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P(AA–SA) latex particle synthesis via inverse miniemulsion polymerization–nucleation mechanism and its application in pH buffering

Ying-Da Luo [a], Chi-An Dai [a,b,*], Wen-Yen Chiu [a,b,c]

[a] *Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China*
[b] *Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China*
[c] *Department of Material Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China*

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ABSTRACT

In this work, poly(acrylic acid-*co*-sodium acrylate) P(AA–SA) latex particles were prepared by inverse miniemulsion polymerization and used as a pH buffering agent for application. The polymerization was quickly initiated by a redox initiator (ammonium persulfate/sodium metabisulfite) at 0–5 °C. Thus the possibility of monomer dissolving in a solvent was reduced, which enhanced the degree of droplet nucleation. The effects of costabilizer and the ratio of SA/(AA + SA) in functional latex particles on the nucleation mechanism and emulsion stability were investigated. The apparent pK_a values of the synthesized P(AA–SA) latex particles were determined by titration experiments. Their properties on pH buffering were also studied, including the pH temporal response and pH buffering ability. The results showed that sodium hydroxide, which was introduced as the costabilizer to enhance the osmotic pressure and to increase the deprotonation of acrylic acid, was effective in guaranteeing droplet nucleation predominantly. Meanwhile, the surfactant concentration was controlled to be less than its critical micelle concentration (CMC) value to avoid micellar nucleation. Furthermore, the P(AA–SA) latex particles thus synthesized were found to be an excellent material for pH buffering. The pH temporal response was very rapid and related to the crosslinking degree of the latex particles. The terminal range of pH buffering for latex particles was controllable by the ratio of SA/(AA + SA).

1. Introduction

For an ideal miniemulsion polymerization, the loci of reaction are in the monomer droplets and the mechanism is called droplet nucleation [1,2]. As a result, monomer droplets in miniemulsion act as nanoreactors for in situ polymerization, resulting in a one-to-one copy of droplets to latex particles synthesized [3,4]. It differs from the conventional emulsion polymerization, where the polymerization occurs in micelles or homogeneous solution. In order to carry out an ideal miniemulsion polymerization, the size of monomer droplets is controlled in the range of 50–500 nm [5,6] by a variety of homogenization process such as high-pressure homogenizer [7,8], ultrasonication [9–12], and other higher shear devices [13]. The stability of miniemulsion must be maintained by its surfactant and costabilizer. The surfactant prevents oil droplets from coalescence either by electrostatic repulsion or steric stabilization [14,15]. The costabilizer used in oil/water miniemulsion, a hydrophobe, creates osmotic pressure in oil droplets to prevent molecular diffusion from small to large droplets [16,17].

As miniemulsion polymerization is carried out in a nonaqueous solvent, such a polymerization is called water-in-oil (W/O) or inverse miniemulsion polymerization. The formulation for inverse miniemulsion is dramatically different. The surfactant used now is a nonionic surfactant or amphiphilic block polymer [18,19] and the costabilizer is usually a highly hydrophilic salt. For a successful inverse miniemulsion, it is preferable to have droplet nucleation in order to precisely control size and size distribution of nanoparticles synthesized.

Landfester et al. [18] prepared PAA latex particles by inverse miniemulsion polymerization at 65 °C. The partition of acrylic acid in cyclohexane with different costabilizers was examined by ^{1}H NMR. The results showed that the percentage of acrylic acid dissolving in cyclohexane at 65 °C ranged from 7 to 87%, depending on the experimental conditions. Since the interfacial tensions of miniemulsions before and after polymerization were very similar, they concluded that droplet nucleation was the main initiation mechanism.

The originality and novelty of this work is as follows. Polymerization was carried out at 0–5 °C by using a redox initiator.

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[*] Corresponding author at: Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China. Fax: +886 2 33663051. Postal address: No. 1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106.
E-mail address: polymer@ntu.edu.tw (C.-A. Dai).

