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KINETIC STUDIES ON EMULSION COPOLYMERIZATION OF VINYL ACETATE AND ACRYLICS IN THE BATCH PROCESS

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Abstract—The batch emulsion copolymerization of vinyl acetate and acrylic monomers (acrylic acid, methyl acrylate and acrylamide) was investigated at 25°C with a redox initiator system and a complex emulsifier. The kinetic behaviour of the copolymerization and the structure of the resulting copolymers, as well as the particle size and the number density of the latexes, were studied as a function of the conversion and the reaction time. The results show that the copolymerization process has a three-stage feature under the conditions of the optimum concentration of the initiator and the emulsifier being 0.2 wt% and 2.0 wt%, respectively. During the process, the particle size and the number density change drastically and finally reach limiting values of 120 nm and 2.5×10^{14} mL^{-1}, respectively, for VAc–AA–AM terpolymer. A special mechanism of particle formation is proposed. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

It is well known that the nature of the polymerization process can affect the kinetic behaviour, microstructure, molecular weight (MW) and homogeneity of the resulting copolymers. In the emulsion copolymers, vinyl acetate (VAc) latexes have been of interest for a long time owing to their various industrial applications, such as adhesives, textile sizes and coatings [1, 2]. Many studies have been devoted to their preparation by an emulsion process because of their relatively low cost, ready availability, wide compatibility and excellent adhesive characteristics. The mechanism of VAc emulsion polymerization is shown to deviate noticeably from the classical emulsion polymerization theory. This behaviour is related to the physical characteristics of the monomer: water solubility, large polymer swellability and high reactivity of the growing radical. In the emulsion polymerization of VAc, homogeneous nucleation plays an important role owing to its high water solubility [3–5]. In the emulsion copolymerization of VAc/acrylics, other problems will be encountered due to the large discrepancy in their reactivity ratios. Only a few studies have dealt with the VAc/acrylics multi-polymerization. This prior work showed the influence of the synthesis process on the mechanical properties of films cast from those latexes, and some researches were done on the surface and colloidal properties of the latexes [6, 7]. It seems that the emulsion copolymerization of the system leads to the latexes of various structures, merely by changing the polymerization process [8]. The purpose of the present work is to study the kinetics of the batch emulsion copolymerization of VAc/acrylics, including the effects of the monomer ratios, effect of level of the complex emulsifiers and concentration of the redox initiator system on the conversion or rate, copolymer composition, molecular weight (MW) and particle size. The semi-continuous process will be reported in another paper.

EXPERIMENTAL

Materials and reagents

Vinyl acetate (VAc), methyl acrylate (MA), acrylic acid (AA) and acrylamide (AM) are of A.R.-grades and were treated just before use to remove the inhibitors. The complex emulsifier of polyvinyl alcohol 1090 (PVA, the degree of hydrolysis and average degree of polymerization being 90% and 1000, respectively)/sodium dodecylsulfate (SDS) and the redox initiator system of potassium persulfate (KPO)/bisulfite were used without purification.

Emulsion copolymerization and kinetics

The VAc/acrylics emulsion copolymerization was run using the batch process. The reactor is a 500-mL double wall, four-neck glass flask equipped with a lune type Teflon blade. The agitation was maintained at 200 rpm. During the polymerization, nitrogen was purged to displace the atmosphere in the reactor and the samples were withdrawn by a sampling device at a definite time interval. The whole comonomer mixture with emulsifier-deionized water solution was added into the flask at the beginning of the polymerization, then the persulfate/bisulfite solution was added to start the polymerization at 25°C. The duration of the polymerization is 5–7 hr so that the conversion is high enough.

