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Polymer Particles

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Polymer Particles

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Preface

In this special volume on polymer particles, recent trends and developments in the synthesis of nano- to micron-sized polymer particles by radical polymerization of vinyl monomers in environmentally friendly heterogeneous aqueous and supercritical carbon dioxide fluid media are reviewed by prominent worldwide researchers. Polymer particles are prepared extensively as synthetic emulsions and latexes, which are applied as binders in the industrial fields of paint, paper and inks, and films such as adhesives and coating materials. Considerable attention has recently been directed towards aqueous dispersed systems due to the increased awareness of environmental issues. Moreover, such polymer particles have already been applied to more advanced fields such as bio-, information, and electronic technologies. In addition to the obvious commercial importance of these techniques, it is of fundamental scientific interest to completely elucidate the mechanistic details of macromolecule synthesis in the "microreactors" that the polymer particles in these heterogeneous systems constitute.

In the first chapter, Professor Nomura et al. review features of emulsion polymerization, which is applied for the synthesis of submicron-sized polymer particles, with particular emphasis on particle nucleation and growth and polymer structure development. In the second chapter, Professor Schork describes the basic features of miniemulsion polymerization, which is deeply related to emulsion polymerization, but offers advantages for the synthesis of hybrid particles in which hydrophobic substances are included. This chapter also covers controlled/living radical polymerization, which has been developed over the past 10 years. It is of great importance both from an academic and industrial perspective to make controlled/living radical polymerization compatible with heterogeneous systems. In the third chapter, Professsor Gan and coworkers review microemulsion polymerization and its applications for the synthesis of polymer nanoparticles and nanocomposites of polymeric/inorganic substances. In the fourth chapter, Professors Kawaguchi and Ito review various features of dispersion polymerization, which is a useful technique for the synthesis of micron-sized monodisperse polymer particles, focusing on the preparation of novel functional particles and the control of particle size. In the final chapter, heterogeneous polymerization of fluoroolefins in supercritical carbon dioxide fluids is reviewed. One of the authors,

Professor DeSimone, is the pioneer of heterogeneous polymerizations in supercritical carbon dioxide.

As the editor of this Special Volume on "Polymer Particles", I would like to thank all of the authors who made valuable contributions in spite of their undoubtedly busy schedules. I believe this work will be of great use for scientists in both academia and industry.

Kobe, November 2004 Masayoshi Okubo

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Emulsion Polymerization: Kinetic and Mechanistic Aspects

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Abstract The current understanding of the kinetics and mechanisms of batch and continuous emulsion polymerizations is summarized from the viewpoints of particle formation and growth and polymer structure development. There are numerous factors that affect these processes; among them, studies on the radical transfer and monomer partitioning between phases, which are key factors for particle formation and growth, are reviewed and discussed. Attention is also focused on the effects of initiator type, additives and impurities in the recipe ingredients, and agitation, each of which sometimes exert crucial influences on the processes of particle formation and growth. In relation to polymer structure development, important aspects of the molecular weight distribution and branched/crosslinked polymer formation are highlighted.

Keywords Emulsion polymerization · Kinetics · Particle nucleation · Particle growth · Molecular weight distribution · Nonlinear polymers

Abbreviations

AA	acrylic acid
AAm	acrylamide
AN	acrylonitrile
APS	ammonium persulfate
AIBN	2,2′-azobis-isobutyronitrile
BA	butyl acrylate
Bu	butadiene
CCTVFR	continuous Couette-Taylor vortex flow reactor
CLTR	continuous loop-tubular reactor
CMC	critical micellar concentration
CSTR	continuous stirred tank reactor
CTR	continuous tubular reactor
DVB	divinylbenzene
E	ethylene
KPS	potassium persulfate
MA	methyl acrylate
MAA	methacrylic acid
MC	Monte Carlo
MMA	methyl methacrylate
MWD	molecular weight distribution
NaLS	sodium laurylsulfate
n-BA	*n*-butyl methacrylate
PSD	particle size distribution
PSPC(R)	pulsed sieve plate column (reactor)
PT(R)	pulsed tubular (reactor)
S-E	Smith and Ewart
SEC	size exclusion chromatography
St	styrene
VAc	vinyl acetate
VCl	vinyl chloride
A_m	total surface area of micelles per unit volume of water
A_p	total surface area of polymer particles per unit volume of water
a_s	surface area occupied by a unit amount of emulsifier
d_m	diameter of a micelle
d_p	diameter of a polymer particle
D_w	diffusion coefficient for radicals in the aqueous phase

