerization processes covering all of these techniques in a comparative manner is surprisingly lacking in the literature. In addition, or probably for this reason, the terms suspension, emulsion, and dispersion are not always used consistently in the literature. Some authors refer to emulsion polymerization as dispersion polymerization or vice versa, or to suspension polymerization as emulsion polymerization. Some polymerization literature show the terms suspension, emulsion, and dispersion as equivalents or synonyms. This situation is particularly confusing for students and non-polymer scientists whose work may involve the use of polymer products obtained by heterogeneous polymerization techniques. The present article is aimed to provide a concise methodological description of all of the major heterogeneous polymerization processes, namely, suspension, emulsion, dispersion, and precipitation polymerization of vinyl monomers. A similar coverage of suspen-

sion, dispersion, and interfacial polycondensation processes is the subject of a forthcoming publication [1].

#### General features of heterogeneous polymerization processes

Heterogeneous (or particle forming) polymerization processes are usually two-phase systems in which the starting monomer(s) and/or the resulting polymer are in the form of a fine dispersion in an immiscible liquid. The polymerization initiator may be soluble in the monomer or the liquid, and it may or may not be present within the polymer particles during their formation. In addition to the monomer(s), polymerization medium and the initiator, one or more additives is also added to the polymerization mixture to emulsify the monomer, and/or to stabilize the monomer droplets and the resulting polymer particles. Various combinations of the above-named possibilities are employed under empirically adjusted conditions to produce spherical (or irregularly shaped) polymer particles within relatively narrow size ranges from about 50 nm to 1–2 mm or larger.

There are basically four different techniques employed for the manufacture of particulate polymer products by addition polymerization of vinyl monomers. These are conventionally termed "emulsion" or "suspension" processes on the basis of the size of the polymer particles produced. An arbitrary dividing line between emulsion and suspension is the droplet/particle size of  $1\ \mu\text{m}$  (1000 nm). Fluids containing droplets/particles smaller than about  $1\ \mu\text{m}$  are known as emulsions (latex or colloids), and those containing particles larger than about  $1\ \mu\text{m}$  as suspension. The upper limit of particle size for suspension systems may, for the purpose of the present discussion, be regarded as being about 1–2 mm. The term "dispersion polymerization" has been adopted because the technique replaced the process of polymer dispersion in the paint industry. Polymerization processes leading to the formation of macroscopically apparent polymer precipitates are referred to as "precipitation polymerization". The word "dispersion" is also used to describe liquid/solid dispersions in a general sense.

The terminology of heterogeneous polymerization systems adopted here is the one employed by most polymer chemists, and the terms "suspension", "emulsion", "dispersion," and "precipitation" are clearly distinguished on the basis of the following four criteria.

- 1) Initial state of the polymerization mixture;
- 2) Kinetics of polymerization;

- 3) Mechanism of particle formation; and
- 4) Shape and size of the final polymer particles.

The interdependence of the above factors will become abundantly clear throughout the present discussion, and the clarification is hoped to encourage a more universally consistent usage of the terms suspension, emulsion, and dispersion polymerization. Kinetic features and the size range of polymer particles produced by different heterogeneous polymerization processes are presented in Fig. 1.

It is here necessary to gather a brief idea of the nature and role of various components of heterogeneous polymerization systems in general, before discussing the details of individual processes. Thus, the monomer is usually referred to as the "monomer phase" or "dispersed phase". The liquid phase containing the dispersed monomer is defined as the "polymerization medium", or "medium" for the sake of brevity. The polymerization medium may also be referred to as the "continuous phase" or the "outer phase". In addition to the monomer(s) and the polymerization medium, another liquid (which must be miscible with the monomer and immiscible with the medium) may also be added to the monomer. This liquid is known as the "monomer diluent", or "diluent" for short. The use of the term solvent is deliberately avoided in the present discussion, because the diluent may be a good, poor, or non-solvent, or a precipitant for the polymer.

Polymerization mixtures composed of an aqueous phase and a nonaqueous phase are generally

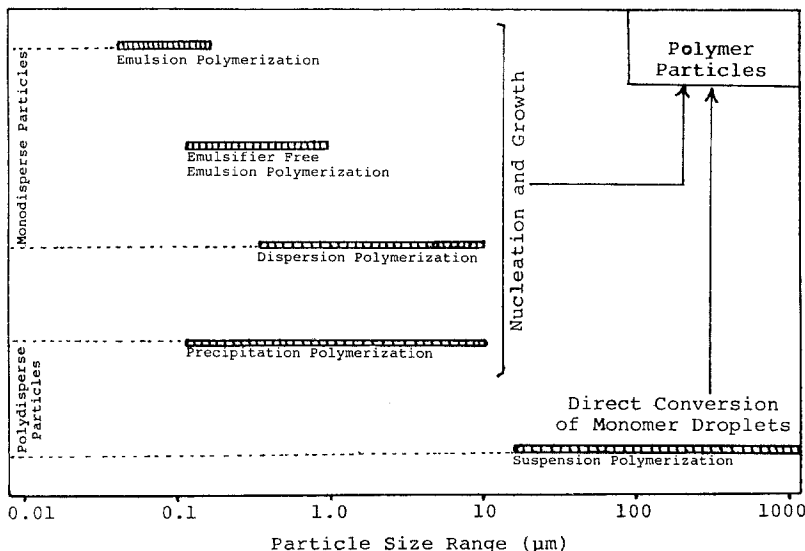


Fig. 1. General kinetic features and particle size ranges of heterogeneous (particle forming) polymerization processes

classified into oil-in-water (O/W) or water-in-oil (W/O) systems. The use of the terms "inverse suspension" and "inverse emulsion" should be avoided, because they imply a narrow definition of the terms "suspension" and "emulsion".

## Suspension polymerization

### Process description

In suspension polymerization [2, 3],\* the initiator is soluble in the monomer, and these two are insoluble in the polymerization medium. The volume ratio of the monomer phase to the polymerization medium is usually kept within 0.1–0.5, but, in principle, it can be as high as unity or even higher. The monomer phase is, by means of a stirrer and a suitable droplet stabilizer (suspension agent), suspended in the medium in the form of small droplets (microdroplets). The polymerization is then initiated at the desired temperature (20–100 °C), and is usually allowed to proceed to completion (~100%). Under these conditions, the monomer "microdroplets" are converted directly to the corresponding polymer "microbeads" of approximately the same size.

Basic aspects of suspension polymerization have been discussed in early papers by Hohenstein and Mark [4], Trommsdorff and coworkers [5], and later by Hopff et al. [6]. On the basis of these studies, it is generally assumed that polymerization kinetics in suspension polymerization are similar to those of bulk or solution polymerization, depending on the absence or presence of a monomer diluent in the monomer droplets. In this sense, suspension polymerization may be regarded as "microbulk" or "microsolution" polymerization, because individual monomer droplets represent tiny bulk or solution polymerization reactors. The suspension medium housing the "microreactors" acts as an efficient heat transfer agent. As a result, high rates of polymerization can be maintained to achieve complete conversion during relatively short periods of time.

Examples of industrially important polymers produced by oil-in-water (O/W) suspension polymerization include polystyrene, poly(vinyl chloride) (PVC), polyacrylates and poly(vinyl acetate).

