Terminology of polymers and polymerization processes in dispersed systems (IUPAC Recommendations 2011)*

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Abstract: A large group of industrially important polymerization processes is carried out in dispersed systems. These processes differ with respect to their physical nature, mechanism of particle formation, particle morphology, size, charge, types of interparticle interactions, and many other aspects. Polymer dispersions, and polymers derived from polymerization in dispersed systems, are used in diverse areas such as paints, adhesives, microelectronics, medicine, cosmetics, biotechnology, and others. Frequently, the same names are used for different processes and products or different names are used for the same processes and products. The document contains a list of recommended terms and definitions necessary for the unambiguous description of processes, products, parameters, and characteristic features relevant to polymers in dispersed systems.

Keywords: dispersed systems; glossary; IUPAC Polymer Division; polymer terminology; polymerization processes; terminology.

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1. INTRODUCTION

A large group of industrially important polymerization processes is carried out in dispersed systems. These processes differ with respect to their physical nature, mechanism of particle formation, particle morphology, size, charge, types of interparticle interactions, and many other aspects. Polymer dispersions, and polymers derived from polymerization in dispense systems, are used in diverse areas such as paints, adhesives, microelectronics, medicine, cosmetics, biotechnology, and others. Frequently, the same names are used for different processes and products or different names are used for the same processes and products. The present list of recommended terms and definitions is necessary for the unambiguous description of processes, products, parameters, and characteristic features relevant to polymers in dispersed systems.

For ease of reference, the terms in each section, subsection, etc. are listed alphabetically and numbered sequentially. Cross-references to terms defined elsewhere in the document are denoted in italic typeface. If there are two terms in an entry on successive lines, the second is a synonym.

2. POLYMER PARTICLES

2.1 polymer particle

Particle of polymer of any shape.

Note: For the description of a particle, the expression “size” is often used. However, because this expression does not have a sufficiently precise meaning its usage is not recommended.

2.2 polymer bead

Sphere of polymer, usually with a diameter in the range from one-tenth to a few millimeters.

2.3 polymer microparticle

Particle of polymer of any shape with an equivalent diameter from approximately 0.1 to 100 μm.

2.3.1 polymer microsphere

Polymer microparticle of spherical shape.

2.3.2 polymer microcapsule

See microcapsule.
2.4  polymer nanoparticle
Particle of polymer of any shape and an *equivalent diameter* from approximately 1 to 100 nm.

2.4.1  polymer nanosphere
*Polymer nanoparticle* of spherical shape.

2.4.2  polymer nanocapsule
See *nanocapsule*.

2.5  polymer gel particle
Particle of gel in which the *network* component is a polymer.

2.5.1  gel microparticle
*microgel*
Particle of gel of any shape with an *equivalent diameter* of approximately 0.1 to 100 μm.

*Note:* Definition based on ref. [1].

2.5.2  gel nanoparticle
*nanogel*
Particle of gel particle of any shape and an *equivalent diameter* of approximately 1 to 100 nm.

2.5.3  microgel
See *gel microparticle*.

2.5.4  nanogel
See *gel nanoparticle*.

2.6  polymer network particle
Particle having any shape and composed of a polymer network and possibly species of finite molar mass.

2.7  latex
Colloidal dispersion of polymer particles in a liquid.

*Note:* The polymer in the particles may be organic or inorganic.

2.7.1  artificial latex
Latex obtained by emulsification of a polymer or oligomer solution in a liquid or by emulsification of a liquid polymer or liquid oligomer in a liquid.
2.7.2 hybrid latex

a. Latex comprising a polymer of relatively high molar mass and an oligomer or an alkyd resin, in
which there is usually chemical bonding between the two components, formed either during latex
synthesis or subsequently after formation of a film from the latex.

b. Latex comprising multicomponent particles that contain both organic and inorganic material
phases.

2.7.3 inverse latex

Nonaqueous latex in which the dispersed phase comprises hydrophilic polymer usually swollen with
water.

Note: An inverse latex is usually formed by inverse emulsion, inverse micro-emulsion, or
inverse mini-emulsion polymerizations in which water-soluble monomer(s) dissolved in
the dispersed phase is (are) polymerized.

2.7.4 latex particle

Polymer particle that is present in a latex.

2.7.5 natural latex

Latex, the dispersed phase of which is obtained from various plants.

Note 1: The dispersed phase is often polyisoprene (2-methyl-1,3-butadiene). An example is
latex from the rubber tree, Hevea brasiliensis.

Note 2: Many plants when wounded produce a milky, sticky sap that is referred to as a latex.

2.7.6 synthetic latex

Latex obtained as a product of an emulsion, mini-emulsion, micro-emulsion, or dispersion polymeriza-
tion.

3. PARTICLE DIAMETERS, AVERAGE PARTICLE DIAMETERS, AND
PARTICLE-DIAMETER DISPERSITY

3.1 equivalent particle diameter, SI unit: nm

Diameter of a hypothetical spherical particle of the same composition that, using a given particle-size
determination method, would give the same diameter as a substance composed of spherical or non-
spherical particles at the same concentration.

Note: Although the equivalent particle diameter is not a precisely defined quantity, as its value
depends on the experimental method used for its determination, it is useful for particle
characterization.
### 3.2 average particle diameters and particle-diameter dispersity

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Symbols and formulae</th>
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</thead>
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<tr>
<td><strong>3.2.1 number-average particle diameter</strong></td>
<td>$\langle d_N \rangle = \bar{d}_N = \frac{\sum N_i d_i}{\sum N_i}$</td>
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<tr>
<td><strong>3.2.2 surface-average particle diameter</strong></td>
<td>$\langle d_s \rangle = \bar{d}_s = \frac{\sum N_i d_i^3}{\sum N_i d_i^2}$</td>
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<td><strong>3.2.3 mass-average particle diameter</strong></td>
<td>$\langle d_m \rangle = \bar{d}_m = \frac{\sum N_i d_i^4}{\sum N_i d_i^3}$</td>
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<tr>
<td><strong>3.2.4 z-average particle diameter</strong></td>
<td>$\langle d_z \rangle = \bar{d}_z = \left(\frac{\sum N_i d_i^5}{\sum N_i d_i^4}\right)^{1/3}$</td>
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<tr>
<td><strong>3.2.5 volume-average particle diameter</strong></td>
<td>$\langle d_v \rangle = \bar{d}_v = \left(\frac{\sum N_i d_i^3}{\sum N_i d_i^2}\right)^{1/3}$</td>
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<tr>
<td><strong>3.2.6 particle-diameter dispersity</strong></td>
<td>$D_d = \frac{\langle d_m \rangle}{\langle d_N \rangle} = \frac{\bar{d}_m}{\bar{d}_N} = \frac{\sum N_i d_i^4}{\sum N_i d_i^3}$</td>
</tr>
</tbody>
</table>