After the polymerization was started, 1–2 mL of the reaction mixture was sampled at a definite time interval for the conversion measurement. The sample was placed in a tared weight dish along with three drops of a short-stop solution (5% phenol in water–alcohol solution) and dried overnight in an oven at 75°C. The solid percentage and conversion were determined gravimetrically from the dried sample weights based on the total amount of the monomer mixture. The film sample was used for the measurement of

Table 1. The copolymer wt% in the emulsion copolymerization

	VAc	MA	AA	AM
1	50–85	—	50–15	—
2	30–60	30–50	10–20	—
3	30–65	15–30	5–10	15–30
4	50–80	—	5–20	15–30

copolymer composition using Fourier Transform Infrared Spectrometry (FTIR, Nicolet DX).

Characterization of particle size and average molecular weight

The particle size of the latex was determined by the dynamic light scattering method using a Malvern Autosizer II. A drop of latex withdrawn from the reactor was diluted with distilled water to a concentration of 1–3%, then thoroughly distributed by means of an ultrasonic distributor. The particle size of the sample was measured at 25°C.

The specific viscosity was determined with an Ubbelodhe viscometer at 30°C and was then used to calculate the average molecular weight.

The surface property of the latex was measured with a surface tensiometer (model JZHYI-180) at 25°C.

RESULTS AND DISCUSSION

Selection of the recipes

Component of comonomers. The studies on the VAc/acrylics multi-polymerization are of particular interest, because they lead to an important material for a textile size. According to the requirements of the size, such as the adhesives, stability and water dispersity, the components of comonomers were first studied as shown in Table 1. The reactivity ratios of monomer pairs are listed in Table 2.

The primary results showed that the first, second and third recipes were not successful, because the precipitations were often obtained after the latexes stayed at room temperature for a period of over one week. However, the above phenomena did not occur when using the fourth recipe and the copolymerization was successful. Therefore, the fourth recipe was used to study the copolymerization kinetics further.

Along with conversion–time data, the copolymer composition, average molecular weight (MW) and particle size were selected as the objective parameters to be studied in the emulsion copolymerization.

Ratio and concentration of the complex emulsifier. The type, ratio and concentration of emulsifier have a strong effect on the conversion, stability and particle size of the latex. In the present work, SDS and PVA were selected to form a complex emulsifier in VAc emulsion copolymerization, which was different from only PVA used in VAc homopolymerization. The effects of the ratio and concentration of SDS/PVA on the stability of

Table 2. Reactivity ratios of monomer pairs [9]

	r_1	r_2
VAc–AA	0.01	10
VAc–AM	0.016	6.291
AA–AM	1.43	0.60

Table 3. The stability of the monomer latex under different emulsifier ratios and concentrations[a]

SDS:PVA	Conc. (wt%)	Precipitation time (min)
1:1	2	30
2:1	2	5
3:1	2	5
1:2	2	45
1:3	2	165
1:3	0.5	10
1:3	1	30
1:3	3	115
1:3	4	5

Stirring speed: 200 rpm; stirring time: 30 min; VAc:AA:AM = 77:7.5:15.5.

monomer droplets and the surface tension of the system are shown in Table 3 and Fig. 1. The surface tension of the system decreases gradually as the SDS component, relative to PVA, increases at a constant concentration of 2 wt%. Generally, the lower the surface tension, the finer the dispersion of the monomers. On the other hand, the smaller the amount of agent used to reach the surface tension of the system, the better the emulsification ability of the complex emulsifier. In this special system, the emulsification ability is good when the concentration and the ratio of SDS and PVA are 2 wt% and 1:3, respectively (Table 3).

Initiator. In the emulsion copolymerization, the conversion (X, %) and MW of the resulting copolymers are affected by the redox initiator system (KPO/bisulfite), as shown in Table 4. The conversion increases with an increase of the level of initiator, while the average MW decreases. Obviously, when the concentration of the initiator is lower than 0.15%, the conversion is quite low. As a result, 0.2 wt% initiator (based on the monomer weight) is optimum in order to get higher conversion, as shown in Fig. 2.