Styrene-based resins used for the preparation of ion exchange resins and polymer supports [7–9] are also obtained by O/W suspension copolymerization of styrene and divinylbenzene (and a functional monomer). For all of these preparations the initiator is usually an azo compound (e.g., azo-bis-2-methylpropionitrile, AIBN), or an organic peroxide (e.g., benzoyl peroxide), and the polymerization is performed at a temperature of about 50–100 °C. Among typical droplet stabilizers used for O/W suspension polymerization are polyvinylpyrrolidone (PVP) and poly[(vinyl alcohol)-co-(vinyl acetate)]. The latter polymer is obtained by partial (85–92%) hydrolysis of poly(vinyl acetate). A wide range of other water soluble organic polymers, including natural gums, cellulose ethers, and synthetic polymers are also used. Scarcely soluble inorganic salts such as talc, phosphates, and sulfates may also be employed, either alone or in combination with organic stabilizers [2, 3].

Major examples of polymers produced by water-in-oil (W/O) suspension polymerization include polyacrylamide and water soluble acrylates. Acrylamide based polymer supports [10–11] are also prepared by W/O suspension copolymerization of acrylamide with bisacrylamide (and a functional monomer). Here, an aqueous solution containing the monomer(s) and the initiator is suspended in liquid paraffin or a chlorocarbon (polymerization medium), followed by polymerization at a temperature of 20–50 °C. A water-soluble catalyst may also be used for these preparations. The most typical combination of initiator and catalyst for W/O suspension polymerization is that of potassium peroxydisulfate and N,N,N',N'-tetramethylethylenediamine. Stabilizers used for W/O suspension polymerization include ethylcellulose, cellulose acetate butyrate, and various amphiphilic oligomers such as Span and Tween [2, 3].

Figure 2 shows a cylindrical reactor vessel with symmetrically matching stirring arrangement designed [3, 12] for laboratory scale suspension polymerization. The spiral stirring arrangement provides a relatively turbulent-free and uniform distribution of the mixing force throughout the suspension mixture. This, in turn, leads to the formation of relatively uniform monomer droplets and, hence, production of polymer particles with correspondingly narrow size distribution. In addi-

\*) See also a recent review by Yuan HG, Kalfas G, Ray WH (1991) JMS-Rev Macromol Chem Phys C31 (2–3):215

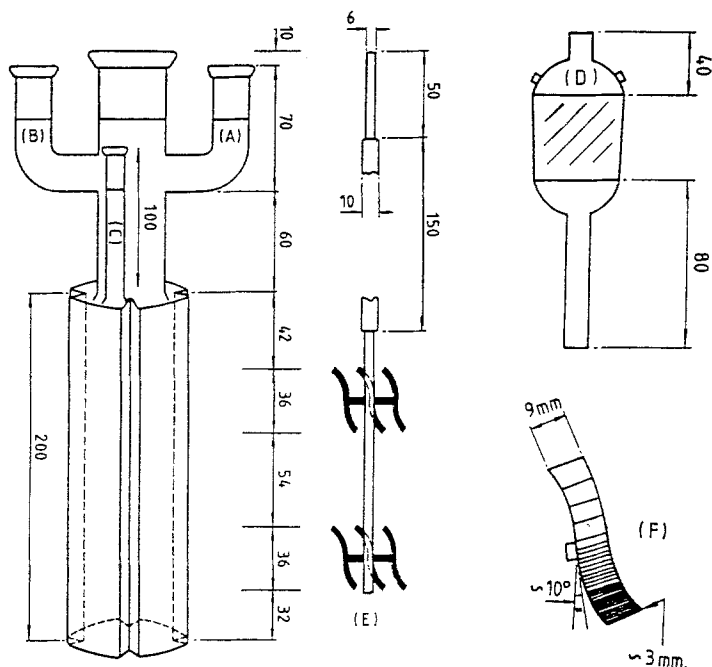


Fig. 2. Cylindrical glass reactor with symmetrically matching stirrer designed for laboratory scale suspension polymerization

tion, uniform distribution of the stirring force throughout the mixture produces a relatively stable suspension system, and minimizes the chance of inadvertent particle coagulation and experimental failure.

Quality of the beaded polymer products obtained by suspension polymerization depends, in addition to reactor design, on operational parameters governing the overall stability of the suspension system. In practice, efficient management of a suspension polymerization process is as much an art [3, 13] as it is based on exact scientific principles. Figure 3 shows examples of polymer particles produced by suspension polymerization, using the reactor vessel described above. In micrograph A, the particles are irregular agglomerates of smaller microspheres. This product was obtained from a low viscosity monomer mixture and a poorly stabilized suspension system. Micrograph B, on the other hand, shows relatively uniform individual microspheres obtained from a normal polymerization run under carefully controlled conditions [10, 12].

#### Droplet/particle size control

Suspension polymerization can, in principle, be employed to produce polymer particles within any size range, from about 100 nm up to about 1–2 mm

or larger. For the routine practice of addition polymerization of vinyl monomers, however, suspension polymerization is suitable for polymer particles within the size range of about 20  $\mu\text{m}$ –2 mm. Preparation of particles smaller than about 20  $\mu\text{m}$  by suspension polymerization becomes increasingly complicated as a result of emulsion polymerization [3, 14].

The average size of the monomer droplets (and, hence, that of the resulting particles) can be readily controlled by varying the stirring speed, volume ratio of the monomer to suspension medium, concentration of the stabilizer, and the viscosities of both phases according to Eq. (1). This equation represents most of the empirical relationships reported by Arshady and Ledwith [3], Hopff and coworkers [6], Kavarov and Babanov [15], Mersmann and Grossman [16], and Sculles [17]:

$$\bar{d} \equiv k \frac{D_v \cdot R \cdot \nu_d \cdot \varepsilon}{D_s \cdot N \cdot \nu_m \cdot C_s}, \quad (1)$$

where  $\bar{d}$  = average particle size;  $k$  = parameters such as apparatus design, type of stirrer, self stabilization, etc.;  $D_v$  = diameter of vessel;  $D_s$  = diameter of stirrer;  $R$  = volume ratio of the droplet phase to suspension medium;  $N$  = stirring speed (or power of mixing);  $\nu_d$  = viscosity of the droplet phase;  $\nu_m$  = viscosity of the suspension medium;

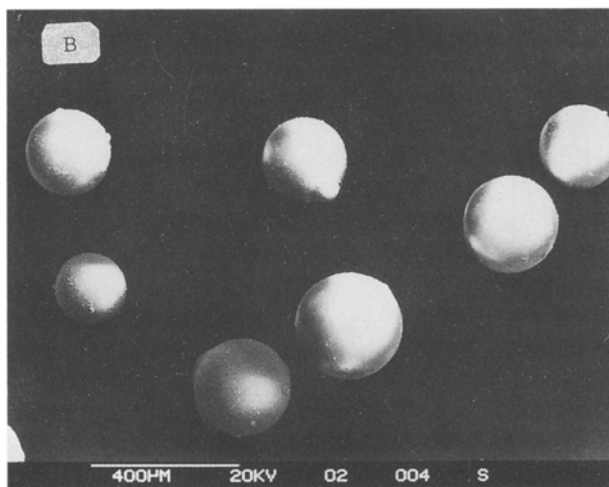
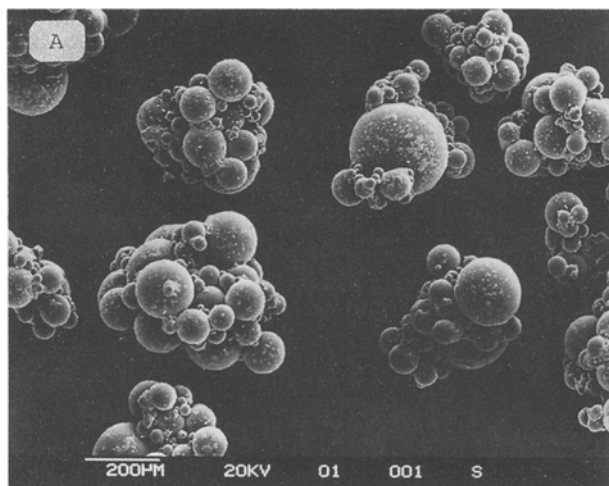


