Porous Acrylonitrile/Itaconic Acid Copolymers Prepared by Suspended Emulsion Polymerization

Mengmeng Yu, Hou Chen, Ying Liang, Hengli Cui, Wenying Zhou, Xianqiang Cui, Dongmei Li

School of Chemistry and Materials Science, Ludong University, Yantai 264025, China

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ABSTRACT: Porous acrylonitrile (AN)/itaconic acid (IA) copolymers were successfully prepared by suspended emulsion polymerization for the first time, with potassium peroxydisulfate (KPS) as an initiator, poly(vinyl alcohol) (PVA) as a dispersant agent, and Span80 as an emulsifier. The effects of the water/monomer mass ratio, agitation conditions, KPS concentration, PVA concentration, Span80 concentration,s and IA concentration on the average particle size and size distribution, particle morphology, and porosity of the AN/IA copolymers were investigated. The results show that the final AN/IA copolymers formed with agglomerates of primary particles had a porous structure, low particle density, and uniform particle size and did not agglomerate easily between the particles. The preparation conditions for the AN/IA copolymers were optimized as follows: (1) the water/monomer mass ratio was 0.3 : 1; (2) the concentrations of KPS, IA, PVA, and Span80 were 0.5, 12.4, 0.1, and 0.5 wt %, respectively, based on the weight of AN separately; (3) the agitation rate was 400 rpm; (4) the polymerization temperature was 70°C; and (5) the reaction time was 3 h. The size of the final AN/IA copolymer particles was in the range 200–400 μm. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2761–2768, 2009

Key words: copolymerization; morphology; particle size distribution

INTRODUCTION

Polyacrylonitrile (PAN) resins have been widely used as absorbing materials and reinforcing materials in the automobile, aerospace, recreational, and various other industries; their application may be more widespread by further improvement of their performance.[1–4] In addition, PAN-based fibers remain one of the best materials for making carbon fibers, where high strength and modulus, high thermal and corrosion resistance, and low density are the prime requirements.[5–7] Acrylonitrile (AN) homopolymers result in a poorer quality of the final products. It has been modified to improve its properties, including the mechanical strength, elasticity, and plasticity, by the incorporation of suitable acidic comonomers, such as itaconic acid (IA), during polymerization.[8–16]

Several polymerization techniques have been successfully used to synthesize AN copolymers, such as solution, aqueous suspension, and solvent water suspension techniques.[17–22] However, the polymer particles obtained by these methods all had some defects of compact structure and unworkability. It is important to select a suitable technique and optimize the conditions of polymerization for the synthesis of porous and workable AN copolymers. Vindevoghel et al.[23,24] proposed a suspended emulsion polymerization process and applied this process to prepare porous poly(vinyl chloride) particles. Suspended emulsion polymerization is a new polymerization process developed from suspension and emulsion polymerization to prepare porous polymers. Polymers of porous structure are beneficial to thermal and solvent immersion and can be processed under mild conditions. Bao et al.[25,26] investigated the particle features, formation mechanism, and influence conditions on the particle characteristic of avpoly (vinyl chloride) resin prepared by suspended emulsion polymerization. Bao et al.[27] also discussed the suspended emulsion polymerization of methyl methacrylate because methyl methacrylate could dissolve their polymers and had a relatively high solubility in water. It was difficult to obtain porous polymers by normal suspended emulsion polymerization unless cyclohexane was used as porogen. To the best of our knowledge, porous AN/IA copolymers have not been obtained. Thus, the suspended emulsion

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Correspondence to: H. Chen (sdchenhou@hotmail.com).

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polymerization of AN with IA was first attempted in this study.

In this study, porous AN/IA copolymers were prepared by suspended emulsion polymerization for the first time. A detailed study of the effects of the water/monomer mass ratio, agitation conditions, potassium peroxydisulfate (KPS) concentration, IA concentration, poly(vinyl alcohol) (PVA) concentration, and Span80 concentration on the average particle size and particle size distribution, particle morphology, and porosity of AN/IA copolymers are described.

EXPERIMENTAL

Materials

AN (analytical reagent grade, Tianjin Kermel Chemical Reagents Co., Tianjin, China) was freshly distilled *in vacuo*. KPS (analytical reagent grade, Tianjin Reagent Chemical Co., Tianjin, China) was used as an initiator. IA (chemically pure grade, Shanghai Yingyuanka Chemical Co., Shanghai, China) was recrystallized from acetone and was used as a comonomer. PVA (Shanghai Aibi Chemical Co., Shanghai, China; polymerization degree = 1750 ± 50) was used as the dispersant agent. Span80 (analytical reagent grade, Tianjin Fuchen Chemical Reagents Factory, Tianjin, China) was used as the emulsifier. Deionized water was adopted as the polymerization medium.

