

Emulsion Polymerization of Methyl Methacrylate in Concentrations of Emulsifiers Below Their CMCs—Polymerization Rate, Particle Size, and Particle-Size Distribution

ZAI-ZHANG YU,* BO-GENG LI, MING-JIAN CAI, BAO-FANG LI, and KUN CAO

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

SYNOPSIS

The emulsion polymerization of methyl methacrylate (MMA) in concentrations of emulsifiers below their critical micelle concentrations (CMCs) initiated by $K_2S_2O_8$ (KPS) was studied. It was observed that the initiator concentration has little effect on both polymerization rate and particle size. However, the polymerization rate is faster and particle size is smaller obviously when decreasing the ratio of the water/monomer or increasing the temperature of polymerization or the amount of the emulsifier. In the range of a 200–400 rpm stirring speed, the polymerization rate is almost unchanged although the particle size becomes larger with increase in the stirring speed. The monodisperse particle (size about 100–200 nm) can be obtained using this process. The mechanism of emulsion polymerization of MMA in the emulsifier concentration below its CMC is discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Emulsion polymerization is usually carried out in an emulsifier concentration above its critical micelle concentration (CMC). However, many experimental studies have been made to demonstrate that the emulsion polymerization could be performed in the absence of an emulsifier. In this soap-free process, a stable polymer latex with a monodisperse size of particles can be obtained when a relatively large amount of water-soluble initiator is used or a hydrophilic or ionic monomer is copolymerized. However, the polymerization rate of the soap-free emulsion polymerization is much lower than that in normal emulsion polymerization. The mechanism of the soap-free emulsion polymerization was considered as “homogeneous nucleation” or “oligomer nucleation” because of the absence of micelles.¹ Most of articles focused on the polymerization of styrene; only a few articles involved the soap-free emulsion

polymerization of methyl methacrylate (MMA) carried out in the presence of persulfate.^{2,3} To improve the reaction rate of soap-free emulsion polymerization, in this article, the emulsion polymerization of MMA initiated by potassium persulfate (KPS) using various emulsifiers in concentrations below their CMCs was studied in detail.

EXPERIMENT

The emulsion polymerization of MMA was carried out in a 1 L jacketed reactor equipped with stirrer, condenser, thermometer, N_2 gas pipe, and monomer feed inlet. The temperature of the reaction was controlled by pumping the thermostatic water into the jacket of the reactor through a water thermostat. A mixture of sodium dodecylbenzene sulfonate (SDBS) and octylphenol poly(ethylene oxide) with 10 units of ethylene oxide (OP-10) was used as the emulsifier. SDBS, sodium lauryl sulfate (SLS), SLS/OP-10, and $C_{17}H_{35}COOK$ were also used as emulsifiers in the experiments for comparison. The monomer was distilled, and the initiator KPS and

* To whom correspondence should be addressed.

emulsifiers were prepared into an aqueous solution before polymerization.

Water, emulsifier, and monomer were added into the reactor and stirred for 0.5 h before polymerization; the initiator was fed into the reactor after the temperature of the content in the reactor reached a desired level. As polymerization proceeds, samples were taken at suitable time intervals for measuring the monomer conversion by the weight method. The final particle size and particle-size distribution were determined by a Malvern submicron particle size analyzer. The particle size and particle-size distribution are showed as the z -average value (dz) and the "poly" value, respectively. The value of "poly" ranged between 0 and 1. The closer to 0 the value of "poly," the narrower the PSD. The weight-average particle size (dw), the number-average particle size (dn), and the index of the particle-size distribution (dw/dn) were obtained also by calculation of the data of the particle-size distribution.

POLYMERIZATION RATE, PARTICLE SIZE, AND PARTICLE-SIZE DISTRIBUTION

The effects of polymerization conditions on polymerization rate, particle size, and particle-size distribution in the emulsion polymerization of MMA using various emulsifiers in concentrations below their CMCs were studied in detail; the results are as follows.

Initiator Concentration

The amount of persulfate used in this process was as much as five times that in normal emulsion polymerization. The fragment of initiator links onto the end of polymer chain and polymeric surfactant formed *in situ* to stabilize the latex.

Table I The Effect of Concentration of Initiator on Particle Size and Particle-Size Distribution of Latex^a

	KPS/100 M				
	0.2	0.4	0.6	0.8	1.0
dz (nm)	142.6	127.7	142.4	144.9	139.8
poly	0.096	0.013	0.005	0.004	0.004
dw/dn	1.143	1.043	1.013	1.012	1.012

^a Polymerization conditions are the same as in Figure 1.

