

A Comparative Study on Emulsion Polymerization Processes of Styrene Initiated by Water-soluble and Oil-soluble Initiators

Liu Xiao-Jing, Tian Yu-He, Lu Yang-Cheng

Cite this article as:

Liu Xiao-Jing, Tian Yu-He, Lu Yang-Cheng. A Comparative Study on Emulsion Polymerization Processes of Styrene Initiated by Water-soluble and Oil-soluble Initiators[J]. *Chinese J. Polym. Sci.*, 2019, 37(2): 142-148. doi: 10.1007/s10118-019-2186-3

View online: <https://doi.org/10.1007/s10118-019-2186-3>

Articles you may be interested in

SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE CdSe NANOPARTICLES CAPPED BY AOT

Chinese J. Polym. Sci. 2013, 31(9): 1284 <https://doi.org/10.1007/s10118-013-1329-1>

HYDRATION AND PHASE SEPARATION OF TEMPERATURE-SENSITIVE WATER-SOLUBLE POLYMERS

Chinese J. Polym. Sci. 2011, 29(1): 13 <https://doi.org/10.1007/s10118-010-1018-2>

Synthesis of Water-soluble, Polyester-based Dendrimer Prodrugs for Exploiting Therapeutic Properties of Two Triterpenoid Acids

Chinese J. Polym. Sci. 2018, 36(9): 999 <https://doi.org/10.1007/s10118-018-2124-9>

水溶性和油溶性引发剂引发 γ -甲基丙烯酰氧基丙基三甲氧基硅烷/苯乙烯细乳液共聚合的比较

MINIEMULSION COPOLYMERIZATION OF γ -METHACRYLOXYPROPYLTRIMETHOXYSIANE AND STYRENE INITIATED BY OIL-SOLUBLE AND WATER-SOLUBLE INITIATORS

高分子学报. 2008(10): 941 <https://doi.org/10.3724/SP.J.1105.2008.00941>

一种带疏水长链的水溶性偶氮引发剂的合成及端基疏水聚合物疏水缔合效应研究

Synthesis of Water-soluble Azo Initiator with Hydrophobic Long Chain and Study on Associative Effect of Hydrophobically End-capped Polymer

高分子学报. 2016(8): 1128 <https://doi.org/10.11777/j.issn1000-3304.2016.16003>

水溶性共轭聚合物在生物传感中的应用

Water-soluble Conjugated Polymers for Biosensor Applications

高分子学报. 2018(2): 186 <https://doi.org/10.11777/j.issn1000-3304.2018.17269>

A Comparative Study on Emulsion Polymerization Processes of Styrene Initiated by Water-soluble and Oil-soluble Initiators

Xiao-Jing Liu, Yu-He Tian, and Yang-Cheng Lu*

State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract The solubility of initiator determines its distribution and the roles played in emulsion polymerization as well as the final products, but this is still lack of systematic investigation. The present work focuses on this issue by comparing the kinetic behaviors and product properties of styrene emulsion polymerization initiated by 2,2-azoisobutyronitrile (AIBN) and potassium persulphate (KPS). Compared to KPS-initiated emulsion polymerization, the AIBN-initiated polymerization was found to be insensitive to the type of emulsifier, and have high polymerization rate as well as narrow molecular weight distribution and particle size distribution. This result indicates the effective free radicals are generated in micelles or colloids, which could decrease the proportion of homogeneous nucleation and make the process and product more controllable. As a consequence, there is a linear relationship between molecular weight of product and AIBN concentration in lg-1g coordinate. It provided a reference for the preparation of latexes with specified molecular weight and supported the possibility of the coexistence of multiple free radicals in one micelle or colloid when using oil-soluble initiator.

Keywords Emulsion polymerization; Oil-soluble initiator; Water-soluble initiator; Styrene; Reaction mechanism

Citation: Liu, X. J.; Tian, Y. H.; Lu, Y. C. A comparative study on emulsion polymerization processes of styrene initiated by water-soluble and oil-soluble initiators. *Chinese J. Polym. Sci.* 2019, 37, 142–148.

INTRODUCTION

Emulsion polymerization is an environmentally friendly approach to producing high performance polymeric materials, compared to the processes using volatile organic solvents like solution polymerization or precipitation polymerization. The water-borne emulsion polymers are widely used as important components in adhesives, inks, paints, synthetic rubbers, coatings, drug delivery systems, thermoplastics, immune-diagnosis tests, and cosmetics.^[1–3]

Conventional emulsion polymerization process involves the emulsification of monomers in water containing emulsifier and following polymerization reaction in micelles or colloids. When using water-soluble initiator as a typical case, the mechanism of emulsion polymerization has been thoroughly investigated to reach a common view of micellar nucleation scheme, which is described as Smith and Ewart model.^[4–6] In detail, water-borne free radicals initiate the polymerization of monomers dissolved in aqueous phase firstly to generate hydrophobic oligomeric radicals, and then the oligomeric radicals are captured by micelles and further react with the monomer therein. However, it is difficult to avoid other scenarios. For examples, abundant free radicals and deficient monomers in the aqueous phase may result in the generation of low-molecular-weight polymers; the nucle-

ation in aqueous phase may take place once the oligomeric radicals reach high polymerization degree before being captured by micelles,^[7] and Ozdeer *et al.*^[8] even obtained latex products with bimodal particle size distribution by the KPS-initiated emulsion copolymerization of styrene and butyl acrylate. In the past few decades, the usage of oil-soluble initiators (*e.g.* AIBN) has been reported in emulsion polymerization,^[9–12] providing alternatives and offering some good performance. For instance, Ali *et al.*^[13] studied the emulsion polymerization of 2-hydroxyethyl methacrylate (HEMA) and found that stable latex products were produced only as using oil-soluble initiators in combination with alkyl sulfate. Our group successfully prepared monodispersed polystyrene nanolatex with poly(vinyl alcohol) (PVA) as the sole stabilizer by using AIBN as initiator,^[14] which is difficult to be realized by conventional emulsion polymerization with water-soluble initiators due to the formation of coagulum during relatively long reaction time.^[15,16] Besides, oil-soluble initiators are fit to produce non-ionic latex products, while water-soluble initiators could decompose into ions to affect surface charge properties of particles.^[17]