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It ensured that the amount of acrylic acid dissolved in cyclohexane was minimized and the possibility of homogeneous nucleation was largely reduced. In addition, DLS measurements were applied to compare the size distributions of droplets and the corresponding latex particles. It is a direct method for evaluating the degree of droplet nucleation during miniemulsion polymerization. The criteria of performing droplet nucleation were established in this research. Besides the investigation of nucleation mechanism in inverse miniemulsion polymerization, the application of P(AA–SA) latex particles in pH buffering was also examined in this work.

2. Materials and methods

2.1. Materials

Acrylic acid (AA; Acros), sodium chloride (NaCl; Acros), sodium hydroxide (NaOH; Showa), *N*,*N*-methylenebisacrylamide (MBA; Acros), ammonium persulfate (APS; Acros), sodium metabisulfite (SMBS; Showa), Span 80 (Showa), and cyclohexane (Acros) were used without further purification. Distilled and deionized water was used throughout the work.

2.2. Preparation of latex particles by inverse miniemulsion polymerization

All chemicals used in this study were divided into three parts including a dispersed phase, a continuous phase, and an SMBS solution. The ingredients are shown in Table 1. In the preparation of the dispersed phase, two steps were used. First, the NaOH solution and monomer AA were mixed in an ice bath in order to prevent excessive high temperature resulting from the exothermic reaction of partial neutralization of AA. Second, as the solution temperature returned to room temperature, the crosslinking agent MBA, deionized water, and APS were added under stirring. The well-mixed dispersed phase was then introduced to the continuous phase solution, Span 80/cyclohexane mixture under stirring in an ice bath (0–5 °C) with ultrasonication (Dr. Hielscher UP-50H, 100% amplitude output for 20 min). After that, the SMBS solution was introduced to the mixture solution slowly under ultrasonication for an additional 20 min. SMBS and APS act as a pair of redox initiators and the polymerization proceeded rapidly within several minutes on mixing under ultrasonication. However, in order to ensure a maximum conversion of monomer, the reaction time was kept for roughly 30 min. After the polymerization, the latex particles were centrifuged and washed using cyclohexane several times. The sample was dried in a vacuum oven at 95 °C until the sample weight remained constant.

2.3. Characterization

The morphological analysis of P(AA–SA) composite particles was performed by using a JOEL JEM-1230 transmission electron microscope (TEM) with a CCD camera. The size distributions of both monomer droplets and latex particles were characterized by using a dynamic light scattering (DLS) instrument (Malvern Zeta Sizer 3000H). When droplet nucleation was the dominant route during polymerization, the size distributions of droplets and the corresponding latex particles should be similar. The pH buffer ability of latex particles was evaluated by the following method. Aqueous solutions with different pH values at 3, 5, 9, and 11 were prepared first by using sodium hydroxide and hydrogen chloride. Then, 0.05 g of the dried sample was added to the 50 ml aqueous solution with different pH values. The pH regulation capacity of the latex sample as a function of time was measured while the solution was under ultrasonication. The final pH value was also plotted in the vertical axis and the initial pH value was plotted in the horizontal axis in order to investigate their ultimate capacity for pH buffering.

Table 1
Symbols and recipes for the synthesized latex particles.[a]

Sample code[b]	Costabilizer	MBA/AA (molar ratio)	Span 80 (g)	Costabilizer/AA (molar ratio)
A0	–	0.014	1	0
A1	NaOH	0.014	1	0.36
A2	NaOH	0.014	1	0.54
A3	NaOH	0.014	1	0.72
S1	NaOH	0.014	1	0.54
S2	NaOH	0.014	3.5	0.54
M1	NaOH	0	1	0.54
M2	NaOH	0.014	1	0.54

[a] A 0.5 g SMBS dissolved in 2 ml deioned water was called the SMBS solution. The amounts of acrylic acid, APS, and deionized water in the dispersed phase were 5, 0.5, and 10 g, respectively, in each formulation.