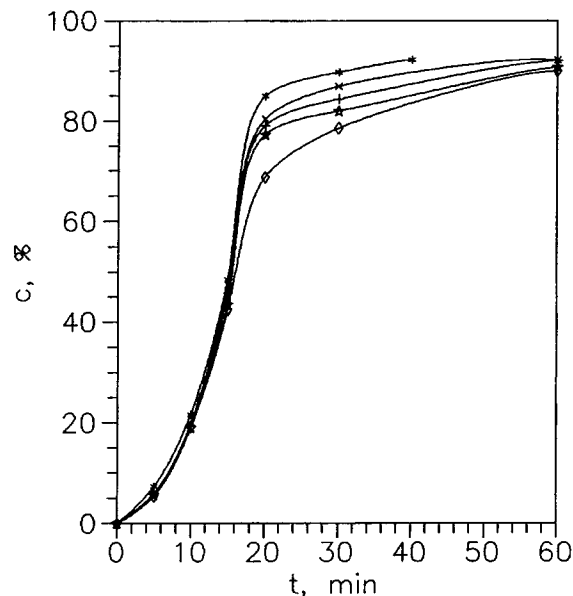


Figure 1 The effect of initiator concentration on the rate of emulsion polymerization; M , 100; H_2O , 500; E , 0.8; $65^\circ C$; 400 rpm. I : ($\diamond \diamond \diamond$) 0.2; ($\star \star \star$) 0.4; ($+++$) 0.6; ($\times \times \times$) 0.8; ($***$) 1.0.

The effects of the amount of initiator on particle size, particle-size distribution, and polymerization rate are showed in Table I and Figure 1, respectively.

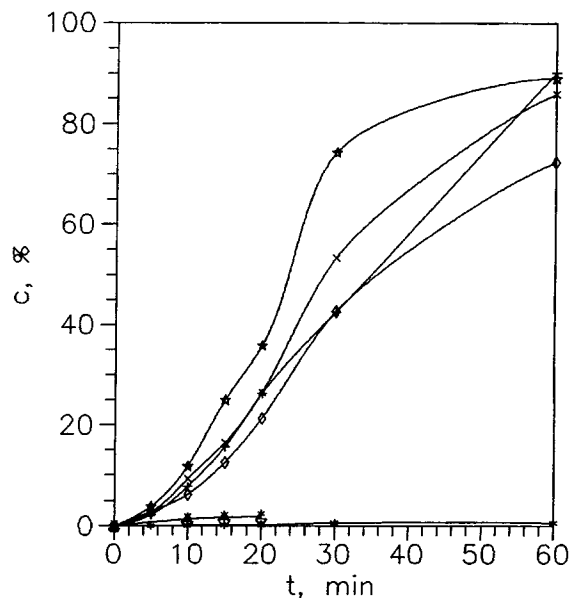


Figure 2 The effect of emulsifier kind on rate of polymerization; M , 100; H_2O , 500; I , 0.6; $55^\circ C$; 400 rpm; E , 3.53×10^{-3} mol/L. E : ($\diamond \diamond \diamond$) SDBS/OP; ($\star \star \star$) SDBS; ($+++$) SLS; ($\times \times \times$) SLS/OP; ($***$) $C_{17}H_{35}COOK$; ($\text{⊗} \text{⊗} \text{⊗}$) OP.

Table II The Effect of Kinds of Emulsifiers on Particle Size and Particle-size Distribution of Latex^a

	Kinds					
	SDBS/OP	SDBS	SLS/OP	SLS	C ₁₇ H ₃₅ COOK	OP
<i>dz</i> (nm)	175.3	115.4	144.1	122.2	1939	282.1
poly	0.024	0.037	0.004	0.022	1.00	0.029
<i>dw/dn</i>	1.078	1.104	1.012	1.064	12.30	1.08

^a Polymerization conditions are the same as in Figure 2.

It can be seen from Table I and Figure 1 that as the concentration of initiator increases both the polymerization rate and particle size are almost unchanged, but the particle-size distribution becomes narrower.

Kind and Amount of Emulsifier

Figure 2 and Table II show that the polymerizations using different kinds of emulsifier have great influence on the polymerization rate, particle size, and particle-size distribution. It may be due to the different Hydrophile-Lipophile Balance (HLB) values, surface tensions, and protective actions of colloids by these emulsifiers.

