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Particle Nucleation Loci in Styrene-Butyl Acrylate Miniemulsion Copolymerization

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Summary

Miniemulsion polymerizations of styrene and butyl acrylate in the presence of sodium dodecyl sulfate (SDS) as the surfactant and stearyl methacrylate (SMA) as reactive cosurfactant were carried out by using water-soluble (potassium persulfate) and oil-soluble (2,2-azobisisobutyronitrile) (AIBN) initiators respectively. Effects of the two initiators on the particle nucleation mechanisms are investigated. By comparison with the mean diameter of monomer droplets and polymer particles, it is shown that both homogeneous nucleation and monomer droplets nucleation coexist in the presence of a water-soluble initiator but homogeneous nucleation becomes less significant with SDS concentration increasing. Meanwhile, using oil-soluble initiator, the possibility of homogeneous nucleation is depressed effectively. As a result, monomer droplets are definitely the main loci of particle nucleation.

Introduction

Several mechanisms of nucleation have been postulated in emulsion polymerization: (i) nucleation in monomer-swollen micelles.(ii) nucleation in the aqueous phase with subsequent precipitation of the oligomeric radicals being formed, and (iii) nucleation in monomer droplets.[1] The first two mechanisms of nucleation have been intensively studied in conventional emulsion polymerization, but the monomer droplets are not considered to be significant locus of polymerization because of their relatively smaller specific surface area compared to that of the monomer-swollen micelles.

In 1973, Ugelstad et al.[2] were the first to demonstrate that under conditions in which the droplet size is small enough, nucleation of monomer droplets could account for an important part of the particles formed. In his work, he stirred cetyl alcohol (CA) with water and sodium lauryl sulfate (SLS) at 60°C and then styrene was added under stirring. After polymerized at 60°C and it was found that a large fraction of polymer particles were formed by droplet nucleation when a relatively modest amount of surfactant was used.

C.S.Chern et al.[3]used alkyl methactylates such as dodecyl methacrylate(DMA) or stearyl methacrylate (SMA) as the cosurfactant in the miniemulsion polymerization of styrene. It was demonstrated that both DMA and SMA can act as a conventional cosurfactant in stabilizing the homogenized monomer droplets. Furthermore, the methacrylate group may be chemically incorporated into latex particles in the subsequent miniemulsion polymerization. This technique may thus eliminate the need for removing the low molecular weight cosurfacant from latex products to alleviate the VOC problem.

Although the potential importance of droplet polymerization in miniemulsion systems has been recognized by a number of workers, the particle formation mechanisms under various preparation conditions are not entirely clear. A more quantitative investigation of these miniemulsion systems is therefore required. In this paper, miniemulsion polymerizations of styrene-butyl acrylate prepared with water-soluble (potassium persulfate) and oil-soluble (2,2-azobisisobutyronitrile) (AIBN) initiators were carried out to provide a fundamental understanding of the nucleation mechanisms involved in the miniemulsion systems.

Experimental

Materials

Potassium persulfate and 2,2-azobisisobutyronitrile were recrystallized twice from water and ethanol respectively. Styrene and butyl acrylate were vacuum-distilled and stored at -2°C. All other reagents were used as received without further purification.

Preparation of monomer miniemulsions

The monomer miniemulsion was prepared by dissolving SDS in water and SMA in the monomer respectively. The both oily and aqueous solutions were mixed with a mechanical agitator for 30 min. The resultant emulsion was then homogenized by the numerical controlled sonifier-KB2200DB (KunShan Co.), operated at 80% of total energy output for 20 min.

Polymerization process

Polymerization was carried out in a 250ml reactor equipped with a two-bladed fan turbine agitator, a thermometer and a reflux condenser. Immediately after homogenization, the resultant miniemulsion was charged into the reactor and then purged with N_2 for 10 min while the reactor temperature was brought to 75°C. Polymerization temperature was kept at 75°C for 6 hours.

Determination of monomer droplets size (or latex particle size)

The average sizes of monomer droplet (or latex particle) were determined by dynamic light scattering method (BrookHaven BI-200SM). The sample was diluted with water to adjust the number of photons counted per second (cps) to 8000-12000. The dilution water was saturated with surfactant and monomers and consequently, diffusion of

SDS, ST and BA from monomer droplets (or monomer-swollen latex particles) into water was prohibited. The reported data represent an average of at least three measurements and the errors have been estimated to be 8% or less.