**Note 1:** In the formulae, $N_i$ denotes the number of particles of diameter $d_i$.

**Note 2:** Averages may be denoted by $\langle \cdot \rangle$ or by $\bar{\cdot}$.

**Note 3:** In principle, any method suitable for measuring the diameters of single particles (e.g., electron microscopy) could be used for the determination of all the averages given in the table. However, some experimental methods allow determination only of particular diameter averages.

**Note 4:** Average diameters are defined and calculated by using relations or ratios between the main momentums of a representative statistical distribution that is the particle diameter distribution (e.g., $z$-average diameter is the fifth momentum over the fourth one).

**Note 5:** The definition of mass-average diameter is meaningful only for latexes where the particles all have the same density.

**Note 6:** The definition of the $z$-average diameter is meaningful only for latexes where the particles all have the same density and refractive index.

**Note 7:** The term “particle-diameter dispersity” and the symbol $D_d$ are an extension of the terms molar-mass dispersity ($D_M$) and degree-of-polymerization dispersity ($D_X$), where $D_m = \frac{M_m}{M_n}$ and $D_X = \frac{X_m}{X_n}$ [2].

**Note 8:** For “particle-diameter dispersity”, the term “diameter-polydispersity index” is not recommended as “polydispersity” is an undefined quantity. The term “non-uniformity factor” is also not recommended.
4. PARTICLE MORPHOLOGY

4.1 composite particle

See multicomponent particle.

4.2 homogeneous particle

Particle that is spatially uniform with respect to chemical composition of the constituent polymer(s).

Note: A particle that is chemically homogeneous but has a radial distribution function of composition that is not step-like is not a homogeneous particle. Similarly, a block-copolymer micelle is not a homogeneous particle, although all constituent copolymer molecules can have identical compositions.

4.3 multicomponent particle
structured particle
composite particle

Inhomogeneous particle consisting of two or more immiscible components.

Note 1: The components can be solid, liquid, or gaseous.

Note 2: Multicomponent particles are often obtained by sequential polymerizations of different monomers or monomer mixtures.

4.3.1 core-shell particle

Polymer particle comprising at least two phase domains, one of which (the core) lies within the other(s) that form the polymeric outer layer(s) (the shell(s)).

Note 1: Examples of core-shell particles are shown in Fig. 1. A core may be composed of one single-phase domain of one type of polymer or copolymer block in a shell of a different type of polymer (or copolymer block).

Note 2: Core-shell particles may be obtained by seeded emulsion polymerization in which the seed particles form the cores of the new particles, and polymer produced in the second stage and subsequent stages, if any, forms the shell.

Note 3: Core-shell particles in which polymer synthesized in the second stage is located within one single domain, and the particles and polymer constituting the initial seed are located in the shell are usually called inverted core-shell particles.

4.3.1.1 microcapsule

Core-shell particle with an equivalent particle diameter in the approximate range 0.1 to 100 μm, wherein the core is a fluid (liquid or gas) or a solid that may subsequently be released.

4.3.1.2 nanocapsule

Core-shell particle with an equivalent particle diameter in the approximate range from 1 to 100 nm, wherein the core is a fluid (liquid or gas) or a solid that may subsequently be released.
4.3.2 inverted core-shell particle
Core-shell particle in which polymer synthesized in the second stage is located in the core of the particle and polymer constituting the initial seed is located in the shell.

Note: See Fig. 1.

4.3.3 multilayered particle
Multicomponent particle made of at least two different polymers, with an inner core of one polymer and with at least two layers of different polymers.

Note: See Fig. 1.

4.3.4 occluded particle
Multicomponent particle in which one polymer forms more than one phase domain within a matrix of another polymer.

Note 1: See Fig. 1.

Note 2: The number and size of the domains can vary, and their spatial distribution within the particles is often not uniform.

Note 3: This type of particle is also referred to as having microdomain morphology.

4.3.5 partially engulfed particle
Multicomponent particle in which one or more polymer(s) cover(s) most, but not all, of the particle surface.

Note 1: See Fig. 1.

Note 2: The degree of coverage may vary when neither polymer is preferentially covering the other one. The morphology is commonly referred to as a hemisphere.
4.4 **macroporous particle**
Particle containing pores of diameters exceeding about 50 nm.

*Note:* For definition of macropores, see ref. [3].

4.5 **mesoporous particle**
Particle containing pores of diameters between approximately 2 and 50 nm.

*Note:* For definition of mesopores, see ref. [3].

4.6 **microporous particle**
Particle containing pores of diameters not exceeding 2 nm.

*Note:* For definition of micropores, see ref. [3].

4.7 **structured particle**
See *multicomponent particle*.

5. **COLLOIDAL AND RELATED SYSTEMS**

5.1 **dispersed phase**
Phase constituted of particles of any size and of any nature dispersed in a *continuous phase* of a different composition.

5.2 **continuous phase**
Phase not interrupted in space

*Note:* The continuous phase may be gaseous, liquid, or solid.

5.3 **dispersion medium**
Matrix for the *dispersed phase*

*Note 1:* The dispersion medium is the *continuous phase* of the dispersion.

*Note 2:* If the continuous phase is a gas, the dispersion is called an aerosol [1].

5.4 **dispersion**
Material comprising more than one phase where at least one of the phases consists of finely divided phase domains, often in the *colloidal* size range, dispersed throughout a *continuous phase*.

*Note 1:* Modification of definition in ref. [1].

5.4.1 **nonaqueous dispersion**
*Dispersion* in which the *continuous phase* is nonaqueous.
5.4.2 polymer dispersion

Dispersion in which the dispersed phase consists of a polymer.

5.5 colloid

Short synonym for colloidal system.