The results of polymerization at different

amounts of the emulsifier SDBS/OP-10 are shown in Figure 3 and Table III. The CMC of SDBS/OP-10 is about 3×10^{-3} g/mL.⁴ It is observed that when the concentration of emulsifier is increased the changes of the polymerization rate are only to a small extent although the particle sizes are obviously decreased. These facts imply that a different mechanism from the normal emulsion polymerization may exist in the emulsion polymerization in an emulsifier concentration below its CMC.

Temperature

As shown in Figure 4 and Table IV, the polymerization rate, particle size, and particle-size distri-

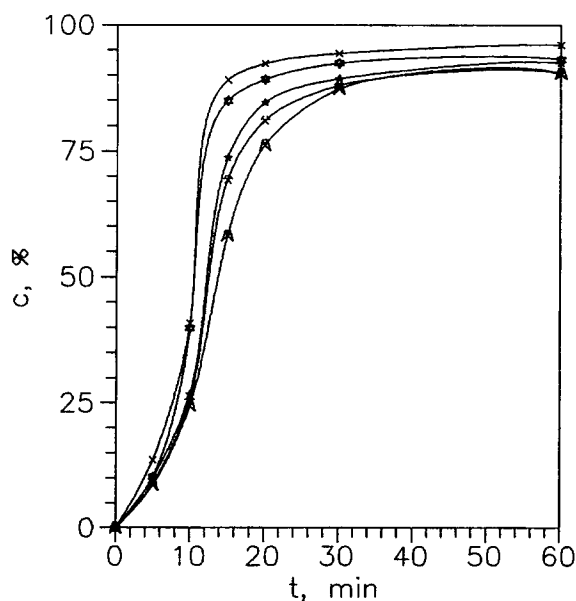


Figure 3 The effect of emulsifier concentrations on rate of emulsion polymerization: *M*, 100; H₂O, 500; *I*, 1.0; 70°C; 400 rpm. *E*: (▲▲▲) 0.4; (×××) 0.5; (★★★) 0.6; (☆☆☆) 0.7; (×××) 0.8.

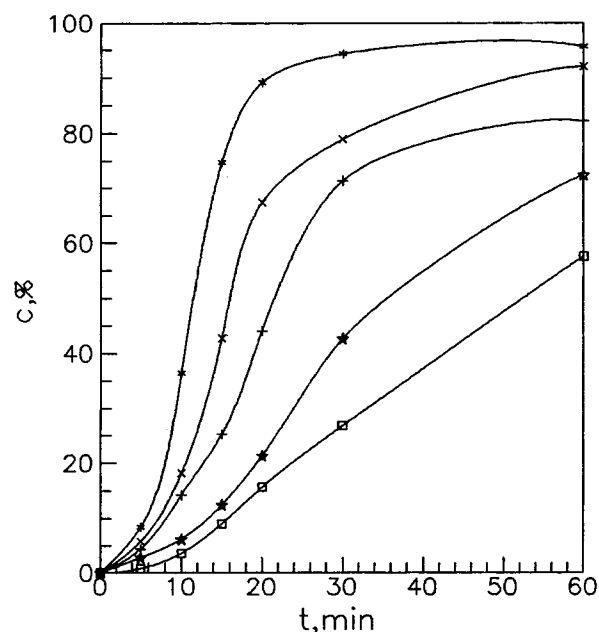


Figure 4 The effect of temperature on rate of emulsion polymerization: *M*, 100; H₂O, 500; *I*, 0.6; *E*, 0.8; 400 rpm. *T*(°C): (□□□) 50; (☆☆☆) 55; (+++++) 60; (x x x) 65; (***) 70.

Table III The Effect of Amounts of Emulsifier on Particle Size and Particle-Size Distribution^a

	E/100 M					
	0.4	0.5	0.6	0.7	0.8	1.0
g/mL H ₂ O, 10 ³	0.8	1	1.2	1.4	1.6	2
dz (nm)	338.2	154.7	138.1	109.5	96.3	83.7
poly	0.456	0.017	0.002	0.038	0.049	0.036
dw/dn	7.893	1.073	1.054	1.027	1.013	1.104

^a Polymerization conditions are the same as in Figure 3.

bution are affected drastically by the temperature of polymerization. As temperature increased, not only the decomposition rate of the initiator but also the solubility of MMA in water increased and the number of particles nucleated also increased.