Fig. 3. Scanning electron micrographs of typical polymer samples produced by suspension polymerization. A) broad size distribution and aggregation resulting from a poorly stabilized droplet suspension; B) individually spherical particles with narrow particle size distribution resulting from a well-stabilized droplet suspension

$\varepsilon$  = interfacial tension between the two immiscible phases; and  $C_s$  = stabilizer concentration.

Quantitative expressions reported by different authors [3, 6, 15–17] for various parameters in Eq. (1) differ from each other to some extent, depending on the details of the suspension system studied. However, Eq. (1) provides a useful guide for planning a new suspension polymerization process, as well as a semiquantitative basis for understanding particle size data of the product thus produced.

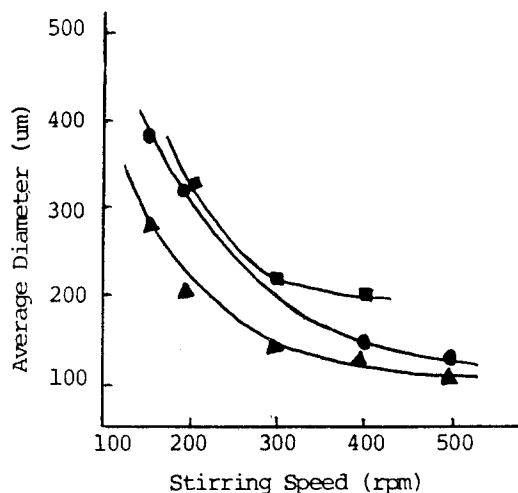


Fig. 4. Effect of stirrer speed on particle size in suspension polymerization of styrene in the presence of 0.2% (■), 0.3% (●), or 0.4% (▲) of a hydrophobically modified polyoxyethylene stabilizer (adapted from [18])

Among the parameters indicated in Eq. (1), stirrer speed is by far the most convenient means of controlling particle size. A typical example of the dependence of particle size on stirrer speed is provided by the graphs in Fig. 4 for suspension polymerization of styrene [18]. This pattern of particle size control by stirrer speed is generally observed for well-stabilized suspension systems; although the slope of the curve may vary, depending on the magnitude of other parameters of Eq. (1).

#### Particle morphology

An important aspect of polymer particles obtained by suspension polymerization is the surface and bulk morphology of the individual beads. This morphology is basically related to the degree by which the polymer dissolves, swells or precipitates in the monomer phase. When the polymer is soluble (or swellable) in its monomer mixture, the resulting polymer particles have a smooth surface and a relatively homogeneous (nonporous) texture. On the other hand, when the polymer is not soluble (or swellable) in its monomer mixture, the final particles have a rough surface and a porous morphology. For example, polystyrene and poly(methyl methacrylate) dissolve (swell) in their own monomers and produce smooth and translucent microbeads. On the other hand, poly(vinyl

chloride) and polyacrylonitrile are insoluble (i.e., precipitate) in their own monomers, and produce corrugated (or porous) particles.

The degree of resin porosity and the details of pore structure is of particular interest in the production of crosslinked ion exchange resins and polymer supports. For these materials, particle morphology can be strongly influenced by the use of a suitable monomer diluent (not to be confused with water used as polymerization medium). Thus, for the preparation of polymer supports and ion exchange resins, the monomer is diluted by an inert liquid which may be a good or poor solvent, or a precipitant for the resulting polymer particles. In this way, polymer particles with a wide range of porosities can be produced, depending on the

nature and the percentage of the monomer diluent and the extent of polymer crosslinking [19, 20].

Figure 5 shows scanning electron micrographs (SEM) of cross-sections of nonporous and porous beads produced by suspension copolymerization of styrene with 2,4,5-trichlorophenyl acrylate and divinylbenzene. The polymers were obtained in the presence of chlorobenzene (A, a good solvent), or chlorobenzene-octane (B, a poor solvent) [9].

### Emulsion polymerization

#### *Process description*

In (classical) emulsion polymerization [21–23], the monomer is insoluble (or scarcely soluble) in

