

Effect of pH Value on the Aqueous Precipitation Copolymerization of Acrylonitrile and Vinyl Acetate

Zhen Yao,¹ Huan-Jin Chen,¹ Yi-Xiu Qin,¹ Kun Cao^{1,2}

¹Department of Chemical and Biological Engineering, Institute of Polymerization and Polymer Engineering, Zhejiang University, Hangzhou 310027, China

²State Key Laboratory of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: The aqueous precipitation copolymerization of acrylonitrile (AN) and vinyl acetate (VAc) with NaClO₃/NaHSO₃ redox initiation system is carried out continuously in a 10L pilot-plant reactor. The effects of pH value on ionization equilibrium of NaHSO₃, polymerization rate, particle morphology, particle size and its distribution, molecular weight and its distribution have been investigated. It has been found that effective concentration of reductant H₂SO₃ increases with the decrease in pH value. On the other hand, decreasing pH value intensifies the coalescence among particles and then reduces dif-

fusion rate of monomer and radicals into particles. Experimental data shows that the increase of pH value results in higher conversion. It indicates that pH value's effect on particle stability prevails its influence on effective concentration of the reductant. This conclusion is verified by the molecular weight, particle size, and particle morphology. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1486–1491, 2011

Key words: aqueous precipitation copolymerization; acrylonitrile; pH value; vinyl acetate

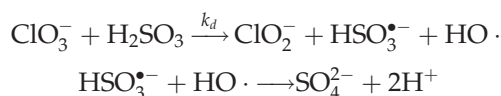
INTRODUCTION

The common polymerization techniques used for producing polyacrylonitrile (PAN) include solution polymerization,^{1–3} aqueous precipitation polymerization,^{4–12} and mixed-solvent precipitation polymerization.^{13,14} Aqueous precipitation polymerization is favored as the commercial production process for acrylic fiber due to being free of organic solvent and stabilizer. Because of the radical segregation in heterogeneous polymerization process, PAN copolymers synthesized with this technique have high molecular weight, which is very important for producing high-performance fibers. Furthermore, there are no extra impurities in an aqueous copolymerization system.⁵ Therefore, it is becoming a more noticeable method for producing PAN with high quality.

Aqueous precipitation polymerization is a special emulsion polymerization without stabilizers for producing polymer particles with uncontrolled-size.¹⁵ For emulsion polymerization of acrylamide (AM) and acrylic acid (AA) salts, the polymerization rate strongly depends on pH value of the aqueous phase due to the formation of ion pair on the end of prop-

agating macroradicals at higher pH value.¹⁶ Kato et al.¹⁷ also found that pH value can influence the emulsion polymerization process and size of the obtained latex particles by affecting the physicochemical properties of emulsifier.

The aqueous precipitation polymerization of acrylonitrile (AN) is mostly initiated by redox initiation system for its superiority in initiating efficiency at low polymerization temperature and high molecular weight of resultant products. The redox pair used in industries includes persulfate-bisulphite, chlorate-bisulphite, hydroxylamine sulfonate-bisulphite, etc. The application of new redox pairs in aqueous polymerization process, such as K₂CrO₄-NaAsO₂,^{4,18} potassium persulfate (K₂S₂O₈)-thiourea,¹⁹ Ce(IV)-sucrose,²⁰ chloramine-T/hydrogen,²¹ Ce(IV)-oxalic acid,²² were also investigated. The reductants are usually weak acid salts, which generate effective ingredient by ionization in aqueous solution at certain pH value. According to different initiating mechanism, effective reductive ingredient should differ from each initiation system. For example, the initiating process for NaClO₃-NaHSO₃ initiator system takes place according to the following mechanism.^{23,24}



Here, the effective reductive ingredient is H₂SO₃.

Correspondence to: K. Cao (kcao@che.zju.edu.cn).

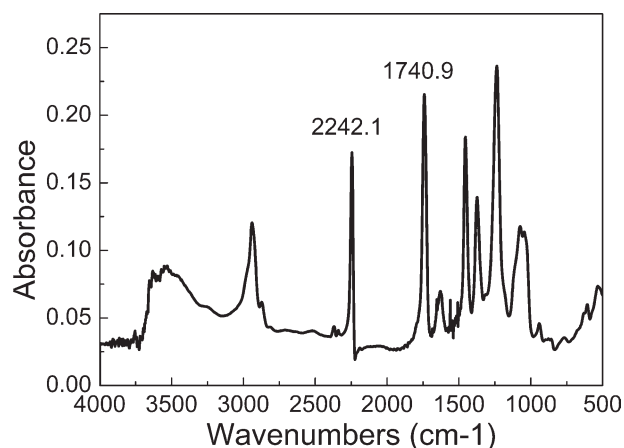


Figure 1 A typical FTIR spectrum of the obtained copolymer of AN and VAc.