D_p	diffusion coefficient for radicals inside a polymer particle
$E(t)$	residence time distribution function
F	absorption efficiency factor defined in Eq. 8
f	initiator efficiency
f_i	fraction of i-radicals in the polymer particle phase
I_0, $[I_0]$	initial initiator concentration
k_d	rate constant for initiator decomposition
k_{em}	mass transfer coefficient for micelles defined by Eq. 7
k_{ep}	mass transfer coefficient for polymer particles defined by Eq. 7
k_f	rate coefficient for radical desorption per particle
k_{mf}	chain transfer rate constant to monomer
k_{tw}	rate coefficient for bimolecular radical termination in the aqueous phase
k_{Tf}	chain transfer rate constants to chain transfer agent (CTA)
m_d	partition coefficient for monomer (monomeric radicals) between particle and aqueous phases defined by $m_d=[M]_p/[M]_m$
M_m	aggregation number of emulsifier molecules per micelle
M_0	initial monomer concentration
$[M]_{pc}$	constant monomer concentration in polymer particles at saturation swelling
$[M]_w$	monomer concentration in the aqueous phase
$\bar{n}_A$	average number of A-radicals per polymer particle
N_n	number of polymer particles containing n radicals
R_p	rate of polymerization
$[R_w^\star]$	radical concentration in the aqueous phase
S_0	initial emulsifier concentration
S_m	concentration of emulsifier forming micelles
v_p	volume of a polymer particle
X_{Mc}	critical monomer conversion where monomer droplets disappear from the aqueous phase
α_w	nondimensional parameter defined by $\rho_w v_p/k_{tp}N_T$
ε	defined by $(k_{ep}/k_{em})M_m$ in Eq. 37
λ	partition coefficient for radicals between particle and water phase
μ	volumetric growth rate per polymer particle
θ	mean residence time
ρ	radical entry rate per polymer particle defined by Eq. 12
ρ_e	overall rate of radical entry into polymer particles
ρ_p	polymer density
ρ_w	rate of radical generation per unit volume of water

1 Introduction

There are four main types of liquid-phase heterogeneous free-radical polymerization; microemulsion polymerization, emulsion polymerization, miniemulsion polymerization and dispersion polymerization, all of which can produce nano- to micron-sized polymeric particles. Emulsion polymerization is sometimes called macroemulsion polymerization. In recent years, these heterophase polymerization reactions have become more and more important

technologically and commercially, not only as methods for producing high-performance polymeric materials, but also from an environmental point of view. It is well known that microemulsion, miniemulsion and dispersion polymerizations bare many similarities to emulsion polymerization in the kinetics of particle nucleation and growth and in polymer structure development. Therefore, for optimal design and operation of these heterophase free radical polymerizations, it is important to have detailed knowledge of the kinetics and mechanisms of emulsion polymerization. In this article, recent developments in emulsion polymerization are reviewed from kinetic and mechanistic perspectives.

Between 1995 and 1997, three excellent books on emulsion polymerization were published and provide extensive reviews of the subject up to 1995 [1–3]. Therefore, this review article will focus on research work that has appeared since ~1996. We will also include historically important work from before 1995 in this review article.

2
Emulsion Polymerization Kinetics

2.1
Generally Accepted Kinetics Scheme

Emulsion polymerization takes place over a number of steps, where various chemical and physical events take place simultaneously during the process of particle formation and growth. Figure 1 depicts the generally accepted scheme for the kinetics of emulsion polymerization.

Three major mechanisms for particle formation have been proposed to date. Figure 1a shows the proposed scheme for particle formation in emulsion polymerization initiated by water-soluble initiators. Particle formation is considered to take place when either: (1) a free radical in the aqueous phase enters a monomer-swollen emulsifier micelle and propagation proceeds therein (*micellar nucleation*); (2) the chain length of a free radical growing in the aqueous phase exceeds its solubility limit and precipitates to form a particle nucleus (*homogeneous nucleation*), or; (3) a free radical growing in the aqueous phase enters a monomer droplet and propagation proceeds therein (*droplet nucleation*). However, if the resultant polymer particles are not stable enough, the final number of polymer particles produced, regardless of the mechanism of particle formation, is determined by coagulation between the existing particles (*coagulative nucleation*).

In the process of particle growth, various chemical and physical events occur in both the aqueous and particle phases, as illustrated in Fig. 1b [1]. We now know that the polymerization takes place exclusively in the resultant polymer particle phase, wherever the free radicals are generated. Smith and Ewart [4] were the first to establish a quantitative description of the processes of parti-