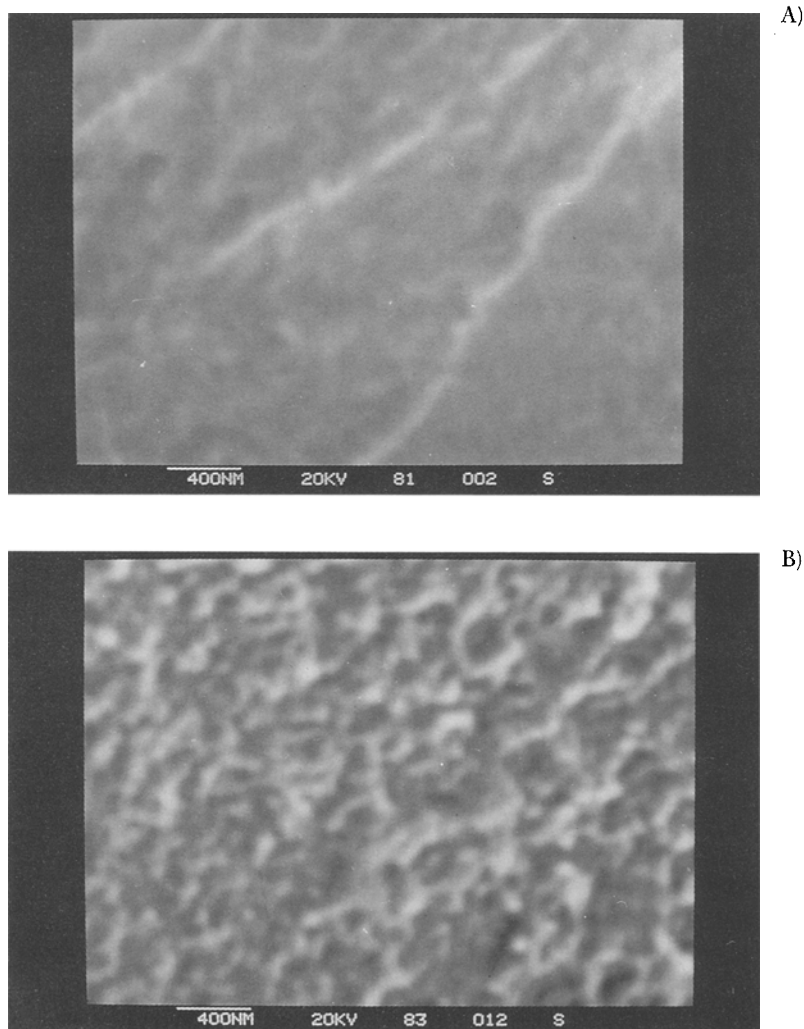


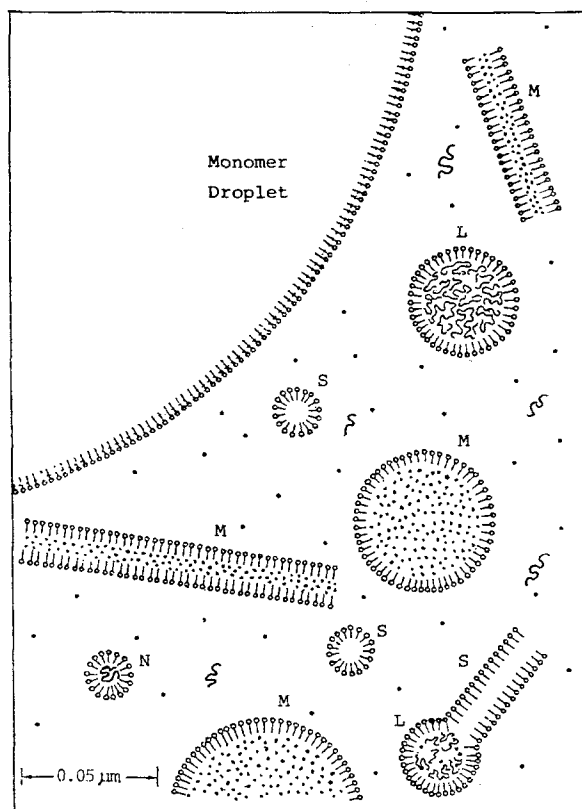
Fig. 5. Cross-sections of nonporous (A) and porous (B) particles produced by suspension polymerization of styrene with 2,4,5-trichlorophenyl acrylate and divinylbenzene in the presence of a monomer diluent: chlorobenzene (A), or chlorobenzene-*n*-octane (B)

the polymerization medium, but it is emulsified in it by the aid of a surfactant (emulsifier or soap). The initiator is, unlike in suspension polymerization, soluble in the medium, and not in the monomer. Under these conditions, the monomer is present in the mixture partly in the form of droplets (about 1–10  $\mu\text{m}$  or larger), and partly in the form of soap-coated micelles (ca. 50–100 Å), depending on the nature and concentration of the emulsifier. A small percentage of the monomer is also molecularly dissolved in the medium. For example, solubility of styrene in water at 70 °C is about 4 g/l.

The volume ratio of the monomer phase to the medium in emulsion polymerization is usually within about 0.1–0.5, and the polymerization is carried out at 40–80 °C. The state of the polymerization mixture in the early stages of emulsion polymerization is schematically presented in Fig. 6. Since the initiator is present only in the medium, the initial locus of polymerization is in the medium (i.e., outside the droplets and micelles). The oligoradicals formed in the polymerization medium are either surrounded by the dissolved monomer and emulsifier molecules, or they are absorbed by the already present soap-coated monomer micelles.

In either case, the initially formed oligoradicals produce stabilized nuclei (primary particles) [24, 25]. Subsequently, emulsifier-stabilized polymer nuclei become the main loci of polymerization by absorbing further oligoradicals and monomer molecules from the medium, or in effect from the monomer droplets. In this way, the nuclei/particles grow gradually until the monomer is completely consumed. The size of the latex particles thus produced is usually in the range of 50–300 nm. It is noteworthy, however, that exact details of particle formation and growth are strongly dependent on the nature of the polymerization mixture, as has been outlined recently by Lagaly and colleagues [22].

For O/W emulsion polymerization (e.g., those of styrene or methyl methacrylate in water), potassium peroxydisulfate and sodium dodecylsulfate are commonly used as initiator and emulsifier, respectively. Combinations of ionic and nonionic emulsifiers may also be used. An interesting example is the use of sodium dodecylsulfate and Triton X-100, as reported by Woods et al. for the preparation of monodisperse polystyrene particles (ca. 250 nm) [26].



• = Monomer molecule, M = Monomer containing micelle  
S = Soap micelle, S<sup>o</sup> = Growing macroradicals  
N = Polymer nucleus, L = Growing latex particle

Fig. 6. Schematic presentation of early stages of emulsion polymerization (adapted from B. Vollmert, *Polymer Chemistry*, Springer Verlag, New York, 1973)

For water soluble monomers, an aqueous solution of the monomer is emulsified in a water immiscible liquid (an oil), in the presence of a water-in-oil (W/O) emulsifier, and an oil soluble initiator. Examples of W/O emulsion polymerization [27–29] are those of acrylamide and sodium 4-vinylbenzenesulfonate in toluene, in the presence of benzoyl peroxide initiator. Fatty esters of polyhydroxy compounds (e.g., sorbitan monooleate) are often used as W/O emulsifiers. A recent recipe described by Pichot et al. [27] uses an aqueous solution of acrylamide and methacrylic acid in toluene, in the presence of sorbitan esters and AIBN. This polymerization is carried out at 40 °C for 1–4 h to obtain a high yield of the latex copolymer containing 30–70% methacrylic acid.

### Alkyl cyanoacrylate nanospheres

An interesting example of O/W emulsion polymerization is that of alkyl cyanoacrylates by anionic initiation (i.e.,  $\text{HO}^-$  ions present in water). A very low concentration of  $\text{HO}^-$  is required for the polymerization to proceed in a controlled manner. In practice, pH is adjusted to 1–3 to achieve a  $\text{HO}^-$  concentration of about  $10^{-13}$ – $10^{-11}$  mole/l. Poly(alkyl cyanoacrylate) latex (nanospheres, nanocapsules) are biodegradable, and have attracted considerable interest for potential pharmaceutical use [30, 31].

Douglas et al. have studied the details of emulsion polymerization of butyl cyanoacrylate in the presence of polyoxyethylene-b-polyoxypropylene copolymers or low molecular weight polysaccharides as emulsifier [32]. Since these emulsifiers carry free hydroxy groups, it is reasoned [33] that the emulsifier may act also as initiator and, hence, covalent attachment to the latex particles (Fig. 7).

### Particle size control

The size of latex particles in emulsion polymerization has no direct relationship with the size of the initially formed monomer droplets or micelles. These do not contain any initiator and, hence, are not directly converted to the corresponding polymer particles. Instead, the fraction of the monomer molecularly dissolved in the polymerization medium plays a key role in determining the size of the final polymer particles. The size of the latex particles in emulsion polymerization is also influenced by a number of other factors, including emulsifier concentration and polymerization temperature. Figure 8 shows electron micrographs of polyvinyltoluene particles prepared by emulsion

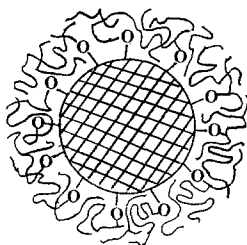


Fig. 7. Schematic presentation of stabilizer-grafted poly(alkyl cyanoacrylate) particles produced by emulsion polymerization in the presence of dextran used as emulsifier

polymerization at different temperatures, under otherwise similar conditions [34].