Unlike the water-soluble initiators, the oil-soluble initiators still face controversy in the mechanism of active species generation and transportation during emulsion polymerization, such as the position that effective radicals generate,^[18,19] although the polymerization kinetics might be similar when using different initiators.^[20] One opinion^[21–24] considers that the initiator dissolved in the aqueous phase generates the effective radicals since the pair of radicals formed in micelles

* Corresponding author: E-mail luyc@tsinghua.edu.cn

Received July 4, 2018; Accepted August 30, 2018; Published online September 25, 2018

or colloids tend to terminate once being formed. Another opinion^[25,26] considers that the desorption rate of the newly formed radicals from the micelles or colloids is greater than the rate of termination, so the initiators in micelles or colloids could provide most effective radicals. The former is similar to what happens in emulsion polymerization initiated by water-soluble initiator; the latter may result in a different scenario without the transfer of oligomeric radicals from aqueous phase to micelles. Therefore, the mechanism of emulsion polymerization initiated by oil-soluble initiator may be further revealed through systematically comparing this process with the emulsion polymerization initiated by water-soluble initiator.

In this work, typical oil-soluble initiator AIBN and water-soluble initiator potassium persulfate (KPS) were selected to conduct emulsion polymerization of styrene comparatively. To cognize how the polymerization takes place, the time profile of monomer conversion and the morphology, size, and molecular weight distribution of final products were determined carefully. For different initiators, the effects of emulsifier type and the ratio of initiator to monomer were investigated separately to explore their differences. Then, by proposing that the micelles are the dominant sites of free radical generation and polymerization for oil-soluble initiator initiated emulsion polymerization, the experimental results were explained thoroughly from mechanism. The potential advantages were discussed at last about oil-soluble initiator initiated emulsion polymerization in the uniformity of products and the usage of nonionic emulsifier.

EXPERIMENTAL

Chemicals and Materials

Styrene (St, Sinopharm) was washed with sodium hydroxide aqueous solution (5 wt%) and water sequentially to remove the polymerization inhibitors, and then purified by distillation under reduced pressure. Then, St and water were stripped with nitrogen gas to remove dissolved oxygen for at least 1 h before use. AIBN (J&K) was recrystallized twice from ethanol. Water-soluble initiator KPS (Xilong Chemical), the emulsifiers sodium lauryl sulfate (SLS, J&K), sodium dodecyl benzene sulphonate (SDBS, Sinopharm), Tween 20 (Xilong Chemical), and NaNO_2 were used as received. The water used throughout experiments was ultra-

pure water produced from water purification machine (Center 120FV-S).

Polymerization Reaction

The polymerization process with Tween 20 as emulsifier was taken as an example for illustration. Tween 20 aqueous solution was used as the continuous phase to dissolve water-soluble initiator KPS. St was used as the dispersed phase to dissolve oil-soluble initiator AIBN. The schematic of experimental set-up for polymerization reaction was based on our previous report.^[14] The continuous phase and the dispersed phase were fed into a three-necked flask and homogenized by continuous mechanical stirring ($800 \text{ r} \cdot \text{min}^{-1}$) for 30 min under nitrogen atmosphere at room temperature. The obtained emulsion was pumped through a stainless steel coil emerged in thermostat to reach the desired reaction temperature rapidly ($< 30 \text{ s}$), and injected into a 100 mL three-necked flask with magnetic stirrer ($300 \text{ r} \cdot \text{min}^{-1}$) under nitrogen atmosphere. A water bath was used to control the reaction temperature. Timing started as the injection was just finished. Samples were drawn from the reactor at preset time, in which the products were precipitated by ethanol, separated out by filtration, and dried in vacuum oven at 40°C for further characterization. The conditions of polymerization experiments are listed in Table 1.

Analysis and Characterization

For latex particles, the morphology was characterized with scanning electron microscopy (SEM, JSM 7401F, JEOL). The test sample was prepared by sprinkling a trace amount of dried polymer sample over the SEM sample stage which was coated with a film of conducting resin, and then coated with gold nanoparticles to prevent charge buildup from the electron beam. The number-average molecular weight (M_n) and polydispersity index (PDI) of the polymers were measured with a Waters gel permeation chromatography (GPC) instrument comprised of a Waters 2707 auto sampler, a 1515 Isocratic HPLC pump, a 2414 refractive index detector, and three GPC columns thermostated at 38°C . The instrument was calibrated with polystyrene standards. The mobile phase was tetrahydrofuran (THF), of which the flow rate was $1.0 \text{ mL} \cdot \text{min}^{-1}$. The data were processed by the Breeze 2 software from Waters. The monomer conversion was determined gravimetrically.