Ratio of H₂O/Monomer

The emulsion polymerization rate of MMA becomes slower, the particle size smaller, and the particle-size distribution narrower, respectively, when the ratios of H₂O/M are increased from 4 to 9 as shown in Figure 5 and Table V. These phenomena result from the decrease of concentrations of initiator, emulsifier, and monomer when the amount of water is increased. Otherwise, the aggregations of oligomer radicals and the polymer particles are unimportant.

Ionic Strength

Figure 6 and Table VI indicate that, as in the normal emulsion polymerization, the polymerization rate and especially the particle size and particle-size distribution of latex are affected by adding a small amount of NaCl before polymerization. The particle size is larger when a small amount of NaCl is added.

Table IV The Effect of Temperature on Particle Size and Particle-size Distribution^a

	T (°C)				
	50	55	60	65	70
dz (nm)	183.1	175.3	145.7	137.8	123.6
poly	0.043	0.024	0.044	0.004	0.004
dw/dn	1.127	1.075	1.133	1.013	1.012

^a Polymerization conditions are the same as in Figure 4.

It is observed that the relationship between particle size and ionic strength is linear, as shown in Figure 7. Using this result, a method for controlling the particle size of latex could be obtained.

Stirring Speed

The polymerization rates are almost unchanged when the stirring speeds are in the range of 200–400 rpm, but they decrease drastically at higher stirring speeds, e.g., at 500–600 rpm as shown in Figure 8, which may be a consequence of O₂ infiltration at

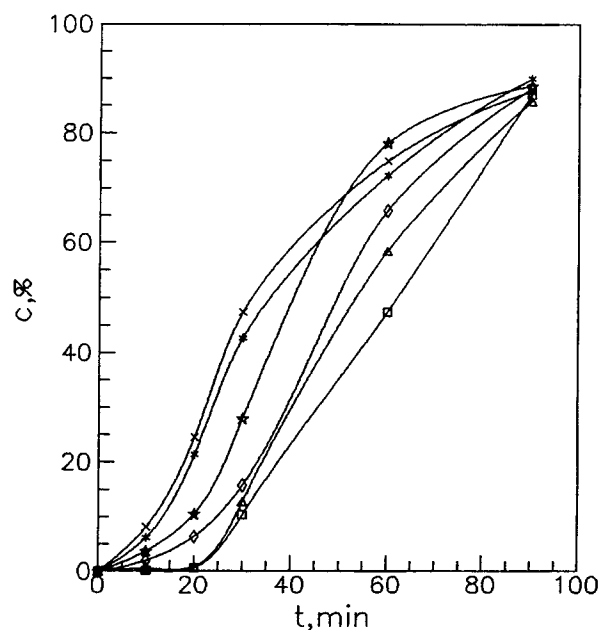


Figure 5 The effect of ratio of H₂O/M on rate of emulsion polymerization: M, 100; I, 0.6; E, 0.8; 55°C; 400 rpm. H₂O/M: (x x x) 4; (* * *) 5; (☆ ☆ ☆) 6; (◇ ◇ ◇) 7; (△ △ △) 8; (□ □ □) 9.

Table V The Effect of Ratio of H₂O/M on Particle Size and Particle-size Distribution^a

	H ₂ O/M					
	4	5	6	7	8	9
<i>dz</i> (nm)	357.3	157.8	111.7	96.7	88.6	72.6
poly	0.435	0.062	0.058	0.112	0.101	0.044
<i>dw/dn</i>	3.554	1.180	1.173	1.343	1.295	1.131

^a Polymerization conditions are the same as in Figure 5.

Table VI The Effect of Ionic Strength on Particle Size and Particle-size Distribution^a

	NaCl (10 ³ mol/dm ³)				
	0	1	3	5	8
Ionic strength, ^b 10 ³	13.3	14.3	16.3	18.3	21.3
<i>dz</i> (nm)	175.3	186.4	206.3	258.6	295.8
poly	0.024	0.013	0.050	0.039	0.025
<i>dw/dn</i>	1.075	1.047	1.158	1.130	1.112

^a Polymerization conditions are the same as in Figure 6.

^b Both concentrations of NaCl and KPS were considered.

the higher stirring speeds. The peak in particle size is exhibited and distribution is wider when the stirring speed is either faster or slower (Table VII).