Polymerization

All polymerizations were performed in 100-mL, round-bottom flasks. A typical procedure was as follows: the required amounts of KPS, IA, deionized water, dispersant agent, emulsifier, and freshly distilled AN were injected into the reaction system in that order. The system was charged with N_2 for 5 min and was sealed under N_2. The mixture was stirred at room temperature until all of the solid dissolved. Then, the flask was wholly immersed in an oil bath held at 70°C by a thermostat to start the polymerization. The reaction was carried out under stirring for a definite time. The polymerization was terminated by the cooling of the flask in ice water. The polymerization product was obtained after filtration, washing, and drying. All of the ingredients used are summarized in Table I.

TABLE I
Standard Recipe for the Suspended Emulsion Polymerization of AN with IA

Ingredient	Dosage (g)
AN	40.3
H_2O	14.0
KPS	0.20
IA	5.00
PVA	0.04
Span80	0.20

The conditions were as follows: the temperature was 70°C, the time was 3 h, the agitation rate was 400 rpm, the water/monomer mass ratio was 0.3 : 1, and the weight of AN was kept at 40.3 g. The concentrations of KPS (0.5 wt %), IA (12.4 wt %), PVA (0.1 wt %), and Span80 (0.5 wt %) were all based on the weight of AN.

Characterization

The volume-average particle size and particle size distribution of the AN/IA copolymer particles were measured with a laser particle size analyzer (LS13320, Beckman Coulter, Los Angeles, CA), and the size distribution was indicated by the coefficient of variability. The coefficient of variability measures the distribution of particle size as a proportion of its average particle size. It is the ratio of the standard deviation to the average particle size and is often expressed as a percentage.

The particle morphology of the AN/IA copolymers was observed with scanning electron microscopy (SEM; JSM-5610LV, Jeol, Tokyo, Japan), and the samples were sputter-coated with Au film before the examination.

The porosity of the AN/IA copolymers was characterized by surface area and a porosity analyzer (Micromeritics 2020, Micromeritics, Atlanta, GA). The Barrett–Joiner–Halenda (BJH) average pore diameter (nm) and BJH pore volume (cm^3/g) in the dry state were determined from low-temperature nitrogen adsorption–desorption isotherms at 77 K with a high-vacuum volumetric apparatus.

RESULTS AND DISCUSSION

Effects of the water/monomer mass ratio on the average particle size and size distribution

Water, acting as the dispersed phase, was suspended in the continuous monomer phase in the suspended emulsion polymerization system. Figure 1 displays the variation in the average particle size and coefficient of variability relative to different water/monomer mass ratios. The average particle size decreased and the size distribution became wide with increasing water/monomer mass ratio.

The copolymerization of AN with IA mainly proceeded in the dispersed water droplets through the emulsion polymerization mechanism because of the solubility of the monomer in the water and the application of the water-soluble initiator. The size of the initial water droplets governed the size of the grains in the polymerization system and changed with various water/monomer mass ratios.[27] With

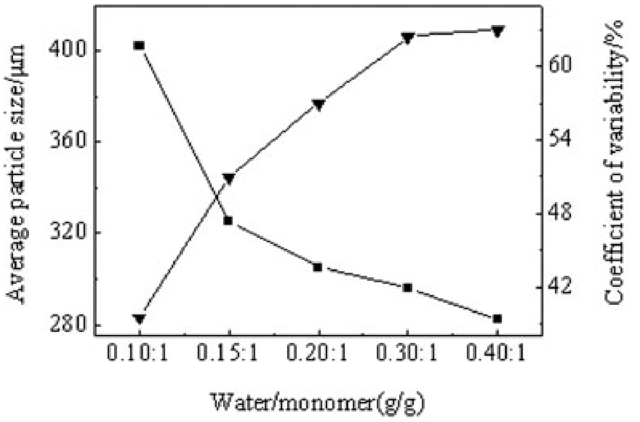

Figure 1 (■) Average particle size and (▼) coefficient of variability of AN/IA copolymers prepared by suspended emulsion polymerization with various water/monomer mass ratios (rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

increasing water/monomer mass ratios, the number of latex particles increased, the diameter of latex particles decreased and became nonuniform, the final particles formed with agglomerates of the primary particles became small, and the size distribution became wide.