Table 1 Collection of experimental conditions and product characterization results ^a

Entry	Content (g)						$M_n \times 10^{-5}$	PDI
	AIBN	KPS	Tween 20	SDBS	SLS	NaNO_2		
1	0.1	—	1.8	—	—	—	1.87	3.08
2	—	0.1	1.8	—	—	—	0.889	4.05
3	—	0.01	1.8	—	—	—	5.39	2.69
4	0.1	—	1.8	—	—	0.41	0.372	2.17
5	0.005	—	1.8	—	—	—	7.21	1.89
6	0.01	—	1.8	—	—	—	6.14	2.07
7	0.05	—	1.8	—	—	—	4.04	2.44
8	0.5	—	1.8	—	—	—	0.603	2.41
9	1	—	1.8	—	—	—	0.348	2.52
10	0.1	—	—	—	0.744	—	1.37	4.02
11	0.1	—	—	0.738	—	—	1.78	3.42
12	—	0.1	—	0.738	—	—	1.37	6.10

^a The contents of styrene and water were 10 and 60 g, respectively, for all experimental conditions.

RESULTS AND DISCUSSION

Emulsion Polymerization Processes with Tween 20 as Emulsifier

Two series of emulsion polymerization experiments were carried out with Tween 20 as emulsifier, in which KPS and AIBN were used as initiator, respectively. Fig. 1 presents the time profiles of the conversion. It was found that the monomer conversion of AIBN-initiated emulsion polymerization (entry 1) was always higher than that of KPS-initiated emulsion polymerization (entry 2). After 50 min, the conversion, M_n , and PDI for the AIBN-initiated polymerization were over 90%, 1.87×10^5 , and 3.08, respectively, and those for the KPS-initiated polymerization were less than 70%, 0.889×10^5 , and 4.05, respectively. Compared with KPS, AIBN seems to initiate the polymerization more effectively and contribute to obtaining polymer with lower PDI.

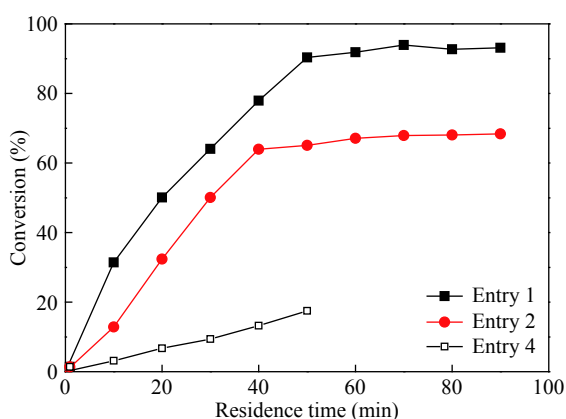


Fig. 1 Time profiles of monomer conversion of various polymerization processes with Tween 20 as emulsifier. The initiator was AIBN for entries 1 and 4, KPS for entry 2. NaNO_2 was added for entry 4 as well. The quantitative conditions included: initiator, 1 wt% of monomer; Tween 20, 3 wt% of water; phase ratio, 1:6; $T = 70^\circ\text{C}$.

As well known, for KPS-initiated emulsion polymerization, the aqueous solution is the main site where the effective free radicals are generated. The radical flux of KPS can be calculated by $R_i = 2fk_d[I]$, where $f = 0.5$,^[27] $k_d = 2.5 \times 10^{-5} \text{ s}^{-1}$ is the decomposition rate constants, $[I] = 6.17 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ is the molar concentration of KPS in aqueous solution and the calculated value of radical flux is $R_i = 1.54 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$. Similarly, if the effective free radicals of AIBN are generated in water, the radical flux will be $R_i = 1.41 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, where $f = 0.6$,^[27] $k_d = 4.47 \times 10^{-5} \text{ s}^{-1}$, $[I] = 2.625 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ on the basis of its solubility in water.^[27] The calculated value of radical flux of KPS is around ten times larger than that of AIBN. However, Fig. 1 shows a fact that AIBN with lower radical flux rate corresponds to higher polymerization rate. This contradiction implies for the AIBN-initiated emulsion polymerization, other sites may have significant contribution to free radical generation.

Since AIBN is soluble in styrene, it is undoubted that most of them exist in the micelles and monomer droplets. Luo *et al.*^[28] stated that the addition of NaNO_2 could destroy free radicals both within the micelles and in the aqueous phase, and left the polymerization in monomer droplets alone, so

we carried out polymerization experiments in the presence of NaNO_2 to reveal the contribution of polymerization in monomer droplets (entry 4). As seen, both the polymerization rate and the molecular weight were quite low. Evidently, the polymerization in monomer droplets presented insignificant enhancement of monomer conversion in AIBN-initiated process. On the other hand, Tween 20 has dendritic hydrophilic part in molecular structure, prone to generating micelles with thick shell. Weiss, *et al.*^[29] measured the size of Tween 20 micelles before and after solubilization with *n*-hexadecane and found that the oil molecules may be packed in the shell of micelles. In this work, most styrene and AIBN might exist in the shell of micelles as well, which could prevent the *in situ* generated free radicals from bimolecular termination. So they could initiate polymerization effectively. Van der Hoff^[30] also supposed that the effective free radicals of oil-soluble initiators in emulsion polymerization may be formed in the emulsifier layer at monomer-water interface.