Even with the same reductant, KPS-NaHSO₃ combination follows a different mechanism²⁵:



Here, HSO₃⁻ is the effective reductive ingredient.

The ionization equilibrium of reductant is greatly influenced by pH value, leading to various concentration of effective reductive ingredient. Aqueous precipitation polymerization of AN/methyl acrylate (MA)/sodium methallyl sulfonate (MAS) using NaClO₃-Na₂SO₃ as the initiation system was studied by Chen et al.²⁶ They found that final conversion increased correspondingly when increasing pH value from 0.5 to 4.0 and the maximum of initial polymerization rate was achieved when pH value was 2.0.

At present, few systematic work has been conducted to study the effect of pH value on the behavior of aqueous precipitation polymerization of AN. In addition to the ionization equilibrium, would pH value also affect particle morphology, and consequently influence the polymerization rate and molecular weight? This needs further investigation. In this article, continuous aqueous precipitation copolymerization of AN and vinyl acetate (VAc) with the NaClO₃-NaHSO₃ initiation system is investigated. The article focuses on the effects of pH value on ionization equilibrium of NaHSO₃, polymerization rate, particle morphology, particle size and its distribution, molecular weight and its distribution.

EXPERIMENTAL

Materials

AN as technical grade is purified by heat distillation under ordinary pressure. VAc as chemically pure is purified by distilling under vacuum. NaClO₃ as chemically pure is also refined before polymeriza-

tion. NaHSO₃, H₂SO₃, and NaOH as analytically pure are used as received. Deionized water is adopted as the polymerization medium.

Preparation

The aqueous precipitation polymerization of AN and VAc are carried out in a 10L continuous stirred tank reactor (CSTR). The given monomers (AN and VAc), oxidant (NaClO₃ solution) and reductant (NaHSO₃ solution) are filtered and pumped into the reactor continuously. The feeding concentration of AN, VAc, NaClO₃, NaHSO₃ are 5.00, 0.48, 0.02, 0.06 mol/L, respectively. Feeding rate is 12.77 or 13.64 L/hr corresponding to the residence time of 47 min or 44 min. The polymerization temperature is 60°C. Real-time measurement of pH value is conducted by an on-line pH detector. With the data from the pH detector, pH controller regulates the flow of pH control agent to obtain the desired pH value.²⁷ Reactant slurry flows out from top of the reactor and enters a termination tank. The polymerization is terminated by adding 2 wt % NaOH solution. The produced copolymers are purified by washing with deionized water and being filtered. The samples are dried in a vacuum oven at 80°C to constant weight to remove the residual monomer and water. The mass conversion is measured gravimetrically.

Characterization

Copolymer composition

IR spectra of the resultant AN/VAc copolymers are recorded by a Nicolet 5700 FTIR spectrometer. Both nitrile's C≡N at 2240 cm⁻¹ and ester's C=O at 1740 cm⁻¹ are strong peaks. A typical FTIR spectrum is shown in Figure 1. The calibration curve with linear regression equation is obtained in Figure 2 by

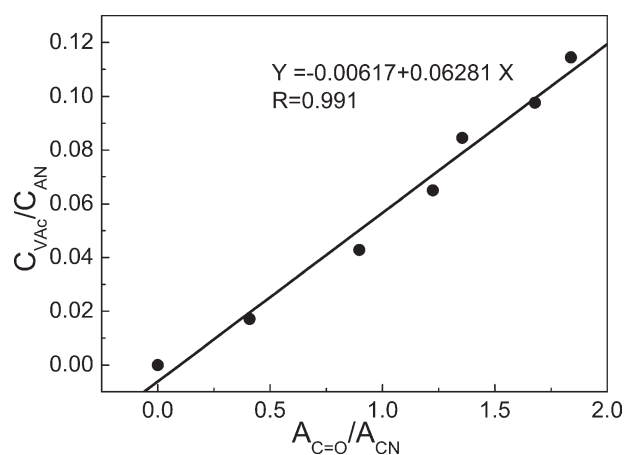


Figure 2 Calibration curve with linear regression equation between peak area ratio by FTIR and composition ratio by ¹H-NMR.

plotting the peak area ratio determined by FTIR against the composition ratio determined by $^1\text{H-NMR}$ measurement, which is recorded by a Varian NMK 300 spectrometer with 3000 scans in DMSO- d_6 solution at 120°C .

