Chemical Engineering Science 138 (2015) 41–58

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Emulsion terpolymerization of St/MMA/BuA: Modeling of composition, number of particles and the influence of *n*-DDM on the molecular weights

Javier Alejandro Díaz-Ponce [a,*,1], Humberto Vázquez-Torres [a,2], Carlos Martínez-Vera [b,3]

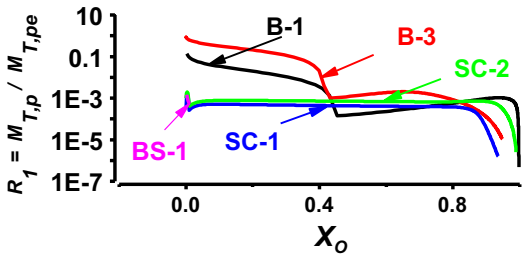
[a] Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, Col. Vicentina, Apdo. Post. 55-534, México, D.F. C.P. 09340, México

[b] Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, Col. Vicentina, Apdo. Post. 55-534, México, D.F. C.P. 09340, México

HIGHLIGHTS

- Systematic study of gel effect in batch, semicontinuous and seeded processes.
- Simple mathematical kinetic modeling with a good fitting to experimental data.
- Analysis of the dependence of mass transfer of *n*-DDM on the feed monomer composition.
- Simulation of the behavior of number of particles in emulsion terpolymerization.
- Contribution to the design of process strategies to emulsion terpolymerization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 December 2014
Received in revised form
2 July 2015
Accepted 29 July 2015
Available online 10 August 2015

Keywords:
Emulsion polymerization
Gel effect
Number of particles
Chain transfer agent
Kinetic modeling

ABSTRACT

The influence of *n*-dodecyl mercaptan (*n*-DDM) on the molecular weights distribution of the styrene/methyl methacrylate/butyl acrylate (St/MMA/BuA) terpolymer was studied. First, a kinetics emulsion terpolymerization model based on Nomura's model for copolymerization was developed. The predicted data by this model was compared with those obtained for batch, semicontinuous polymerization, as well as seeded experiments for the St/MMA/BuA system. A composition near to the unitary azeotrope of methyl methacrylate (MMA) was calculated and used to estimate the M_w of a terpolymer uniform in composition synthesized by a seeded process. It was established that a higher proportion of BuA makes the model of weight fraction of polymer W_p in the particle more suitable for simulating the gel effect on the propagation rate coefficient k_p. Likewise, this model of gel effect upon k_p is significant for both the semicontinuous processes with lower monomer addition rate and the seeded process.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Emulsion polymerization is a heterogeneous phase free radical polymerization, in which water, emulsifier micelles, oil monomer droplets and polymer swollen particles are involved. In this process, the polymer particles are built up by the absorption of radicals from the aqueous phase to the micelles (micellar nucleation) or by growing

* Corresponding author. Tel.: +52 5558044625.
E-mail addresses: qjavier2002@yahoo.com (J.A. Díaz-Ponce), hvto@xanum.uam.mx (H. Vázquez-Torres), cmv@xanum.uam.mx (C. Martínez-Vera).
[1] Postdoctoral position.
[2] Tel.: +52 5558044625.
[3] Tel.: +52 5558041232.

http://dx.doi.org/10.1016/j.ces.2015.07.050
0009-2509/© 2015 Elsevier Ltd. All rights reserved.

aqueous soluble olygomer radicals until they form new particles stabilized by emulsifier molecules (homogeneous nucleation). This constitutes the classical interval I of emulsion polymerization within a conversion of 5–10 wt%. In the interval II, monomers diffuse from oil droplets (monomers reservoirs) to the growing particles and the emulsion polymerization rate is constant up to 50–60 wt% of conversion. Interval III starts when the monomer droplets disappear and the polymerization rate begins to fall off (Napper and Gilbert, 1989; Nomura et al., 2005). The emulsion polymerization of three monomers is commonly carried out for tailoring materials with a good balance of adhesion, thermal aging, and tensile strength, among others, by controlling their composition, as is the case of the methacrylic acid-methyl acrylate-vinyl acetate terpolymer (Moustafa, 2006). On the other hand, mechanical and rheological properties can be adjusted by controlling the molecular weight distribution (MWD) of the terpolymer (Bersted and Anderson, 1990) which can be accomplished by a chain transfer agent (CTA). In academic research, as can be concluded from an analysis of scientific literature, terpolymerization is performed without CTA (Huo et al., 1988; Khan et al., 2009; Masa et al., 1993; Soljic et al., 2010; Srour et al., 2009; Urretabizkaia et al., 1994; Urretabizkaia and Asua, 1994; Wang and Hutchinson, 2011) in spite of its common use in industrial polymerization (Duggal and Slayton, 2008). Thiols are the most used CTAs for polymer synthesized by emulsion polymerization, in particular *n*-DDM, as in emulsion polymerization of monomers such as styrene St (Cunningham and Ma, 2000; Dietrich, 1988; Harelle et al., 1994; Mendoza et al., 2000; Salazar et al., 1998; Uraneck and Burleigh, 1970) and butadiene (Bd) (Weerts et al., 1991). Similarly, studies on molecular weights in copolymerization have been reported for styrene/butadiene (St/Bd) (Uraneck and Burleigh, 1970; Václavek, 1967), styrene/butyl acrylate (St/BuA) (Benyahia et al, 2010; Ginsburger et al., 2003; Zoco et al., 2003), methyl methacrylate/butyl acrylate (MMA/BuA) (Sayer et al., 2001), and vinyl acetate/butyl acrylate (VAc/BuA) (Sweetman et al., 2006) by using *n*-DDM as chain transfer agent.

