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Suspended Emulsion Copolymerization of Acrylonitrile with Methyl Acrylate: Effects of Reaction Parameters on the Polymerization

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Acrylonitrile/methyl acrylate copolymers were synthesized by suspended emulsion polymerization with water as dispersed phase and monomers as continuous phase, potassium peroxydisulphate (KPS) as initiator, Span-80 as emulsifier, and poly(vinyl alcohol) (PVA) as suspending agent. Effects of reaction parameters such as water/monomer mass ratio, concentration of initiator, polymerization temperature and agitation rate on polymerization conversion and the particle size distribution of acrylonitrile/methyl acrylate copolymers were studied. It was found that polymerization conversion increased with an increase of water/monomer mass ratio, concentration of initiator and polymerization temperature, while the agitation rate had no significant effect on the polymerization conversion. Particle size distribution became narrower with an increase of water/monomer mass ratio and agitation rate. Under the same initiator concentration and polymerization temperature, particle size distribution became wider along with polymerization time. The differential scanning calorimetry (DSC) results indicated that the peak temperature of the copolymers decreased with increasing MA content.

Keywords: Suspended emulsion polymerization, acrylonitrile, methyl acrylate, particle size distribution

1 Introduction

Polyacrylonitrile (PAN) is one of the important precursors for polymer materials. It has been widely used as reinforcing materials in automobile, aerospace, recreational and other industries, and its application may be broader with its performance further improved (1–6). Acrylonitrile (AN) homopolymer has good processibility and electrochemical stability, but it is brittle for the reason that the interaction of adjacent cyano groups which enhances the resistance of interior rotation of the main chain and decreases the flexibility of main chain (7). These drawbacks can be made up to some extent by forming copolymers through copolymerization with suitable comonomer like methyl acrylate (MA) (8–12).

Copolymerization of AN with other comonomers can be approached by various methods such as solution, emulsion, aqueous suspension and solvent water suspension polymerization (13–16). Chen et al. (17) discussed the influencing factors of acrylonitrile aqueous suspension copolymerization system. It was found that the polymerization conversion increased with an increase of initiator concentration and polymerization temperature, the agitation rate should be controlled in a definite range to keep a steady polymerization. Wang et al. (18) studied the free-radical solution copolymerization of itaconic acid (IA) and AN, the final polymerization solution was spun to form PAN precursors of carbon fiber. Chen et al. (19) firstly investigated the copolymerization of amino ethyl-2-methyl propenoate and acrylonitrile by solvent water suspension method to produce a kind of high-performance acrylic fiber. However, the polymer particles obtained by the above methods universally have some defects of compact structure and unworkability. It is important to select a suitable technique and optimize the conditions of polymerization for synthesis of workable AN copolymers.

In the 1990s, Vindevoghel et al. (20, 21) proposed the suspended emulsion polymerization process and applied this process to prepare porous poly(vinyl chloride) (PVC) resin with homogeneous distribution of primary particles, and investigated the effects of dispersants and surfactants on the particles properties of PVC resin. Suspended emulsion polymerization is a new polymerization process in which a water phase containing the initiator is suspended in an organic phase containing the monomer, and the polymer formed is insoluble in both organic and water phase. The polymerization starts in the water droplets in the presence

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of monomers dissolved in water and were initiated by a water-soluble initiator. The primary particles are formed through the emulsion polymerization mechanism and coagulate at the later polymerization stage due to the low colloidal stability of primary particles. As a result, porous polymer particles in supermicron size would be formed. About ten years later, Bao et al. (22, 23) investigated the particles formation mechanism and kinetics of PVC and PMMA resins prepared by the suspended emulsion polymerization.

In this paper, AN/MA copolymers were prepared by suspended emulsion polymerization. Effects of polymerization conditions such as water/monomer mass ratio, concentration of initiator, polymerization temperature, agitation rate on polymerization conversion and the particle size distribution of AN/MA copolymers were described.