Determination of monomer conversion

Final monomer conversion was determined by the gravimetric method.

Results and discussion

Polymerized by water-soluble initiator

Table 1 Basic recipe of miniemulsion polymerization using potassium persulfateas initiator

Monomer (mol•L^{-1})	1.0
H_2O (mL)	100
SDS (mmol•L^{-1})	5-14
SMA (mmol•L^{-1})	20-56
$K_2S_2O_8$ (mmol•L^{-1})	0.133
$NaHCO_3$ (mmol•L^{-1})	0.133

Recipes for the systems studied are listed in Table 1. In this series of experiments, the concentration of SDS ([SDS]) was varied from 5 to 14 mmol•L^{-1}. The influences of concentration of SDS on the size of monomer droplets and polymer particles were presented in Table 2. It is shown that with the concentration of SDS increasing, both d_m and d_p decrease gradually and then increase when the concentration of SDS is larger than 10 mmol•L^{-1}. This is due to the fact that the ratio of SDS to SMA is fixed at constant in the experimental system, which means SMA increases proportionally with concentration of SDS increasing. In this situation SMA does not only act as the cosurfactant, but becomes the co-monomer as well, i.e., the total concentration of monomer increases accordingly. Therefore, at the relatively lower level of concentration of SDS, SDS plays a significant role in controlling the size of dispersed phrase and the result shows that both d_m and d_p decrease with concentration of SDS increasing. After d_p reaching the minimum, increase in total solid content becomes somewhat sharply and leads to particle size larger unavoidably.

Table 2 Variation of the mean diameter of monomer droplet (d_m) and polymer particle (d_p) with surfactant concentration using water-soluble initiator

[SDS] (mmol•L^{-1})	[SMA] (mmol•L^{-1})	d_m (nm)	d_p (nm)
5	20	336.2	159.3
8	32	317.4	151.1
10	40	234.9	125.1
12	48	248.6	149.7
14	56	276.0	212.3

From the data of dm and dp, some information can be got about the particle nucleation. The dm is not only the basic parameter to infer the adsorption status of SDS on the surfaces of monomer droplets but also a crucial factor to decide whether micelle present in aqueous phase, which refer to the loci of the particle nucleation. The information concerning the particle nucleation loci could be illustrated clearly according to the following equations:

$$N_m = \frac{m}{\frac{\pi}{6} d^3{}_m \rho_m} \quad \textbf{(1)}$$

$$S = \pi d_m{}^2 N_m \quad \textbf{(2)}$$

$$M_{theor} = \frac{S}{a_s N_A} \quad \textbf{(3)}$$

$$M_{total} = M_{theor} + M_{cmc} \quad \textbf{(4)}$$

$$M_{\exp er} = \frac{w}{M} \quad \textbf{(5)}$$

$$N_p = \frac{m[\rho_m X + \rho_p (1-X)]}{\frac{\pi}{6} d_p{}^3 \rho_m \rho_p} \quad \textbf{(6)}$$

Here d_m --- mean diameter of monomer droplets (cm)
ρ_m --- monomer density ($g{\bullet}cm^{-3}$)
N_m --- number of monomer droplets (mL^{-1})
m --- initial monomer weight ($g{\bullet}mL^{-1}$)
S --- total surface area of monomer droplets ($cm^2{\bullet}mL^{-1}$)
a_s --- coverage area per molecular of SDS on the surface of monomer droplets (cm^2) (a_s is taken as $4.72\times10^{-15}cm^2$ from reference[4])
M_{theor} --- amount of SDS for theoretical minimum requirement where surfaces of monomer droplets are covered with SDS ($mol{\bullet}mL^{-1}$)
M_{CMC} --- critical micelle concentration of SDS in water (Here M_{CMC} is taken as 8.2 $mmol{\bullet}L^{-1}$ form reference[5])
M_{total} --- theoretical minimum amount of SDS presumed the critical micelle concentration of SDS is reached in the miniemulsion systems ($mol{\bullet}mL^{-1}$)
w --- experimental SDS weight ($g{\bullet}mL^{-1}$)
M --- mole mass of SDS ($g{\bullet}mol^{-1}$)

M_{exper} --- experimental amount of SDS (mol•mL^{-1})
N_A --- Avogadro Constant (mol^{-1})
N_p --- number of polymer particles (mL^{-1})
d_p --- mean diameter of polymer particles (cm)
ρ_p --- polymer density (g•cm^{-3})
X --- final monomer conversion

According to the equations 1-4, the relationship between the experimental amount of SDS (M_{exper}) and the theoretical minimum amount of SDS (M_{total}) presumed the micelle present in the systems is shown in the Table 3.