Fig. 2 shows the SEM images of the products of entries 1 and 2. For the AIBN-initiated polymerization, the particle size of the products was around 100 nm and relatively narrow distributed. For the KPS-initiated polymerization, the particle size of the products was distributed around two quite different values, and numerous particles far smaller than 100 nm existed. An explanation is that these small particles just generated due to nucleation in aqueous phase. When using AIBN or other oil soluble initiator, the aqueous solution is lack of free radicals, and the chain propagation in the aqueous phase and perhaps nucleation can be inhibited dramatically, which is favourable for the uniformity of particle size.

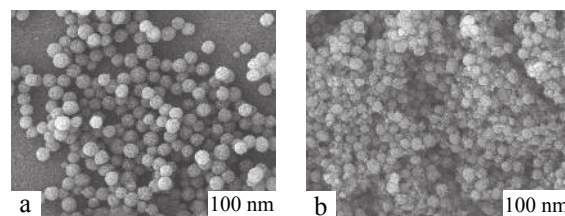


Fig. 2 SEM images of products of emulsion polymerization using Tween 20 as emulsifier. The initiators were (a) AIBN and (b) KPS, respectively. The quantitative conditions included: initiator, 1 wt% of monomer; Tween 20, 3 wt% of water; phase ratio, 1:6; $T = 70^\circ\text{C}$.

Effects of Emulsifier Type

Emulsifier plays important roles in emulsion polymerization. The type of emulsifier determines the stability and rheology of the resulting latexes and the polymerization rate.^[31,32] Weiss *et al.*^[33] reported that the mass transfer rate of monomer from droplets into the micelles depended closely on the molecular structure of the surfactant. They further suggested that the interfacial mass transport coefficient of Tween 20 micellar solution was relatively low. Herein, contrast to the nonionic emulsifier Tween 20, conventional anionic emulsifiers SDBS and SLS were selected to carry out emulsion polymerization as well. These anionic emulsifiers could form small monomer-swollen micelles with thin surface layer.^[31] The time profiles of monomer conversion are shown in Fig. 3. The polymerization rate was obviously increased with the substitute of Tween 20 by ionic emulsi-

fiers, although the ratio of concentration to critical micelles concentration (CMC) for SDBS or SLS (about 5) was far lower than that for Tween 20 (about 500). The results were related to the high interfacial mass transport resistance of Tween 20, which hindered the monomer supply to micelles and then slowed down the propagation rate of polymer chains.

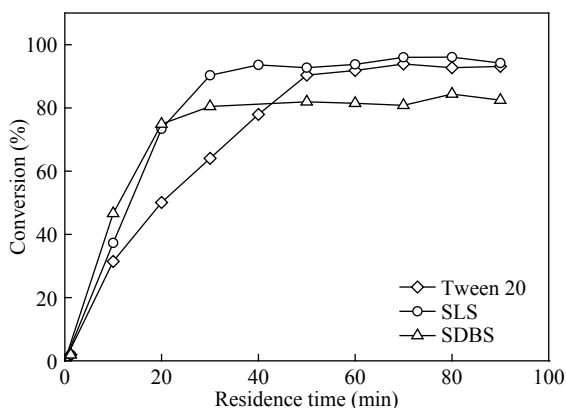


Fig. 3 The time profiles of monomer conversion of AIBN-initiated emulsion polymerization with different emulsifiers. The experimental formulations correspond to entries 1, 10, and 11; initiator was 1 wt% of monomers; Tween 20 was 3 wt% of water; SDBS was 1.23 wt% of water; SLS was 1.24 wt% of water; the phase ratio was 1:6; $T = 70^\circ\text{C}$.

Comparison was also extended to the emulsion polymerization initiated by KPS, as shown in Fig. 4. No matter which initiator was used, the emulsion polymerization rate with SDBS as the emulsifier was always higher than that with Tween 20 as the emulsifier. For the KPS-initiated emulsion polymerization, the monomer conversion reached nearly 80% after 10 min polymerization when using SDBS, but only reached 12% when using Tween 20. Compared with the AIBN-initiated process, the KPS-initiated process was more sensitive to emulsifier type and micellar structure. A plausible explanation is that the effective free radicals of AIBN mainly generated in micelles or colloids and did not need to get into emulsifier micelles like the oligomeric radicals initiated by KPS did.

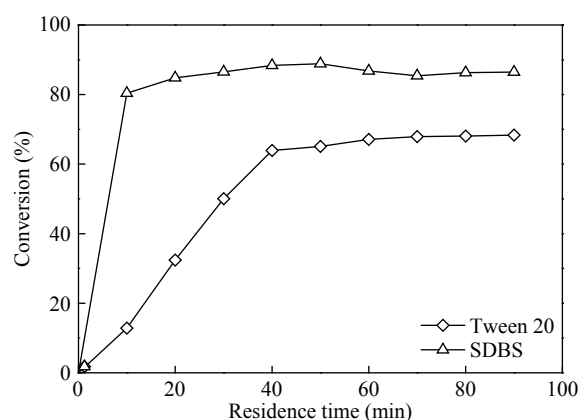


Fig. 4 The time profiles of monomer conversion of KPS-initiated emulsion polymerization with different emulsifiers. The experimental formulations correspond to entries 2 and 12; initiator was 1 wt% of monomers; Tween 20 was 3 wt% of water; SDBS was 1.23 wt% of water; the phase ratio was 1:6; $T = 70^\circ\text{C}$.