[b] The sample codes denoted as A2, S1, and M2 have the same formulation. Different codes were used for different parameter comparisons.

2.4. Titration of latex particles

The amount of 0.05 g of the dried latex sample was dispersed homogeneously into 50 ml deionized water and the steady pH value of the solution was recorded, followed by titration with a 0.02 N NaOH solution. The variation of pH value was recorded in the process of titration until a constant pH value was attained. By differentiating the pH curve with the titrating volume of NaOH solution, the number of COOH groups per gram of latex particles could be determined according to the peak position. In addition, a 0.02 N hydrogen chloride (HCl) solution was used to titrate the latex sample solution. The titration process was the same as noted above. In this case the number of COO^- groups per gram of latex particles could be determined. After the contents of COOH and COO^- groups in P(AA–SA) latex particles were known, the apparent pK_a of P(AA–SA) could be calculated from the following equation:

$$pK_a = pH + \log \frac{[COO^-]}{[COOH]}. \qquad (1)$$

3. Results and discussion

3.1. Nucleation mechanism and morphology of PAA latex particles

3.1.1. Effect of costabilizer

The role of a costabilizer in miniemulsion polymerization is to suppress molecular diffusion or so-called Ostwald ripening effects by introducing an osmotic pressure to maintain the droplet stability during polymerization. In our experiments, a formulation without any costabilizer was performed first for comparison. However, in such a reaction condition, macroscopic phase separation of the miniemulsion was significant and visible after stopping agitation. One of the phases was a milky emulsion containing latex polymer particles, and the other phase was a transparent solution from the coarsening of original droplets. The severe phase separation resulted in a low monomer conversion (10%) after polymerization. It indicated that the existence of costabilizer was important. TEM photographs of latex particles without adding any costabilizer in formulation are shown in Fig. 1a. It demonstrated a core–shell structure, in which PAA was formed on the shell layer and water was present in the core. The morphology was resulted from the phase separation of PAA with water and an enhanced tendency of PAA diffusing out to the solvent phase.

When NaCl was used as the costabilizer and the molar ratio of costabilizer/monomer was 0.54 in the formulation. The surfactant (Span 80) concentration was controlled below the CMC

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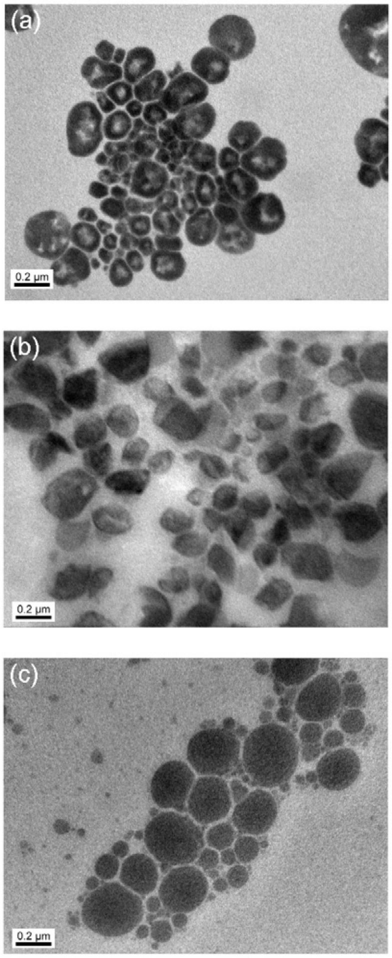

Fig. 1. TEM photographs of the synthesized latex particles with different amounts of costabilizer (a) A0, (b) A1, and (c) A3.

value (3.2 g/80 ml cyclohexane) to avoid the micellar nucleation. The phase separation of miniemulsion was prevented to some extent but still visible after stopping agitation. Although the final monomer conversion was increased to 69%, the poor stability of miniemulsion resulted in large amount of latex particles produced from homogeneous nucleation during the synthesis. As a result, NaCl was not an effective costabilizer to achieve droplet nucleation dominantly.

