

Effect of carboxylic acid monomer and butadiene on particle growth in the emulsifier-free emulsion copolymerization of styrene–butadiene–carboxylic acid monomer

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Abstract

Carboxylated styrene–butadiene rubber (XSBR) latexes were prepared by emulsifier-free batch emulsion copolymerization of styrene and butadiene with different types of carboxylic acid monomers (AA, MAA, IA). It was found that the particle growth is dependent on the hydrophilic nature of carboxylic acid monomers. SEM studies showed that N_p is almost constant in the particle growth stage (conversion above 10%). Through some calculations by data obtained from DLS technique, average diameter of monomer swollen polymer particles of all the XSBR latexes at the same conversion of 0.4 was obtained to be 368.91, 174.17 and 437.15 nm for AA, MAA and IA, respectively. Several kinetic parameters related to the particle growth stage such as the average number of growing chain per particle were calculated to be 0.474, 0.370 and 1.685 for AA, MAA and IA, respectively. It was observed that these kinetic parameters increase with increasing average diameter of monomer swollen polymer particles, which is consistent with the emulsion polymerization kinetics. Moreover, results indicated that the polymerization rate per particle or equivalently the average number of the growing chain per particle (particle growth stage) decreases by replacing a part of styrene with butadiene in the emulsion copolymerization recipe of styrene–carboxylic acid monomer.

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1. Introduction

Water-soluble carboxylic acid monomers such as acrylic acid (AA), methacrylic acid (MAA) and itaconic acid (IA) are widely used in emulsion polymerization for the production of carboxylated latexes used for paper coatings, textile coatings and adhesives. The incorporation of the carboxyl groups on the latex particle surface, even in small amounts, provides many advantages, such as enhanced colloidal stability, mechanical and freeze–thaw stability, rheology and adhesion to

various substrates [1,2]. Conventional emulsion polymer systems often use monomers that are relatively water-insoluble such as styrene, acrylonitrile and butadiene. The primary reaction locus is inside the polymer particles, and aqueous-phase polymerization is usually considered to be negligible. Many industrial reaction systems, however, employ one or more monomers that have a significant solubility in water. The concentration and extent of reaction of these water-soluble monomers in the aqueous phase may be significant, and conventional emulsion polymerization kinetics does not readily apply to these systems. Carboxylated styrene–butadiene rubber (XSBR) latexes comprise an important class of industrial emulsion polymer systems involving water-soluble carboxylic acid monomers [1,2]. Carboxylic acid monomers are often completely soluble in water. However, they will still partition to varying extents into the organic phase depending on their

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Nomenclature

$X_{ov}(t)$	overall mass conversion at time t
$SC(t)$	solid content at time t
$SC(\text{initial})$	solid content at the beginning of reaction
$SC(\text{final})$	solid content at the end of reaction
R_p	polymerization rate per unit volume of the continuous phase
$C_{M,0}$	initial monomer concentration (moles per unit volume of the continuous phase)
$\theta(t)$	overall molar conversion at time t
f_0	mole fraction of monomers i to j in the initial feed
F	instantaneous mole fraction of monomers i to j in the copolymer chain
$\bar{F}$	cumulative average mole fraction of monomers i to j in the copolymer chain at any conversion
$\bar{F}_i$	cumulative average mole fraction of monomer i in the copolymer chain at any conversion
μ	molecular weight ratio of monomers i to j
$\bar{n}$	average number of growing chain per particle
N_p	number of latex particles per unit volume of the aqueous phase
C_{MP}	overall monomer concentration in the polymer particles at interval II
N_{av}	Avogadro's number
P/W	weight ratio of polymer to water
M/W	weight ratio of monomer(s) to water
ρ_P	average density of the polymer
ρ_W	density of water
ρ_M	density of the swelling monomer at the liquid state
d_p	average particle diameter
d_{pswol}	average diameter of monomer swollen particles
M_M	molecular weight of the swelling monomer
F_i	instantaneous mole fraction of monomer i in the copolymer chain
f_i	instantaneous mole fraction of monomer i in the feed (unreacted monomer) at any conversion
f_i^0	f_i in the initial state
r_i	reactivity ratio of monomer i
$\bar{k}_p$	average propagation rates constant in the particle phase
$k_{p,ii}$	coefficient of propagation rate in homopolymerization of monomer i
$k_{p,jj}$	coefficient of propagation rate in homopolymerization of monomer j
α_i	partition coefficient of carboxylic acid monomer i between styrene and water
M_i	molecular weight of monomer i
$\bar{M}_M$	average molecular weight of the swelling monomer mixture in particle phase
ρ_i	density of monomer i at the liquid state
$\bar{\rho}_M$	average density of the swelling monomer mixture in particle phase

x_i	mole fraction of monomer i in the reaction mixture (particle phase)
ϕ_i	volume fraction of monomer i in the reaction mixture (particle phase)

relative hydrophobicity. In this case, significant amounts of carboxylic acid monomer may exist in both the organic and aqueous phases.

Despite the presence of several studies on preparation and properties of XSBR latexes [1–6], there are few reports about the effect of carboxylic acid monomer on the nucleation process and particles' growth in the literature [7–9]. These are among the most important parameters, which should be assigned in emulsion polymerization technique. However, in recent years due to high progresses in analytical techniques, investigation of these parameters has become plausible [10–16].

Although the conversion of monomer to polymer in conventional emulsion polymerization systems is believed to take place primarily in the monomer swollen polymer particles, the oligomeric radicals formed in the aqueous phase can play a major role in particle nucleation and stabilization and in the characteristics of the final latex products. The number of particles formed during the reaction is closely related to the amount and type of the carboxylic acid monomer, the pH and the ionic strength [9,16–18]. In addition, the particle growth process is also affected by the presence of carboxylic acid monomers [16,19,20]. Shoaf and Poehlein [19,20] developed a model that describes the kinetics of particle growth in seeded emulsion copolymerization of styrene with acrylic and methacrylic acids. These authors confirmed the influence of events taking place in the aqueous phase on the basic mechanisms operating in the particle growth stage. In the presence of a completely water-soluble monomer, the events in the water phase should be emphasized. Most of the reported studies in the literature for emulsion polymerization systems involving carboxylic acid monomers have focused on the overall kinetic scheme in order to predict reaction rates, copolymer composition, particle concentrations and particle size. Recently, Slawinski et al. [10–12] evaluated the average number of growing chains per particle during interval II of the emulsion polymerization process for seeded batch emulsion copolymerization of styrene and acrylic acid. The results indicate that pH generally has a minor influence on the polymerization rate and average number of growing chains per particle in the seeded systems. Yuan et al. [13–15] investigated experimentally the formation of water-soluble oligomers during the emulsion polymerization of styrene–butadiene–acrylic acid and determined their relevance to the kinetics and mechanism of particle nucleation and growth. Mahdavian and Abdollahi [16] investigated the effect of carboxylic acid monomer amount on both particle nucleation and growth in emulsifier-free batch emulsion copolymerization of styrene (St)–butadiene (Bu)–acrylic acid by DLS technique for the first time. It was observed that the number of latex particles per unit volume of the aqueous phase and thus polymerization rate

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