Kinetic feature of VAc emulsion copolymerization

Conversion–time curves of copolymerization. From the reactivity ratios of three comonomer-pairs shown in Table 2, it may be expected that the conversion–time curve will be unusual and that the composition of the resulting copolymers will shift drastically with
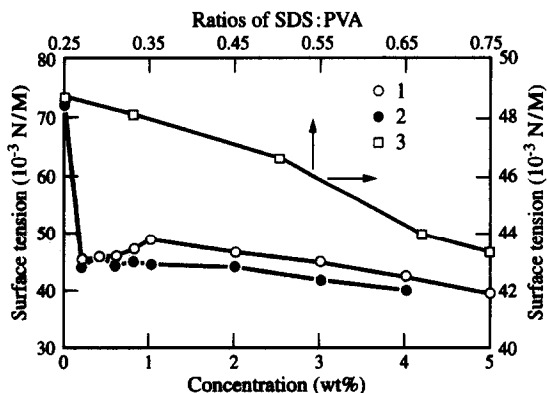

Fig. 1. The effects of ratios and concentration of complex emulsifier on the surface tension of the system. 1— SDS:PDA = 1:1, 2—SDS:PVA = 2:1, 3—concentration of emulsifier = 2 wt%.

Table 4. The effects of the redox system levels on the conversion and MW (VAc:AA:AM = 77:7.5:15.5)

I (wt%)	X (%)	η_{sp}
0.05	43.7	17.09
0.1	52.1	6.89
0.15	89.6	6.21
0.2	92.1	3.40
0.3	99.3	1.36

Fig. 3. Conversion–time curves of VAc copolymerization. 1—VAc = 100%, 2—VAc:AA = 85:15, 3—VAc:AA:AM = 77:7.5:15.5.

the conversion owing to the great discrepancy in the reactivity ratios. The conversion–time curves of VAc copolymerization are shown in Fig. 3.

Curve 1 in Fig. 3 is a typical conversion–time curve of VAc homopolymerization. Firstly, VAc polymerizes rapidly until 80% conversion. Thereafter, the rate decreases and levels off gradually. However, the curves of VAc copolymerization (curves 2 and 3 in Fig. 3) are quite different from that of its homopolymerization. The conversion–time curve of VAc/AA copolymerization (curve 2) may be divided into three stages. The rate of stage I is more rapid. In stage I, AA is the main monomer unit (>70 mol%) in the copolymer, owing to its higher reactivity ratio, while VAc is the comonomer unit in a considerable amount (20–30 mol%) because of its higher percentage in the recipe. Most of the AA polymerizes (~60 mol%) and is consumed during stage I. Stage II of curve 2 is a nearly horizontal line. It means that the copolymerization rate is very slow for the cross-termination of these two types of comonomers with different reactivities. After stage II, the rate increases rapidly because it may be regarded as VAc homopolymerization. Actually, VAc is the main monomer (>95%), with only a small amount (<5%) of AA, if it is present at all, as the comonomer in stage III. The overall product is practically a mixture of AA/VAc copolymer at stage I and PVAc with a trace of AA at stage III.

For the AA/AM pair, r_1 (=1.43) is little different from r_2 (=0.60), and the reactivity ratio of VAc/AA (=0.01/10) approaches that of VAc/AM (=0.016/6.291). The VAc/AA/AM terpolymerization may be treated kinetically as VAc/acrylics binary copolymerization. Actually, the features of curve 3 (VAc/AA/AM terpolymerization) are similar to those of curve 2 (VAc/AA copolymerization). At stage I,
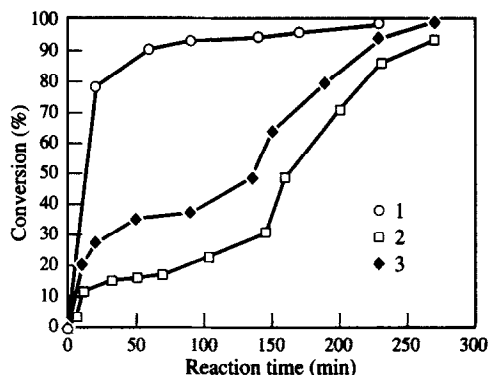
the copolymerization rate is more rapid, and the terpolymer is mainly composed of AA and AM with a considerable amount of VAc because of its high content in the monomer mixture, though r_1 (=0.01–0.016) is much smaller than r_2 (=10–6.3). After the slow stage II, the rate increases rapidly in stage III. VAc is the main component of the terpolymer, with small amounts of AA and AM, if present, in the last stage. The overall product is a mixture of the copolymers with different compositions and possesses two glass transition temperatures in the DSC spectrum, as shown in Fig. 4.

