

Partition of Initiators in Quasi-static Precipitation Polymerization of AAm/MAc*

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Abstract In order to investigate the partition of initiators for quasi-static precipitation polymerization of acrylamide (AAm) and methacrylic acid (MAc) in ethanol, azo-initiators were employed with various functional groups such as $-\text{COOCH}_3$ (V-601, dimethyl 2,2'-azobis(isobutyrate)), $-\text{CN}$ (V-65, 2,2'-Azobis(2,4-dimethylvaleronitrile)), $-\text{COOH}$ (V-501, 4,4'-azobis(4-cyanovaleric acid)) and $-\text{NH}-$ (VA-061, 2,2'-azobis[2-(2-imidazolin-2-yl)propane]), respectively. Particle size, induction time and kinetics of polymerization were investigated by the scanning electron microscopy (SEM) and gravimetry. It was observed that the polymerization parameters, such as the particle size, induction time and polymerization rate, were considerably affected by the functional groups of initiators. Besides, the monomer concentration also played important roles in the particle formation. By using V-601, the polymerization rate was strongly correlated with the total surface area of particles and the concentration of initiators. However, by using V-501, the polymerization rate was strongly related to $W_0C_{i,0}$, where W_0 is the initial concentration of monomers and $C_{i,0}$, the initial concentration of initiators. The results indicated that the different functional groups determined the different partition types of initiators between the minimonomer droplets and the continuous phase due to the molecular interactions of initiator and monomers. V-601 was all partitioned in the continuous phase, but a part of V-65 was partitioned in the minimonomer droplets. Besides the V-501 dissolved in the continuous phase, a part of V-501 was adsorbed on the surface of minimonomer droplets. VA-061 destroyed the stability of minimonomer droplets by the formation of zwitterions with MAA.

Keywords: Partition of initiator; Precipitation of polymerization; Quasi-static state; Methacrylic acid and acrylamide.

INTRODUCTION

Mechanism of emulsion polymerization and dispersion/precipitation polymerization has been argued for decades^[1,2]. A well-known mechanism is the hypothesis of homogeneous nucleation suggested by Fitch *et al*^[2]. Its main contents are briefly outlined as following. The initial polymerization takes place in the continuous phase wherein the monomer is saturated and all initiator exists. As the polymerization progresses in chain length, the lyophobicity of chain increases. At a critical chain length, the chain begins to precipitate to form a nucleus. Thereafter, the nuclei are swollen by monomer and capture the oligoradicals generated in the continuous phase. Thereby the main loci of polymerization in the system commence to shift from the continuous phase to the swollen nuclei. The particles are produced by the polymerization in the nuclei. This mechanism is primarily deduced from the facts of particle formation in the heterogeneous polymerization systems without any additional surfactant such as the soap-free emulsion polymerization, and apparently supported by the experimental results of precipitation polymerization systems where the systems are considered to be homogeneous prior to the

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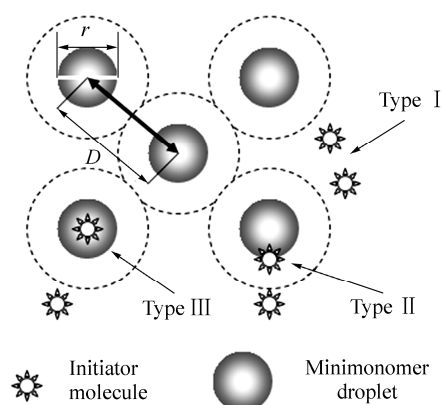
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particle formation. However, it has been found that this mechanism was not only contradictory with many experimental facts recently observed^[3–8], but also, based on it, the kinetics of polymerization had to be explored on some unimaginable assumptions^[1, 2]. For example, the agitation factor is not included in the mechanism though it is a key factor to the success of most emulsion polymerizations. Moreover, according to this mechanism, the initial polymerization rate in the continuous phase must be extraordinarily fast, even though sometimes the monomer concentration such as styrene is extremely low^[1, 2]. Furthermore, some precipitation polymerization systems have been checked carefully by the modern equipments^[9–12]. It is evidenced that these systems are not homogeneous prior to the start of polymerization.

Hence, a new mechanism is postulated^[4–6]. It declares that the microspheres is originated from the polymerization within the micro-/minimonomer droplets pre-existing in the system. The micro-/minimonomer droplets may be created normally by two approaches, *i.e.* the temperature induced decrease of monomer solubility and the disturbance of interfacial layer between the monomer phase and the continuous phase by agitation. This mechanism has been rationalized experimentally in recent decades^[7–18]. According to this mechanism, a kinetic model is logically deduced, namely that prior to the polymerization, the partition of initiator molecules should be considered. As shown in Scheme 1, three types of partition are possible, *i.e.* Type I, all initiator in the continuous phase; Type II, initiator in the continuous phase and on the surface of micro-/minimonomer droplets; Type III, initiator exists in the continuous phase and the micro-/minimonomer droplets, according to properties of initiator and monomer. Here, a noticeable one is the Type III. It is familiar to the so-called suspension polymerization where the monomer phase is slashed into small droplets containing the oil-soluble initiator by the mechanical stirrer^[1, 2]. Conventionally, Type III is considered not to fit for the preparation of nano-scale particles due to the energy-deficient of mechanical agitation. However, this viewpoint has been overtaken with the results of semi-batch soap-free emulsion polymerization of styrene/4-vinyl pyridine (St/4VP)^[6]. Hence, the new mechanism is regarded as a consistent mechanism for all the polymerization systems by which the particles, microspheres or beads are prepared. However, such partitions imply that the kinetics of polymerization should be different by using different initiator. Micro-/minimonomer droplets are formed thermodynamically, thus their stability is dependent on the interfacial tension. For example, the initiator partitions of Type II and III may change the interfacial tension of micro-minimonomer droplets. As well known, as a turnout of stability, the number of droplets is important to the overall polymerization rate.