Using sodium hydroxide as the costabilizer, the molar ratio of NaOH/AA (neutralization degree) in the formulation was varied from 0.36, 0.54, to 0.72 (sample code A1–A3, respectively). That was also almost the molar ratio of SA/(AA + SA) in the P(AA–SA) latex particles after polymerization. The surfactant (Span 80) concentration was controlled below the CMC value to avoid the micellar nucleation. In such a system, phase separation was not observed before and after the polymerization. The conversion was almost complete if the molar ratio of costabilizer/monomer was higher than 0.36. The results indicated that NaOH not only introduced an osmotic pressure but also increased the hydrophilicity of the acrylic acid monomer by deprotonation of carboxylic acid. Thus, the monomer solubility in cyclohexane decreased and the stability of inverse miniemulsion was enhanced.

Presented in Fig. 2 are the size distributions of droplets and latex particles with different concentrations of costabilizer, NaOH. With increasing the concentration of costabilizer, the monomer (AA–SA) was more hydrophilic in nature. It decreased the solubility of monomer in cyclohexane, thus the monomer droplets increased slightly in size. The TEM photographs in Fig. 1 exhibited variations of particle size with different concentrations of NaOH. The size of the particles without costabilizer was smaller than that in the presence of the costabilizer. Without costabilizer, NaOH, the solubility of monomer in cyclohexane increased. It resulted in monomer droplets becoming smaller after ultrasonication, compared to the case with NaOH as the costabilizer. Furthermore, the shape of latex particles with less costabilizer (sample A1) was not spherical compared with the sample of A3. When monomer was more hydrophilic (sample A3), the higher interfacial tension resulted in a spherical morphology of latex particles. If a less hydrophilic one was applied (sample A1), an irregular shape of latex particles was observed due to the lower interfacial tension. The morphological transition from core–shell to homogeneous structure of the synthesized latex particles was also observed in Fig. 1. When the costabilizer was absent, a core–shell structure was obtained. When the concentration of costabilizer was higher (sample A3), the morphology was homogeneous. In a formulation with a medium amount of costabilizer (sample A1), the transition state morphology of latex particles from core–shell to homogeneous structure was demonstrated. In addition, some small particles were observed in these three samples (samples A1–A3). It implied that the possibility of homogeneous nucleation could not be ruled out during the particle growth. The lower interfacial tension increased the coagulation of latex particles; thus, fewer small particles were seen in sample A1. In samples A3, higher interfacial tension prevented the latex particles from coagulation to some extent and small latex particles from homogeneous nucleation were observed. However, the volume percentage of small latex particles from homogeneous nucleation was small in the DLS experiment. In summary, the similar size distribution curves of monomer droplets and the corresponding latex particles suggested that droplet nucleation was the dominant route in particle synthesis with NaOH as a costabilizer.

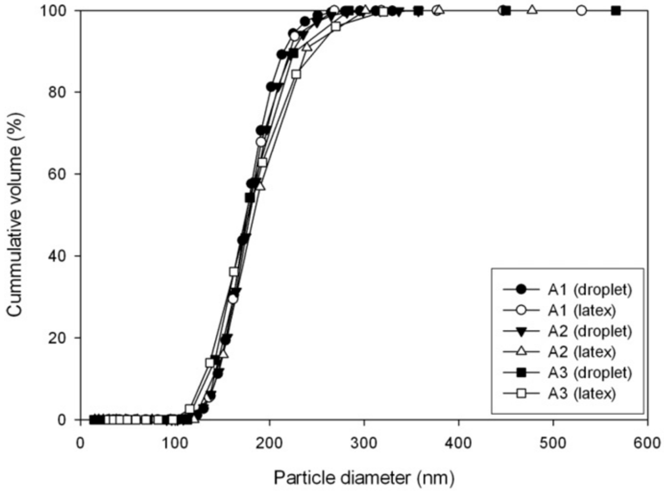

Fig. 2. Size distributions of monomer droplets and latex particles with different amounts of costabilizer, NaOH. The formulation is shown in Table 1.