Effects of Initiator Concentration

During the emulsion polymerization process, the initiator concentration, referred as the ratio of initiator to monomer, has direct influence on the probability of chain initiation and the polymerization degree of propagating chain. Higher initiator concentration corresponds to more but shorter propagating chains in common, decreasing the molecular weight of obtained polymer. When using water-soluble initiator, shorter propagation chains which possess less chance to get into micelles, are more probably consumed by chain termination reaction in aqueous solution. Therefore, with the increasing of initiator concentration, more products would generate in the aqueous solution, widening the molecular weight distribution in general, as indicated by the comparison of entries 2 and 3 in Table 1. With the KPS concentration increasing from 0.1 wt% to 1 wt%, M_n decreased from 5.39×10^5 to 0.889×10^5 , and PDI increased from 2.69 to 4.05. Furthermore, Fig. 5(a) shows the time profiles of monomer conversion in entries 2 and 3. As can be seen, the increase of KPS concentration can accelerate the polymerization process at initial but make the final monomer conversion decrease. Capek *et al.*^[31,34] also found that for emulsion polymerization of styrene with non-ionic emul-

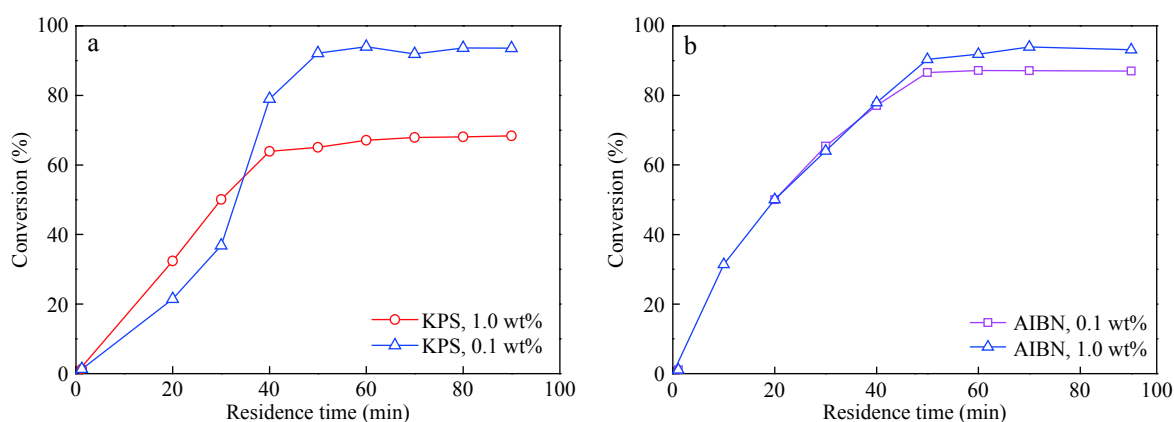


Fig. 5 Effects of initiator concentration on the time profile of monomer conversion in emulsion polymerizations initiated by (a) KPS and (b) AIBN. The experimental formulations correspond to entries 1, 2, 3, and 6. Tween 20 was 3 wt% of water; the phase ratio was 1:6; $T = 70^\circ\text{C}$.

sifiers, the maximal rate of polymerization decreased with increasing initiator (APS) concentration, despite an increase in particle concentration. An explanation is that the increasing of initiator in aqueous phase might act against the propagation of oligomeric radicals, and increase the probability of chain termination between oligomeric radicals. Therefore, to prepare relatively uniform latex product, the initiator concentration should be selected carefully for the emulsion polymerization using water-soluble initiator, and high initiator concentration is not appropriate.

Comparatively, AIBN-initiated emulsion polymerizations were carried out with various AIBN concentrations, as entries 1 and 6 in Table 1. Fig. 5(b) shows the time profiles of monomer conversion. The results were quite different from that shown in Fig. 5(a). The curves are almost overlapped, and the effect of initiator concentration is little. Correspondingly, as the concentration of AIBN increased from 0.1 wt% to 1 wt%, M_n decreased from 6.14×10^5 to 1.87×10^5 , and PDI increased from 2.07 to 3.08. Compared with the KPS-initiated emulsion polymerization, the variances have the same tendency but are relatively small. This is because for AIBN-initiated emulsion polymerization, the chain initiation and chain propagation proceeded in micelles mostly, which is independent of the initiator concentration. It may endow the AIBN-initiated emulsion polymerization with the merits of favorable flexibility and controllability in polymerization performance.

Features and Potentials of Emulsion Polymerization Initiated by Oil-soluble Initiator

Based on above comparisons on apparent kinetics and products between the emulsion polymerization processes initiated by AIBN and KPS, it was supposed that there exist different scenarios depending on the solubility of initiator.

Fig. 6 shows the schematics of emulsion polymerization processes, in which Figs. 6(a)–6(f) correspond to those using oil-soluble initiator, while Figs. 6(g)–6(l) correspond to those using water-soluble initiator. Both groups involve three common stages: initiation outside monomer droplets, nucleation in micelles, and particle growth to deplete monomer.