Molecular weight

Molecular weight and molecular weight distribution (MWD) of copolymers are determined by a Waters 150ALC/GPC gel permeation chromatography (GPC) using three styrene gel (HR4, HR3, HR1) columns in series. The parameters for Mark-Houwink equation used in this work are: $K = 2.78 \times 10^{-4}$ dL/g and $\alpha = 0.76$.²⁸ *N,N*-dimethyl formamide (DMF) is used as the eluent at a flow rate of 1.0 mL/min.

Particle size

Particles of AN-VAc copolymer are well dispersed with ultrasound in deionized water media. The size distribution of particles is determined by a Coulter LS230 particle size analyzer.

Sedimentation value

Solutions for the measurements of sedimentation value are prepared by adding NaOH solution to 40 mL of slurry until its pH value reaches 7. After being kept in a sealed 100 mL cylinder for 48 h to obtain sedimentation volume (V_s), the solutions are then dried in a vacuum oven at 80°C to constant weight (W_s). Sedimentation value Φ_s (mL/g) can be calculated from the following equation:

$$\Phi_s = V_s/W_s$$

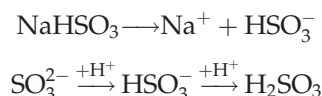
Particle morphology

Morphologies of particles are observed using a SIRON field emission scanning electron microscopy (FESEM).

RESULTS AND DISCUSSION

Ionization equilibrium of NaHSO_3

In aqueous solution, NaHSO_3 are ionized into HSO_3^- , SO_3^{2-} , and H_2SO_3 .



The existing of H^+ can affect the ionization process and change concentration of the three species. To study the ionization equilibrium of NaHSO_3 at

various pH values, we introduce the distribution coefficient of the three species, δ_i , which are defined as following:

$$\begin{aligned} \delta_1 &= \frac{[\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]} \\ &= \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 - K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \\ \delta_2 &= \frac{[\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]} \\ &= \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \\ \delta_0 &= 1 - \delta_1 - \delta_2 \end{aligned}$$

where, δ_0 is distribution coefficient of H_2SO_3 , δ_1 is distribution coefficient of HSO_3^- , δ_2 is distribution coefficient of SO_3^{2-} , K_{a1} and K_{a2} are equilibrium constant for first and secondary ionization of H_2SO_3 , respectively. According to published data,²⁹ $K_{a1} = 0.0172$, $K_{a2} = 6.24 \times 10^{-8}$ at 25°C .

The ionization equilibrium at 25°C is shown in Figure 3. It can be found that concentration of the three species have quite different variation trends according to the change of pH value. With the increase in pH value, the concentration of H_2SO_3 decreases, whereas the concentration of SO_3^{2-} increases. The curve of HSO_3^- concentration versus pH value shows a typical mountain shape with maximum concentration at pH = 4.5.

To further study the influence of temperature on ionization equilibrium, it is essential to obtain both K_{a1} and K_{a2} at different temperature. A series of pH value of H_2SO_3 solution are obtained by adding NaOH solution at 60°C .

Combining the mass balance and the charge balance, the following equation can be obtained:

$$[\text{H}^+] = \frac{K_w}{[\text{H}^+]} + \frac{c_0 V_0}{V + V_0} \delta_1 + 2 \frac{c_0 V_0}{V + V_0} \delta_2 - \frac{cV}{V + V_0} \quad (1)$$

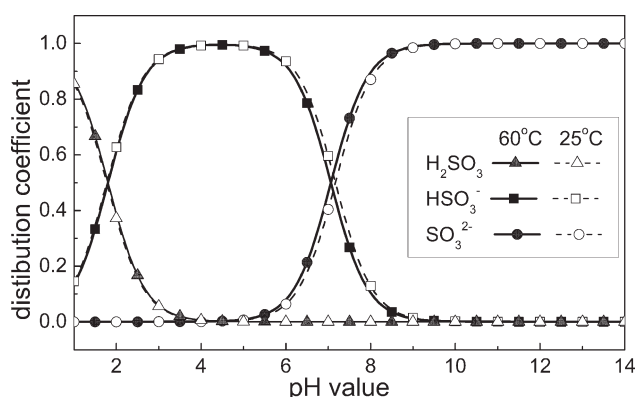


Figure 3 Equilibrium concentration of H_2SO_3 , HSO_3^- and SO_3^{2-} at various pH value.