The internal morphologies of the AN/IA grains prepared with different water/monomer mass ratios are shown in Figure 2. When the water/monomer mass ratio increased, the porosity of the target product increased. Figure 3 shows the BJH desorption pore size distributions of the AN/IA copolymers at different water/monomer mass ratios. With increasing water/monomer mass ratio, the pore size became relatively uniform. The final polymer grains had the best porosity when the water/monomer mass ratio was 0.3 : 1. With increasing amount of water in the system, more water was sealed in the space accumulated with the primary particles, and more pores existed in the interior of the polymer grains. Therefore, the final particles were more porous.

Effects of the agitation condition on the average particle size and size distribution

The size of the dispersed water droplets and AN/IA copolymers particles were influenced by the agitation rate when the polymerization recipe was fixed.[26] The effects of various agitation conditions on the average particle size and coefficient of variability are illustrated in Figure 4. Upon increasing agitation rate, the average particle size decreased considerably and then increased, and the size distribution was the widest at 600 rpm. Figure 5 shows the SEM microphotographs of the AN/IA particles prepared at 200, 400, and 600 rpm. Figure 6 shows the BJH desorption pore size distributions of the AN/IA copolymers at different agitation rates. With increasing agitation rate, the pore size did not change significantly. The final particles had the best porosity at 400 rpm as shown by comparison of the internal morphologies of the AN/IA grains under different agitation conditions. The agitation rate was too slow to overcome the viscosity of the system. However, if

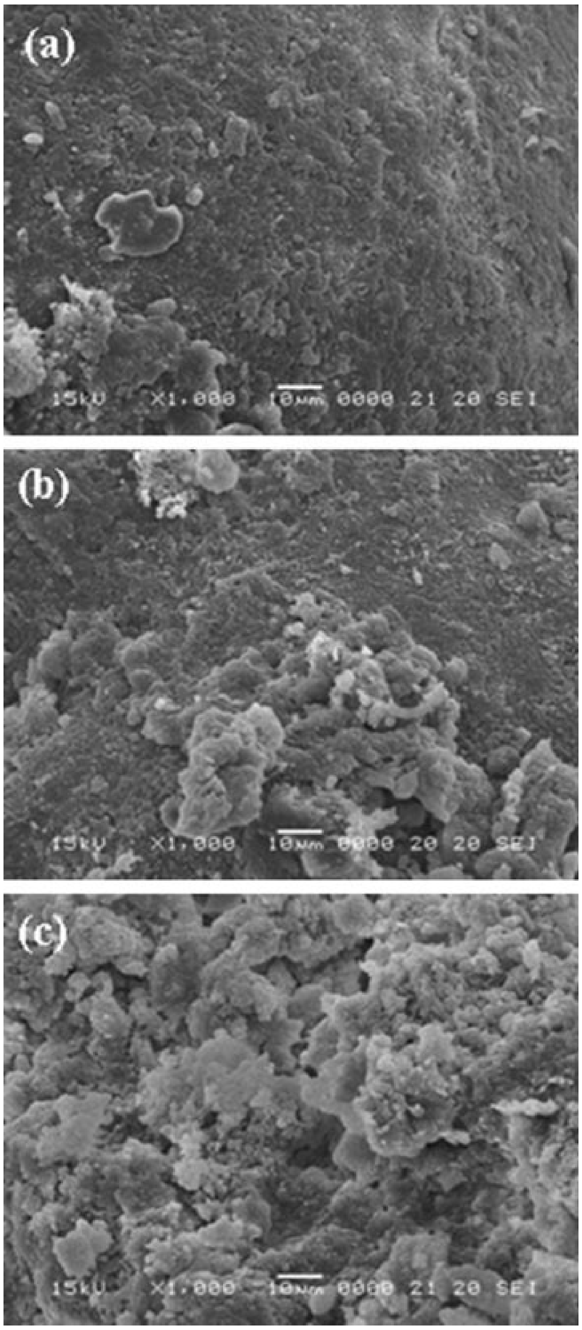

Figure 2 SEM microphotographs of particles prepared with different water/monomer mass ratios: (a) 0.1 : 1, (b) 0.15 : 1, and (c) 0.3 : 1 (rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