2 Experimental

2.1 Materials

Acrylonitrile (AN, Tianjin Kermel Chemical Reagent Co., A.R. grade, China) was distilled to get 76–78°C distillation just before polymerization. Methyl Acrylate (MA, Tianjin Kermel Chemical Reagent Co., A.R. grade, China). Potassium peroxydisulphate (KPS, Tianjin Reagent Chemical Co., A.R. grade, China) was used as an initiator. Polyvinyl alcohol (PVA, Shanghai Aibi Chemical Co. polymerization degree = 1750 ± 50) with the trade name of LW124 was used as the dispersant agent. Span-80 (Tianjin Kermel Chemical Reagent Co., A.R. grade, China) was used as the emulsifier. Deionized water was adopted as the polymerization medium.

2.2 Polymerization

AN/MA copolymerization was carried out in a 100 ml round bottomed flask. A typical example of the general procedure was as follows: Water, a mixture of AN (84–90 mol%) and MA (10–16 mol%), dispersant agent PVA and emulsifier Span-80 were placed in the flask and stirred for 10 min before polymerization. KPS solution was fed into the reactor when the content in the reactor reached the designed polymerization temperature. The reactor was agitated from periodically. The polymerization was terminated by cooling down the flask to 40°C rapidly after a definite reaction time. The copolymers were obtained after filtrating, washing and drying.

2.3 Characterizations

Infrared spectrum was recorded on a Nicolet MAGNA-IR550 spectrophotometer; test conditions: potassium bromide pellets. Scanning 32 times, the resolution is 4 cm^{-1}. The data was treated with Thermo Nicolet Corporation OMNIC32 (version 6.0a) software.

Conversions were determined with the conventional gravimetric method. The conversion was calculated as follows:

$$\mathrm{Cv} = \mathrm{M}/(\mathrm{M}_{\mathrm{AN}} + \mathrm{M}_{\mathrm{MA}})$$

Where Cv is the calculated conversion, M is the weight of AN/MA copolymers, M_{AN} is the weight of monomer AN and M_{MA} is the weight of comonomer MA.

The volume particle size distribution of AN/MA copolymers particles were measured by a laser particle size analyzer (LS-13320, Beckman Coulter, Los Angeles, CA).

Differential scanning calorimetry (DSC) was performed using a Netzsch DSC204F1 Phoenix instrument, in nitrogen atmosphere at a heating rate of 10°C/min.

The molecular weight ($\overline{M}_\eta$) of AN/MA copolymers was determined by the intrinsic viscosity measurements. The intrinsic viscosity $[\eta]$ of AN/MA copolymers was measured at 25°C in N,N—dimethyl formamide (DMF) using an Ubbelohde viscometer, and the molecular weight was calculated from the following equation (17):

$$[\eta] = 2.78 \times 10^{-4} \overline{M}_\eta^{0.76}$$

3 Results and Discussion

3.1 FTIR Characterization

FTIR spectrum of the AN/MA copolymer prepared by suspended emulsion polymerization is given in Figure 1. The sharp absorption at 2243 cm^{-1} due to C≡N characteristic peak, the strong band in 1732 cm^{-1} was present in AN/MA copolymer due to C=O stretching introduced by ester group in MA comonomer. FTIR spectrum indicates that MA monomer successfully copolymerized with AN.

3.2 Effect of the Initial Water/Monomer Mass Ratio

Figure 2 displays variations of polymerization conversion with water/monomer mass ratio at a different time. The concentration of KPS and Span-80, polymerization temperature and agitation rate were kept constant, while the initial water/monomer mass ratio was varied. From Figure 2, a general conclusion can be found that polymerization conversion increased with an increase of water/monomer mass ratio. Furthermore, it can also be observed that polymerization conversion increased as polymerization time prolonged. In the suspended emulsion polymerization, the initiator is a water-soluble system so that an emulsion polymerization takes place in the water phase from the dissolved monomer and the radicals coming from the initiator (20). Monomers easily dissolved in water phase and were initiated by KPS with an increase of water/monomer mass ratio, corresponding to the increase of active sites, growing