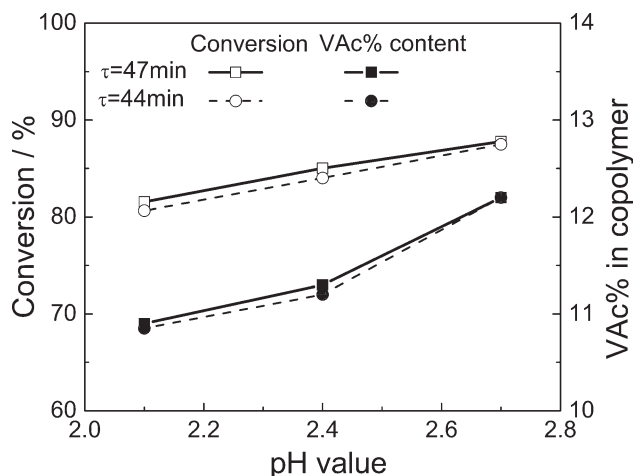


Figure 4 Influence of pH value on the conversion and VAc content of obtained copolymers.

$$V = \frac{c_0\delta_1 + 2c_0\delta_2 - \left([H^+] - \frac{K_w}{[H^+]}\right)}{[H^+] - \frac{K_w}{[H^+]} + c} V_0 \quad (2)$$

where, c_0 is the initial concentration of H_2SO_3 solution mol/L; c is the concentration of NaOH solution mol/L; V_0 is the initial volume of H_2SO_3 solution mL; V is the addition of NaOH solution mL; K_w is the ion product of water, $K_w = 1.01 \times 10^{-14}$ at 25°C.³⁰

K_{a1} and K_{a2} can be obtained by fitting the experimental data of V versus pH value using eq. (2). The two constants determined by this method at 25°C ($K_{a1} = 0.0169$ and $K_{a2} = 6.78 \times 10^{-8}$) are in good agreement with the literature values ($K_{a1} = 0.0172$ and $K_{a2} = 6.24 \times 10^{-8}$),²⁹ which demonstrates the reliability of this model. With the same method, ionization constants can be obtained as $K_{a1} = 0.0158 = K_{a2} = 8.63 \times 10^{-8}$ at 60°C, which show little difference with the ones at 25°C. The ionization equilibrium at 60°C are also plotted in Figure 3, which indicates that temperature hardly influence the ionization equilibrium.

Effect of pH value on conversion

H_2SO_3 acts as the effective ingredient in the $NaClO_3/NaHSO_3$ redox initiation system. One would expect that the monomer conversion increases with the decrease in pH value as the concentration of H_2SO_3 increases with the decreasing pH value. The dependence of conversion on pH value is experimentally studied at residence time τ of 47 min and 44 min in the continuous reactor. As shown in Figure 4, lower conversion is obtained in polymerization with lower pH value.

Mass transfer of both monomer and radicals between aqueous continuous phase and polymeric

particles phase during the AN aqueous precipitation polymerization process has been confirmed by various researchers.^{31,32} Monomer and radicals dissolved in aqueous solution are absorbed by the polymers particles. Primary radicals created in the polymer phase by chain transfer of radicals to monomer can be desorbed to aqueous phase, which is believed to be much slower than absorption. Therefore, polymerization takes place in both phases and then particle phase gradually become the main location for polymerization as the conversion increases.

Since neither surfactant nor stabilizer is added in the aqueous precipitation polymerization, the resulting particles are stabilized by the terminal residue of persulfate with ionic segment on the surface.³³ Either decreasing pH value or adding electrolyte will thin the electrical double layer, which intensifies the coalescence among particles and decreases total surface area. The transfer rate of monomer and radicals into the particles should be reduced. Since particles are the main location for polymerization, this would subsequently decrease reaction rate and conversion. From our experimental data, it can be concluded that the effect of pH value on particle coalescence is more significant than it is on the redox initiator system. It will be discussed in the following particle size section.

Effect of pH value on MW and MWD

The effects of pH value on the molecular weight and MWD (M_w/M_n) are shown in Figure 5. It can be found that the molecular weight of polymers produced at higher pH value is higher than those produced at lower pH value. On the other hand, the MWD is barely affected by the pH value.