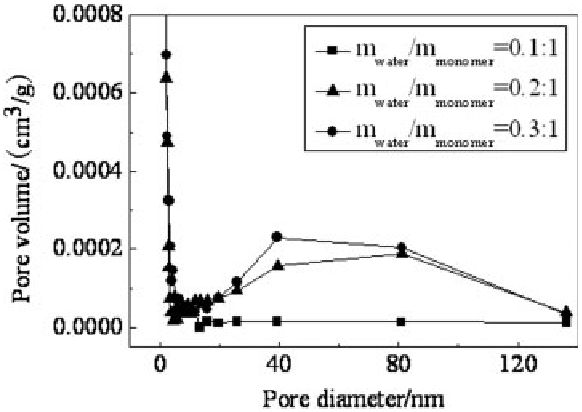

Figure 3 Pore size distributions of AN/IA copolymers prepared by suspended emulsion polymerization with various water/monomer mass ratio ($m_{\mathrm{water}}/m_{\mathrm{monomer}}$) values (rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

the agitation rate was too high, the collision probability of latex particles increased. To obtain AN/IA copolymers with good porosity and high workability strength, the agitation rate should be controlled in a definite range.

Effects of the initiator concentration on the average particle size and size distribution

AN/IA copolymers were prepared by suspended emulsion polymerization with the formation of radicals in the water phase, and the radicals were captured by the existing particles inside the water phase.[25,26] The effects of various KPS concentrations based on the weight of AN on the average particle size and coefficient of variability of the AN/IA copolymers are shown in Figure 7. With increasing KPS concentration, the average particle size decreased, and the size distribution became narrow. The initiator concentration had enormous impact on the copolymerization of AN with IA. The concentration of KPS needs to be in a certain range to ensure that the reaction proceeds smoothly.[27] With

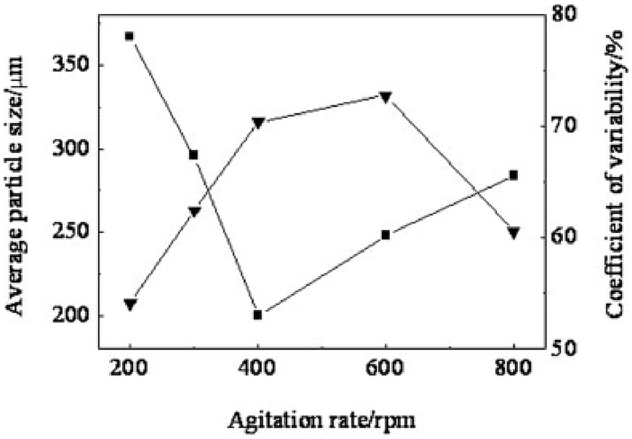

Figure 4 (■) Average particle size and (▼) coefficient of variability of AN/IA copolymers prepared by suspended emulsion polymerization with various agitation conditions (water/monomer mass ratio = 0.3 : 1, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