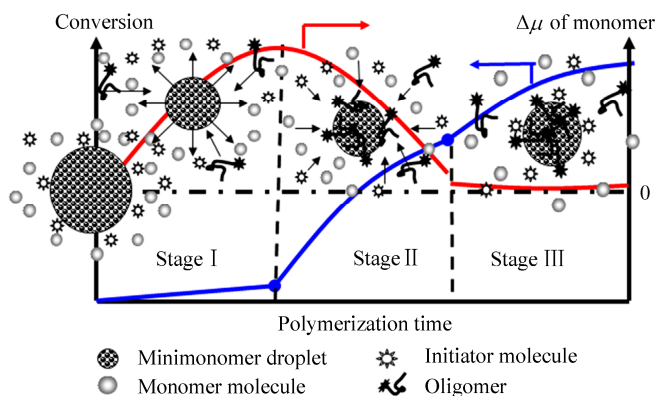
Scheme 1 Partition types of initiator in the polymerization system

Another deduction from this model is concerned with the packing of micro-minimonomer droplets in the continuous phase, in analogous to the crystalline lattice. It implies that, for preparing the stable latex, two limited concentrations of monomer should exist, the minimum concentration of monomer under which the minimonomer droplets cannot form and the maximum concentration of monomer above which the space of continuous phase cannot contain so many stable particles. For example, the closest packing model of lattice is

the face-center-cubic model where the volume occupation ratio of atoms is $\sim 74\%$. If the packing of minimonomer droplets adopts this model, the maximum concentration should be less than $\sim 9.25\%$, provided that the contacting distance of two droplets is equal to the diameter of droplets (Scheme 1). It is to say, in a precipitation polymerization system where the minimonomer droplets are spontaneously created by the decrease of solubility, the monodispersed microspheres cannot be prepared with the concentration more than $9.25\% (V/V)$, irrespective of the composition, agitation rate and crosslinking agent. These two concentrations have been reported in references^[9, 10, 12]. For example, in the precipitation polymerization of AAm/Mac in ethanol, with 10 wt% or more concentration of monomers, the microspheres were not prepared, instead, the coagulum was obtained^[12].

Certainly, it is complicated in the conventional emulsion polymerization where the monomer phase exists. The volume of continuous phase may increase at the expense of monomer phase. Nevertheless, at least so far, the evidence has not been observed, inferring the possibility of preparing particles with a solid content higher than 70% by the emulsion polymerization or precipitation polymerization.

As for the process of particle formation, it is also easily deduced from the new mechanism in light of the common thermodynamic knowledge. As shown in Scheme 2, taking Type I as an example and taking no account of the monomer transfer from the monomer phase, the process of particle formation can be divided into three stages. At stage I, the polymerization consumes up monomer in the continuous phase. It triggers off the Ostwald ripening of minimonomer droplets due to the increase of chemical potential of monomer in the droplets. Namely, the monomer molecules will escape from some smaller droplets to complement the loss of monomer in the continuous phase. At meanwhile, the oligoradicals are generated. At stage II, the survived minimonomer droplets capture the oligoradicals, thereby the polymerization starts in the minimonomer droplets. It decreases the chemical potential of monomer. The non-equilibrium flux force drives the monomer molecules and oligoradicals in the continuous phase to condense on the minimonomer droplets. Hence, the polymerization rate is accelerated. At stage III, the diffusion of radicals dominated the overall polymerization rate in the vicinity of thermodynamic equilibrium state until the monomer in the particles is consumed up. At this stage, the polymerization rate is gradually decelerated. With respect to the difference of Type I, Type II and Type II, there should exhibit at the stage I where, for Type II, the period is shorter, whilst for Type III, the stage I is negligible.



Scheme 2 Three polymerization stages of particle formation

However, the above deduced results from the new mechanism need the verification of experimental facts. In our previous work, a quasi-static precipitation polymerization system (QSPS) of methacrylic acid (MAc)/acrylamide (AAm) in ethanol was developed to prepare the monodispersed microspheres^[19]. Besides the energy-saving, a merit of this system is that all of the behaviors of species are purely dominated by the thermodynamic factors because the mechanical agitation is not imposed. It provides a simple system for us to further understand the mechanism of particle formation because there is no process of monomer transfer from

the bulk monomer phase to the growing particles, no mechanical agitation, no stabilizer, *etc.* which usually make the problem complicated. Moreover, employing this system and V-65 as initiator, a surprising result was observed that, passing through the induction period, the polymerization rate was strongly correlated to the term of $W_0 C_{i,0}^{1/2}$ where W_0 and $C_{i,0}$ were the initial concentrations of monomers and initiator, respectively^[19]. It reminds us of the classical equation of bulk free-radical polymerization. It evokes our confidence to explore a mathematical model for this new mechanism.

Therefore, in order to further understand the mechanism of particle formation, in this paper, several initiators carrying different functional groups, and also various decomposition coefficients, will be employed to carry out the quasi-static precipitation of MAA/AAM in ethanol. If the partition types are true, these initiators must impact different effects on the polymerization kinetics. This is our purpose of this paper. It is believed that understanding of QSPS is the base for insight into the complicated dynamic polymerization systems, where the factors such as stabilizer, agitation and the monomer transfer must be considered.

EXPERIMENTAL

Materials

All the reagents and solvents used in this paper were purchased from Wako Pure Chemical Industries, Ltd. Japan. Monomer methacrylic acid (MAc) was purified by distillation under reduced pressure. Monomer acrylamide (AAm), all initiators and solvent ethanol (EtOH, dehydrated) were used without further purification. The main properties and functional groups of the used initiators are listed in Table 1.