Note: Quotation from refs. [1,4].

5.5.1 colloidal

State of subdivision such that the molecules or polymolecular particles dispersed in a medium have at least one dimension between approximately 1 nm and 1 μm, or that in a system discontinuities are found at distances of that order.

Note: Quotation from refs. [1,4].

5.5.2 colloid stabilizer

Compound increasing stability of a colloid.

Note: A colloid stabilizer may be added to a colloid or synthesized during colloid preparation.

5.6 polymer colloid

Colloidal dispersion in which at least one of the phases is a polymer, either organic, or inorganic or some combination of the two.

Note 1: For the definition of colloidal dispersion, see ref. [4].

Note 2: The term “polymer colloid” is more general than latex. In a latex the dispersed phase is always a polymer, whereas in a polymer colloid this need not be so.

Note 3: Particles of a liquid or a gas dispersed in a polymer, particles comprising “empty” shells made of polymers, and aerosols of polymer particles are all known examples.

5.7 suspension

Dispersion of solid particles in a liquid.

Note: Definition based on that in ref. [4].

5.7.1 colloidal suspension

System in which particles of colloidal size of any nature (e.g., solid, liquid, or gas) are dispersed in a continuous phase of a different composition (or state) [1,4].

Note: The definition is based on refs. [1,4].

5.8 emulsion

Fluid system in which liquid droplets are dispersed in a liquid.

Note 1: The definition is based on the definition in ref. [4].
Note 2: The droplets may be amorphous, liquid-crystalline, or any mixture thereof.

Note 3: The diameters of the droplets constituting the dispersed phase usually range from approximately 10 nm to 100 μm, i.e., the droplets may exceed the usual size limits for colloidal particles.

Note 4: An emulsion is termed an oil/water (o/w) emulsion if the dispersed phase is an organic material and the continuous phase is water or an aqueous solution and is termed water/oil (w/o) if the dispersed phase is water or an aqueous solution and the continuous phase is an organic liquid (an “oil”).

Note 5: A w/o emulsion is sometimes called an inverse emulsion. The term “inverse emulsion” is misleading, suggesting incorrectly that the emulsion has properties that are the opposite of those of an emulsion. Its use is therefore not recommended.

5.8.1 polymer emulsion

Emulsion in which the dispersed phase is a liquid polymer or a polymer solution.

Note: The dispersing phase may be a low-molecular-weight liquid or a solution of another polymer.

5.8.2 macro-emulsion

Emulsion in which the particles of the dispersed phase have diameters from approximately 1 to 100 μm.

Note 1: Macro-emulsions comprise large droplets and thus are “unstable” in the sense that the droplets sediment or float, depending on the densities of the dispersed phase and dispersion medium. Separation of the dispersed and continuous phases usually occurs within time periods from a few seconds to a few hours, depending upon the viscosity of the fluid medium and the size and density of the droplets.

Note 2: Macro-emulsions usually contain low-molecular-weight or polymeric surfactants that decrease the rates of coalescence of dispersed droplets. Droplets of the dispersed phase may be also stabilized by adsorption of solid particles onto their surface (so-called Pickering stabilization).

5.8.3 mini-emulsion

Emulsion in which the particles of the dispersed phase have diameters in the range from approximately 50 nm to 1 μm.

Note 1: Mini-emulsions are usually stabilized against diffusion degradation (Ostwald ripening [1]) by a compound insoluble in the continuous phase.

Note 2: The dispersed phase contains mixed stabilizers, e.g., an ionic surfactant, such as sodium dodecyl sulfate (n-dodecyl sulfate sodium) and a short aliphatic chain alcohol (“co-surfactant”) for colloidal stability, or a water-insoluble compound, such as a hydrocarbon (“co-stabilizer” frequently and improperly called a “co-surfactant”) limiting diffusion degradation. Mini-emulsions are usually stable for at least several days.
5.8.4 micro-emulsion
Dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm.

Note 1: In a micro-emulsion the domains of the dispersed phase are either globular or interconnected (to give a bicontinuous micro-emulsion).

Note 2: The average diameter of droplets in macro-emulsion (usually referred to as an “emulsion”) is close to one millimeter (i.e., $10^{-3}$ m). Therefore, since micro- means $10^{-6}$ and emulsion implies that droplets of the dispersed phase have diameters close to $10^{-3}$ m, the micro-emulsion denotes a system with the size range of the dispersed phase in the $10^{-6} \times 10^{-3} = 10^{-9}$ m range.

Note 3: The term “micro-emulsion” has come to take on special meaning. Entities of the dispersed phase are usually stabilized by surfactant and/or surfactant-cosurfactant (e.g., aliphatic alcohol) systems.

Note 4: The term “oil” refers to any water-insoluble liquid.

5.9 gel
Nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid [1].

Note 1: A gel has a finite, usually rather small, yield stress.

Note 2: A gel can contain:

(i) a covalent polymer network, e.g., a network formed by crosslinking polymer chains or by nonlinear polymerization;

(ii) a polymer network formed through the physical aggregation of polymer chains, caused by hydrogen bonds, crystallization, helix formation, complexation, etc., that results in regions of local order acting as the network junction points. The resulting swollen network may be termed a “thermoreversible gel” if the regions of local order are thermally reversible;

(iii) a polymer network formed through glassy junction points, e.g., one based on block copolymers. If the junction points are thermally reversible glassy domains, the resulting swollen network may also be termed a thermoreversible gel;

(iv) lamellar structures including mesophases ([3] defines lamellar crystal and mesophase), e.g., soap gels, phospholipids, and clays;

(v) particulate disordered structures, e.g., a flocculent precipitate usually consisting of particles with large geometrical anisotropy, such as in $V_2O_5$ gels and globular or fibrillar protein gels.

Note 3: Corrected from [4], where the definition is via the property identified in Note 1 (above) rather than of the structural characteristics that describe a gel.

5.9.1 polymer gel
Gel in which the network component is a polymer network.
Note: Definition quoted from ref. 1,4.

5.9.1.1 hydrogel
Gel in which the swelling agent is water.

Note 1:  The network component of a hydrogel is usually a polymer network.

Note 2:  A hydrogel in which the network component is a colloidal network may be referred to as an aquagel.