Concepts related to the emulsion polymerization are the partition of the monomers among different phases (Gugliotta et al., 1995) and the number of particles in the emulsion. Concepts associated to the terpolymerization are the rates of polymerization and termination, with the corresponding glass and gel effects. A concept linked to both the emulsion and the terpolymerization is the average number of radicals in the particles, which can be calculated by different ways (Li and Brooks, 1993). Tacit in the average number of radicals in emulsion polymerization is the phenomenon of radical compartmentalization (Buttè et al., 2002), which influences the MWD of the terpolymer and hence a high molecular weight can be attained with a high rate of polymerization. Likewise, the concentration of the *n*-DDM in the particles $[n\text{-DDM}]_p$ has been calculated by Nomura by analyzing the mass transfer from the droplets to the particles. Nomura considers that the main barrier to the mass transfer is from the surface of the droplets to the water and that the disappearance of the monomer droplets gives a jump in the transfer of the *n*-DDM to the particles (Nomura et al., 1994). On the other hand, Cunningham determined the concentration in the particle of *n*-DDM, $[n\text{-DDM}]_p$, through the characterization of the instantaneous MWD; nevertheless, this procedure cannot be used for online industrial applications as the Nomura's model (Cunningham and Ma, 2000).

In this work, an experimental as well as a theoretical study of the terpolymerization of St/MMA/BuA for batch, monomer feed semicontinuous, and batch-semicontinuous processes is presented. The model of the polymerization process proposed here is validated through the comparison of the experimental results with the simulations, as pointed out elsewhere (Mendoza et al., 2000) This work deals with the analysis of M_n and M_w of the terpolymer St/MMA/BuA in the presence of *n*-DDM as chain transfer agent because the study of the terpolymerization of the system St/MMA/BuA and their molecular weights is important in its application as an acrylic resin in industrial paints (Khan et al., 2009; Borthakur et al., 2010) or in nanocomposite coatings (Rong et al., 2011). The terpolymerization model was built up from the theoretical assumptions of the copolymerization of styrene/methyl methacrylate St/MMA system given by Nomura and Fujita (1985). In order to have a better fitting of the conversion curve and to include the homogeneous and micellar nucleation, and the coagulation phenomena, the experimental determination of the particle diameter D_p was carried out. In addition, the concentration of monomers in the particle in intervals I–II was calculated through the monomer partition model, given by Schoonbrood et al. (1994) and well explained by Lovell (1997). The dissolution of the monomers in water was taken into account through the partition coefficients; whereas in interval III, the partition coefficients and the monomer mass balance were considered. The average number of radicals in the particle "n" was estimated through the semiempirical Nomura's model (Nomura and Fujita, 1985; Nomura et al., 2005). The models of Hamielec, Ray, and W_p; the later with two variants, the one used by Benyahia et al. (2010) and another one resulting from a modification made in this work. All these models were compared among them by analyzing the gel effect through the classical concepts of free volume and entanglements (O'Neil and Torkelson, 1997). As a new procedure to calculate the influence of the chain transfer agent in the molecular weight of the polymers, a correction factor F_c for the quantity of *n*-DDM in the particle calculated through Nomura's model allowed to adjust the experimental M_n and M_w values with the simulated kinetic of the terpolymerization. In this context, the termination rate in the batch processes was considered for calculating the molecular weight distribution MWD moments in order to obtain M_n and M_w, in accordance with the analysis of Baillagou and Soong for free radical polymerization (Baillagou and Soong, 1985). The termination rate was not considered in the semicontinuous processes, as Broadhead proposed (Broadhead et al., 1985), due to the negligible number of chains produced by termination reactions. In this case, the Nomura's model for desorption and capture of radicals by the particles (Nomura et al., 1982) allowed us to estimate the molecular weights. The actual efforts in emulsion polymerization are focused on the optimization of the molecular weight and particle size distributions (Srour et al., 2009). In the case of molecular weight, the optimization of the polymerization with a chain transfer agent in homopolymers (Tjiam and Gomes, 2014) and copolymers (Benyahia et al., 2010, 2013) has been done, and Wang and Hutchinson, 2011 included the penultimate effect, β-scission and backbiting in the simulation of the polymerization. In our work, the effect of the chain transfer agent in terpolymerization has been included in the model through the use of average values of k_p an k_t of BuA, which include the effect of backbiting. As a novel perspective, we have compared different k_p-gel models in order to analyze the gel effect in different reaction processes, that is, batch, semicontinuous and batch semicontinuous.

2. Experimental

2.1. Materials

Styrene St (PEMEX, industrial grade), methyl methacrylate MMA (Celanese, industrial grade, $>99\%$), butyl acrylate BuA (Celanese, industrial grade), deionized water (H_2O), sodium lauryl sulfate (SLS, Aldrich, industrial grade), potassium persulfate ($K_2S_2O_8$, Productos Químicos Monterrey, analytical grade), sodium carbonate (Na_2CO_3, Técnica Química, analytical grade), sodium sulfate (Na_2SO_4, Aldrich), sodium hydroxide (NaOH, Aldrich), and *n*-dodecyl mercaptan

Download English Version:

https://daneshyari.com/en/article/154581

Download Persian Version:

https://daneshyari.com/article/154581

Daneshyari.com