The micrographs in Fig. 8 indicate that the size of the particles decreases as the temperature of polymerization increases. This observation is in accordance with the nucleation mechanism outlined above [24, 25], and reflects the dependence of particle size on the rate of nucleation ( $\equiv$  rate of polymerization). Other kinetic parameters which control the rate of polymerization reaction (i.e., concentrations of initiator, emulsifier, and salt), also influence the size of the latex particles [22, 24, 25, 34, 35]. Salt concentration controls the viscosity and ionic strength of the medium, both of which influence the course of the nucleation process.

### Soapless emulsion polymerization

In emulsifier-free (or soapless) emulsion polymerization [36–38], the polymerization is carried out in the same way as in classical emulsion polymerization, except that no emulsifier is used. Accordingly, nucleation takes place by precipitation of macroradicals (and macromolecules), as compared with micelle formation in normal emulsion

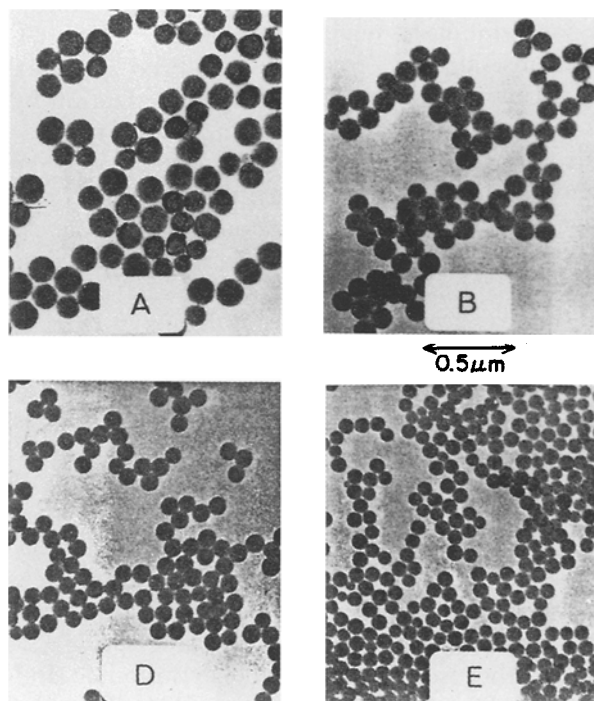


Fig. 8. Polyvinyltoluene particles produced by emulsion polymerization at 23 °C (A), 50 °C (B), 70 °C (D), and 80 °C (E) [84]



polymerization. Since there is no emulsifier present in the medium, the nuclei thus formed are not stabilized by any emulsifier or stabilizer. As a result, the initially formed polymer nuclei collide and form larger and larger particles as the polymerization proceeds.

However, latex particles produced in the absence of emulsifier are, to some extent, stabilized by the orientation of their own polymer chains, notably the chain ends originating from initiator molecules. For example, in the case of potassium peroxydisulfate initiator, the chain end groups are  $\sim\text{OSO}_3^- \text{K}^+$ . As the particles grow, their surface charge increases, and at a certain size (usually  $> 100 \text{ nm}$ ), the particles become stabilized by their own electrostatic charge. Latex stabilization by the use of amidinium initiators (Fig. 9) producing positively charged latex particles has also been studied by Goodwin et al. [36b]. Monomer to water ratio in emulsifier-free emulsion polymerization is usually much smaller than that in normal emulsion polymerization. In most cases, monomer concentration is less than 5%, and the size of the resulting particles is in the region of about 100–1000 nm.

## Dispersion polymerization

### Process description

In dispersion polymerization [39–41] the monomer and the initiator are both soluble in the polymerization medium, but the medium is a poor

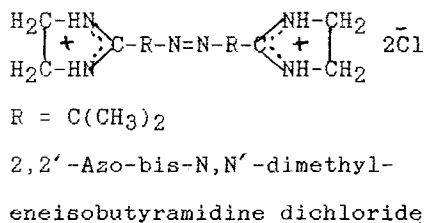
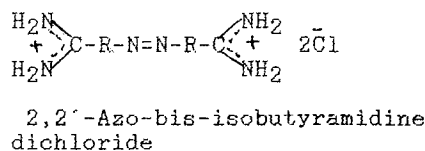


Fig. 9. Amidinium-azo initiators used in soapless emulsion polymerization to produce positively charged latex particles [36b]

solvent for the resulting polymer. Accordingly, the reaction mixture is homogeneous at the onset, and the polymerization is initiated in homogeneous solution. Depending on the solvency of the medium for the resulting macroradicals and macromolecules, phase separation occurs at an early stage. This leads to nucleation and the formation of primary particles, as illustrated in Fig. 10. However, primary particles thus formed in dispersion polymerization are swollen by the polymerization medium and/or the monomer. As result, polymerization proceeds largely within the individual particles, leading to the formation of spherical particles in the region of about 0.1–10  $\mu\text{m}$ .

Typical examples of dispersion polymerization are those of styrene and methyl methacrylate in hydrocarbons or in  $\text{C}_1\text{--C}_5$  alcohols. Various aspects of dispersion polymerization in petroleum hydrocarbons were discussed in a monograph edited by Barret [39]. Almog et al. [40], and Ober et al. [41] have reported on dispersion polymerization of styrene and methyl methacrylate in alcohols and various alcohol-ether or alcohol-water mixtures. More recently, Tseng et al. have studied the effects of medium solvency, and concentrations of

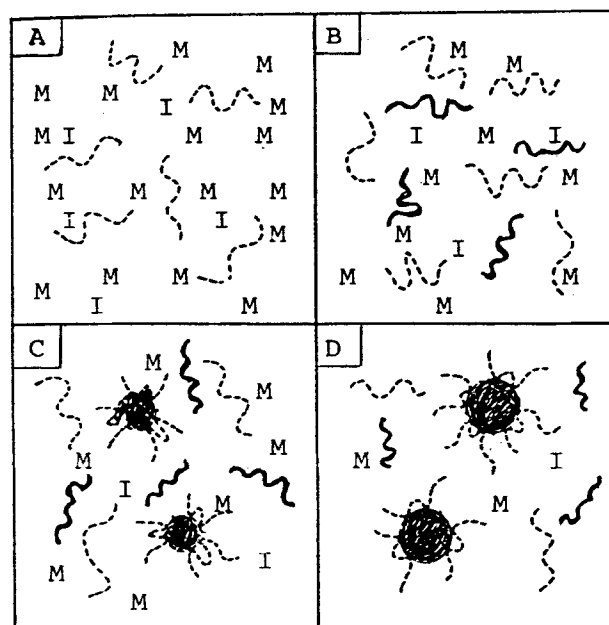


Fig. 10. Schematic presentation of nucleation and particle growth in dispersion polymerization. M = monomer; I = initiator; ---- = stabilizer; — = macromolecule/macroradical