Note 3:  Definition quoted from refs. [1,4].

5.9.1.2 aerogel
Gel comprised of a microporous solid in which the dispersed phase is a gas [1].

Note 1: Microporous silica, microporous glass, and zeolites are common examples of aerogels.

Note 2: Corrected from ref. [4], where the definition is a repetition of the incorrect definition of a gel (see Note 3 of 5.9) followed by an inexplicit reference to the porosity of the structure.

5.10 micelle
Particle of colloidal dimensions that exists in equilibrium with the molecules or ions in solution from which it is formed.

Note: Based on definition in ref. [4].

5.10.1 hemi-micelle
Type of micelle that exists in relatively small numbers below the critical micelle concentration.

5.10.2 ad-micelle
Surfactant bilayer formed on a charged adsorbing surface.

Note 1: Ad-micelles are usually formed on inorganic particles.

Note 2: In the case of particles with charged surfaces the surfactant molecules are oriented with their charged head-groups toward the particle surfaces. In the case of further addition of surfactant, a surface bilayer may form, which is termed an ad-micelle (adsorbed micelle).

5.10.3 micellar aggregation number
micellar degree of association
Number of molecules constituting a micelle.

5.10.4 micellar charge
Combined charge of the surfactant ions and counterions tightly bound to a micelle.

Note 1: Micelle with tightly bound ions behaves as a unit carrying the net charge.

5.10.5 micellar degree of association
See micellar aggregation number.

5.10.6 micellar molecular weight
See micellar relative molar mass.

5.10.6 micellar relative molar mass
micellar molecular weight
Mass of a mole of micelles divided by the molar mass constant. The relative molar mass of micelles (mic) is thus $M_{r,\text{mic}} = \frac{M_{\text{mic}}}{M_u}$.

Note 1: 1/12 of the molar mass of $^{12}\text{C}$ is termed “molar mass constant” with symbol $M_u = \frac{M(^{12}\text{C})}{12} = N_A m_u$ and unit g mol$^{-1}$ where $m_u$ is the “atomic mass constant” with unit u or Da, and $N_A$ is the Avogadro constant.

Note 2: The micellar relative molar mass refers to a neutral micelle and thus includes the mass of counterions that compensate the charge of surfactant molecules in micelles.

5.11 vesicle
Closed structure formed by amphiphilic molecules that contains solvent (usually water).

5.12 particle number concentration, $C_p$, accepted for use with SI unit: L$^{-1}$
Number of particles per volume of suspending medium.

5.13 solids content of a polymer dispersion
Mass fraction of nonvolatile material in a polymer dispersion.

5.13.1 polymer content
Mass fraction of polymer in a polymer dispersion.

5.14 dispersed-phase (amount) concentration, $[A]_p$ for species A, $[M]_p$ for monomer, accepted for use with SI unit: mol L$^{-1}$
particle-phase (amount) concentration
Amount concentration of a species within the dispersed phase.

Note: If the dispersed phase depends on quantities such as radius, $r$, time, $t$, etc., the recommended symbols are $[A]_p(r,t,...)$ and $[M]_p(r,t,...)$. 

5.15 continuous-phase (amount) concentration, \([A]_{\text{cont}}\) for species A, \([M]_{\text{cont}}\) for monomer, accepted for use with SI unit: mol L\(^{-1}\)

Concentration of species within the continuous phase of a dispersion.

Note 1: If the continuous phase is water, the symbols \([A]_{w}\) and \([M]_{w}\) are usually used.

Note 2: If the continuous-phase concentration depends on quantities such as time \(t\), etc., the recommended symbols are \([A]_{\text{cont}}(t,...)\) and \([M]_{\text{cont}}(t,...)\).

5.16 particle-phase concentration

See dispersed-phase concentration.

5.17 polymer mass fraction, \(w_p\)

Mass fraction of polymer within the dispersed phase.

6. POLYMERIZATION PROCESSES

6.1 emulsion polymerization

Polymerization whereby monomer(s), initiator, dispersion medium, and possibly colloid stabilizer constitute initially an inhomogeneous system resulting in particles of colloidal dimensions containing the formed polymer.

Note: With the exception of mini-emulsion polymerization, the term “emulsion polymerization” does not mean that polymerization occurs in the droplets of a monomer emulsion.

6.1.1 ab initio emulsion polymerization

Emulsion polymerization in which no seed particles are added.

6.1.2 batch emulsion polymerization

Emulsion polymerization in which all the ingredients are placed in a reactor prior to reaction.

6.1.3 continuous emulsion polymerization

Emulsion polymerization in which all the ingredients are added continuously and the product latex is removed continuously.

6.1.4 emulsifier-free emulsion polymerization

Emulsion polymerization carried out without the addition of a colloid stabilizer.

Note 1: In an emulsifier-free emulsion polymerization, a colloid stabilizer is produced in situ (e.g., the polymerization of styrene initiated with potassium persulfate yields macromolecules with anionic end groups providing ionic stabilization of the colloidal polystyrene particles).

Note 2: Other names, such as emulsifier-less, soap-less, soap-free, surfactant-less, and surfactant-free emulsion polymerization, that are sometimes used, are not recommended.
6.1.5 **encapsulating emulsion polymerization**

*Emulsion polymerization* leading to the encapsulation of a solid within polymer particles or liquid polymer droplets.

*Note:* An encapsulating emulsion polymerization is often performed inside *ad-micelles*.

6.1.6 **inverse emulsion polymerization**

*Emulsion polymerization* in a nonaqueous medium in which the *dispersed phase* is usually an aqueous solution, initially of monomer(s), and finally of polymer.

6.1.7 **monomer-flooded emulsion polymerization**

*Semi-continuous emulsion polymerization* in which the monomer(s) is(are) fed to the reactor at a rate that exceeds the rate of polymerization.

*Note:* A monomer-flooded emulsion polymerization refers to a state where the monomer concentration in the polymer particles is at or greater than its equilibrium swelling value and therefore droplets may be formed.

6.1.8 **monomer-starved emulsion polymerization**

*Semi-continuous emulsion polymerization* in which the polymerization rate is controlled by the feed rate(s) of monomer(s), in such a way that, for most of the process, the polymerization rate equals the monomer(s) feed rate(s).