Table 1. Initiators and their properties used in the experiments

Initiator	Code	Functional groups	T^* (°C)
2,2'-Azobis(2,4-dimethylvaleronitrile)	V-65	—CN	51
2,2'-Azobis[2-(2-imidazolin-2-yl)propane]	VA-061	—NH—**	61
4,4'-Azobis(4-cyanovaleric acid)	V-501	—CN, —COOH	69
Dimethyl 2,2'-azobis(isobutyrate)	V-601	—COOCH ₃	66

* Temperature of 10 h half-life provided by the manufacturers, ** Imidazole ring

Methods

All polymerization was performed in a 1.5 L sonoreactor (40 kHz, 300 W) (SR-1500, Shinka Industry Co. Ltd., Kawasaki, Japan), equipped with a water jacket, an stainless ultrasonic irradiator, a condenser, a set of nitrogen inlet and a rubber stopper for adding the initiator with a syringe. Experimental method of QSPS has been described in detail in Ref. [19]. Briefly, the weight ratio of AAm/MAC was 3/1 and the total amount of reagents was always 800 g, (~1 L) in all experiments. It took about 10 s to inject the hot water (60 °C) into the water jacket. The temperature rising rate near to the central irradiator in the reaction system was measured as soon as the jacket was filled up. It was 0 min, 26 °C; 3.1 min, 45 °C; 6.8 min, 50 °C; 10.6 min, 55 °C and 17.9 min, 60 °C. The hot water of 60 °C in jacket was cycled with a water pump throughout the polymerization.

As for the agitated polymerization, the addition process of reagents was described elsewhere^[4]. The ultrasonic pulse (2 min irradiation and 1 min stop, 50% output of power (150 W)) was selected as the agitator. It irradiated in the whole polymerization process. It should be remarked that the preliminary experimental results indicated that the ultrasonic irradiation did not initiate polymerization in the absence of initiator.

Characterization

The conversion of monomer was determined by gravimetry. Reaction mixture, ~3 g, was extracted out with a syringe, and then cleaned twice by the recycling centrifugation (13000 r/min, 2 min)-redispersion in ethanol-centrifugation, and finally dried under vacuum at room temperature. The samples were weighted at about 24 h for the first time and then returned to vacuum oven until no weight loss in two 4-h-intervals. These samples, the dried powders, were further applied for the observation of scanning electron microscopy (SEM) (JSM-5600, JEOL, Tokyo, Japan) by which the SEM diameters of particles were determined^[4-6]. The number-average diameter and the average root-square deviation of diameters were used for the characterization

of diameter and its distribution.

The induction time was defined as the period from the moment that the temperature of system rose to 60 °C to the moment that the color of faint blue was observed by nude eyes. The normalized diameter was defined elsewhere^[19].

RESULTS AND DISCUSSION

Induction Time, Particle size and Surface Area

As described in the section of Introduction, there are three types of initiator partition according to their properties. Therefore, in order to check this hypothesis, four types of initiators were selected. As shown in Table 1, the similar half-life spans of initiators are selected except for V-65, which is a little bit faster than others. It is said, in most cases, the decomposition rate will not be a factor to affect the polymerization. Moreover, these initiators carry different functional groups. For example, V-65 carries —CN interacting with MAA with hydrogen-bond. V-501 carries —COOH and —CN. It means that V-501 interacts with both MAA and AAm. VA-061 is special because the group of imidazole ring can interact with MAA to form zwitterionic salt. V-601 has ester group, thus the weakest interaction of V-601 with monomers is anticipated. Even though, it is still unknown how these initiators partition in the system.

As we know, oxygen is a good probe to detect the existence of free-radicals. It can quench the activity of free-radicals. Accordingly, reminiscent of Scheme 2, provided that the most of oxygen molecules exist in the continuous phase, the stage I should be the most sensitive stage to the existence of oxygen. For example, the free-radicals may be quenched if the initiator is dominantly partitioned in the continuous phase. As a turnout, the induction time is normally elongated. Inversely, if most of initiator is partitioned in the minimonomer droplets, the induction time of polymerization should be less affected by the existence of oxygen. Such a difference of oxygen effects is not imaginable in the conventional mechanism of homogeneous nucleation because all the initiators are presumably considered to be partitioned in the continuous phase^[1, 2]. Moreover, according to Scheme 2, the effects of agitation should be different according to the different types of initiator partition. For example, for Type I, the agitation is of importance because it increases the encountering possibility of free-radicals and minimonomer droplets, in turn to shorten the induction time, regardless the existence of oxygen. Based on these considerations, the polymerizations performed under three conditions were deliberately designed. These were 1) at atmosphere, *i.e.* without deoxygenating, 2) deoxygenating, 3) ultrasonic agitation at atmosphere. The results are shown in Table 2.

Table 2. Induction time, normalized diameters and their deviation of particles prepared under oxygen, non-oxygen and ultrasonic conditions

Normalized diameter (nm)	V-65 (mg/800 g)			V-501 (mg/800 g)				V-601 (mg/800 g)			
	50	100	200	50	100	200	400	50	100	200	400
No O ₂	574.5	522.1	472.8	—	897.4	868.1	842.1	654.6	623.3	586.2	544.1
O ₂	530.3	466.3	465.0	—	—	751.3	740.9	—	580.7	574.5	503.3
O ₂ (Ultrasonic)*	538.0	493.6	471.4	—	754.0	689.4	588.5	718.4	590.4	577.8	570.5
Deviation of diameter (%)											
No O ₂	2.5	2.3	2.0	—	4.7	4.4	3.9	3.0	2.7	2.5	2.5
O ₂	2.8	2.6	2.3	—	—	5.8	5.2	—	3.1	2.7	2.4
O ₂ (Ultrasonic)*	3.6	2.9	2.5	—	3.9	3.6	3.7	3.5	3.0	3.0	2.8
Induction time of polymerization (min)											
No O ₂	6	6	4	—	10	9	6	18	13	6	5
O ₂	44	33	18	—	—	66	39	—	57	32	25
O ₂ (Ultrasonic)*	6	4	2	—	13	10	5	24	20	12	7

Note: Solid content, 5 wt%; * Ultrasonic agitation; No O₂, deoxygenated with N₂ for 1 h; O₂, without deoxygenating