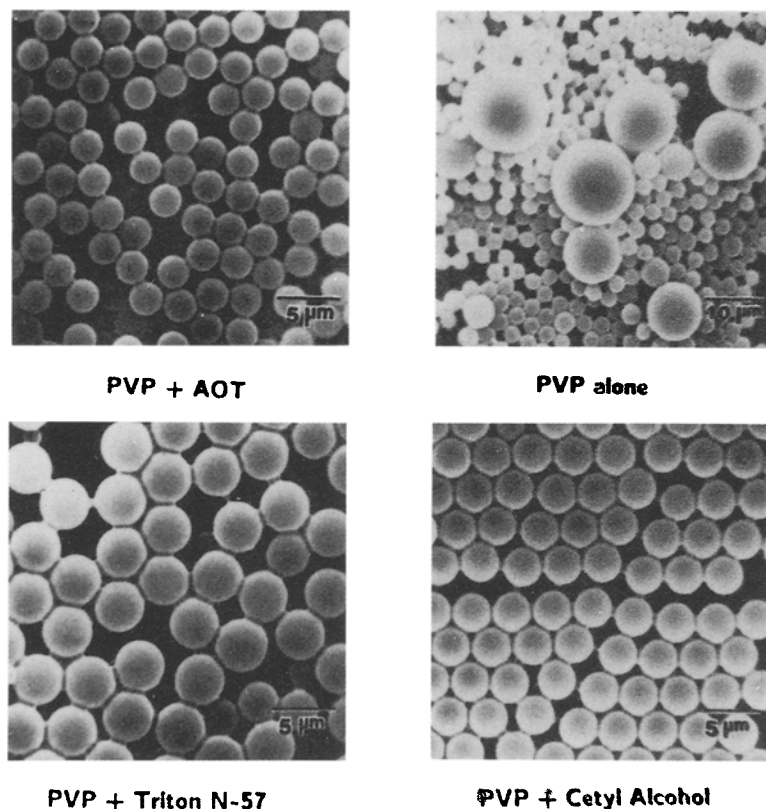


Fig. 11. Polystyrene particles produced by dispersion polymerization in ethanol in the presence of polyvinylpyrrolidone (PVP) and different costabilizers (AOT, aerosol OT) (from [42])

monomer, stabilizer, and initiator on the size of polymer particles formed in dispersion polymerization. They have also discussed the preparation of reactive and crosslinked particles. Figure 11 shows electron micrographs of typical polystyrene particles reported by this group [42]. Egan and Winnick [43] have also described an interesting study of dispersion polymerization of vinyl acetate in isooctane involving the copolymerization of fluorescent monomers such as methacryl derivatives of pyrene or phenanthrene.

#### Particle stabilization

Particle dispersions produced by dispersion polymerization in the absence of any stabilizer are not sufficiently stable and may coagulate during their formation. Addition of a small percentage of a suitable stabilizer to the polymerization mixture produces stable particle dispersions. Particle stabilization in dispersion polymerization is usually referred to as "steric stabilization", as compared with emulsifier or charge stabilization in emulsion

polymerization. Good stabilizers for dispersion polymerization are polymer and oligomer compounds with low solubility in the polymerization medium and moderate affinity for the polymer particles. For example, methacrylic polymers carrying oligostearic grafts (PMMA-g-OSA) have been found [39] particularly suitable for dispersion polymerization of hydrophobic monomers in petroleum hydrocarbons. For dispersion polymerization in alcohols and other polar solvents, a wide range of polar organic polymers such as polyvinylpyrrolidone, poly(vinyl alcohol), and cellulose derivatives, with or without costabilizers have been used [40–42].

In many instances [39], the stabilizer may be grafted onto the surface of the polymer particles either during, or after, the polymerization process. An interesting recent example is that of stabilizer-grafted monodisperse poly(methyl methacrylate) particles reported by Antl et al. [44]. In a typical preparation, a charge of 750 g of the polymerization solution (Table 1) is refluxed to achieve complete polymerization within about 2 h. The

Table 1. Typical recipe for dispersion polymerization involving stabilizer grafting<sup>a</sup>) to the polymer particles [44]

Polymerization ingredients	Parts by weight
Methyl methacrylate containing 1.8% methacrylic acid	42
Polymeric stabilizer carrying glycidyl groups	2.1
<i>n</i> -Hexane	35.2
Aromatic hydrocarbons (b.p. 230–250 °C)	17.0
Azo-bis-2-methylpropionitrile (AIBN)	0.4

<sup>a</sup>) Grafting via coupling of glycidyl groups to methacrylic acid residues on the particles

low boiling solvent is then distilled off at 120 °C and replaced by a high boiling hydrocarbon. An amine catalyst is subsequently added, and the mixture is maintained at 120 °C until the stabilizer is coupled to the particles. The reaction is assumed to take place via the esterification of the carboxylic residues on the polymer by the glycidyl groups on the stabilizer. By adjusting the solvency of the polymerization medium (i.e., the ratio of aliphatic to aromatic hydrocarbons), particles in the size range of 0.8–2.6  $\mu\text{m}$  are produced [44].

#### Particle size control

Particle size in dispersion polymerization is governed by the temperature of polymerization, concentrations of monomer and initiator, and the type and concentration of stabilizer. In addition, the solvency of the polymerization medium strongly influences particle size. Effect of medium solvency on particle size in dispersion polymerization of styrene in C<sub>1</sub>–C<sub>5</sub> alcohols is shown in Table 2 [40]. For the dependence of particle size on stabilizer type see Fig. 11.

#### Precipitation polymerization

In precipitation polymerization, the initial state of the reaction mixture is the same as that in dispersion polymerization, i.e., a homogeneous solution. However, in this case, primary particles do not swell in the medium, and the polymerization is literally a “precipitation polymerization”. Under these conditions, initiation and polymerization take place largely in the homogeneous medium. This leads to continuous nucleation and the coagulation of the resulting nuclei to form larger and

Table 2. Effect of medium solvency ( $\Delta\delta$ )<sup>a</sup>) on particle size in dispersion polymerization of styrene [40]

Polymerization medium	$\Delta\delta$ (cal/ml) <sup>1/2</sup>	Mean particle diameter ( $\mu\text{m}$ )
Methanol	14.5	1.8
Ethanol	12.7	2.8
<i>n</i> -propanol	11.9	2.6
Isopropanol	11.5	3.2
2-Butanol	10.8	1–22
<i>t</i> -Butanol	10.6	5.2

<sup>a</sup>)  $\Delta\delta = |\delta_p - \delta_m|$ ;  $\delta_p$  and  $\delta_m$  are solubility parameters of polystyrene and the polymerization medium, respectively.

larger particles. Thus, precipitation polymerization produces irregularly shaped and polydisperse particles, as shown in Fig. 12 for the polymerization of tetrafluoroethylene in water [45]. Another example of precipitation polymerization is that of acrylonitrile in bulk.

An interesting illustration of the difference between precipitation and dispersion polymerization is provided by the work of Carezza and Palma [46] on radiation polymerization of acrylonitrile and acrylonitrile-butyl acrylate. Figure 13 shows micrographs of homo- and copolymer particles obtained by  $\gamma$ -irradiation of the monomers in bulk, under similar conditions. The homopolymer particles (A) are irregularly shaped and polydisperse (i.e., precipitation polymerization), whereas the copolymer particles are spherical and uniform (i.e., dispersion polymerization).

The criterion of medium solvency for the polymer is generally a useful guide for distinguishing between dispersion and precipitation polymerization, even though a sharp distinction may not always exist. The use of particle stabilizers in precipitation polymerization may produce more uniform particles, but the particles remain irregularly shaped due to their growth mechanism. It is also noteworthy that suspension polymerization of monomers such as vinyl chloride is, in effect, a precipitation polymerization taking place in tiny monomer droplets.