Nevertheless, they have original difference in the location of initiator. When using water-soluble initiator, the polymerization is initiated in aqueous solution to generate oligomeric radicals. Quite a few oligomeric radicals may penetrate into micelles to carry out further polymerization. However, due to the steric hindrance of the shell of micelle, some oligomeric radicals may still stay in aqueous solution to produce oligomers by chain termination reactions. The proliferation of these oligomers in aqueous solution can result in the decrease of M_n , the broadening of PDI, and the appearance of small particles (< 100 nm) through homogeneous nucleation and growth.^[35] Such a case is more likely to occur as using non-ionic emulsifier due to the proneness of generating micelles with thick shell.^[36] When using the oil-soluble initiator, the polymerization proceeds in micelles dominantly, and the generation of oligomers in aqueous solution will be insignificant. Moreover, the shell of micelle does not exclude free radicals from micelles but prevent them from bimolecular termination, resulting in the acceleration of polymerization process. Therefore, using oil-soluble initiator in emulsion polymerization could benefit the control on molecular weight and particle size, and diminish the effects of micellar structure and aqueous phase polymerization. These advantages over using water-soluble initiator have been confirmed by comparative emulsion polymerization experiments with Tween 20 as emulsifier, which may help to expand the application of non-ionic emulsifiers to varieties of emulsion polymerization systems.

Another advantage of using oil-soluble initiator to initiate emulsion polymerization over using water-soluble initiator is the capability of providing simple and confirmed sites for various chain reactions. It could evade the complexity for controlling and adjusting the molecular weight distribution of products. Herein, the concentration of AIBN was adjusted within an extended range from 0.05 wt% to 10 wt% to explore the potential of the AIBN-initiated emulsion polymerization in molecular weight regulation. Fig. 7(a) shows the time profiles of monomer conversion. When the concentration of AIBN was in the range from 0.1 wt% to 10 wt%, it had no obvious difference in the polymerization rate, al-

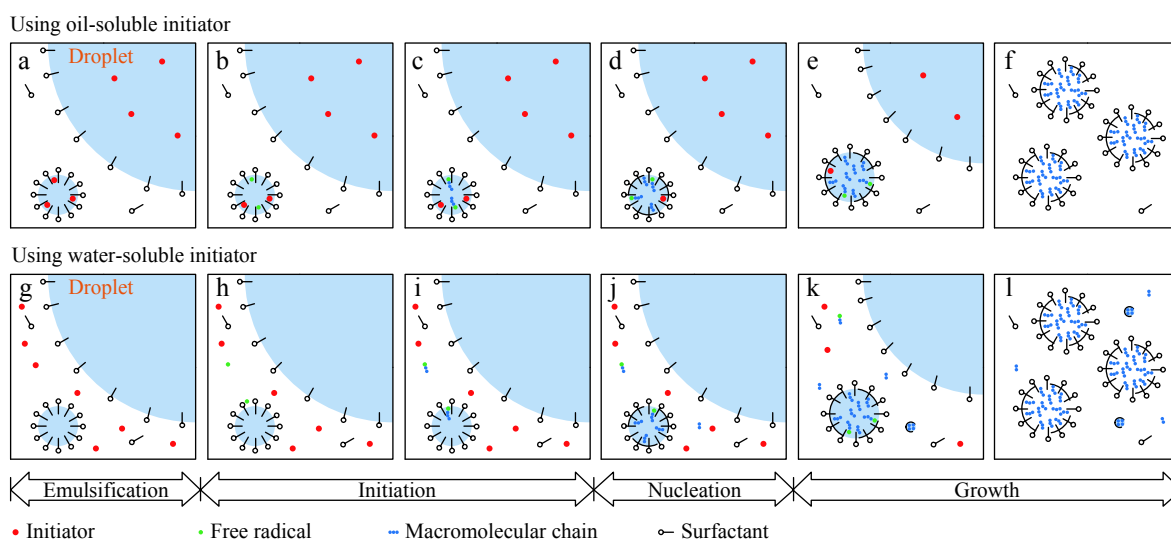


Fig. 6 Schematics of emulsion polymerization processes initiated by oil-soluble initiator and water-soluble initiator

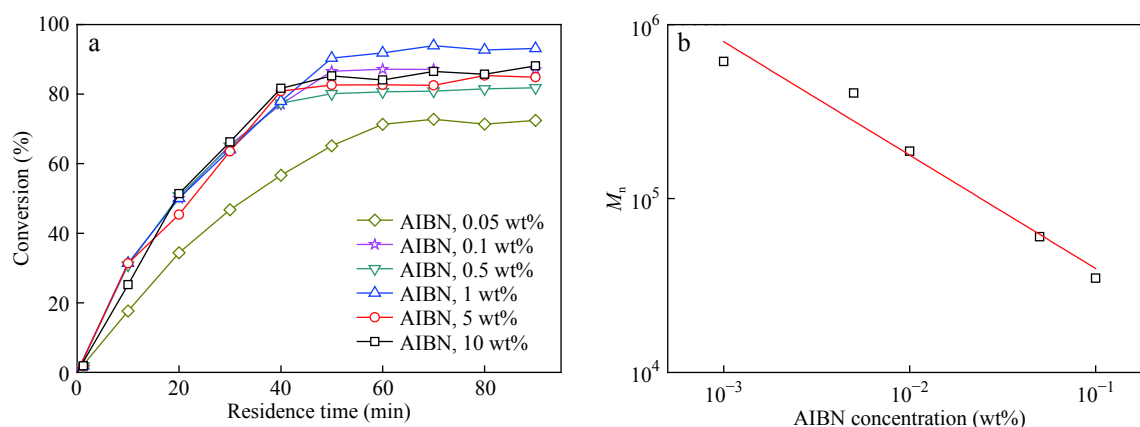


Fig. 7 Controllability of AIBN-initiated emulsion polymerization process with respects of (a) monomer conversion and (b) product molecular weight. The experimental formulations correspond to entries 1, 5, 6, 7, 8, and 9. Tween 20 was 3 wt% of water; the phase ratio was 1:6; $T = 70\text{ }^{\circ}\text{C}$.