Copolymer composition. From the large discrepancy of reactivity ratios it may be expected that the copolymer composition will shift drastically from the monomer composition. In VAc–AA copolymerization ($r_1 = 0.01$, $r_2 = 10$), the monomer compositions (f_1, f_2) and average copolymer compositions ($\bar{F}_1, \bar{F}_2$) at a different conversion (X, %) may be calculated from the integration equation of a copolymer composition and the results are listed in Table 5.

At 12.5% conversion (from Table 5), it may be seen that the average copolymer compositions are $\bar{F}_1 = 0.292$ for VAc and $\bar{F}_2 = 0.708$ for AA, and that VAc has only consumed 4.43 mol%, but AA has consumed 52.3 mol% when the residual monomer fractions are $f_1 = 0.90$ for VAc and $f_2 = 0.10$ for AA, respectively. It means that AA is the main monomer with a considerable amount of VAc as a
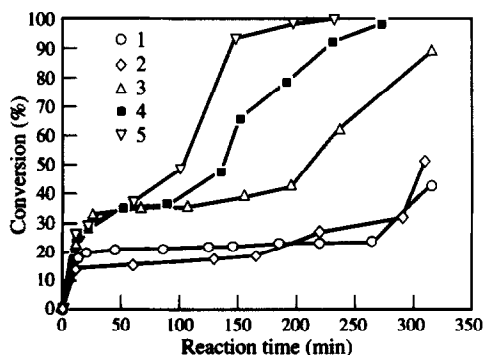

Fig. 2. Conversion–time curves of VAc copolymerization a. different initiator levels. 1—0.05%, 2—0.1%, 3—0.15%, 4—0.2%, 5—0.35%.
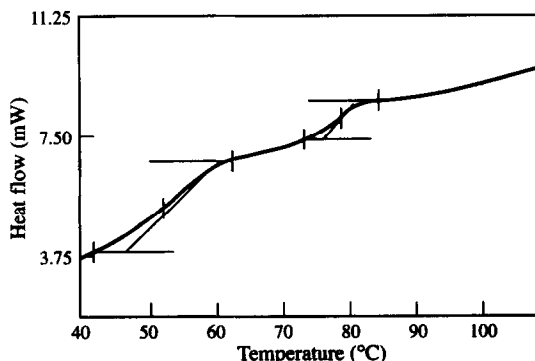

Fig. 4. DSC spectrum of VAc–AA–AM terpolymer.

Table 5. The monomer compositions (f_1, f_2) and average copolymer compositions (F_1, F_2) at different conversions (X %) ($r_1 = 0.01$, $r_2 = 10$; $f_1^0 = 0.824$, $f_2^0 = 0.176$)

X (%)	4.4	12.5	20.2	27
f_1	0.85	0.90	0.95	0.99
f_2	0.15	0.10	0.05	0.01
F_1	0.259	0.292	0.326	0.375
F_2	0.741	0.708	0.674	0.625
XF_1/f_1^0 (%)	1.38	4.43	7.99	12.3
XF_2/f_2^0 (%)	18.5	52.3	77.4	95.9

Table 6. The specific viscosity (η_{sp}) of terpolymer vs conversion (X) (VAc:AA:AM = 77:7.5:15.5)

T (min)	X (%)	η_{sp}
30	36.7	5.72
45	39.2	5.76
75	44.2	6.04
105	48.8	6.24
320	94.5	6.75

comonomer in the VAc/AA copolymer at stage I (<15% conversion). In the copolymer composition, AA content decreases from 0.741 to 0.625, and VAc increases from 0.259 to 0.375 (in mole fraction), when the conversion increases from 4.4 to 27%.