As shown in Table 2, a noticeable result is the variation of induction time. In the absence of oxygen, V-65 gave the shortest induction time, whilst V-501 gave the longest among the three initiators. In addition, the effect

of V-65 amount on the induction time was insignificant, whereas for V-501, the effect was serious. For example, with 50 mg of V-501, the induction time was infinitely long (not detectable in 4 h), but with 100 mg of V-501, the induction time was cut down to 10 min. The effect of V-601 amount was moderate. The induction time was impacted severely by the existence of oxygen. It was greatly elongated by oxygen. However, the quenching efficiency of oxygen was quite different. As shown in Table 2, for V-65, the induction time was always detectable though it was so long as 44 min at 50 mg V-65, but for V-501, it was not detectable even though 100 mg of V-501 was added. It implies that oxygen was more effective to quench V-501 free radicals. The quenching efficiency of oxygen to V-601 was moderate among them. However, when the ultrasonic agitation was loaded, the effect of oxygen was greatly bated, irrespective of the properties of initiators. It seems that the ultrasonic agitation can eliminate the effect of oxygen. Moreover, compared to the data without agitation, it indicated that the agitation was more effective to reduce the induction time of V-501 system. Based on these results, it was summarized that the induction time of V-501 system was the most sensitive one to oxygen and agitation, whereas that of V-65 system was the most inert one.

On the other hand, as shown in Table 2, a general result was that the normalized diameters decreased as the concentration of initiators increased, irrespective of the types of initiators and the conditions. It is normal in accordance with the process of particle formation shown in Scheme 2. The more initiator the shorter the induction time was. Hence, the smaller number of minimonomer droplets were degraded due to the effect of Ostwald ripening (Scheme 2, stage I). It was coincident to the results obtained from the variation of diameter deviations. As shown in Table 2, the deviation of diameter increased with the increase of induction time under the same conditions. In addition, for V-65 and V-601, the ultrasonic agitation greatly bated the induction time, but enlarged the deviation of diameter. This result indicated that the rate of Ostwald ripening was promoted by the drastic agitation. An exception was of V-501. The deviation of diameter was greatly improved by the ultrasonic agitation. As shown in Table 2, the deviations of diameter were even smaller than those in the absence of oxygen. It further confirmed that the system of V-501 was very sensitive to the agitation. In contrast, the system of V-65 was the most inert one because the variation of deviation was insignificant though the polymerization conditions changed drastically. Finally, the normalized diameters listed in Table 2 should be addressed. It is clear that the diameters prepared by using V-501 were always the biggest, whilst they were the smallest by using V-65. The bigger diameter is always corresponding to the smaller number of particles. Two factors could result in this result. The first one was that the interfacial tension of minimonomer droplets was high due to the presence of V-501. The second one was the effect of Ostwald ripening occurring in the process of polymerization. The earlier formed particles grew up at the expense of the minimonomer droplets, more heavily the later formed particles. Of course, the high interfacial tension rendered the droplets to be more easily suffered from the Ostwald ripening. Hence, comprehensively considering all the data listed in Table 2, the first one, namely the interfacial tension, was the primary factor. A result supporting this proposal was that the diameter changed little, though the amount of V-501 increased greatly. If the effect of Ostwald ripening was dominant, it should be greatly depressed by the increase of polymerization rate. However, as shown in Table 2, with 100 mg of V-501, the diameter was 897.3 nm, but as the amount of V-501 increased to 400 mg, it was 842.1 nm. The decrement was just ~55 nm. In contrast, the decrement of diameter was closed to 80 nm when V-601 was used. Furthermore, when 800 mg of V-501 was used, instead of the continuous decrease of diameter, the diameter abnormally increased to 883.5 nm (not shown in Table 2).

The effects of initial concentration of monomers on the particle formation were also investigated. It should be noted at first that the induction time was usually decreased as the concentration of monomers increased. Figure 1 shows the total surface area and number of particles prepared by using different initiators in the absence of oxygen. It indicated that, as shown in Fig. 1(b), no matter whether the total surface area was calculated with the normalized diameter (W_0/D' , where W_0 was the initial concentration of monomer (wt%), and D' , the normalized diameter (m)) or the SEM diameter (W_0X/D , where X was the conversion of monomer (%) and D , the number averaged diameter (m) measured with the SEM photos), the results were consistent. This result evidenced that the normalization of diameter was rational. On the other hand, as shown in Fig. 1, it was observed

the index representing the number of particles (W_0X/D^3) prepared at 2.5 wt% was always the biggest, whereas the index indicating the total surface area (W_0/D') was the smallest, regardless to the amount and types of initiators. It should be remarked that, as discussed in the next section, in almost all of the cases, the polymerization rate of 2.5 wt% was the slowest. Therefore, this result implies that the number of particles was not the decisive factor for the polymerization rate, or at least, was not the dominant factor. It was completely contradictory with the viewpoint of the conventional mechanisms^[1, 2]. Moreover, it was common in Fig. 1 that the higher the concentration of monomers, the bigger the diameters were. However, it did not mean that the corresponding total surface area was smaller as usual. Inversely, as shown in Fig 1, the total surface area generally increased with the increase of the initial concentration of monomers. It is said, the higher concentration of monomers turned out the bigger diameters and larger total surface area of particles. A little difference should be marked that, in the system of V-601 (Fig. 1a), the increment of total surface area was negligible when the concentration of monomers increased from 5.0 wt% to 7.5 wt%. For example, at the level of 200 mg/800 g V-601, when the concentrations of monomers were 2.5 wt%, 5.0 wt% and 7.5 wt%, the corresponding indices of total surface area were 6.25, 8.53 and 8.64. It was similar to the results of V-65 previously reported^[19]. In contrast, the increment of surface area was significant in the system of V-501. As shown in Fig. 1b), at the level of 200 mg/800 g V-501, when the concentrations of monomers were 2.5 wt%, 5.0 wt% and 7.5 wt%, the corresponding indices of total surface area were 4.82, 5.57 and 6.26. It indicated that, compared with those of V-601 and V-65, the total surface area of particles was more sensitive to the concentration of monomers in the presence of V-501. Furthermore, the total surface area was also affected by the concentration of initiators. At the same level of concentration of monomers, the total surface area increased with the increase of initiators in general. Relatively, the effect of V-501 was more pronounced (Fig. 1b). However, compared with those of monomer concentration, the effects of initiator concentration were subordinate. For example, as shown in Fig. 1, at 2.5 wt%, the total surface area was almost constant to the variation of initiator concentrations. These results indicated that the total surface area of particles was dominated by the concentration of monomers. Finally, comprehensively compared the total surface area of particles prepared by using V-601 and V-501, respectively, it was observed that, in use of V-601, the total surface area of particles was always much larger than that prepared by using V-501. For example, as shown in Fig. 1a), the total surface area of particles (W_0/D') prepared by V-601 varied in the range from 5.78 to 9.37, but for V-501 (Fig. 1b), it varied in the range from 4.29 and 8.17. Taking account of V-65^[19], it could be concluded that, with the same amount of initiator and concentration of monomers, V-65 contributed the largest surface area to particles, whereas V-501 contributed the smallest. It further supported the above proposal that the big diameter of particles prepared by V-501 was primarily attributed to the high interfacial tension of minimonomer droplets. The smallest surface area benefitted the droplets to bate the surface energy so as to stabilize the droplets.