*Note:* Usually a monomer-starved emulsion polymerization refers to a state where the monomer concentration in the polymer particles is less than its equilibrium swelling value.

6.1.9 **power-feed emulsion polymerization**

*Semi-continuous emulsion copolymerization* in which the instantaneous composition of the formed copolymer is the same as that of the added monomer mixture(s).

*Note:* A power-feed emulsion polymerization is normally achieved by feeding to the reactor monomer mixture(s) from one or more reservoirs under monomer-starved conditions. In the simplest case, reservoirs I and II are initially filled with monomers A and B, respectively. During polymerization the contents of reservoir I are continuously pumped into the reactor and the contents of reservoir II are continuously pumped into reservoir I at definite rates.

6.1.10 **seeded emulsion polymerization**

*Emulsion polymerization* with seed particles (see definition 6.9) are formed in situ or added initially to the polymerizing mixture.

*Note:* Under certain conditions the seed particles capture enough radical species from the aqueous phase so that no new particles are formed. In such polymerization, the number of growing particles is equal to the number of seed particles.
6.1.11 semi-continuous emulsion polymerization

Semi-batch emulsion polymerization

Emulsion polymerization in which some of the ingredients are initially placed in a reactor and the remaining ingredients are added during the polymerization.

6.1.12 vesicle polymerization

Polymerization inside the bilayer of a vesicle leading to formation of polymer inside the bilayer.

Note 1: The bilayer may contain polymerizable and non-polymerizable molecules.

Note 2: Usually phase separation occurs leading to entities with inhomogeneously distributed polymer (e.g., entities that contain a latex particle inside the vesicle's bilayer).

Note 3: The morphology of such entities is called “parachute” morphology, owing to similarity of their shape to the shape of parachute canopy.

Note 4: In the case of reactive copolymerizing surfactants (i.e., surmers; see definition 7.11.1) hollow spherical entities can sometimes be obtained with a homogeneous distribution of polymer in the bilayer.

6.2 micro-emulsion polymerization

Emulsion polymerization in which the starting system is a micro-emulsion and the final latex comprises colloidal particles of polymer dispersed in an aqueous medium.

Note: Diameters of polymer particles formed in the micro-emulsion polymerization usually are between 10 and 50 nm.

6.2.1 inverse micro-emulsion polymerization

Emulsion polymerization in which the starting system is a micro-emulsion and the final system is composed of an organic continuous phase with an aqueous polymer solution as the dispersed phase.

6.3 micellar polymerization

Polymerization of a polymerizable surfactant in solution above its critical micelle concentration.

Note: The initial micellar structure usually is not preserved during the polymerization.

6.4 mini-emulsion polymerization

Polymerization of a mini-emulsion of monomer in which all of the polymerization occurs within pre-existing monomer particles without the formation of new particles.

6.4.1 inverse mini-emulsion polymerization

Emulsion polymerization in which the starting system is a mini-emulsion and the final system is composed of an organic continuous phase with an aqueous polymer solution as the dispersed phase.
6.5 precipitation polymerization
Polymerization in which monomer(s), initiator(s) and colloid stabilizer(s) are dissolved in a solvent and this continuous phase that is a nonsolvent for the formed polymer beyond a critical molecular weight.

6.5.1 dispersion polymerization
Precipitation polymerization in which monomer(s), initiator(s), and colloid stabilizer(s) are dissolved in a solvent forming initially a homogeneous system that produces polymer and results in the formation of polymer particles.

Note: The process usually results in polymer particles of colloidal dimensions.

6.5.1.1 seeded dispersion polymerization
Dispersion polymerization in which seed particles are formed in situ or added prior to initiation of the polymerization.

6.5.2 precipitation polycondensation
Precipitation polymerization proceeding by polycondensation.

Note: See ref. [1] for the definition of polycondensation.

6.5.2.1 dispersion polycondensation
Dispersion polymerization proceeded by polycondensation.

Note: See ref. [1] for the definition of polycondensation.

6.5.3 precipitation polyaddition
Precipitation polymerization proceeding by polyaddition.

Note: See ref. [1] for the definition of polyaddition.

6.5.3.1 dispersion polyaddition
Dispersion polymerization proceeding by polyaddition.

Note: See ref. [1] for the definition of polyaddition.

6.6 suspension polymerization
Polymerization in which polymer is formed in monomer, or monomer-solvent droplets in a continuous phase that is a nonsolvent for both the monomer and the formed polymer.

Note 1: In suspension polymerization, the initiator is located mainly in the monomer phase.

Note 2: Monomer or monomer-solvent droplets in suspension polymerization have diameters usually exceeding 10 μm.
6.6.1 micro-suspension polymerization

Suspension polymerization in which the diameter of the monomer droplets is of the order of a few μm.

7. TERMS RELATED TO POLYMERIZATION PROCESSES

7.1 average number of radicals per particle, \( <N> \) or \( \bar{N} \)

Ratio of the total number of radicals in particles to the number of particles.

7.2 critical oligomer degrees of polymerization

7.2.1 critical oligomer degree of polymerization for irreversible entry, \( z_{\text{crit}} \)

Lowest degree of polymerization of aqueous-phase oligomer-radicals needed for irreversible capture by colloidal particles, micelles, or both during a polymerization.

7.2.2 critical oligomer degree of polymerization for precipitation, \( j_{\text{crit}} \)

Lowest degree of polymerization of oligomer-radicals that precipitate from the continuous phase during a polymerization.

Note: \( j_{\text{crit}} \) is usually equal to the degree of polymerization at which oligomer-radicals undergo a coil-to-globule transition.

7.3 intervals in emulsion polymerizations

Periods in an emulsion polymerization defined by the formation of polymer particles, and the presence or absence of monomer droplets in the polymerizing mixture.

Note: In naming particular intervals, the word “interval” is always written with a capital I.

7.3.1 Interval 1 in emulsion polymerization

Period in a batch ab initio emulsion polymerization (see definitions 6.1.1 and 6.1.2) during which the formation of particles takes place.

7.3.2 Interval 2 in emulsion polymerization

Period in an emulsion polymerization during which no new particles are formed and monomer droplets are present.

Note: This interval is associated with an approximately constant value of the average number of radicals per particle, an approximately constant value of monomer concentration in the particles, and, thus, an approximately constant rate of polymerization.