From the sequence distribution calculation at stage I of VAc/AA copolymerization, most of the AA is in monomeric unit (31.9%), diad (21.7%) and triad (14.8%) with a considerable amount of tetra-ad (10.1%) and penta-ad (6.9%), but VAc is mainly monomeric unit (95.5%) with a small amount of diad (4.3%). It means that VAc/AA copolymerization has an alternative tendency, especially for VAc. It may be recognized from $r_1 \cdot r_2 = 0.1$ initially.

The overall product may be regarded as a mixture of AA–VAc copolymer at stage I and PVAc with a small amount of AA at stage III. The intermediate product of stage II is only in small amount. The composition change of VAc–AA–AM terpolymer with conversion is shown in Fig. 5.

From the polymer chemistry point of view, the batch process is not usually used to run VAc/acrylics copolymerization because of the larger discrepancy in their reactivity ratios. But from the fabric size materials point of view, the VAc co- or terpolymers from the batch process are suitable for their applications, though the semi-batch process is much better. A paper on VAc/acrylics emulsion copolymerization in the semi-batch process will be published later.

Average molecular weight of copolymer. The average MW (or specific viscosity, η_{sp}) increases slightly during the copolymerization, as shown in Table 6. This means that the lifetime of the growing chain is very short and that it meets the mechanism of the free radical polymerization.
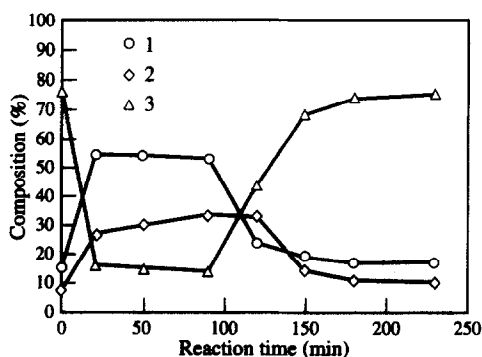
Particle size and number density of copolymer. The solubility of VAc in water is about 25 g/L at 25°C, while AA (or ALM) is soluble in both water and VAc. Two phases will coexist in the VAc–AA–water tertiary system: the oil phase is VAc droplets containing a certain amount of AA, and the aqueous phase is an emulsion solution containing AA and a small amount of VAc. AA is distributed in these two phases. This phenomena is the basis for the interpretation of the particle formation mechanism.

The particle size and the number density of the particle are related to the comonomers and the conversion as shown in Fig. 6.

It is known that the change of the average particle diameter of co- or terpolymers with the soluble comonomers is different from that of the normal emulsion (co)polymer [10]. At the beginning of copolymerization, the VAc (with a certain amount of AA or AA–AM) droplet is about 440 nm in diameter, much smaller than the monomer droplets (-1000 nm) in conventional emulsion polymerization. The primary radicals are produced from the redox reaction of KPO/bisulfite and initiate VAc or AA in the aqueous solution to propagate somewhat. The VAc, AA or VAc–AA oligomeric radicals diffuse to the surface of the droplets and initiate VAc–AA polymerization there. The composition of the VAc–AA copolymer changes as shown in Table 5. F_2 for AA is in the range of 0.741–0.708 mol% at 4.4–12.5% conversion. It may be expected that the VAc–AA copolymer of this composition is more hydrophilic and is swollen with water to form larger drops. The swollen drops may be regarded as an emulsified sap composed of AA or AA/AM copolymer with a certain amount of VAc. As the copolymerization progresses, the diameter of drops becomes larger and larger, up to 4000 nm at stage I, then the drops break up and the colour of the latex
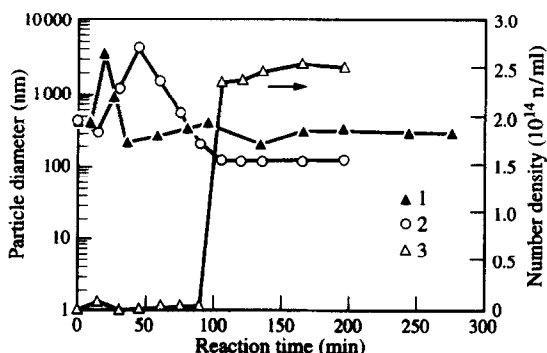