though the generation rate of free radicals varied significantly.^[37] This implies that the rate-limiting step of these polymerization processes might not be the polymerization itself but the mass transfer feeding monomer. However, when the concentration of AIBN decreased to 0.05 wt%, the polymerization rate decreased obviously, indicating the polymerization reaction in micelles became the rate-limiting step due to the deficiency of AIBN therein. Overall, once the AIBN concentration was not less than 0.1 wt%, it was supposed that the molecular weight of the product would be determined by the amount of effective free radicals. Considering the relationship between effective free radical and initiator, the correlation between molecular weight and initiator is reasonable. Fig. 7(b) shows a linear relationship between molecular weight of polystyrene and mass ratio of AIBN to styrene in lg-lg coordinate, which fits well with an exponential function:

$$M_n = 8823w^{-0.65} \quad (1)$$

where M_n means the molecular weight of obtained polystyrene, w means the mass ratio of AIBN to styrene. The fitting equation is a reference for the preparation of polymer with specific molecular weight. The strong correlation between M_n and initiator concentration, as well as the confirmed site where polymerization reaction takes place, also reflects the potential coexistence of multiple free radicals in one micelle or colloid when using oil-soluble initiator.

CONCLUSIONS

To clarify how the solubility of initiator influences emulsion polymerization in terms of process and product, the kinetic behaviors and product properties of emulsion polymerization of highly hydrophobic styrene initiated by AIBN and KPS were compared systematically in this work. It was found that compared with KPS-initiated emulsion polymerization, the polymerization initiated by AIBN was insensitive to the type of emulsifier. In addition, the latter had higher polymerization rate as well as provided narrower molecular weight distribution and particle size distribution than the former did when using the non-ionic Tween 20 as emulsifier. These results indicated that the effective free radicals of oil-soluble

initiators were generated in micelles or colloids and did not need to penetrate their interface, which were different from the scenario of water-soluble initiators. Besides, due to the poor solubility of AIBN in water, the AIBN-initiated emulsion polymerization decreased the proportion of homogeneous nucleation and was more controllable in the morphology and molecular weight distribution of polymer products. Therefore, oil-soluble initiators were thought to be more adaptive to emulsion polymerizations stabilized by non-ionic emulsifiers or that have high quality demand on the particle size or molecular weight distribution of products. A linear relationship was also established between molecular weight of emulsion polymer and the concentration of AIBN in lg-lg coordinate. The concentration of AIBN covers from 0.01 wt% to 10 wt% and molecular weight from 3.48×10^4 to 6.14×10^5 , providing a reference for the preparation of latexes with specified molecular weight. Moreover, this study implies the potential coexistence of multiple free radicals in one micelle or colloid when using oil-soluble initiator.

ACKNOWLEDGMENTS

The authors granted the financial support of the National Natural Science Foundation of China (Nos. 21422603 and U1662120).

REFERENCES

- Asua, J. M. Emulsion polymerization: From fundamental mechanisms to process developments. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, 42, 1025–1041.
- Zhao, B.; Deng, J. P. Emulsion polymerization of acetylenics for constructing optically active helical polymer nanoparticles. *Polym. Rev.* **2017**, 57, 119–137.
- Jiang, S.; Van Dyk, A.; Maurice, A.; Bohling, J.; Fasano, D.; Brownell, S. Design colloidal particle morphology and self-assembly for coating applications. *Chem. Soc. Rev.* **2017**, 46, 3792–3807.
- Smith, W. V.; Ewart, R. H. Kinetics of emulsion polymeriza-