#### Other techniques

##### Bimodal polymerization

Any polymerization process constituting more than one set of conditions defining suspension,

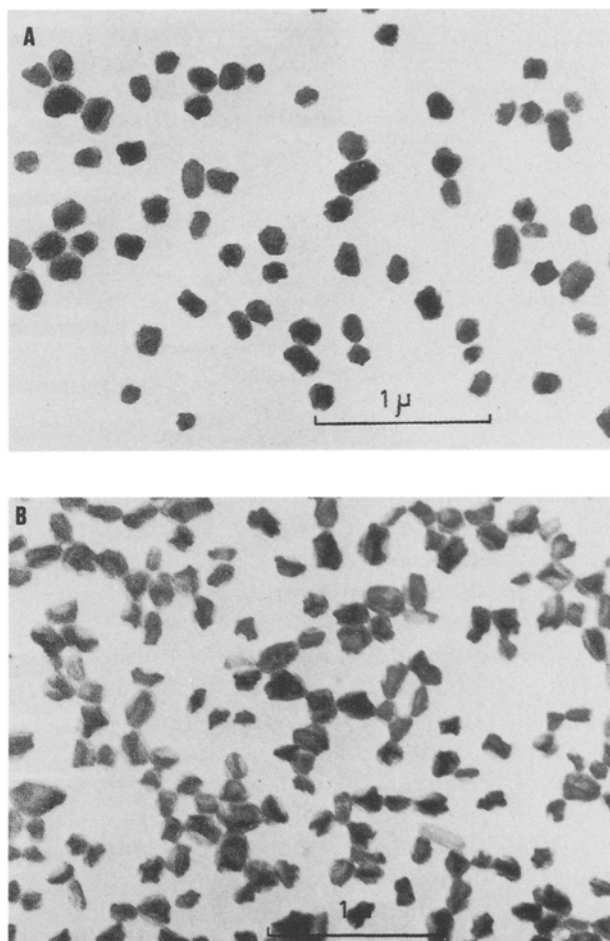


Fig. 12. Polytetrafluoroethylene (PTFE) particles produced by precipitation polymerization in water. Polymerization time: A) 30 min; B) 60 min [45]

emulsion, dispersion or precipitation polymerization is literally a multimodal polymerization. In practice, bimodal processes involving both suspension and emulsion polymerization are frequently reported. The following are typical examples:

- 1) Polymerization of styrene in water under suspension conditions, but attempting to produce very small particles [14];
- 2) Polymerization of divinylbenzene in water by thermal initiation in the presence of an emulsifier [47];
- 3) Polymerization of styrene in water, in the presence of an oil soluble initiator and an emulsifier [48];

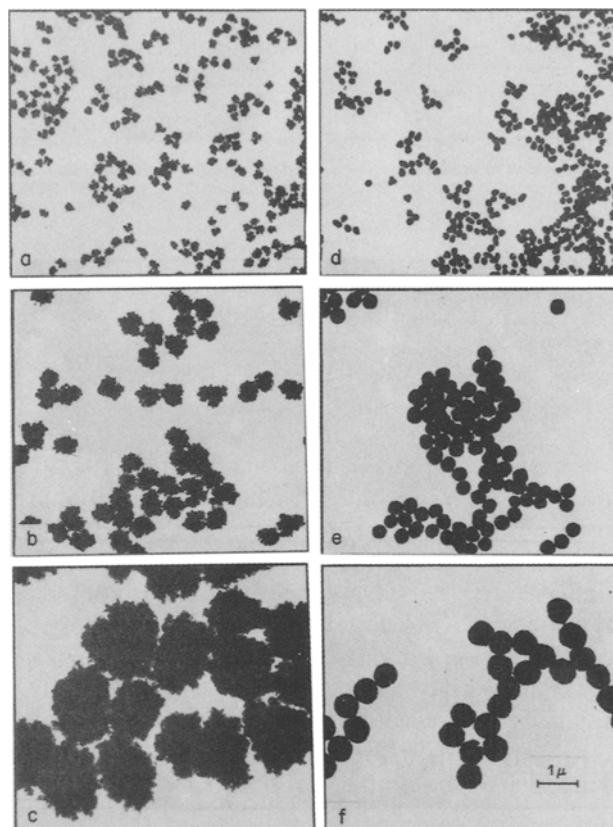


Fig. 13. Polyacrylonitrile (a, b, c) and copoly(acrylonitrile-butyl acrylate) (d, e, f) particles produced by radiation polymerization in bulk [46]

- 4) Copolymerization of aqueous acrylamides in chloroform-toluene with persulfate initiator, but in the presence of an emulsifier [49].

All of these examples involve the formation of polymer particles with very broad particle size distributions, e.g.,  $0.1\text{--}10\ \mu\text{m}$  [47] or  $0.2\text{--}2.0\ \mu\text{m}$  [49]. Figure 14 shows an electron micrograph of a sample of polystyrene particles produced under apparent emulsion conditions, but in the presence of a monomer soluble initiator [48]. Under these conditions, initiation takes place both in the polymerization medium and in the monomer droplets and, hence, a bimodal system involving both suspension and emulsion polymerization.

#### Seeded polymerization

Various modes of emulsion and dispersion polymerization discussed above involve the formation

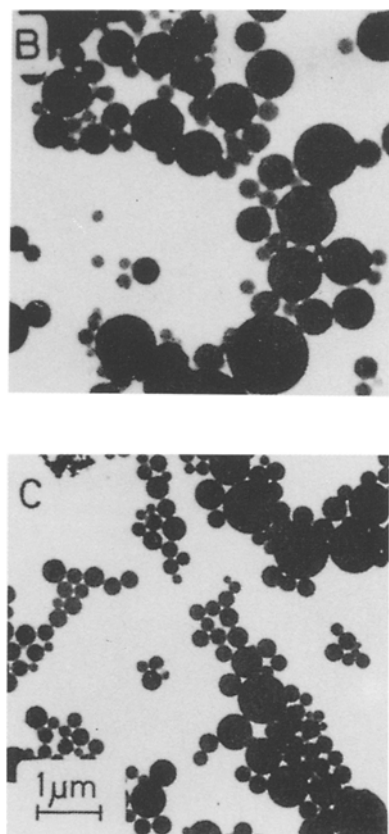


Fig. 14. Bimodal polystyrene particles produced by polymerization in water, in the presence of an emulsifier and a monomer-soluble initiator [48]

of nuclei (primary particles), followed by gradual growth of these nuclei to produce the final polymer particles. In all of these systems, preformed polymer particles (i.e., seeds) can be added to the polymerization mixture at the onset of the polymerization instead of in situ formation of polymer nuclei. However, polymerization conditions (i.e., number of seed particles and concentrations of initiator and stabilizer) must be carefully chosen to avoid the formation of new particles.

Polymerization in the presence of seed particles (seeded polymerization) was first reported by Smith in 1948 [50] to study the kinetics of emulsion polymerization. In more recent years, seeded polymerization has been widely employed for the same purpose (cf. [17, 39, 51]), as well as for the preparation of relatively large monodisperse particles [52, 53].