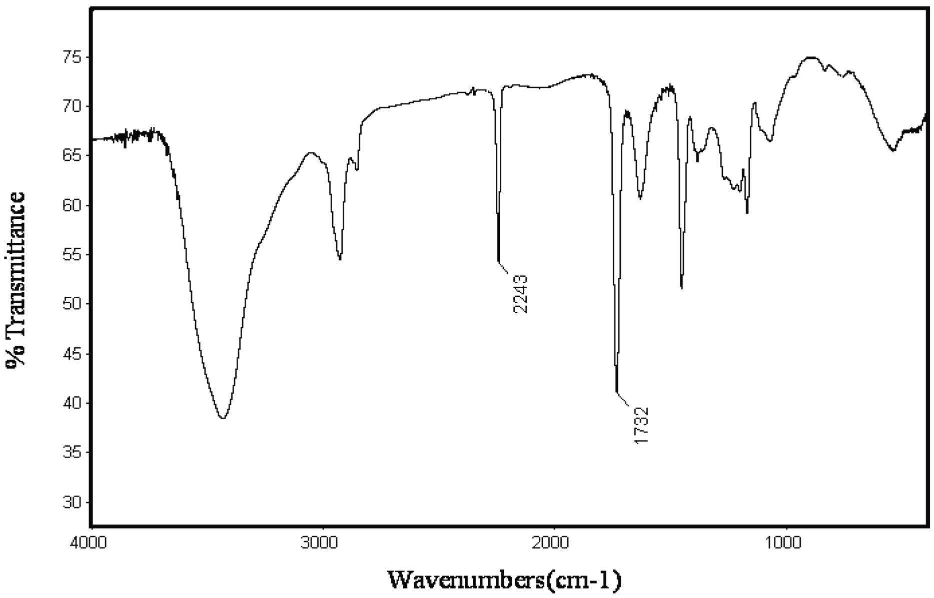

Fig. 1. FT-IR spectrum of AN/MA polymer (after washed with methanol) (water/monomer mass ratio: 0.6:1(m_{water}: 18 g), T: 68°C, Span-80: 4.42 vol%, m_{PVA}: 0.16 g, 500 r/min, t: 2.5 h).

chains and the number of latex particles. The probabilities of the latex particles colliding with each other and forming primary particles were raised, and there were more polymer particles formed by primary particles, thus the polymerization conversion increased.

The liquid-liquid dispersion and the coalescence rate of the system could be affected by the water/monomer mass ratio, thus affecting the dispersed droplets and resin particle size. Figure 3 displays the particle size distribution of AN/MA copolymers with different water/monomer mass ratio. As shown in Figure 3, the particle size distribution became narrower as the water/monomer mass ratio increased. Because the solubility of monomer in water and the application of the water-soluble initiator, AN/MA suspended emulsion polymerization mainly proceeded in dispersed water droplets through the emulsion polymerization mechanism. The size of the initial water droplets in the polymerization system and the characteristics of the final copolymers particles changed with the variation of water/monomer mass ratio (24). Increasing the water/monomer mass ratio, the number of latex particles increased and the particles diameter decreased, the size of particles that agglomerated by the latex particles decreased. At a higher water/monomer mass ratio, the proportion of large grains in the copolymers became lower and the proportion of small grains became higher, the particle size became uniform simultaneously. The volume fraction was

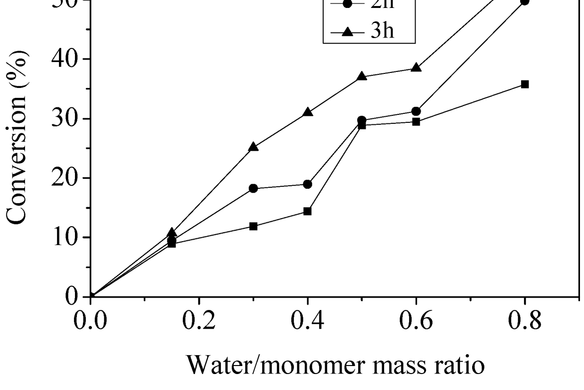

Fig. 2. Variations of polymerization conversion with water/monomer mass ratio at different time (C_{KPS}: 0.00618 mol/L, T: 68°C, m_{PVA}: 0.16 g, Span-80: 4.42 vol%, 500 r/min).