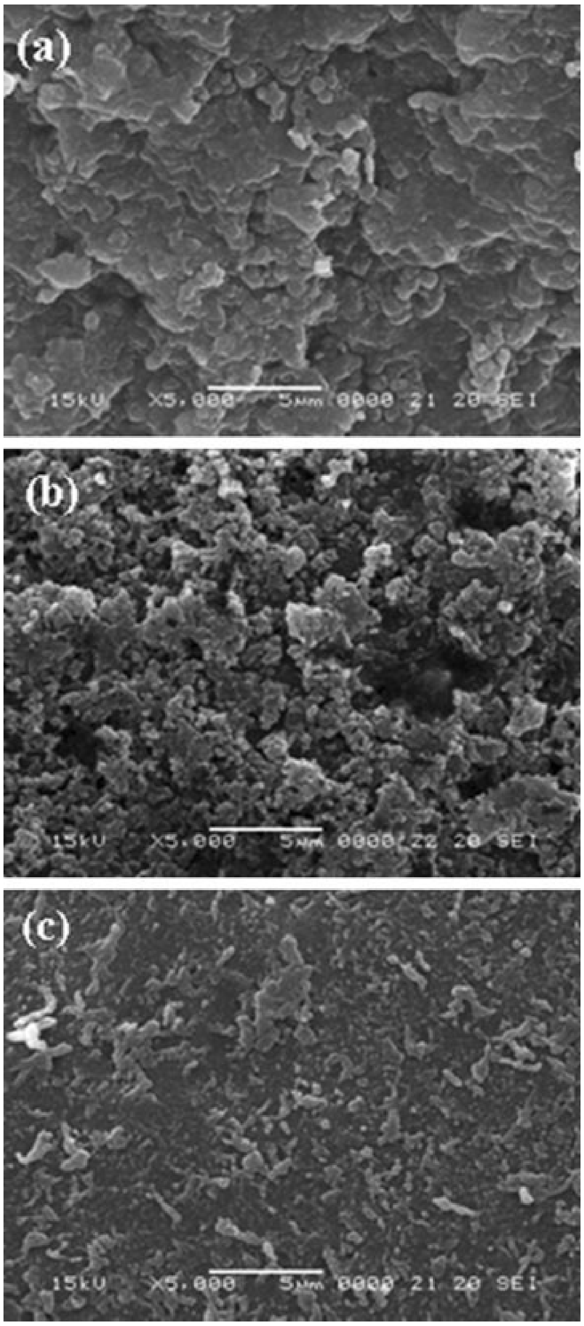

Figure 5 SEM microphotographs of particles prepared under different agitation conditions: (a) 200, (b) 400, and (c) 600 rpm (water/monomer mass ratio = 0.3 : 1, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

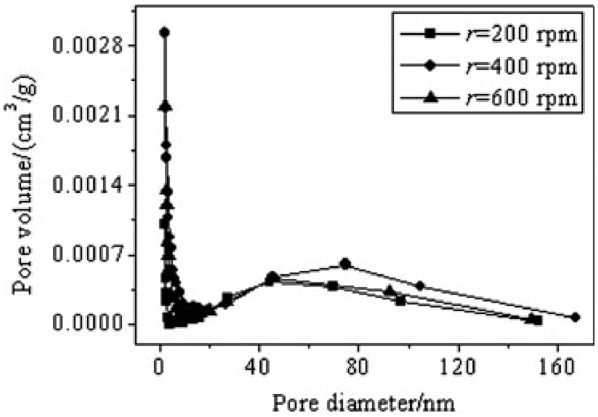

Figure 6 Pore size distributions of AN/IA copolymers prepared by suspended emulsion polymerization under various agitation conditions (r = rate of agitation; water/monomer mass ratio = 0.3 : 1, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

increasing KPS concentration, the number of latex particles and the polymerization rate increased, and the diameter of latex particles decreased; then, the average particle size of the grains formed with agglomerates of latex particles decreased, and the final copolymers with uniform particle size were obtained.

Figure 8 shows the BJH desorption pore size distributions of the AN/IA copolymers. Pores between 1.88 and 146.76 nm were dominant for all products. With increasing KPS concentration, the pore size did not change significantly. The different initiator concentrations led to a change in the total grain number and had no obvious effect on the pore size. However, the final polymer grains had good porosity when the KPS concentration was 0.5 wt %.

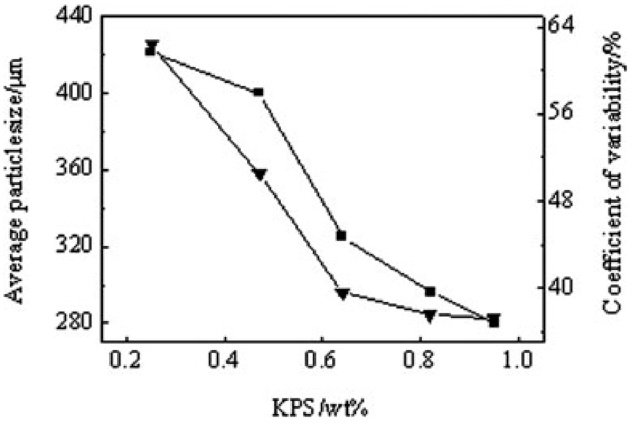

Figure 7 (■) Average particle size and (▼) coefficient of variability of AN/IA copolymers prepared by suspended emulsion polymerization with various initiator KPS concentrations (water/monomer mass ratio = 0.3 : 1, rate of agitation = 400 rpm, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

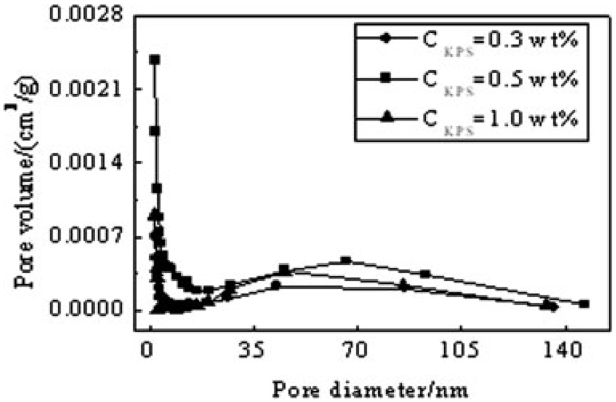

Figure 8 Pore size distributions of AN/IA copolymers prepared by suspended emulsion polymerization with various initiator KPS concentration (C_{KPS}) values (water/monomer mass ratio = 0.3 : 1, rate of agitation = 400 rpm, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