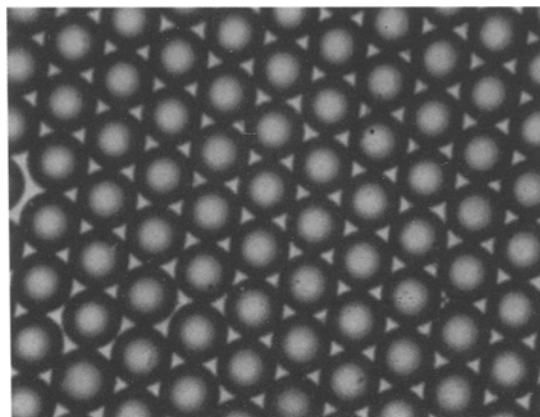


Fig. 15. Monodisperse 20  $\mu\text{m}$  polystyrene-divinylbenzene particles produced by “swollen-seed” polymerization in aqueous medium [54]

The concept of seeded polymerization has been extended by Ugelstad et al. for the preparation of monodisperse particles of up to 50  $\mu\text{m}$  [54]. The method developed by this group is based on the observation that swelling of polymer particles is considerably enhanced in the presence of a small percentage of a second low molecular weight polymer (oligomer). Thus, monodisperse polystyrene latex particles obtained by emulsion polymerization are treated, first with a suitable oligomer, and then with styrene (and DVB) and an oil-soluble initiator. The mixture is allowed to stand until the oligomer and monomer are completely absorbed by the particles. Subsequent polymerization leads to the formation of the correspondingly larger monodisperse particles (Fig. 15) [54]. This method is particularly useful for the preparation of monodisperse polymer microspheres in the region of 5–20  $\mu\text{m}$  which are less readily obtained by basic heterogeneous polymerization techniques.

#### Core-shell polymerization

The formation of core-shell particles [55, 56] by heterogeneous polymerization is superficially similar to seeded polymerization. However, “shell formation” around individual core particles by direct polymerization must take place strictly under the following polymerization conditions.

- 1) The core particles must not swell in the monomer;

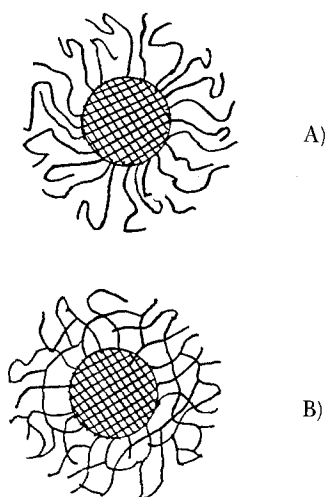


Fig. 16. Schematic presentation of core-shell particles produced by surface grafting (A), or graft polymerization (B)

- 2) The shell polymer must be “formed” or “precipitated” on the core surface;
- 3) Core and shell polymers must not diffuse into each other (i.e., they must be immiscible)

Ideal core-shell structures (Fig. 16) can be obtained by attaching preformed polymer chains to the core surface (A) [57], or graft polymerization on the surface (B) [58]. In the absence of grafting, however, the process of core-shell formation is complicated, and depends on the exact details of experimental conditions (e.g., monomer diffusion into seeds and miscibility of the two polymers) [58–60]. A particularly interesting illustration of these problems is provided by attempted preparation of poly(hydroxyethyl methacrylate)-polystyrene (PHEMA-PS) core-shell particles [60].

Figure 17 shows electron micrographs of core-shell particles obtained by aqueous polymerization of HEMA in the presence of PS core particles (a), and those obtained by aqueous polymerization of styrene in the presence of PHEMA core particles (b). The dark areas in the figure represent PS, and the lighter areas PHEMA. Note that, apart from minor shape irregularities of the particles in micrograph (a), both preparations are remarkably similar, i.e., both experiments lead to the formation of particles with PS core and PHEMA shell.

The rather intriguing result in experiment (b) is a logical consequence of the nature of the two polymers and the aqueous polymerization system employed. PHEMA is *amphiphilic* and PS is *hydro-*

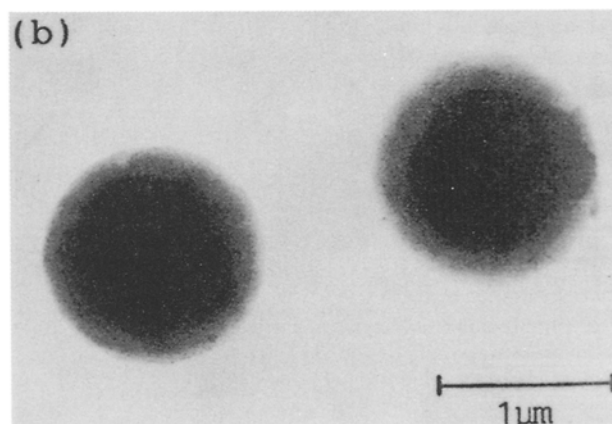
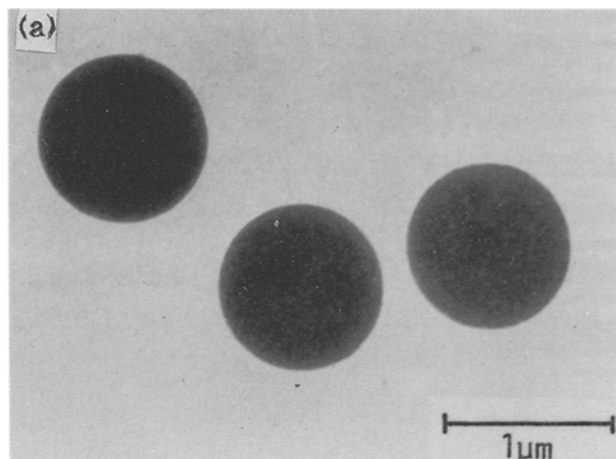


Fig. 17. Core-shell particles produced by a) aqueous polymerization of hydroxyethyl methacrylate (HEMA) in the presence of polystyrene (PS) seeds; and b) aqueous polymerization of styrene in the presence of PHEMA seeds. Note that in both cases the particles are composed of PS core and PHEMA shell

*phobic*. Thus, PHEMA core particles swell in the aqueous polymerization medium and become highly permeable. Under these conditions, styrene (and any PS formed in the aqueous medium) is extracted from the aqueous medium, and resides within the PHEMA core particles. Subsequently, polymerization of styrene and precipitation of PS take place farthest away from the aqueous phase, i.e., in the center of the PHEMA particles. This process may, therefore, be appropriately referred to as “inverted core-shell polymerization”.

## Conclusions and general remarks

A methodological description of heterogeneous polymerization processes, including suspension, emulsion, dispersion, and precipitation polymerization is presented. The discussion focuses on the initial state of the polymerization mixture, mechanism of particle formation, and the shape and size of polymer particles produced in heterogeneous polymerization processes. The influence of manufacturing parameters such as emulsifier, stabilizer, reactor design, and stirring speed on size and morphology of the polymer particles is discussed. Special topics, including emulsifier-free (soapless) emulsion polymerization, seeded polymerization, and the formation of core-shell particles, are also briefly covered. It is shown that different heterogeneous polymerization processes can be clearly distinguished on the basis of one or more of the following four criteria: 1) initial state of the polymerization mixture, 2) mechanism of polymerization, 3) mode of particle formation, and 4) particle form of the final polymer. The discussion should, therefore, assist the comprehension of heterogeneous polymerization processes employed for the production of polymer colloids, particles, and powders. It is also hoped that the concise methodological description will encourage a more universal adoption of the terms "suspension", "emulsion", "dispersion", and "precipitation" polymerization.

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Received May 3, 1991;  
accepted October 30, 1991

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