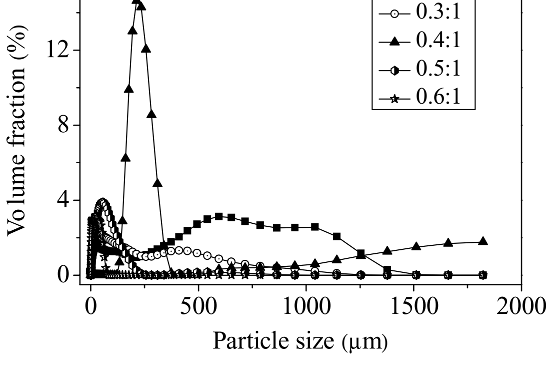

Fig. 3. Effect of water/monomer mass ratio on the particle size distribution of AN/MA copolymers (C_{KPS}: 0.00618 mol/L, T: 68°C, m_{PVA}: 0.16 g, Span-80: 4.42 vol%, t: 2 h, 500 r/min).

the highest and could reach approximately 15% when the mass ratio of water/monomer is 0.4:1, which indicates that particle size dispersion was relatively better under these conditions.

3.3 Effect of Initiator Concentration

KPS was used as the initiator in the copolymerization system of AN/MA. Variations of polymerization conversion vs. initiator concentration with time are displayed in Figure 4. The initial water/monomer mass ratio, polymerization temperature, and the agitation rate were kept constant, and the concentration of KPS was varied.

From Figure 4, it can obviously be found that polymerization conversion increased significantly with the KPS concentration increasing, a similar observation was reported in the case of AN/MA copolymer prepared by aqueous suspension polymerization (17). A relatively high polymerization conversion (about 90%) could be obtained in a short period of time when the initiator concentration was high enough (eg. 0.0185 mol/L). This effect may be explained by an increase of KPS decomposition rate favored by increasing the KPS concentration. The production rate of free radicals resulted from the initiator increased, followed by an increase of active sites and growing chains, led to an increase in the number of latex particles, thus, the polymerization conversion increased.

Initiator concentration can also affect the particle size distribution of the copolymers. When the KPS concentration is 0.0123 mol/L, the particle size distribution of AN/MA copolymers with different polymerization time is given in Figure 5. It is seen that the particle size distribution became wider as polymerization time increased. The copolymerization of monomers could be initiated by KPS to form short chain free radicals, several such short chain free radicals aggregate with each other and flocculate nuclear (primary particles), and monomers constantly diffuse into the nuclear to form latex particles. The initiator decomposed continuously after the formation of latex particles, a large number of free radicals still produced and grew in the water phase. When reaching the critical chain length, the growing free radicals could form new latex particles. New formed free radicals can still initiate copolymerization of AN with MA, formed primary particles and then agglomerated large and non-uniform particles. As a result, the size distribution became wider.

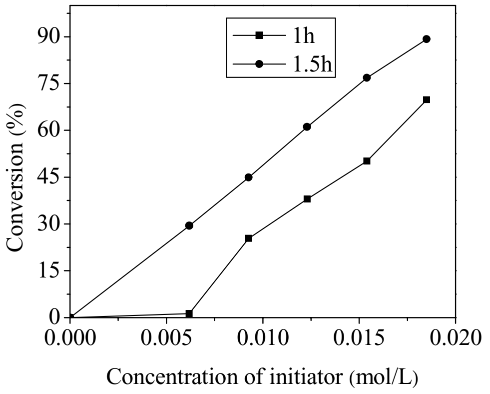

Fig. 4. Variations of polymerization conversion with initiator concentration at different time (Water/monomer mass ratio: 0.6:1(m_{water}: 18 g), T: 68°C, Span-80: 4.42 vol%, m_{PVA}: 0.16 g, 500 r/min).

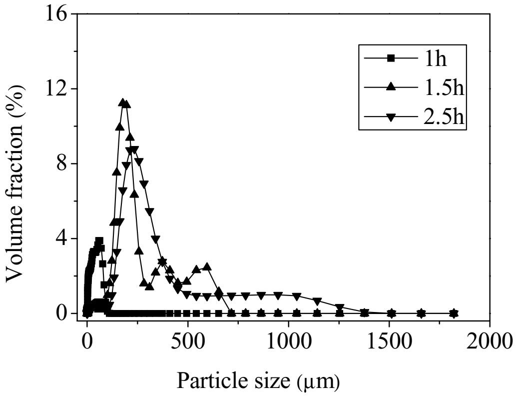

Fig. 5. Particle size distribution of AN/MA copolymers with different polymerization time (Water/monomer mass ratio: 0.6:1(m_{water}: 18 g), C_{KPS}: 0.0123 mol/L, T: 68°C, m_{PVA}: 0.16 g, Span-80: 4.42 vol%, 500 r/min).