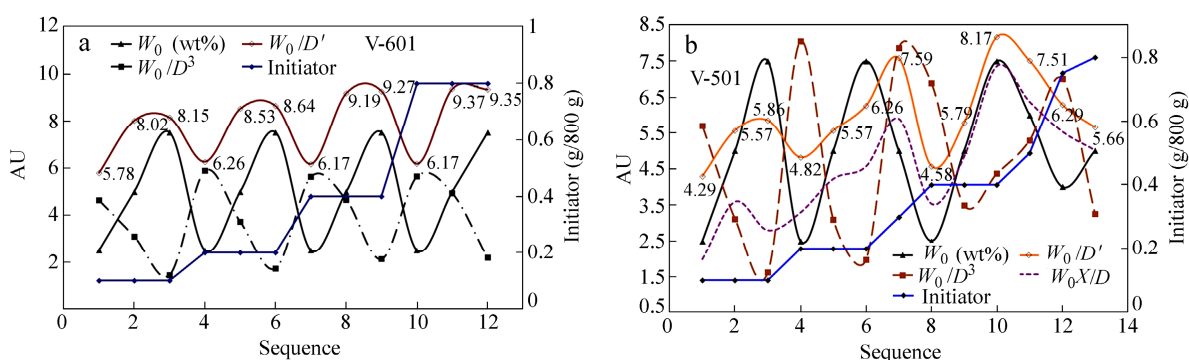


Fig. 1 Number and total surface area of particles prepared under various conditions

Note: orange line, W_0/D' denotes the total surface area calculated by normalized diameter, and dotted pink line, W_0X/D denotes the total surface area calculated by SEM diameter; dotted brown line, W_0X/D^3 denotes the number of particles in 100 g latex.

Figure 2 further shows the normalized diameters versus the initial concentration of monomers. It clearly indicated the diameter was dominantly determined by the concentration of monomers, when V-601 was used as the initiators. The amount of initiator did affect the size of particles, but relative to that of the monomer concentrations, the effect was insignificant. A relationship was founded in Fig. 2 by the linear simulation, namely $R' = 93.7W_0 + 149.4$ where W_0 is the initial concentration of monomers, R' , the normalized diameter. Reminding of V-65, $R' = 75.4W_0 + 149.5$ ^[19], it was observed that the diameter was more dependent on W_0 when using V-601. However, as for V-501, the diameters distributed randomly as W_0 increased (Fig. 2). It indicated that the diameters were dependent on both W_0 and the concentration of V-501.

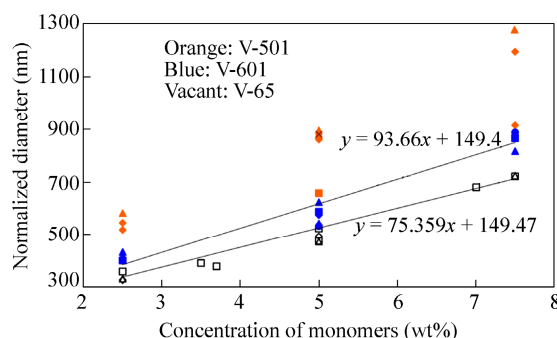


Fig. 2 Normalized diameters versus initial concentration of monomers

At last, the results of polymerization by using VA-061 should be discussed. As shown in Fig. 3, the particles were not prepared, instead, the big and polydispersed floccules were obtained. These floccules were quite different from those aggregations of primary particles as previously reported^[13]. In fact, the phase-separation took place when VA-061 was added into the monomer solution at room temperature. It indicated that the stability of minimonomer droplets was destroyed by VA-061 because the zwitterions of MAA/VA-061 formed. The zwitterions on the surface of minimonomer droplet elevated the interfacial tension of droplet/EtOH, in the meanwhile, weakened the electrostatic repulsion between the droplets.

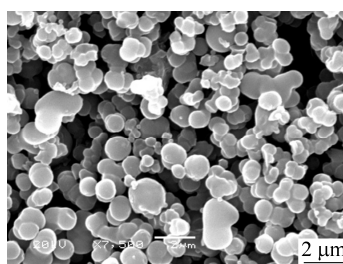


Fig. 3 SEM photo of microspheres prepared by using VA-061

Based on the above discussions, it was summarized that the interaction of initiator molecules with the monomer molecules was of importance to the particle formation. The molecular interaction determined the partition types of initiators in the polymerization systems. According to the above results, V-65 has $-\text{CN}$ groups. It may hydrogen-bonded interact with both MAA and AAm. Therefore, it was possible that some molecules of V-65 entered the minimonomer droplets, namely that it's partition adopted Type III of Scheme 1. Type III gives the shortest induction time, the smallest diameter and the largest total surface area because the rapid nucleation can effectively depress the effect of Ostwald ripening. In addition, adopting Type III, the induction time should be less affected by oxygen provided that oxygen was dominantly in the continuous phase. This proposal was strongly supported by the kinetic result of polymerization. As previously reported^[19], the