Table 3 Relationship between M_{exper} and M_{total} with SDS concentration variation

[SDS] (mmol•L^{-1})	M_{exper} (mol•mL^{-1})	M_{theor} (mol•mL^{-1})	M_{total} (mol•mL^{-1})	M_{exper} / M_{total}
5	5.081×10^{-6}	7.577×10^{-6}	1.578×10^{-5}	0.3220
8	8.145×10^{-6}	8.026×10^{-6}	1.623×10^{-5}	0.5018
10	1.016×10^{-5}	1.085×10^{-5}	1.905×10^{-5}	0.5333
12	1.220×10^{-5}	1.025×10^{-5}	1.845×10^{-5}	0.6612
14	1.424×10^{-5}	9.230×10^{-6}	1.743×10^{-5}	0.8170

It is well known that micelle will present when the residual concentration of the surfactant (SDS) in the water phase exceeds the critical micelle concentration of the surfactant. From Table 3 it can be seen that, in all the cases, the ratios of M_{exper} / M_{total} are all less than 1. It implies that the number of experimental surfactant molecules is less than the total number of surfactant molecules that include the surfactants adsorbed on the surfaces of monomer droplets and dissolved in the system where micelle presents, i.e., although, in some cases, the total surfaces of monomer droplets are covered completely by the amount of the experimental surfactant, the residual amount of the surfactant is not enough to generate micelle in the water phase. Obviously, according to the calculation, it ensures the absence of micelle in the given miniemulsion system. Thus, in the reaction system, the micelle nucleation mechanism can be ruled out. As a result, droplet nucleation and homogenous nucleation are the only two forms of particle formation in the given reaction system.

Based on d_m and d_p, the parameters N_m and N_p can be calculated according to the equations 1 and 6 .The results present in Table 4. It should be pointed out that the ratio of N_p /N_m could explain the particle formation mechanism at some extend. The ratio deviated farther from 1 means that the larger proportion of the resultant latex particles is produced by homogeneous nucleation. From Table 4, it is shown that N_p /N_m decreases from 8.150 to 1.903 with the concentration of SDS increasing from 5 to 14 mmol•L^{-1}. This is obviously different from the conventional emulsion polymerization due to the absence of micelle in the miniemulsion polymerization. It can be expected that N_p increase with the concentration of SDS increasing in a conventional emulsion polymerization system. However, the miniemulsion polymerization system implies that the number of primary particles nucleated in the aqueous phase decreases significantly with increasing concentration of SDS. This is because when the SDS concentration is at the lower level, the mean diameter of the monomer droplets is relatively larger while the specific surface area of the monomer droplets is smaller. Using water-soluble initiator, radicals were produced in the aqueous phase, in which case, the monomer droplets need to capture a radical to be initiated. This indicates that the smaller the specific surface area of the monomer droplet is, the lower the rate that initiators are captured by the monomer droplets is. Therefore, homogenous nucleation plays a significant role at the lower of the concentration of SDS. With the concentration of SDS increasing, the average monomer droplet size decreases, which means that the specific surface area of monomer droplets increases. As a result, the rates that monomer droplets capture initiators and become polymer particles increase sharply and the rates of homogenous nucleation decrease. The final numbers of polymer particles get closer to the numbers of monomer droplets and the ratio of N_p/ N_m decreases.