Effects of the IA concentration on the average particle size and size distribution

The major reason for the superiority of IA over other acidic comonomers is the presence of two carboxylic groups, which increases the activity of the carboxylic group and the nitrile group.[28–31]

Copolymerizations of AN with IA by suspended emulsion polymerization process were carried out at 0.5 wt % KPS relative to the weight of AN. In this experiment, the IA fraction based on the weight of AN was varied from 2.5 to 12.4 wt %. Figure 9 displays the variations in average particle size and coefficient of variability relative to the IA concentration. The average particle size was maximized at 365 μm at 10 wt %, and the size distribution was the widest at 7.4 wt %. However, partially agglomerated

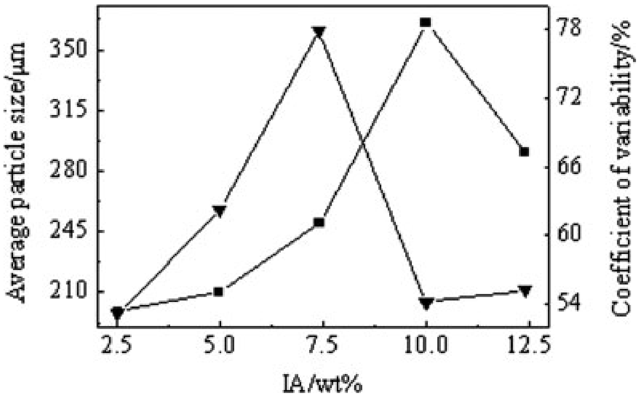

Figure 9 (■) Average particle size and (▼) coefficient of variability of AN/IA copolymers prepared by suspended emulsion polymerization with various comonomer IA concentrations (water/monomer mass ratio = 0.3 : 1, rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, temperature = 70°C, time = 3 h).