Fig. 5. The composition of VAc–AA–AM terpolymer during the copolymerization. 1—AM unit, 2—AA unit, 3—VAc unit. Monomer ratio: VAc:AA:AM = 77:7.5:15.5.

Fig. 6. The particle size and number density of the latexes vs time curves during the polymerization. 1—VAc–AA, 2, 3—VAc–AA–AM.

changes from the glimmer milk sap to soluble type matter at this stage; actually, the average particle number density diminishes rapidly and the value has no significance for the latex. After this abnormal period, the average particle diameter of the VAc–AA copolymer and the VAc–AA–AM terpolymer reaches normal stable values of 240 and 120 nm, respectively. The number density of the VAc–AA–AM terpolymer latex is about 2.5×10^{14} mL^{-1} as shown in Fig. 6. Although curve 1 for copolymerization and curve 2 for terpolymerization have the same tendencies in particle size, the change of the swelling in the copolymerization is earlier than that in the terpolymerization. This may be due to the fact that the discrepancy of the reactivity ratios of VAc–AA is largest in these three comonomer pairs (Table 1) and that AA easily takes part in the copolymerization to form the soluble matter, but the time of the change is shorter than that of the terpolymerization, because the total amount of soluble monomers in the former is less than that in the latter.

After a critical time, AA or AA/AM copolymer with increasing amounts of VAc will precipitate out as the primary particle from the aqueous solution and then proceed to grow. The PVAc with a small amount of AA or AA/AM later formed precipitates and deposits on the primary particle. The copolymer rich in AA or AA–AM formed earlier and the copolymer rich in VAc formed later, will be semi-miscible. It may be correct to reason that VAc–AA or VAc–AA–AM emulsion copolymerization may be run in the batch process to meet the requirement of textile size.

CONCLUSIONS

(1) The recipe of the emulsion copolymerization of VAc/acrylic monomers in a batch process is ascertained as follows:

Monomers
VAc:AA:AM = 77:7.5:15.5 by wt   100 parts by wt
Emulsifiers
SDS:PVA = 1:3 by wt   2
Initiators
Persulfate:bisulfite = 1:1 by mol   0.2

(2) The kinetics of VAc/acrylic monomer(s) co- or terpolymerization are characterized by three stages in the conversion–time curve. Stage I is more rapid in rate due to acrylic/VAc copolymerization and leads to the formation of acrylic/VAc copolymer with acrylic as the main component. The rate of stage II is very slow owing to cross-termination. The rate of stage III increases rapidly and the product is almost entirely PVAc. The overall product is a mixture of a series of acrylic/VAc copolymers with different compositions and possesses two glass transition temperatures. It is suitable to the application in the fabric size.

(3) VAc–AA (or AA–AM) copolymerization has an alternating tendency, especially for VAc.

(4) At stage I, monomer droplets (-440 nm) change into larger copolymer particles (-4000 nm) swollen with water during the copolymerization. Then, the particles break up, and the latex becomes a copolymer solution. Thereafter, new particles nucleate and grow to a constant average diameter of 240 nm for VAc–AA copolymer and 120 nm for VAc–AA–AM terpolymer. The particle number density is about 2.5×10^{14} mL^{-1}.

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