Effects of Alkali Soluble Resin on the Emulsion Polymerization of Butyl Methacrylate

Herng-Dar Hwu and Yu-Der Lee*

Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30043, Taiwan, Republic of China

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Abstract: In this work, alkali soluble resin (ASR) was evaluated as a surfactant in the emulsion polymerization of butyl methacrylate (BMA). Kinetic analysis indicated that the ASR surfactant retarded the reaction rate and reduced the average number of radicals per latex particle. Since the particle nucleation period proceeds until the disappearance of droplets, Interval II does not exist in this system. Experimental results show that the particle number depends on the 0.31 and 0.51 powers of the ASR and KPS concentration, respectively. The particle size distribution of the latex becomes broad with the increase of the ASR concentration in the emulsion polymerization. This phenomenon explains why the period of the particle nucleation is proportional to the ASR concentration used in the reaction.

Keywords: Latex, Polymeric surfactant, Alkali soluble resin, Emulsion polymerization, Retarding effect.

Introduction

Anionic and nonionic emulsifiers [1] are usually used as stabilizers in emulsion polymerization. However, in the applications of polymer products emulsifiers create many drawbacks, such as poor water resistance, poor adhesion, a slowing of film formation and an alteration in polymer properties. Employing a polymeric surfactant in emulsion polymerization is an effective method of overcoming the above drawbacks [2-5]. Owing to its larger molecular structure, a polymeric surfactant is able to eliminate the disadvantages associated with the surfactant migration. Moreover, a polymeric surfactant can provide latex with other features, such as excellent mechanical and freeze-thaw stabilities, because of its steric effect on the particles.

Kiehlbauch and Tsaur [6,7] had examined the feasibility of using alkali soluble resin (ASR) as a polymeric surfactant. They concluded that the resin-fortified emulsion polymers posed many advantages, including substantial Newtonian flow, excellent mechanical stability, fine freeze-thaw stability, good pigment dispersity, and excellent wetting properties. Lee and Kim [8] studied the reaction behaviors of methyl methacrylate and styrene in an ASR aqueous solution. They showed that the ASR formed aggregates in the aqueous solution. They also proposed the grafting of polystyrene to ASR during emulsion polymerization. However, effects of ASR on the reaction behaviors were not investigated thoroughly in their study.

In a previous study [9], the grafting and retarding effects of ASR were found for the emulsion polymerization of SM and MMA, respectively. In this paper, the reaction behaviors with ASR as the surfactant in the emulsion polymerization of butyl methacrylate (BMA) were investigated in detail. The effects of the concentrations of ASR and initiator on the reaction rate, particle size and particle number were evaluated via kinetic analyses, surface tension and GPC measurement.

Theoretical Background

1. Kinetic analysis of emulsion polymerization

The reaction rate of emulsion polymerization is expressed as follows [4,10]:

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*To whom all correspondence should be addressed.
Tel: 886-3-5713304; Fax: 886-3-5715408
E-mail: ydlee@che.nthu.edu.tw

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\[ R_p = \frac{d[M]}{dt} = k_p C_p \overline{N}_p/N_a \] (1)

where \( k_p \) is the rate coefficient for radical propagation, \( C_p \) is the monomer concentration in the polymer particles, \( \overline{N}_p \) is the average number of radicals per particle, \( N_p \) is the number of particles per unit volume of the continuous phase, and \( N_a \) is the Avogadro's number. The rate constant, \( k_p \), can be expressed as follows [11,12]:

\[ k_p = A \exp(-E_a/RT) \] (2)

where \( A \) is the frequency factor, \( E_a \) is the activation energy, \( R \) is the gas constant and \( T \) is the reaction temperature. The particles are saturated with monomer before droplets disappear and the monomer concentration in the particle maintains a constant value during this interval. The number of particles per unit volume of the continuous phase, \( N_p \), is [4,10,13]:

\[ N_p = \frac{6 m_p/X_S \pi D^3d}{d} \quad \text{as} \ X < X_S \] (3)

\[ N_p = \frac{6 m_p/X_S \pi D^3d}{d} \quad \text{as} \ X > X_S \] (4)

where \( m_p \) is the polymer mass per unit volume of the aqueous phase, \( D \) is the diameter of a swollen particle, \( d \) is the density of a swollen particle, \( X \) is the conversion of reaction and \( X_S \) is the conversion of the monomer as droplets disappear. The density of a swollen particle can be calculated as follows [13]:

\[ d = \frac{1}{X_p/d_p + (1-X_S)/d_m} \quad \text{as} \ X < X_S \] (5)

\[ d = \frac{1}{X_p/d_p + (1-X)/d_m} \quad \text{as} \ X > X_S \] (6)

where \( d_m \) is the density of the monomer and \( d_p \) is the density of the polymer. Hence, the average number of radicals per particle (\( \overline{N}_p \)) can be calculated from Eq.(1) with known parameters.

2. Number of polymer particles

The quantitative dependence of the particle number on the surfactant and initiator concentrations was derived by Roe [14] and Smith and Ewart [15], respectively. Similar results were obtained for both micellar and homogeneous nucleation. The relationship is expressed below:

\[ N_p \propto [S]^{0.6} [I]^{0.4} \] (7)

where \([S]\) and \([I]\) are the concentration of surfactant and initiator, respectively. The power dependencies of \(N_p\) on \([S]\) and \([I]\) generally follow the above equation for those monomers with little tendency toward radical desorption [10,16]. However, Eq.(7) cannot predict the particle number well for those monomers with a high tendency toward radical desorption. The predicted dependence of \(N_p\) on \([S]\) and \([I]\) for the formation of particles by coagulative nucleation [10,17] was derived by Feeney as follows:

\[ N_p \propto [S]^{0.4} [I]^{0.4} \] (8)

The occurrence of coagulative nucleation does not alter the 0.4-power dependence of \(N_p\) on \([I]\). However, the mechanism of coagulative nucleation indicates a more complex dependence of \(N_p\) on \([S]\). The exponent of \([S]\) decreases monotonically from 1.2 to 0.4 with increasing \([S]\). The concentration of polymer particles is higher and the nucleation time is longer for systems with a high surfactant concentration. Polymer particle formation becomes less efficient over time as there is a great tendency for the capture of precursor particles by polymer particles when the latter concentration is high.

3. The degree of polymerization

The degree of polymerization can be expressed as [9]:

\[ X_p = \frac{r_p}{r_{p_1} + r_t} \] (9)

where \(X_p\) is the number-average degree of polymerization, \(r_p\) is the propagation rate in the particles, \(r_t\) is the rate of transfer to monomer or to chain transfer agent in the particles. Assuming that the radical is terminated by radical combination only, then the propagation reaction proceeds until another radical is captured by the particle to terminate the propagation reaction. Thus, Eq.(9) can be rewritten as [10]:

\[ X_p = \frac{r_p/r_t = k_p C_p / (N_{u} a 2 f k_d [I] / N_p)} \] (10)

where \(f\) is the initiator efficiency and \(k_d\) is the dissociation constant of the initiator. Because the concentration of monomer in the particles is always kept at the saturation state before the disappearance of the droplets, it is expected that the degree of polymerization is proportional to the number of particles.

Experimental

1. Materials

Reagent grades of butyl methacrylate (BMA, TCI, 99%), potassium persulfate (KPS, Acros, 99%), hydroquinone (Merck, 99%), sodium lauryl sulfate (SLS, TCI, 95%), potassium hydroxide (Merck, 85%), and deionized water were used. The initiator in BMA