3.1.2. *Effect of amount of surfactant*

The function of surfactant was to keep monomer droplets or polymer particles from coalescence and to maintain the stability of emulsion. The surfactant used in this experiment was Span 80 whose CMC was 3.2 g in 80 ml of cyclohexane [20]. By comparing the size distributions of monomer droplets and latex particles in Fig. 3, two distribution curves were nearly identical when the surfactant concentration was below its CMC in S1, but a shrinking feature from droplets to latex particles was observed in S2. This result revealed that a micellar/homogeneous nucleation mechanism was significant if the surfactant concentration was higher than the

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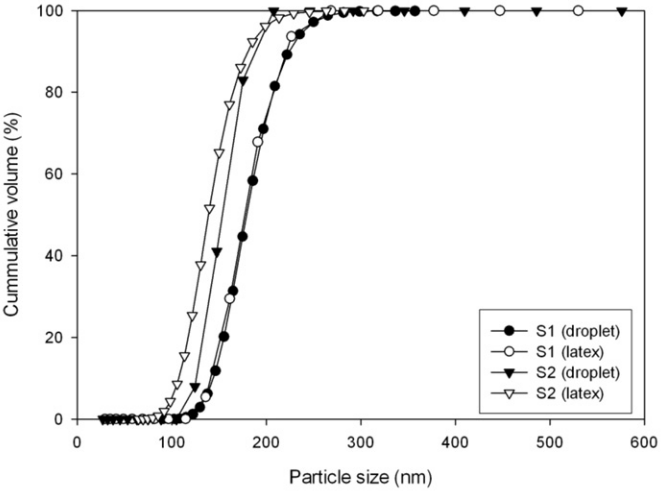

Fig. 3. Size distributions of monomer droplets and latex particles with different amounts of surfactant. The formulation is shown in Table 1.

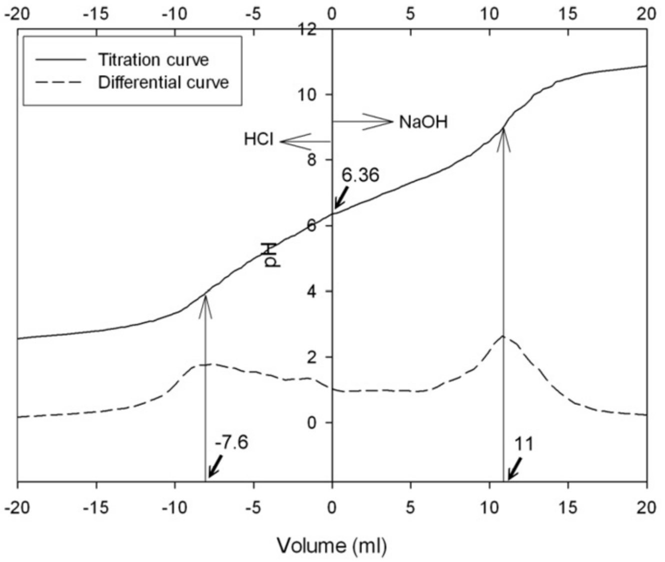

Fig. 4. Titration curve and its differential curve of sample A2. The formulation is shown in Table 1.

CMC in S2. The average size of droplets was in the order of S1 > S2 as expected. The higher concentration of surfactant provided more surface coverage and reduced the size of droplets.