polymerization rate was intensively correlated with the term of $W_0C_{i,0}^{1/2}$ where $C_{i,0}$ was the initial concentration of V-65, similar to the classical equation of bulk free-radical polymerization. V-501 carries $-\text{CN}$ and $-\text{COOH}$ groups. Theoretically, it also hydrogen-bonded interacts with both MAA and AAm. Moreover, it may alter MAA in the interaction of MAA-AAm. Hence, it was deduced that the complexes of V-501-AAm were possibly soluble in ethanol, thus some V-501 was partitioned on the surface of MAA-AAm mini-droplets due to the trimolecular interaction of V-501-AAm-MAA, while the other in form of V-501-AAm existed in the continuous phase. It is to say, V-501 adopted the partition type of Type II (Scheme 1). This proposal could well explain the above results. For example, by Type II, the initiator made the minimonomer droplets instable. As a reward, particles owned the smallest surface area. Moreover, the induction time was the longest and most sensitive to the presence of oxygen since, as shown in Scheme 2, in the induction period (stage I), V-501 on the surface of mini-droplets should diffuse to complement the loss of V-501 in the continuous phase. As for V-601, it has $-\text{COOCH}_3$ groups. It determines that the interaction of V-601 with AAm and MAA is weak. Therefore, a best choice for V-601 is to stay in the continuous phase, *i.e.* Type I of partition. By Type I, the induction time should be also sensitive to the presence of oxygen, but compared with that of V-501, the quenching reaction of oxygen in the continuous phase did not interfere in the diffusion of V-601 free-radicals to the minimonomer droplets.

Anyway, these partition types should be checked by the polymerization kinetics.

Kinetics of Polymerization

In order to investigate the polymerization kinetics, QSPS of MAA/AAm were carried out in the absence of oxygen by using V-601 and V-501 as initiators, respectively. The curves of conversion versus polymerization time by using V-601 are shown in Fig. 4. For easily reading, the curves were grouped with colors according to the concentration of V-601. For example, as shown in Fig. 4, the blue color of curves denoted the concentration of 100 mg/800 g. It is clear that each group has three curves. However, in every group, the curve corresponding to the monomer concentration of 2.5 wt% was always deviated far from the other two curves corresponding to 5 wt% and 7.5 wt% of monomer concentrations respectively. Except for this curve, the curves of each group were closely bound together and distinctly separated from those of the other groups. In addition, as shown in Fig. 4, it was observed that a part of these two curves overlapped, namely that the polymerization rates were equal in a period of polymerization. For example, with 100 mg/800 g V-601 (Fig. 4, blue lines), the two curves overlapped for about 310 min, or in other words, the polymerization rate was not interfered by the concentration of monomers until the conversion attained ~30%. In the case of 200 mg/800 g V-601, the curves overlapped for about 190 min (30% conversion). For the cases of 400 and 800 mg/800 g V601, they were about 130 min (30% conversion) and 60 min (20% conversion), respectively. The above results indicated that the polymerization was dominated by the concentration of V-601, whereas less affected by the monomer concentration. An exception seems to be those with the monomer concentration of 2.5 wt%. However, reminiscent of the total surface area of particles (Fig. 1a), it was understandable readily according to the proposal discussed in the above section, namely that V-601 partitioned in the continuous phase. The free-radicals entered the growing particles completely by the spontaneous diffusion. For example, as shown in Fig. 1(a), the index of total surface area was 6.17 when the polymerization was performed with 800 mg/800 g V-601 and 2.5 wt% monomers, whilst it was 9.27 with 400 mg/800 g V-601 and 7.5 wt% monomers. It is said, the total surface area of 7.5 wt% monomers was nearly 1.5 times as much as that of 2.5 wt% monomers, but the concentration of V-601 at 7.5 wt% monomers was only a half of that at 2.5 wt% monomers. Similar phenomena were also observed in other pairs of recipes, for instance, the pair of 1105 (400, 2.5 wt%) and 1103 (200, 5 wt%) or 1104 (200, 7.5 wt%). Here, the numbering system of samples should be marked that, for instance, 1105 was the serial number, 400 in the parentheses denoted the concentration of initiator and 2.5 wt%, the concentration of monomers. Theoretically, the diffusion rate is determined by the gradient of concentration. It implies that the polymerization rate is benefited from the higher concentration of V-601. However, besides the diffusion rate, the total amount of diffusion is also related to the total area of diffusion section. Accordingly, the larger the total surface area the higher the polymerization rate is. Therefore, although the diffusion rate of V-601 free radicals could not be

calculated here, qualitatively it was rational that the polymerization rate was determined by the product of total surface area and the gradient of V-601 concentration. It was true that, as shown in Fig. 4, the curve of 1108 (800, 2.5 wt%) almost overlapped with the curve of 1106 (400, 5 wt%), meanwhile the curve of 1105 (400, 2.5 wt%) was very closed to that of 1103 (200, 5 wt%). The curve of 1102 (200, 2.5 wt%) was deviated because its total surface area, 6.26, was large relative to that of 1101 (100, 5 wt%), 8.02.