The molecular weight of AN/MA copolymers with different initiator concentration is given in Table 1. As shown in Table 1, the molecular weight decreased with the increase of initiator concentration, a similar observation was also reported in the case of the aqueous suspension polymerization of AN with MA, with a KPS concentration of 0.3%–0.45% to monomer (17).

3.4 Effect of Polymerization Temperature

Temperature is one of the important factors for the suspended emulsion polymerization. The polymerization rate and the resin molecular weight can be affected by temperature. Furthermore, the process of nucleation, morphology and distribution of particles and the performance of the resin are also affected by temperature.

Variations of polymerization conversion vs. temperature with the polymerization time are presented in Figure 6.

Table 1. Molecular weight of AN/MA copolymers with different initiator concentration

Initiator Concentration (mol/L)	*Molecular Weight* ($\overline{M}_\eta$)
0.00618	23.98×10^4
0.0123	23.15×10^4
0.0185	18.57×10^4

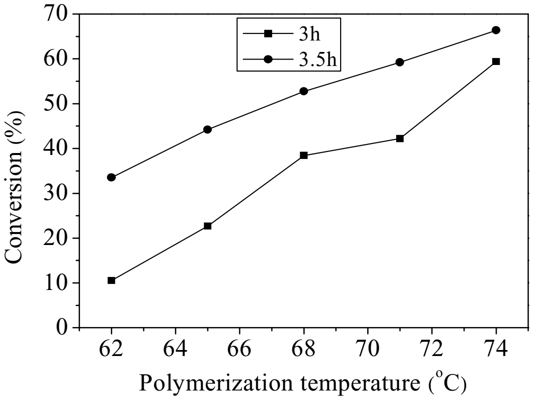

Fig. 6. Variations of polymerization conversion with polymerization temperature at different time (Water/monomer mass ratio: 0.6:1(m_{water}: 18 g), C_{KPS}: 0.00618 mol/L, m_{PVA}: 0.16 g, Span-80: 4.42 vol%, 500 r/min).

The initial water/monomer mass ratio, the concentration of KPS, and the agitation rate were kept constant, the polymerization temperature was varied. From Figure 6, it can be seen that the polymerization conversion increased with an increase of polymerization temperature. Under the same formulation polymerization conditions, there are the same latex grains, and the numbers of the average free radicals in the latex grains are about equal. Upon raising polymerization temperature, the decomposition rate of initiator and monomer solubility in the aqueous phase increased. Polymerization growth rate constant, production rate of free radicals and number of latex particles further increased with the rise of polymerization temperature, resulting in the increase of polymerization conversion.

Figure 7 displays particle size distribution of AN/MA copolymers with a different polymerization time when the polymerization temperature is 68°C. It can be seen from Figure 7 that the particle size distribution became wider as polymerization time increased. It contained a large volume fraction of fine particles in the initial period and the particle size distribution was narrower, as time went on, the volume fraction of fine particles decreased and the particles size of AN/MA copolymers increased. Since polymerization was initiated in water droplets, AN/MA chains would precipitate out from the aqueous phase when they reach a critical polymerization degree. The precipitating AN/MA chains would aggregate to form particles nuclei and primary particles. The grains are formed by coagulation of primary particles. In the early stage, a part of the primary particles cannot coagulate to form grains and some coagulated primary particles would separate from grains under shear during the post-treatment process and the particles size measurement since the coagulation strength of primary particles is weak (25). The coagulation degree and strength of primary particles increase with the extension of polymerization time, therefore, the particles size became non-uniform and the size distribution became wider.