3.2. Dissociation behavior of the synthesized latex particles

P(AA–SA) latex particles with different degrees of protonation of carboxylic acid groups were titrated using NaOH and HCl solutions in order to precisely determine the ratio of $[COO^-]/[COOH]$. The titration curve of sample A2 is shown in Fig. 4, from which the ratio of $[COO^-]/[COOH]$ was obtained as 7.6/11 with an initial pH value of 6.36. According to Eq. (1), the value of pK_a of the latex particles, A2, was calculated to be 6.51. For samples A1 and A3, their pK_a values were 5.93 and 6.78, respectively, based on the same experiment and calculation. The results showed that the dissociation constant pK_a of polyacid varied with the degree of neutralization. With increasing the degree of neutralization, the value of pK_a of P(AA–SA) increased due to the fact that additional proton binding energy was needed for P(AA–SA). More energy was required to dissociate the proton on polyacid if there were many neighboring COO^- groups [21,22]. For monomer acrylic acid, the proton binding energy was weaker; the value of pK_a obtained as 4.2 in our experiment was smaller than the value of polyacid PAA and independent of the degree of neutralization. The distinct dissociation behavior of polyacid makes P(AA–SA) a potential material in the application of pH buffering. The pH value could be adjusted to a desired value by changing the degree of neutralization of P(AA–SA).

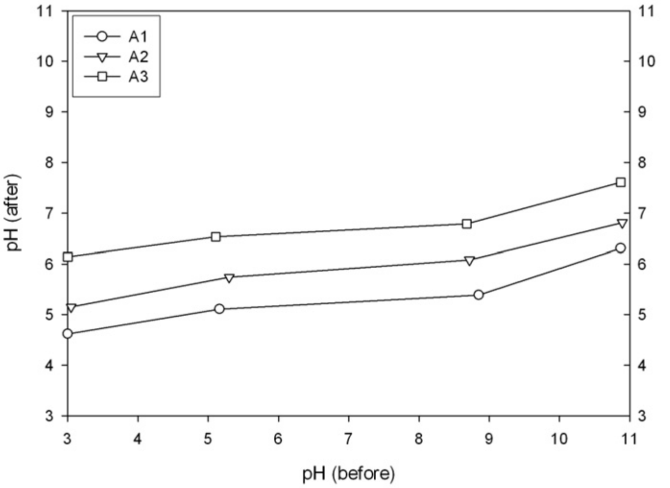

Fig. 5. The ultimate pH buffering property of the latex particles with different amounts of costabilizer. The formulation is shown in Table 1.

3.3. PH buffering properties of the synthesized latex particles

The terminal pH buffering capacity for P(AA–SA) with different SA/(AA + SA) ratios (samples A1–A3) is shown in Fig. 5. It revealed the effectiveness of P(AA–SA) samples in pH buffering. The addition of A1, A2, or A3 sample to a HCl or NaOH testing solution with an initial pH value between 3 and 11 could buffer the testing solution to a pH values of 4.5–6.5, 5–7, and 6–8, respectively. It demonstrates that the partially neutralized PAA latex particles were effective in pH buffering and the pH regulation capacity was closely related to their pK_a values. Fig. 6a shows the temporal response of sample A2 in pH buffering in HCl or NaCl testing solutions with initial pH 3, 5, 9, or 11. The pH values of the testing solutions changed quickly initially and reached steady-state values within 3 min after addition of sample A2. Samples A1 and A3 showed similar response as sample A2. The difference is the ultimate pH regulation range. The results indicated that the synthesized P(AA–SA) latex particles exhibited excellent properties in pH buffering, with fast pH response and adjustable pH regulation capacity.

In addition, the response time was related to the crosslinking degree of the P(AA–SA) latex particles. The sample, M1, did not undergo crosslinking, and its pH temporal response was very quick as shown in Fig. 6b, approaching steady state in 1 min. It was due to the fact that P(AA–SA) latex particles swelled very quickly in water if the chains were not crosslinked in M1.