Table 4 Variation of N_p /N_m with SDS amount using potassium persulfate as initiator

[SDS] (mmol•L^{-1})	X(%)	N_m (mL^{-1})	N_p (mL^{-1})	N_p /N_m
5	95.59	6.065×10^{12}	4.943×10^{13}	8.150
8	96.55	7.027×10^{12}	5.784×10^{13}	8.231
10	96.21	1.778×10^{13}	1.020×10^{14}	5.737
12	95.22	1.500×10^{13}	5.960×10^{13}	3.973
14	96.36	1.096×10^{13}	2.086×10^{13}	1.903

Polymerized by oil-soluble initiator

Table 5 Variation of the mean diameter of monomer droplet (d_m) and polymer particle (d_p) with SDS concentration using oil-soluble initiator

[SDS] (mmol•L^{-1})	[SMA] (mmol•L^{-1})	d_m (nm)	d_p (nm)
5	20	336.2	312.7
8	32	317.4	304.5
10	40	234.9	219.9
12	48	248.6	238.6
14	56	276.0	260.5

For comparison, the miniemulsion polymerizations were carried out with the same recipes and methods of preparation except using oil-soluble initiator instead of water-soluble initiator. The influences of concentration of SDS on the sizes of monomer droplets and polymer particles are listed in Table 5. Also the parameters N_m and N_p can be calculated according to the equations 1 and 6. The results in Table 6 indicate that N_p /N_m fluctuates around 1. It illustrates that the monomer droplet nucleation almost becomes the unique way when oil-soluble initiator is used.

Table 6 Variation of N_p /N_m with SDS amount using AIBN as initiator

[SDS] (mmol•L^{-1})	X(%)	N_m (mL^{-1})	N_p (mL^{-1})	N_p /N_m
5	0.8923	6.065×10^{12}	6.602×10^{12}	1.089
8	0.8821	7.027×10^{12}	7.083×10^{12}	1.008
10	0.8989	1.778×10^{13}	1.896×10^{13}	1.067
12	0.8901	1.500×10^{13}	1.487×10^{13}	0.991
14	0.8955	1.096×10^{13}	1.141×10^{13}	1.041

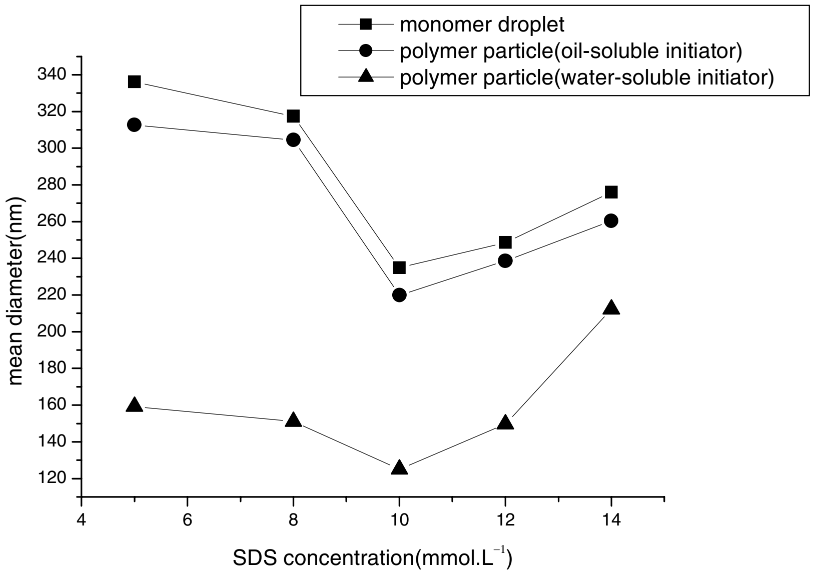

Fig 1. Effect of surfactant concentration on the size of monomer droplet and polymer particle with two kinds of initiators

Figure 1 shows the effect of the surfactant concentration on the size of monomer droplet and polymer particle with two kinds of initiators. It demonstrates clearly that monomer droplet nucleation plays the main role by using oil-soluble initiator, while the system presents a mixed mode of particle nucleation (i.e., monomer droplet nucleation in combination with the homogeneous nucleation) by using water-soluble initiator.

Conclusion

In this study, two kinds of initiators are used with the same recipes and methods of preparation in miniemulsion polymerization. When water-soluble initiator presents, the miniemulsion polymerization occurs a mixed mode of particle nucleation and the result could be proved by the data of N_p /N_m. The ratio of particle nucleation in the aqueous phase decreases sharply with concentration of SDS increasing. Under the same conditions except using the oil-soluble initiator, the data of N_p /N_m strongly proves that the monomer droplet nucleation mechanism almost becomes the unique way to form the polymer particles.

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