3.5 Effect of Agitation Rate

Various polymerization conversions vs. agitation rate with time are presented in Figure 8. The polymerization conditions such as concentration of KPS and Span-80, polymerization temperature and initial water/monomer mass ratio were kept constant, while the agitation rate was varied. From Figure 8, it can be seen that no significant changes in the polymerization conversion have been observed with the difference of agitation rate, but under the same agitation rate condition, the polymerization conversion increased along with polymerization time.

Water acts as a dispersed phase in the suspended emulsion polymerization. The size of dispersed water droplets and AN/MA particles is affected by the agitation rate when the polymerization recipe is fixed (26). In order to obtain AN/MA copolymers of high workability strength,

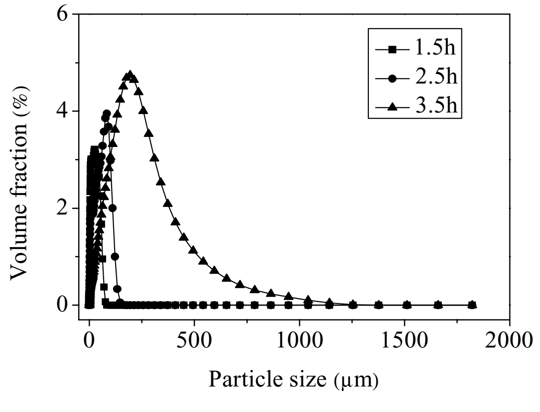

Fig. 7. Particle size distribution of AN/MA copolymers with different polymerization time (Water/monomer mass ratio: 0.6:1(m_{water}: 18 g), C_{KPS}: 0.00618 mol/L, T: 68°C, m_{PVA}: 0.16 g, Span-80: 4.42 vol%, 500 r/min).

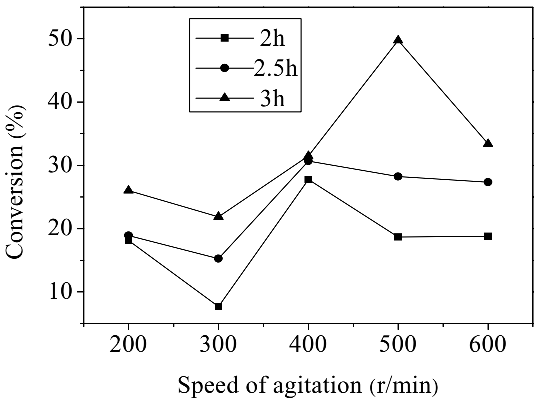

Fig. 8. Variations of polymerization conversion with agitation rate at different time (Water/monomer mass ratio: 0.4:1(m_{water}: 16 g), C_{KPS}: 0.00618 mol/L, T: 68°C, m_{PVA}: 0.16 g, Span-80: 4.42 vol%).

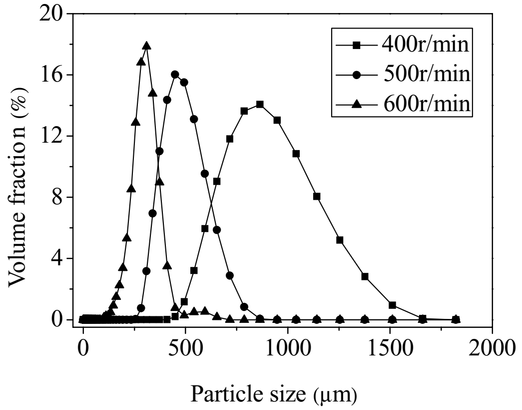

Fig. 9. Effect of agitation rate on the particle size distribution of AN/MA copolymers (Water/monomer mass ratio: 0.4:1(m_{water}: 16 g), C_{KPS}: 0.00618 mol/L, T: 68°C, m_{PVA}: 0.16 g, Span-80: 4.42 vol%, t: 3 h).

the agitation rate should be controlled in a definite range. Particle size distribution of AN/MA copolymers with different agitation rate is given in Figure 9. As shown in Figure 9, the particle size distribution became narrower and the volume fraction became higher as the agitation rate increased. There was no information for low agitation rate such as 200 r/min and 300 r/min, because the particles size was so large that it exceeded the analyzer's extent. Usually, the shearing strength enhanced with the increase of agitation rate, when the agitation rate was slow, it was difficult to overcome the viscosity of the system and tend to form large particles.