7.3.3 Interval 3 in emulsion polymerization

Period in an emulsion polymerization during which no new particles are formed and no monomer droplets are present.
7.4 limiting rate-behaviour in emulsion polymerizations

7.4.1 zero-one behaviour

Limiting behaviour in an emulsion, mini-emulsion, or micro-emulsion polymerization during which the entry of a radical into a particle that contains a growing radical results in termination before significant propagation has occurred.

Note 1: This type of behaviour commonly occurs for small particles, the size of which depends on the type of monomer and on polymerization conditions.

Note 2: The value of the average number of radicals per particle ($\bar{N}$) for a zero-one system can never exceed 0.5.

7.4.1.1 compartmentalization behaviour

Zero-one behaviour wherein radicals are isolated, each being located within a different latex particle.

7.4.2 pseudo-bulk behaviour

Behaviour in an emulsion, mini-emulsion, micro-emulsion, suspension, or dispersion polymerization wherein the kinetics are such that the rate equations are the same as those for polymerization in bulk.

Note 1: In a pseudo-bulk system, the average number of radicals per particle, $\bar{N}$, can take any value.

Note 2: Common extreme cases are (i) when the value of $\bar{N}$ is so high that each particle effectively behaves as a micro-reactor, and (ii) when the value of $\bar{N}$ is low, exit is very rapid and the exited radical re-enters another particle, may grow to a significant degree of polymerization, and so on before any termination event.

7.5 oligomer radical

radical of oligomeric length

Note: For the definition of an oligomer, see ref. [1].

7.6 particle nucleation

7.6.1 homogeneous micellization nucleation

Formation of primary particles as a result of micelle formation from surface-active oligomer radicals formed in a polymerization.

Note: The surface-active oligomer radicals are usually formed by polymerization with initiators providing ionic end-groups.

7.6.2 homogeneous nucleation

Formation of primary particles as a result of the coil-to-globule transition of oligomer radicals that have propagated to the critical oligomer degree of polymerization for precipitation.

7.6.3  
**micellar nucleation**

Formation of *primary particles* as a result of polymerization within monomer-swollen *micelles* initiated by the capture of *primary radicals* or *oligomer-radicals*.

7.6.4  
**coagulative nucleation**

A process combining nucleation by any mechanism with subsequent coagulation being a significant event in formation of colloidally stable particles.

*Note:* The term “coagulative nucleation” does not mean that nucleation is caused by coagulation.

7.7  
**phase-transfer event in a polymerizations in a dispersed system**

Transport of any species (radical, monomer, chain-transfer agent, etc.) from the continuous to the discrete phase and vice-versa.

7.7.1  
**radical desorption**

See *radical exit*.

7.7.2  
**radical entry**

Irreversible transport of a radical from the continuous to the *dispersed phase*.

*Note:* This type of transport frequently involves a radical arising directly from initiator. An example is the sulfate radical anion $SO_4^{2-}$, with the systematic name tetraoxidosulfate ($\cdot 1^{-}$) (where the part in parentheses is pronounced “dot one minus”), propagating with monomer in the aqueous phase until the resulting oligomeric species enters a particle irreversibly.

7.7.2.1  
**entry frequency**

See *radical entry frequency*.

7.7.2.2  
**radical entry frequency, $f_{en}$, SI unit: s$^{-1}$**

*entry frequency*

Average number of entry events per particle per unit interval of time.

*Note:* The term “entry rate coefficient” is incorrect and is not recommended.

7.7.3  
**radical exit**  
**radical desorption**

Reversible or irreversible transport of a radical from the dispersed to the *continuous phase*.

*Note:* This type of transport is frequently through transfer of the radical activity at the end of a macroradical within a particle to a smaller species which may then diffuse irreversibly out of the parent particle into the *continuous phase*.
7.7.3.1 exit frequency

See radical exit frequency.

7.7.3.2 radical exit frequency, \( f_{ex} \), SI unit: \( s^{-1} \)

Average number of exit events per particle per unit interval of time per radical.

Note: The term “exit rate coefficient” is incorrect and is not recommended.

7.8 primary particle

Particle just created by a nucleation process.

7.9 primary radical

Radicals formed from an initiator molecule.

Note: “Primary radical” describes the radical before it reacts with any molecule of monomer.

7.10 seed particle

Particle in a polymer colloid that is the locus of subsequent polymerization.

Note: A seed particle is either added to a polymerization mixture before the polymerization begins, or is formed in situ.

7.11 surfactant related species

7.11.1 surfmer

Monomer with the properties of a surfactant.

Note: For the definition of a surfactant, see ref. [4].

7.11.2 inisurf

Initiator with the properties of a surfactant.

Note: For the definition of a surfactant, see ref. [4].

7.11.3 transurf

Chain-transfer agent with the properties of a surfactant.

Note: For the definition of a surfactant, see ref. [4].

8. AGGREGATION AND RELATED PROCESSES

8.1 aggregation, coagulation, flocculation, and related processes

8.1.1 agglomerate (except in polymer science)

Cluster of primary particles held together by weak physical interactions.
Note 1: A primary particle is the smallest discrete identifiable entity observable by a specified identification technique, e.g., transmission electron microscopy, scanning electron microscopy, etc.

Note 2: The particles that comprise agglomerates can be dispersed again.

Note 3: The definition proposed here is recommended for distinguishing agglomerate from aggregate.

8.1.2 agglomerate (in polymer science)
aggregate (in polymer science)

Cluster of molecules or particles that results from agglomeration.

Note: Quotation from ref. [1].

8.1.3 agglomeration (except in polymer science)
coagulation (except in polymer science)
flocculation (except in polymer science)

Process of contact and adhesion whereby dispersed molecules or particles are held together by weak physical interactions ultimately leading to phase separation by the formation of precipitates of larger than colloidal size.

Note 1: In contrast to aggregation, agglomeration is a reversible process.

Note 2: The definition proposed here is recommended for distinguishing agglomeration from aggregation. Also, see Note 2 of 8.1.1.

Note 3: Quotation from ref. [1].

8.1.4 agglomeration (in polymer science)
aggregation (in polymer science)
coagulation (in polymer science)

Process in which dispersed molecules or particles assemble rather than remain as isolated single molecules or particles.