As discussed in the previous section, effective concentration of the reductant, H_2SO_3 , is relatively low at high pH value. Consequently, less active centers are created and polymer chains with higher degree

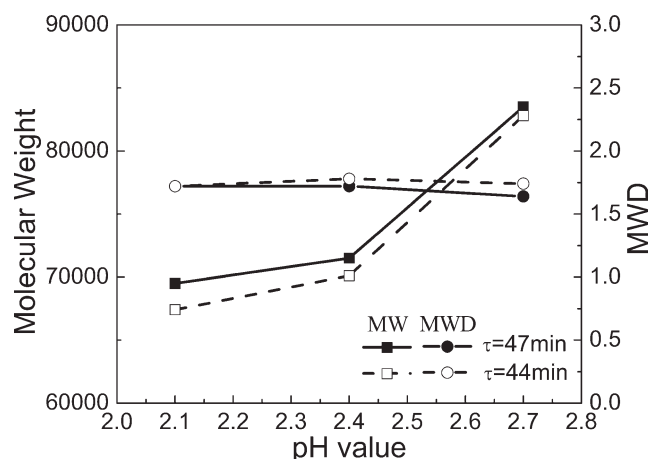


Figure 5 Effect of pH value on the molecular weight and its distribution.

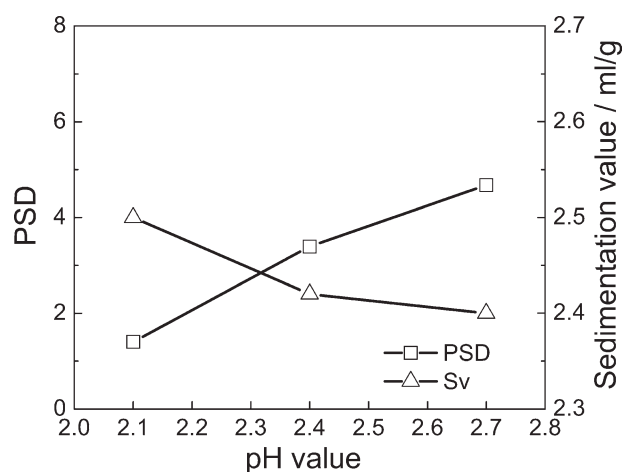


Figure 6 Particle size distribution and sedimentation value at various pH value with $\tau = 47$ min.

of polymerization are generated. Furthermore, particles are more stable and the coalescence between particles is retarded. As a result, the number of radicals in one particle is less at higher pH value. The possibility of termination is reduced, resulting in higher molecular weight.

Effect of pH value on particle size and morphology

Particle morphology is largely determined by the way they are formed. Large particles can either be formed by coalescence or radical growth. With low pH value, particles become unstable because of high ion intensity. Higher pH value reduces the chance of coalescence among particles, increases the polymerization rate and particle growth rate and results in better particle morphology. This is verified by the sedimentation data shown in Figure 6. Sedimentation value, a parameter to characterize particle morphology, is low for round and smooth particles. Seen from Figure 6, the sedimentation value is decreased with increasing pH value.

Wu et al.³⁴ found that the firstly formed primary particles (0.05–0.2 μm) can either absorb radicals or coagulate with other unstable particles in aqueous

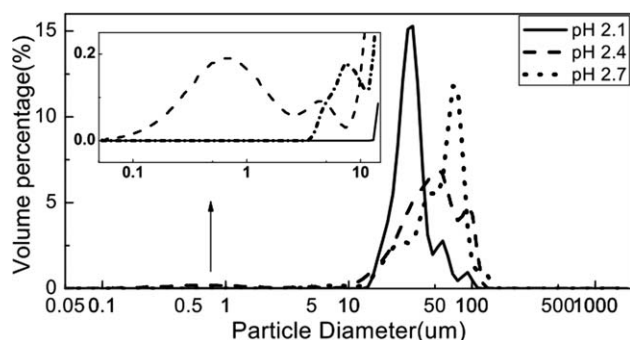


Figure 7 Particle size distribution of the obtained particles at various pH value with $\tau = 47$ min.