- tion. *J. Chem. Phys.* **1948**, *16*, 592–599.
- 5 Gardon, J. L. Emulsion polymerization. I. Recalculation and extension of Smith-Ewart theory. *J. Polym. Sci., Part A: Polym. Chem.* **1968**, *6*, 623–641.
- 6 Gardon, J. L. Emulsion polymerization. II. Review of experimental data in the context of the revised Smith-Ewart theory. *J. Polym. Sci., Part A: Polym. Chem.* **1968**, *6*, 643–664.
- 7 Dong, Y. A molecular theory for particle nucleation: Primary particle formation in emulsion polymerization. *J. Colloid Interface Sci.* **2008**, *326*, 354–359.
- 8 Ozdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. Role of the nonionic surfactant triton X-405 in emulsion polymerization. III. Copolymerization of styrene and *n*-butyl acrylate. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3837–3846.
- 9 Yamamoto, T. Effect of the amount of π electrons in aromatic monomer on the surface potential of polymeric particles obtained through soap-free emulsion polymerization using AIBN. *Chem. Lett.* **2015**, *44*, 1555–1556.
- 10 Yamamoto, T.; Takahashi, Y. Synthesis of hydrocolloid through polymerization of styrene and *N*-vinyl acetamide by AIBN. *Colloid Surf. A* **2017**, *516*, 80–84.
- 11 Liu, B. J.; Wang, Y. J.; Zhang, M. Y.; Zhang, H. X. Initiator systems effect on particle coagulation and particle size distribution in one-step emulsion polymerization of styrene. *Polymers-Basel* **2016**, *8*, 55.
- 12 Zhang, Y. W.; Zhuang, X.; Gu, W. J.; Zhao, J. X. Synthesis of polyacrylonitrile nanoparticles at high monomer concentrations by AIBN-initiated semi-continuous emulsion polymerization method. *Eur. Polym. J.* **2015**, *67*, 57–65.
- 13 Ali, A. M. I.; Tauer, K.; Sedlak, M. Comparing emulsion polymerization of methacrylate-monomers with different hydrophilicity. *Polymer* **2005**, *46*, 1017–1023.
- 14 Lu, Y. C.; Liu, X. J.; Luo, G. S. Synthesis of polystyrene latex via emulsion polymerization with poly(vinyl alcohol) as sole stabilizer. *J. Appl. Polym. Sci.* **2017**, *134*, 45111.
- 15 Suzuki, A.; Matsuda, Y.; Masuda, T.; Kikuchi, K.; Okaya, T. Effect of additives on the initial stage of emulsion polymerization of styrene (St) using poly(vinyl alcohol) as a protective colloid. *Colloid. Polym. Sci.* **2006**, *285*, 193–201.
- 16 Kim, N.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. Comparison of conventional and miniemulsion copolymerizations of acrylic monomers using poly(vinyl alcohol) as the sole stabilizer. *Macromolecules* **2004**, *37*, 2427–2433.
- 17 Lee, S.; Mackay, D.; Rudin, A. A moderately water-soluble azo initiator for emulsion polymerizations. *J. Appl. Polym. Sci.* **1991**, *42*, 3076.
- 18 Autran, C.; de la Cal, J. C.; Asua, J. M. (Mini)emulsion polymerization kinetics using oil-soluble initiators. *Macromolecules* **2007**, *40*, 6233–6238.
- 19 Capek, I. On the role of oil-soluble initiators in the radical polymerization of micellar systems. *Adv. Colloid Interface Sci.* **2001**, *91*, 295–334.
- 20 Alduncin, J. A.; Forcada, J.; Barandiaran, M. J.; Asua, J. M. On the main locus of radical formation in emulsion polymerization initiated by oil-soluble initiators. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1265–1270.
- 21 Nomura, M.; Ikoma, J.; Fujita, K. Kinetics and mechanisms of emulsion polymerization initiated by oil-soluble initiators. IV. Kinetic modeling of unseeded emulsion polymerization of styrene initiated by 2,2'-azobisisobutyronitrile. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2103–2113.
- 22 Nomura, M.; Fujita, K. Kinetics and mechanism of emulsion polymerization initiated by oil-soluble initiators. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 581–587.
- 23 Mork, P. C.; Makame, Y. Compartmentalized polymerization with oil-soluble initiators. Kinetic effect of single radical formation. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2347–2354.
- 24 Capek, I.; Barton, J.; Karpatyova, A. Emulsion polymerization of butyl methacrylate initiated by 2,2'-azoisobutyronitrile. 3. On the applicability of the modified Smith-Ewart model. *Makromol. Chem.* **1987**, *188*, 703–710.
- 25 Asua, J. M.; Rodriguez, V. S.; Sudol, E. D.; El-Aasser, M. S. The free radical distribution in emulsion polymerization using oil-soluble initiators. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3569–3587.
- 26 Shang, Y.; Shan, G. R.; Pan, P. J. Kinetic and molecular weight modeling of miniemulsion polymerization initiated by oil-soluble initiators. *Macromol. Chem. Phys.* **2015**, *216*, 884–893.
- 27 Barton, J.; Karpatyova, A. Emulsion polymerization of butyl methacrylate initiated by 2,2'-azoisobutyronitrile. 1. Kinetic and mechanism. *Macromol. Chem. Phys.* **1987**, *188*, 693–702.
- 28 Luo, Y. W.; Schork, F. J. Emulsion and miniemulsion polymerizations with an oil-soluble initiator in the presence and absence of an aqueous-phase radical scavenger. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3200–3211.
- 29 Weiss, J.; Coupland, J. N.; Brathwaite, D.; McClements, D. J. Influence of molecular structure of hydrocarbon emulsion droplets on their solubilization in nonionic surfactant micelles. *Colloid Surf. A* **1997**, *121*, 53–60.
- 30 Van der Hoff, B. M. E. Kinetics of emulsion polymerization. *Adv. Chem. Ser.* **1962**, *34*, 6–31.
- 31 Capek, I. Sterically and electrosterically stabilized emulsion polymerization. Kinetics and preparation. *Adv. Colloid Interface Sci.* **2002**, *99*, 77–162.
- 32 Chern, C. S.; Lin, S. Y.; Chang, S. C.; Lin, J. Y.; Lin, Y. F. Effect of initiator on styrene emulsion polymerisation stabilised by mixed SDS/NP-40 surfactants. *Polymer* **1998**, *39*, 2281–2289.
- 33 Weiss, J.; McClements, D. J. Mass transport phenomena in oil-in-water emulsions containing surfactant micelles: Solubilization. *Langmuir* **2000**, *16*, 5879–5883.
- 34 Capek, I.; Chudej, J. On the fine emulsion polymerization of styrene with non-ionic emulsifier. *Polym. Bull.* **1999**, *43*, 417–424.
- 35 Chern, C. S.; Lin, C. H. Using a water-insoluble dye to probe the particle nucleation loci in styrene emulsion polymerization. *Polymer* **1999**, *40*, 139–147.
- 36 Ozdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. Role of the nonionic surfactant Triton X-405 in emulsion polymerization. 1. Homopolymerization of styrene. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3813–3825.
- 37 Nomura, M.; Tobita, H.; Suzuki, K. Emulsion polymerization: Kinetic and mechanistic aspects. *Adv. Polym. Sci.* **2005**, *175*, 1–128.