Note: Quotation from ref. [1].

8.1.5 aggregate (except in polymer science)

Cluster of primary particles interconnected by chemical bonds.

Note 1: The particles that comprise aggregates cannot be dispersed again.

Note 2: Alternative definitions of aggregate and agglomerate are used in catalysis [4]. The distinction offered by these definitions is in conflict with the distinction understood in the wider context and with the concepts of aggregation and agglomeration. To avoid confusion the definitions proposed here are recommended.

8.1.6 aggregate (in polymer science)

See agglomerate (in polymer science).
8.1.7 aggregation (except in polymer science)
Process whereby dispersed molecules or particles form aggregates.

Note: In contrast to agglomeration (except in polymer science), aggregation is an irreversible process.

8.1.8 aggregation (in polymer science)
See agglomeration (in polymer science).

8.1.9 breaking of an emulsion
Formation of a system with separate macrophases from an emulsion.

8.1.10 coalescence
Disappearance of the boundary between two particles in contact, or between a particle and a polymer macrophase followed by changes of shape leading to a reduction of the total surface area.

Note 1: Definition modified from that in ref. [4].

Note 2: The coagulation of an emulsion, viz. the formation of aggregates, may be followed by coalescence. If coalescence is extensive it leads to the breaking of an emulsion.

8.1.11 coagulation (in polymer science)
Irreversible formation of aggregates in which particles are in physical contact.

Note: Often the term is used when electrostatically stabilized colloids are destabilized by the addition of a salt.

8.1.11.1 critical coagulation (amount) concentration, \( c_{cc} \), accepted for use with SI unit: mol L\(^{-1}\)
Minimum concentration of electrolyte at and above which rapid coagulation occurs.

Note 1: Rapid coagulation occurs when the only forces between the particles are the attractive van der Waals forces, all other forces being negligible.

Note 2: As the value of the \( c_{cc} \) depends to some extent on the experimental circumstances (method of mixing, time between mixing and determining the state of coagulation, criterion for measuring degree of coagulation, etc.), these should be clearly stated.

8.1.11.2 heterocoagulation
Coagulation of particles of different kinds or sizes, or both.

8.1.11.3 homocoagulation
Coagulation of colloidal particles of the same size and kind.
8.1.12 colloidal crystal
Assembly of colloid particles with a periodic structure that conforms to symmetries familiar from molecular or atomic crystals.

*Note:* Colloidal crystals may be formed in a liquid medium or during drying of particle suspension.

8.1.13 creaming
Macroscopic separation of an emulsion or suspension, under the action of centrifugal or gravitational field, into an upper layer of a highly concentrated emulsion or suspension and a more dense *continuous phase*.

*Note:* Definition modified from that in ref. [4].

8.1.13.1 cream
Highly concentrated emulsion or dispersion formed by *creaming*.

*Note 1:* Definition modified from that in ref. [4].

*Note 2:* The droplets or particles in the cream may be colloidally stable, coagulated, or flocculated but they should not have coalesced.

8.1.14 fast coagulation rate
*rapid coagulation rate*
Rate of coagulation in the absence of any repulsive barrier between particles.

*Note:* The fast coagulation rate is usually measured by adding electrolyte at an increasing concentration, until the observed coagulation rate becomes independent of the electrolyte concentration.

8.1.14.1 fast coagulation rate coefficient, $k_{fast}$, accepted for use with SI unit: L mol$^{-1}$ s$^{-1}$
Rate coefficient for fast coagulation.

8.1.14.2 rapid coagulation rate
*See fast coagulation rate.*

8.1.15 flocculation (in polymer science)
Reversible formation of *aggregates* in which the particles are not in physical contact.

8.1.15.1 floc
*Aggregate* formed by *flocculation*.

8.1.15.2 flocculation rate coefficient, $k_{floc}$, accepted for use with SI unit: L mol$^{-1}$ s$^{-1}$
Rate coefficient for *flocculation*.

8.1.16  micellization
Process in which surface-active molecules or ions aggregate into micelles.

8.1.16.1  critical micelle concentration, $C_{mc}$, accepted for use with SI unit: L mol$^{-1}$ s$^{-1}$
The concentration of surface-active molecules at which micelles start to form in a solution.

*Note:* The above definition is based on explanation given in ref. [4]. “There is a relatively small range of concentrations separating the limit below which virtually no micelles are detected and the limit above which virtually all additional surfactant forms micelles. Many properties of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the cmc. As values obtained using different properties are not quite identical, the method by which the cmc is determined should be clearly stated.”

8.1.17  orthokinetic coagulation
*Coagulation* due to collisions of particles induced by hydrodynamic motion.

*Note:* Orthokinetic coagulation occurs when shear-induced collisions dominate over collisions due to Brownian motion.

8.1.18  particle monolayer
Monolayer of particles deposited at an interface.

*Note 1:* For the definition of monolayer see ref. [4].

*Note 2:* A monolayer of regularly deposited particles is called a two-dimensional colloidal crystal.

8.1.19  perikinetic coagulation
*Coagulation* due to collisions of particles caused by their Brownian motion.

*Note:* Perikinetic coagulation occurs in the absence of mixing or under conditions where shear-induced collisions are negligible compared to diffusion-induced collisions.

8.1.20  slow coagulation rate
Rate of coagulation in presence of repulsive barriers between particles.

8.1.20.1  slow coagulation rate coefficient, $k_{slow}$, accepted for use with SI unit: L mol$^{-1}$ s$^{-1}$
Rate coefficient for slow coagulation.

8.1.21  stability ratio or Fuchs stability ratio, $W$
Ratio $W = k_{fast}/k_{slow}$ or $W = k_{fast}/k_{floc}$, for coagulation or flocculation, respectively, with $k_{fast}$, $k_{slow}$, and $k_{floc}$ measured under the same mixing (or hydrodynamic) conditions.

Note: When comparing $W$ with theory, the fast coagulation rates are often approximated by the Smoluchowski rates of coagulation (for the Smoluchowski kinetic equation of coagulation, see ref. [5]).

8.2 colloidal stability

System in which the particles essentially do not aggregate or sediment.

Note: The definition is based on the definition of colloidal stability given in ref. [4].

8.2.1 electrostatic stabilization

Stabilization of a colloid resulting from the mutual repulsion of the electrical double layers surrounding its particles.