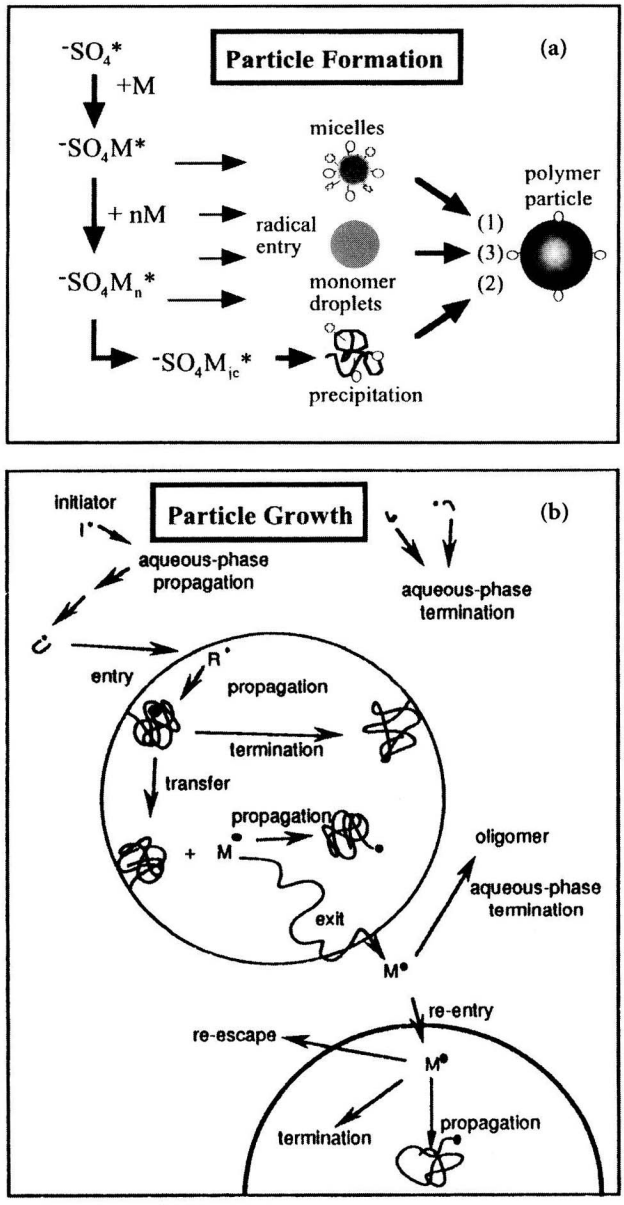

Fig. 1 (**a**) Three major mechanisms of particle formation, and (**b**) various chemical and physical events that occur during the process of particle growth in an emulsion polymerization

cle formation and growth in emulsion polymerization on the basis of the achievements made by Harkins et al. [5]. This is now called the Smith-Ewart theory. It is not an exaggeration to say that almost all of the theoretical developments in emulsion polymerization that have been made so far are based on the Smith-Ewart theory.

2.2 Summary of the Smith-Ewart Theory

The Smith and Ewart theory (the S-E theory) describes the basic concept of emulsion polymerization. Its main points are briefly reviewed here. Smith and Ewart showed that the rate of emulsion polymerization, which proceeds exclusively in the polymer particles, is given by

$$R_p = k_p[M_p]\bar{n}N_T \tag{1}$$

where k_p is the propagation rate constant, $[M]_p$ is the monomer concentration in the monomer-swollen polymer particles, N_T is the number of monomer-swollen polymer particles per unit volume of water and $\bar{n}$ is the average number of radicals per particle, defined as

$$\bar{n} = \sum_{n=1}^{\infty} nN_n \Big/ \sum_{0}^{\infty} N_n = \sum_{n=1}^{\infty} nN_n \Big/ N_T \tag{2}$$

where N_n is the number of polymer particles containing n free radicals. N_n is described by the following balance equation that takes into account three rate processes: (1) radical entry into, (2) radical desorption (exit) from, and (3) bimolecular radical termination inside the polymer particle

$$\begin{aligned} dN_n/dt = {} & (\rho_e/N_T)N_{n-1} + k_f(n+1)N_{n+1} + k_{tp}[(n+2)(n+1)/v_p] \\ & - N_n\{\rho_e/N_T + k_f n + k_{tp}[(n(n-1)/v_p]\} = 0 \end{aligned} \tag{3}$$

where k_f is the rate coefficient for radical desorption per particle, v_p is the volume of a polymer particle, k_{tp} is the rate coefficient for bimolecular radical termination inside the polymer particles, and ρ_e is the overall rate of radical entry into polymer particles, defined by

$$\rho_e = \rho_w + k_f\bar{n}N_T - 2k_{tw}[R_w^*]^2 \tag{4}$$

where ρ_w is the rate of radical production per unit volume of water, k_{tw} is the rate coefficient for bimolecular radical termination in the aqueous phase, and $[R_w^*]$ is the radical concentration in the aqueous phase.

On the other hand, they derived an expression that predicts the number of polymer particles produced, N_T, assuming that (i) a monomer-swollen emulsifier micelle is transformed into a polymer particle by capturing a free radical from the aqueous phase, (ii) the volumetric growth rate per particle μ is constant, at least during particle formation, and (iii) free radical activity does not transfer out of a growing particle

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