3.6 Comparison with Other Polymerization Methods

The variations between different polymerization methods are discussed in Table 2. A briefly methodological description of heterogeneous polymerization processes, including suspension, emulsion, suspended emulsion polymerization is presented. The discussion focuses on the system composition, dispersion condition, initiator, mechanism of polymerization, particle morphology and size. It is shown that different heterogeneous polymerization processes can be clearly distinguished on the basis of one or more of the following four criteria (27): 1) initial state of the polymerization mixture, 2) mechanism of polymerization, 3) mode of particle formation, and 4) particle form of the final polymer.

This thermal event is analyzed in Figure 10. The DSC thermograms show that AN homopolymer exhibits a sharp exothermic cyclization peak at 274°C, while the AN/MA copolymers reduce the rate of this process, and hence, exhibit a broader exotherm in accordance with the literature, and the exotherm peak is shifted to higher temperatures with increasing comonomer content (11, 28). But the peak temperature (319°C) of AN/MA 85/15 copolymer synthesized by suspended emulsion polymerization is lower than

Table 2. Comparison between different polymerization methods

Polymerization methods	*Suspension polymerization*	*Emulsion polymerization*	*Suspended emulsion polymerization*
System composition	Volume ratio of monomer phase/water phase is 0.1–0.5	Volume ratio of monomer phase/water phase is 0.1–0.5	Volume ratio of monomer phase/water phase is 1.2–1.0
Dispersion condition	Monomers are in monomer droplets that dispersed in the continuous water phase	Monomers are in the monomer droplets or micelles that dispersed in the continuous water phase	Water droplets are dispersed in the continuous monomer phase
Initiator	Oil-soluble initiator	Water-soluble initiator	Water-soluble initiator
Mechanism of Polymerization	The bulk polymerization is proceeded in the suspended monomer globule	The polymerization is proceeded in the continuous water phase or latex particles	The polymerization is similar with emulsion polymerization, but proceeded in the water droplets
Mechanism of particle formation	Monomer droplets granulation	Micelles nucleation or homogenous nucleation	Latex particle coacervation
Particle morphology	Normal spherical particles (bead suspension polymerization) or abnormal loose particles (powder suspension polymerization)	Spherical latex particles, latex particles aggregation will be obtained after drying	Similar with the suspension polymerization
Particle size	50–500 μm	0.1–3 μm	Similarly with the suspension polymerization

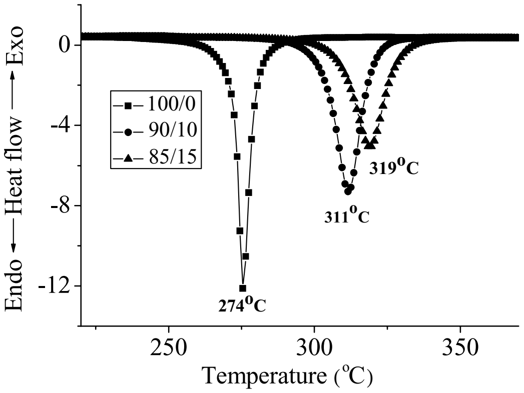

Fig. 10. DSC thermograms for AN homopolymer and copolymer.

that (324°C) of AN/MA 85/15 copolymer synthesized by suspension polymerization and higher than that (318°C) of AN/MA 85/15 copolymer prepared by solution polymerization (28).

4 Conclusions

AN/MA copolymers were synthesized by suspended emulsion polymerization, employing water as dispersed phase and monomers as continuous phase, KPS as initiator, Span-80 as emulsifier, and PVA as suspending agent. The study on AN/MA suspended emulsion polymerization showed that copolymerization conversion increased with an increase of water/monomer mass ratio, concentration of initiator and polymerization temperature, agitation rate had no significant effect on the polymerization conversion. The particle size distribution became narrower with an increase of water/monomer mass ratio and agitation rate. Under the same initiator concentration and polymerization temperature, with an increase of polymerization time, the particle size distribution became wider. The DSC results indicated that the peak temperature of the copolymers decreased with increasing MA content.

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