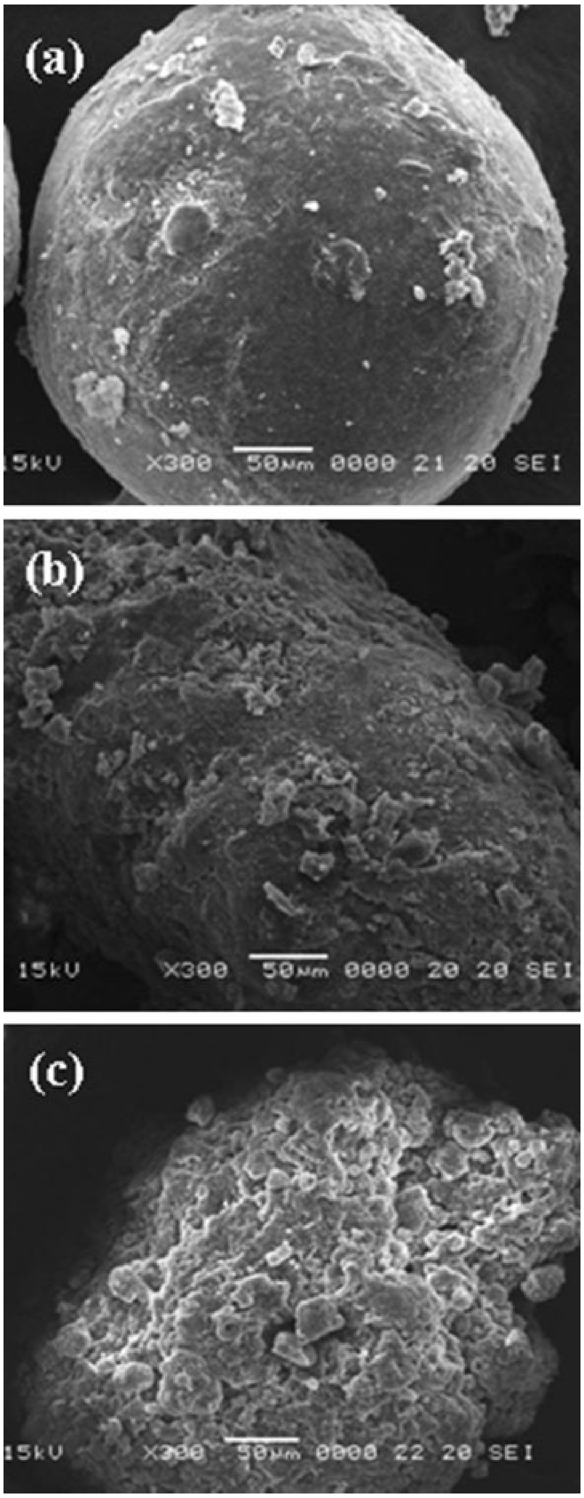

Figure 10 SEM microphotographs of particles prepared with different comonomer IA concentrations: (a) 5.0, (b) 7.4, and (c) 12.4 wt % (water/monomer mass ratio = 0.3 : 1, rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, temperature = 70°C, time = 3 h).

particles were prepared when the IA weight fraction was lower than 2.5 wt % relative to the weight of AN. No particles were obtained at IA weight fractions higher than 12.4 wt %. Figure 10 shows the SEM microphotographs of particles prepared at 5.0, 7.4, and 12.4 wt % with respect to the weight of AN. The target product that had the best porosity was prepared at 12.4 wt % by comparison of the internal morphologies of grains under different IA concentrations. Figure 11 shows the BJH desorption pore size distributions of the AN/IA copolymers at different IA concentrations. The AN/IA copolymer prepared at 12.4 wt % had the best porosity.

The polymerization rate was related to free-radical activity, which was affected by a steric hindrance effect and electronic effect. The molecular dimensions of IA were large, the space steric effect was great in the free-radical reaction, and it was difficult for the radical to attack the quaternary carbon of IA. When IA concentration was lower, the activity of the IA radical was higher than that of AN, and the activation energy of the polymerization decreased. As a result, the average particle size increased, and the size distribution became wide. With continuously increasing IA concentration, the space steric effect played a dominant role and prevented the increasing of the molecular chain; then, the rate of polymerization decreased. As shown in Figures 10 and 11, the average particle size decreased, and the porosity of the polymer was better.

Effects of the PVA dispersant agent concentration on the average particle size and size distribution

Water-soluble polymers as dispersant agents are those usually used in suspension polymerizations; it is generally accepted that they are mainly adsorbed on the surface of the organic phase, where they constitute a protective film. Their role as thickener of

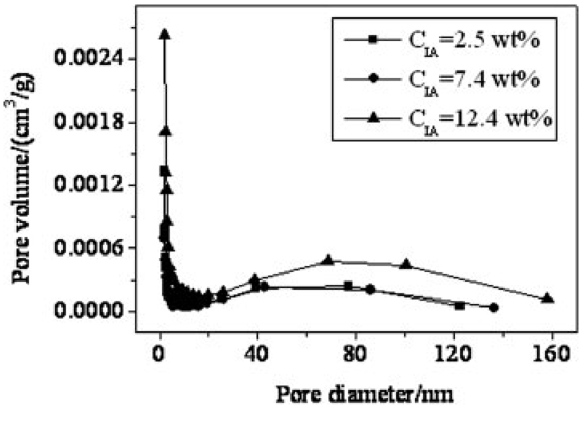

Figure 11 Pore size distributions of AN/IA copolymers prepared by suspended emulsion polymerization with various comonomer IA concentration (C_{IA}) values (water/monomer mass ratio = 0.3 : 1, rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, Span80 concentration = 0.5 wt %, temperature = 70°C, time = 3 h).

the continuous phase is now considered less important. The main difference in suspended emulsion polymerization is that these dispersant agents are now soluble in the dispersed phase. So, their effects may be expected to be very different.[23,24]

A set of experiments was carried out with PVA, namely, LW124. Because PVA did not have good solubility in the solvent, it was prepared in a solution of 2% before the experiments. Their effect relative to various PVA concentrations based on the weight of AN on the average particle size and coefficient of variability are shown in Figure 12. With increasing PVA concentration, the average particle size increased, and the size distribution became narrow. PVA was soluble in water and increased the viscosity of water. PVA had steric hindrance and stabilization effects on the water droplets.[26] With increasing concentration of PVA, more PVA was adsorbed on the surface of the water droplets and constituted a protective film; then, the polymerization proceeded smoothly and stably, and the existence of the primary particles was more stable, and more large particles were formed. As a result, the average particle size increased, and the size distribution became narrow.