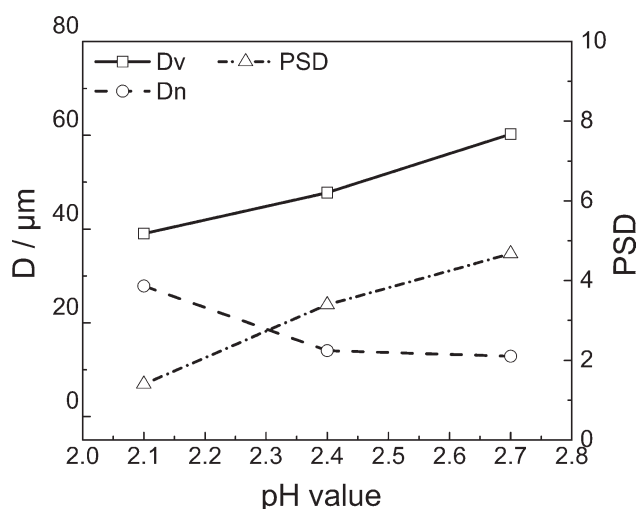


Figure 8 Particle size and its distribution at various pH value with $\tau = 47$ min.

polymerization. As they grow larger, their larger surface areas enable them to absorb more radicals and grow faster. Therefore, there is little limited coagulation occurred between the secondary (0.5–3 μm) and

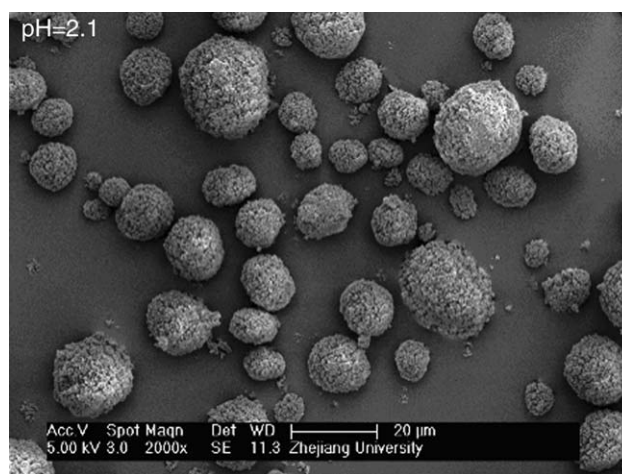


Figure 9 SEM images of the resulting particles at various pH value with $\tau = 47$ min.

larger particles (4–50 μm), which mainly grow by surface polymerization. The particle size distribution (PSD) obtained at different pH value is shown in Figure 7. When pH value increases from 2.1 to 2.4, small particles with size between 0.1 and 3.0 μm appear. These particles grow to 3–11 μm at pH value of 2.7. These further prove that primary particles (0.05–0.2 μm) are more stable at higher pH value, which makes it possible for them to grow to larger ones before coagulate with other particles. Those particles resulting from the coagulation of these grown primary particles, at equal residence time, would ultimately produce particles with larger size.

Figure 8 shows that volume average particle size (D_v) increases with the increase in pH value. On the other hand, number average particle size (D_n) decreases with increasing pH value. PSD becomes broader at higher pH value, which is also confirmed by the PSD (D_v/D_n) data in Figure 8. In the polymerization with low pH value, small particles are unstable. They coagulate with each other until stable larger particles are formed. Therefore, particles generated at lower pH value have more uniform size distribution. High pH value makes it possible for particles to grow individually and eventually formed particles with wider distribution. SEM images of particles produced at pH value 2.1 and 2.7 are shown in Figure 9. It can be seen that particle formed at higher pH value have smooth surface and wider size distribution.

CONCLUSIONS

To classify the effect of pH value on the aqueous precipitation polymerization, copolymerization of AN and VAc is carried out continuously at different pH value. It has been found that the ionization equilibrium of NaHSO_3 is influenced considerably by the pH value. Effective concentration of reductant H_2SO_3 increases with decreasing pH Value. On the other hand, lower pH value intensifies the coalescence among particles and reduces the transfer rate of monomer and radicals into the particles, which lead to lower polymerization rate. Our experimental data shows that the conversion increases with increasing pH value. Therefore, the effect of pH value on particle coalescence is more significant than the effect of pH value on the redox initiator system.

There is no primary particle found in the samples produced at pH = 2.1. Higher pH value stabilizes primary particles and makes it possible to grow to larger sizes before coalescing with others. Those grown primary particles ultimately produce secondary and other generation particles with larger size. Therefore, with increasing pH value, primary particle (small size) and larger size particles coexist, which lead to increasing volume average particle

size and decreasing number average particle size. The increase in pH value also leads to higher molecular weight of polymers because of the reduced concentration of H_2SO_3 and retarded particle coalescence.

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