8.2.2 electrosteric stabilization

Stabilization of a colloid that has both steric and electrostatic stabilization characteristics.

8.2.3 steric stabilization

Stabilization of a colloid resulting from covering particles with a layer of molecules solvated by the continuous medium.

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10. REFERENCES


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<td>Suspension polymerization</td>
<td>6.6</td>
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<td>Particle number concentration</td>
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<td>Synthetic latex</td>
<td>2.7.3</td>
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<td>Particle-phase concentration</td>
<td>5.16</td>
<td>Transurf</td>
<td>7.11.3</td>
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<td>Perikinetic coagulation</td>
<td>8.1.19</td>
<td>Vesicle</td>
<td>5.11</td>
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<td>Phase-transfer events in polymerization in dispersed system</td>
<td>7.7</td>
<td>Vesicle polymerization</td>
<td>6.1.12</td>
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<tr>
<td>Polymer bead</td>
<td>2.2</td>
<td>Volume-average particle diameter</td>
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<td>Polymer colloid</td>
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<td>Polymer content</td>
<td>5.13.1</td>
<td>Z-average particle diameter</td>
<td>3.2.4</td>
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<td>Polymer dispersion</td>
<td>5.4.2</td>
<td>Zero-one behaviour</td>
<td>7.4.1</td>
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<td>Polymer emulsion</td>
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<td>Polymer gel</td>
<td>5.9.1</td>
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### APPENDIX B: LIST OF RECOMMENDED SYMBOLS AND ABBREVIATIONS

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<th>Definition</th>
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<tr>
<td>([A]<em>{\text{cont}}) ([A]</em>{\text{cont}(t,...)})</td>
<td>continuous-phase (amount) concentration for species A</td>
<td>5.15</td>
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<tr>
<td>([A]<em>{p}), ([A]</em>{p(r,t,...)})</td>
<td>dispersed-phase (amount) concentration for species A, particle-phase (amount) concentration for species A</td>
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<tr>
<td>([A]_{w})</td>
<td>(amount) concentration of species A in water</td>
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<tr>
<td>(c_{\text{cc}})</td>
<td>critical coagulation (amount) concentration</td>
<td>8.1.11.1</td>
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<tr>
<td>(\epsilon_{\text{mc}})</td>
<td>critical micelle (amount) concentration</td>
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<td>(\langle d_N \rangle, \bar{d}_N)</td>
<td>number average particle diameter</td>
<td>3.2.1</td>
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<tr>
<td>(D_{\text{DP}}, \langle d_m \rangle/\langle d_N \rangle, \bar{d}_m/\bar{d}_N)</td>
<td>particle-diameter dispersity</td>
<td>3.2.6</td>
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<tr>
<td>(\langle d_p \rangle, \bar{d}_s)</td>
<td>surface average particle diameter</td>
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<td>(\langle d_p \rangle, \bar{d}_v)</td>
<td>volume average particle diameter</td>
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<td>(\langle d_m \rangle, \bar{d}_m)</td>
<td>mass average particle diameter</td>
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<td>(\langle d_z \rangle, \bar{d}_z)</td>
<td>(z)-average particle diameter</td>
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<td>(f_{\text{en}})</td>
<td>radical entry frequency, entry frequency</td>
<td>7.7.2.2</td>
</tr>
<tr>
<td>(f_{\text{ex}})</td>
<td>radical exit frequency, exit frequency</td>
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<tr>
<td>(j_{\text{crit}})</td>
<td>critical oligomer degree of polymerization for precipitation</td>
<td>7.5.2</td>
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<tr>
<td>(k_{\text{fast}})</td>
<td>fast coagulation rate coefficient</td>
<td>8.1.14.1</td>
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<td>(k_{\text{floc}})</td>
<td>flocculation rate coefficient</td>
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<tr>
<td>(k_{\text{slow}})</td>
<td>slow coagulation rate coefficient</td>
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</tr>
<tr>
<td>([M]<em>{\text{cont}}), ([M(t,...)]</em>{\text{cont}})</td>
<td>continuous-phase (amount) concentration for monomer</td>
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<td>([M]<em>{p}), ([M(r,t,...)]</em>{p})</td>
<td>dispersed-phase (amount) concentration for monomer, particle-phase (amount) concentration for monomer</td>
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<td>([M]_{w})</td>
<td>monomer (amount) concentration in water</td>
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<tr>
<td>(&lt;N&gt;, \bar{N})</td>
<td>average number of radicals per particle</td>
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<td>(C_p)</td>
<td>particle number concentration</td>
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<td>(o/w)</td>
<td>oil/water</td>
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<td>(W)</td>
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<td>(w/o)</td>
<td>water/oil</td>
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<td>(w_p)</td>
<td>polymer mass fraction</td>
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<tr>
<td>(z_{\text{crit}})</td>
<td>critical oligomer degree of polymerization for irreversible entry</td>
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</tbody>
</table>
NOTE ADDED IN PROOF

Before this article was ready for printing we found the following errors:

3.2 average particle diameters and particle-diameter dispersity

Replace Note 7 with:

Note 7: The term “particle-diameter dispersity” and the symbol $D_d$ are an extension of the terms molar-mass dispersity ($D_M$) and degree-of-polymerization dispersity ($D_X$), where $D_M = \frac{M_w}{M_n}$ and $D_X = \frac{X_w}{X_n}$ [2].

4.3.5 partially engulfed particle

Figure 1 has been revised. “particle (7.9.)” has been changed to “particle (7.10)” and “polymerization (6.1.9.)” has been changed to “polymerization (6.1.10.)”

Fig. 1 Examples of two-phase particle morphology.

8.1.16.1 critical micelle concentration, $c_{mc}$, accepted for use with SI unit: L mol$^{-1}$ s$^{-1}$

(“$C_{mc}$” has been changed to “$c_{mc}$”).

APPENDIX B: LIST OF RECOMMENDED SYMBOLS AND ABBREVIATIONS

\[ j_{\text{crit}} \] critical oligomer degree of polymerization for precipitation 7.2.2

(“7.5.2” should be “7.2.2”)

\[ W \] stability ratio or Fuchs stability ratio 8.1.21

(added “or Fuchs stability ratio”)