4. Summary

In this work, P(AA–SA) latex particles were synthesized by using inverse miniemulsion polymerization. The polymerization was carried out in cyclohexane at 0–5 °C in the presence of a redox initiator. The particle nucleation and growth loci were mainly in original droplets and only a small amount of particles was produced from homogeneous nucleation when NaOH was used as the costabilizer and the surfactant concentration was less than its CMC value. NaOH not only introduced the osmotic pressure but

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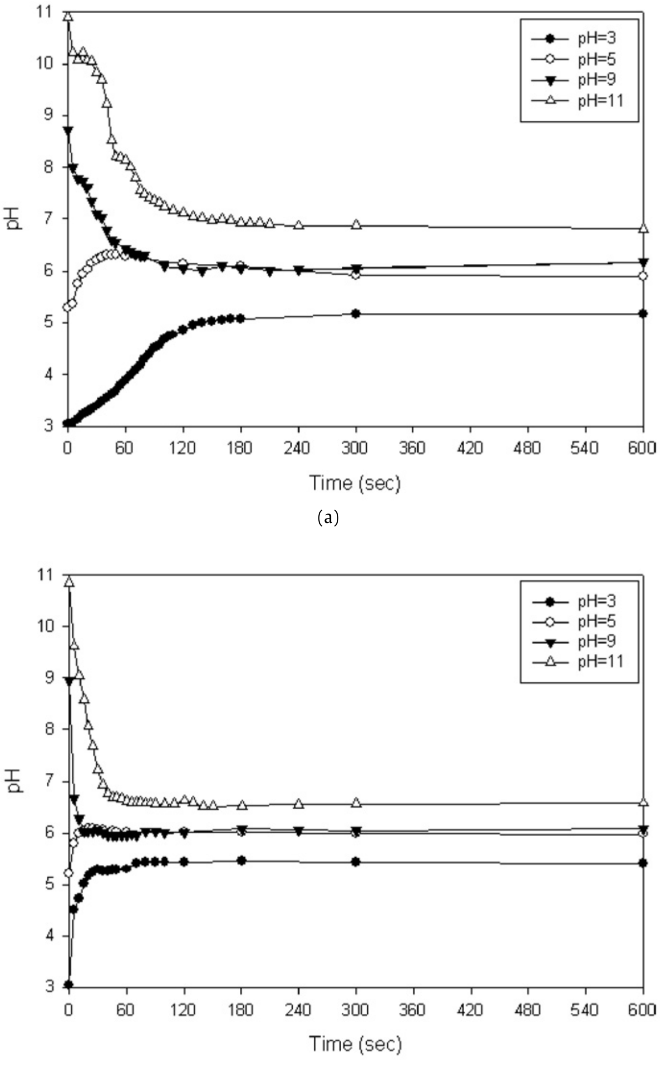

(a)

(b)

Fig. 6. The pH temporal response of samples (a) M2 and (b) M1. The formulation is shown in Table 1.

also increased the hydrophilicity of the monomer by ionization, which retarded the Ostwald ripening and increased the stabilization of the droplets. When the hydrophilicity of monomer droplet was enhanced by the costabilizer, the latex particles synthesized were spherical in morphology due to the increase of interfacial tension.

In addition to the discussion of nucleation mechanism, the P(AA–SA) latex particles prepared were also functional in the application of pH buffering. The pK_a value of the synthesized P(AA–SA) latex particles was controllable in the range of 5–7, depending on the degree of neutralization. The pK_a value of the synthesized latex particles was found to be related to the proton binding energy of COOH groups. When the ratio of NaOH/AA in formulation was changed from 0.36 to 0.72, the pH buffering range shifted to a higher value due to the higher pK_a value of the latex sample. The synthesized P(AA–SA) demonstrated a rapid response, less than 3 min, in the pH buffering experiment. For P(AA–SA) latex particles without crosslinking, the response time was even less than 1 min. It could be concluded that the synthesized P(AA–SA) latex particles exhibited an excellent capacity for pH buffering. Further work to prepare composite latex particles, such as ZnO/P(AA–SA), is ongoing. The potential applications of the composite particles could be extended to UV shielding and piezoelectric devices besides pH regulation.

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