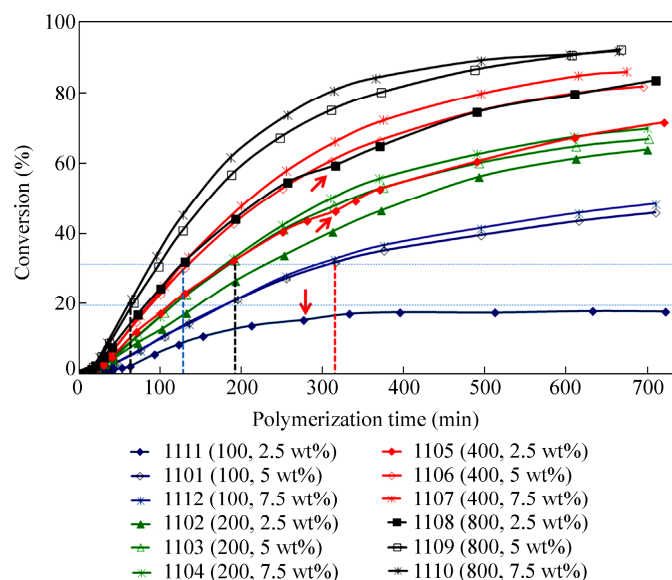


Fig. 4 Kinetic curves of polymerization by using V-601 as initiator

On the other hand, each curve may be divided into two stages in light of the polymerization rate. Here, it should be remarked that the induction period was not included in the curves. As shown in Fig. 4, it was obvious that at the first stage, the polymerization rate was almost constant, but faster than that at the second stage. According to Scheme 2, these two stages were corresponding to the stage II and stage III, respectively. At the stage II, the chemical potential of monomers in the growing particles greatly decreased due to the polymerization. The monomers dissolved in the continuous phase commenced to back to the growing particles. By this way, the concentration of monomers in the growing particles was maintained at a relative constant level. Hence, the polymerization rate was only dependent on the concentration of free-radicals. This was likely the reason that, as discussed above, the curves overlapped before the conversion of monomers attained 30% in some cases. Thereafter, the concentration of monomers commenced to decrease because the monomers in the continuous phase were consumed up. Of course, the rates of decrease were not consistent due to the different sizes of particles.

Finally, the special turn point on the curve of 2.5 wt% monomers should be addressed. As shown in Fig. 4 (pointed by red arrows), it was abnormal that the increase of conversion was suddenly deviated near 300 min, but it was confirmed by sampling more samples (Fig. 4, 1105). This phenomenon was considered to occur at the moment that the polymerization progressed from the stage II to stage III (Scheme 2). Hence, it was possibly ascribed to the smaller size of growing particles. A smaller size is bound to the higher equilibrium concentration of monomers in the continuous phase in accordance with the common thermodynamic knowledge. Taking the small total surface area into account, it was possible that the polymerization in the continuous phase commenced to be prominent at that moment.

The kinetic curves of polymerization by using V-501 are shown in Fig. 5. At a glimpse of Fig. 5, the partly overlap of some curves is clearly visible. Therefore, the overlapped parts of curves are amplified and shown in Fig. 6. It is clear that, as shown in Fig. 6, the overlap does exist at the lower conversions. The measurement

errors can be excluded because the conversions at the deviate point of curves are various according to the concentration of monomers. For example, as shown in Fig. 5, the conversion of deviate point is about 23% for the curves of 1084 (100, 7.5 wt%) and 1079 (100, 5 wt%). It cannot be explained by the measurement errors. Moreover, these curves are obviously grouped with those of the same concentration of V-501. As discussed in the above section concerning with V-601, this result indicated that the polymerization kinetics was dominated by the diffusion of initiator, more exactly the diffusion of free-radicals. It was consistent to the results deduced from the induction time. Namely, at the stage I of polymerization (Scheme 2), most of V-501 on the surface of droplets diffused into the continuous phase, but at the stage II, the free-radicals diffused back to the droplets. Hence, the polymerization rate was determined by the gradient of V-501 concentration and the total surface area of growing particles. Reminiscent of Fig. 1(b), for example, with 100 mg/800 g V-501, the indices of total surface area were 4.29, 5.57 and 5.86, corresponding to the monomer concentrations of 2.5 wt%, 5 wt% and 7.5 wt%, whereas with 400 mg/800 g V-501, those were 4.59, 5.79 and 8.17, corresponding to 2.5 wt%, 5 wt% and 7.5 wt%, respectively. These data explained why the deviation took place and why it was earlier when the concentration of V-501 increased.

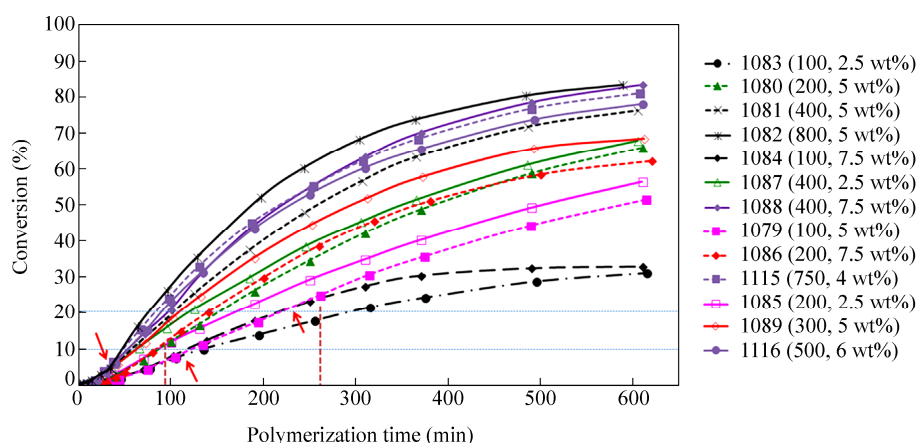


Fig. 5 Kinetic curves of polymerization by using V-501 as initiator

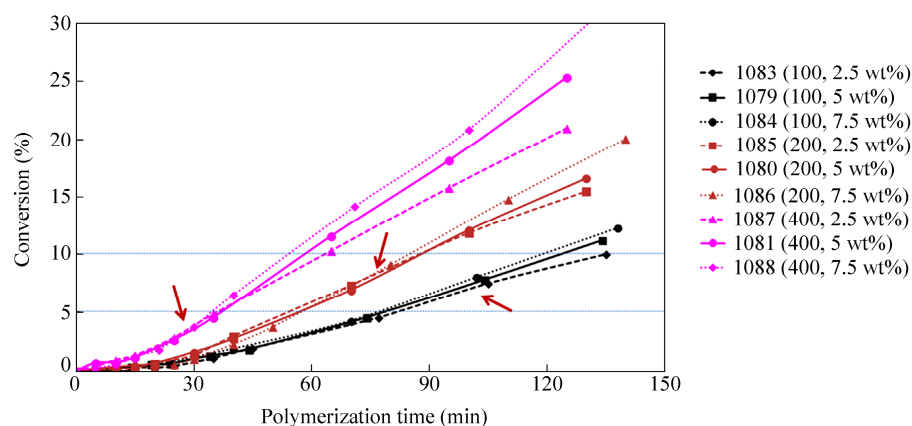


Fig. 6 Amplified diagram of overlapped parts of kinetic curves in Fig. 5

However, returning to Fig. 5, it was apparent that the kinetics of polymerization was quite different from that with V-601 (Fig. 4). Passing through the overlap stage, the varying tendency of conversion against the polymerization time obeyed a principle, namely that it was completely consistent if $W_0C_{i,0}$ was equal. These curves were grouped with the same color in Fig. 5, for instance, the paralleled curves of 1079 (100, 5 wt%) and