Effects of the emulsifier concentration on the average particle size and size distribution

In suspended emulsion polymerization, emulsifiers have reducing interface tension, emulsification, and dispersing effects. The main difference with a conventional emulsion polymerization is that a part of the emulsifier is present at the monomer/water interface and not only at the polymer particle/water interface. Another point is that, in most cases, the amount of the emulsifier is very low, so that the particles formed by the emulsion process are not stable enough and easily coalesce to give much larger primary particles.[23]

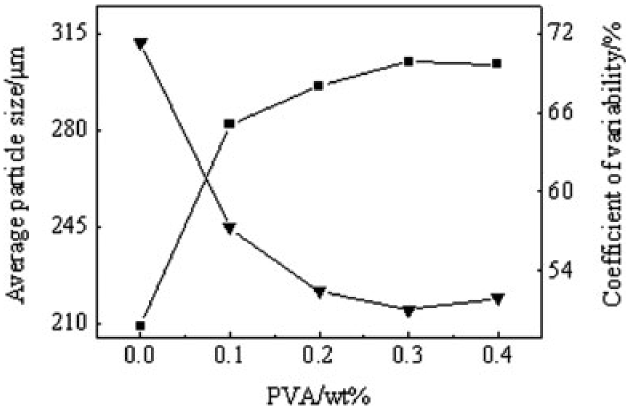

Figure 12 (■) Average particle size and (▼) coefficient of variability of AN/IA copolymers prepared by suspended emulsion polymerization with various dispersant agent PVA concentrations (water/monomer mass ratio = 0.3 : 1, rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, Span80 concentration = 0.5 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

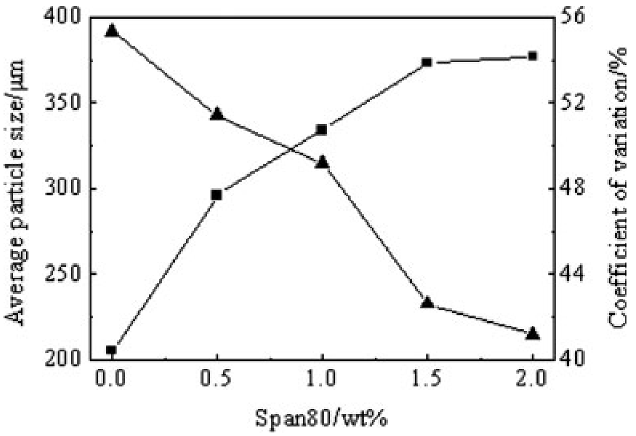

Figure 13 (■) Average particle size and (▼) coefficient of variability of AN/IA copolymers prepared by suspended emulsion polymerization with various emulsifier Span80 concentrations (water/monomer mass ratio = 0.3 : 1, rate of agitation = 400 rpm, KPS concentration = 0.5 wt %, PVA concentration = 0.1 wt %, IA concentration = 12.4 wt %, temperature = 70°C, time = 3 h).

A set of experiments was carried out with Span80 as an emulsifier in a suspended emulsion copolymerization of AN with IA. The effects of various Span80 concentrations based on the weight of AN on the average particle size and coefficient of variability are shown in Figure 13. With increasing concentration of emulsifier, the average particle size increased, and the size distribution became narrow. When Span80 was present, the primary particles formed with agglomerates of latex particles were more stable because of the colloid protection behavior of the emulsifier. With increasing Span80 concentration, the colloid protection behavior was more prominent, and the polymerization proceeded stably; then, the primary particles existed more stably, and more large particles were formed. As a result, the average particle size increased, and the size distribution became narrow.

CONCLUSIONS

Porous AN/IA copolymers were successfully prepared by suspended emulsion polymerization. The final AN/IA copolymers formed with agglomerates of primary particles had a porous structure, low particle density, and uniform particle size and did not agglomerate easily between the particles. The average particle size decreased and the size distribution became wide with increasing water/monomer mass ratio. With increasing KPS concentration, the average particle size decreased, and the size distribution became narrow. With increasing the concentration of PVA, the average particle size increased, and the size distribution became narrow. Suspended emulsion polymerization took place basically by an emulsion mechanism with the formation of the radicals in the water phase, the radicals being captured by the existing particles inside that water phase. The preparation conditions for the AN/IA copolymers were optimized as follows: (1) the water/monomer mass ratio was 0.3 : 1; (2) the concentrations of KPS, IA, PVA, and Span80 were 0.5, 12.4, 0.1, and 0.5 wt %, respectively, based on the weight of AN separately; (3) the agitation rate was 400 rpm; (4) the polymerization temperature was 70°C, and (5) the reaction time was 3 h. The size of the final AN/IA copolymer particles was in the range 200–400 μm.

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