1085 (200, 2.5 wt%), 1080 (200, 5 wt%) and 1087 (400, 2.5 wt%), 1086 (200, 7.5 wt%) and 1089 (300, 5 wt%). The curves of 1088 (400, 7.5 wt%) and 1115 (750, 4 wt%) almost overlapped. The deviated curve of 1116 (500, 6 wt%) was an exception. That is to say, the polymerization rate was strongly correlated with the product of $W_0C_{i,0}$.

In fact, it was difficult to explore an equation to express the polymerization rate when the initiator molecules were adsorbed on the surface of monomer droplets. However, it was deductable that the polymerization rate should be strongly correlated to the total amount of initiator molecules on the surface. Therefore, applying the Gibbs adsorption equation, the following equations were deduced.

$$R_p \propto S_{\text{particle}} \Gamma_{\text{initiator}} \propto -\frac{W_0}{D'} \cdot \frac{C_i d\gamma}{RTdC_i} \quad (1)$$

R_p -polymerization rate; S_{particle} -total surface area of particles; $\Gamma_{\text{initiator}}$ -adsorbed amount of initiator per unit of area; D' -normalized diameter of particles; γ -the interfacial tension; R , T -the common physical constants.

Because the concentration of initiator was very low, it was rational that $\frac{d\gamma}{dC_i} = -b$ where b was a constant. Moreover, according to the Kelvin equation, $\gamma \propto D' \ln C_M$ where C_M was the concentration of monomers in the continuous phase. Hence, $R_p \propto \frac{b\gamma}{\ln C_M} W_0 C_i$. According to this equation, the partition of V-501 was deduced to be Type II that some V-501 molecules were adsorbed on the surface of minimonomer droplets.

Finally, as for V-061, it has $-\text{NH}-$ groups. It chemically interacted with $-\text{COOH}$ of MAC to form zwitterions, $-\text{NH}_2^+-$ and $-\text{COO}^-$. Such interaction obviously damaged the stability of both minimonomer droplets and the growing particles. Therefore, the polymerization kinetics was beyond the scope of this paper and was not investigated, but a fact should be remarked that the induction time was short (~ 10 min) and changed less with the variation of initiator concentration, regardless to the presence of oxygen and agitation. This result indicated that the strong interaction indeed shortened the induction time, *i.e.* the polymerization within droplets directly resulted in the birth of particles.

As a summary, the partition types of initiators were supported by the polymerization kinetics of QSPS. V-601 was all partitioned in the continuous phase, therefore, the polymerization rate was correlated to the diffusion of free-radicals generated in the continuous phase, *i.e.* $R_p \propto (\Delta C_i) S_{\text{particles}}$, where was the difference of concentrations between the continuous phase and the surface of particle. V-501 was partitioned in the continuous phase and the surface of minimonomer droplets. It was complicated and difficult to deduce a equation for the polymerization rate, but experimentally, $R_p \propto W_0 C_{i,0}$.

CONCLUSIONS

In order to investigate the partition of initiators, the quasi-static precipitation polymerization of acrylamide (AAm) and methacrylic acid (MAc) in ethanol was conducted, and azo-initiators were employed with various functional groups such as $-\text{COOCH}_3$ (V-601, dimethyl 2,2'-azobis(isobutyrate)), $-\text{CN}$ (V-65, 2,2'-azobis(2,4-dimethylvaleronitrile)), $-\text{COOH}$ (V-501, 4,4'-Azobis(4-cyanovaleric acid)) and $-\text{NH}-$ (VA-061, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]) functional groups, respectively. It was observed that the induction times of polymerization were dependent on the types of initiators and severely affected by the presence of oxygen. V-65 always exhibited the shortest induction time, whereas V-501 showed the longest. Moreover, the induction time of V-65 was relatively less affected by the presence of oxygen, in contrast, that of V-501 was most seriously affected. Ultrasonic agitation was observed to be an effective factor to greatly shorten the induction times, regardless of the types of initiators. Besides, the monomer concentration also played important roles in the particle formation. By using V-601, the polymerization rate was strongly correlated with the total surface area of particles and the concentration of initiators. However, by using V-501, the polymerization rate was strongly related to $W_0 C_{i,0}$, where W_0 is the initial concentration of monomers and $C_{i,0}$, the initial concentration of

initiators. These results indicated that the kinetics of precipitation polymerization of MAA/AAm was greatly dependent on the properties of initiators. The different functional groups determined the different partition types of initiators between the minimonomer droplets and the continuous phase. According to the molecular interactions of initiator and monomers, three types of initiator partition were summarized as, Type I, all in the continuous phase; Type II, besides a part dissolved in the continuous phase, some adsorbed on the surface of droplets and Type III, some in the minimonomer droplets. According to experimental results, V-601 was considered to be all partitioned in the continuous phase, but as for V-65, a part was partitioned inside the minimonomer droplets. Moreover, besides those in the continuous phase, a part of V-501 was adsorbed on the surface of minimonomer droplets. VA-061 destroyed the stability of minimonomer droplets by the formation of zwitterions with MAA. The polymerization rate at stage II was strongly correlated to the partition types, *i.e.* Type I, $R_p \propto (\Delta C_i) S_{\text{particles}}$; Type II, $R_p \propto W_0 C_{i,0}$; Type III, $R_p \propto W_0 \sqrt{C_{i,0}}$, where R_p was the polymerization rate, $S_{\text{particles}}$, the total surface area of particles and ΔC_i , the gradient of initiator concentration.

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