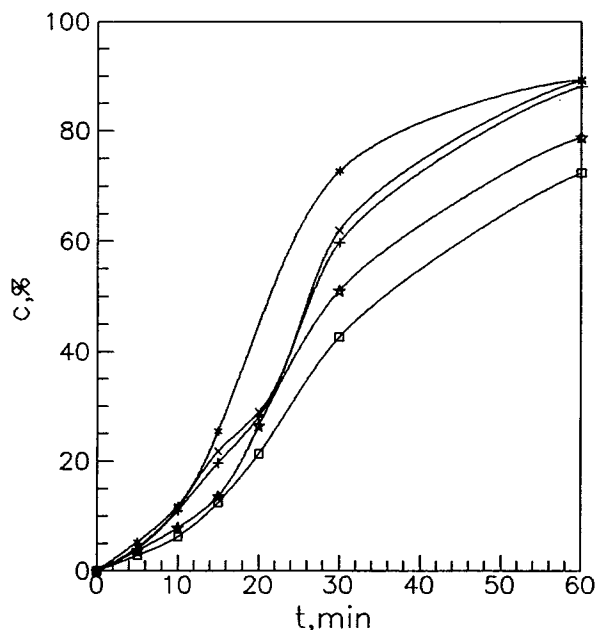


Figure 6 The effect of ion intensity on rate of emulsion polymerization: *M*, 100; H₂O, 500; *I*, 0.6; *E*, 0.8; 55°C; 400 rpm. NaCl (10⁻³ mol/dm³ H₂O): (□□□) 0; (☆☆☆) 1; (+++++) 3; (xxxxx) 5; (****) 8.

DISCUSSION ABOUT MECHANISM

The results described above show that the effects of polymerization conditions on the polymerization rate, particle size, and particle-size distribution in emulsion polymerization of MMA in concentrations of emulsifiers below their CMCs are different from those in normal emulsion polymerization to some extent. It is considered that the polymerization rate and the number of nuclei are dependent mainly on the concentration of MMA in the aqueous medium, because the solubility of MMA in water is larger than that of styrene. When the temperature and concentration of emulsifier increases and ratio of H₂O/monomer decreases, the amount of MMA in the aqueous medium and the number of nucleated particles will be increased, so that the polymerization rate becomes faster and particle size becomes smaller. The amount of initiator exerts an insignificant influence on the nucleation and polymerization rate since the concentration of free radicals generated from the initiator is more than enough for nucleation.

In addition, according to the data of the particle size, the particle number of the latex at the end of polymerization was calculated to be 10¹⁴/mL, this value smaller by 1–2 orders than that in normal emulsion polymerization. Another characteristic of

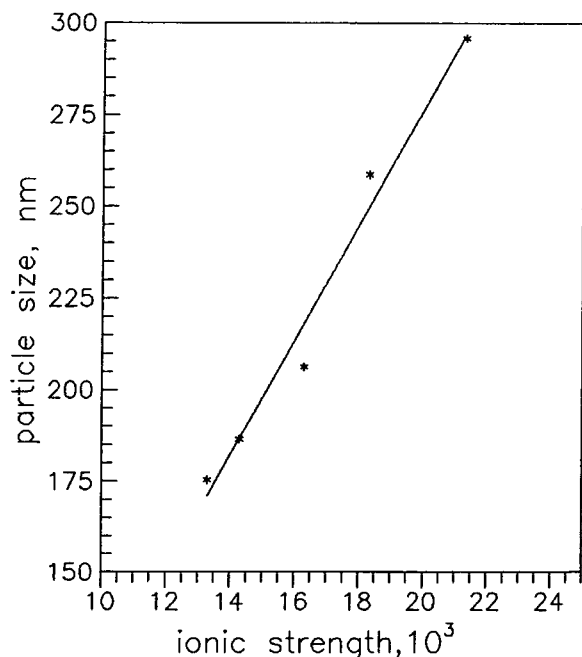


Figure 7 The relation between ionic strength in the system and particle size: (* * *) NaCl only.

the emulsion polymerization of MMA initiated by KPS and in lower emulsifier concentration than its CMC is that the monodisperse particles can be obtained in consequence of the short period of nucleation.

CONCLUSION

From the results described above, the emulsion polymerization of MMA in the emulsifier concentration below its CMC initiated by $K_2S_2O_8$ can be summarized as follows:

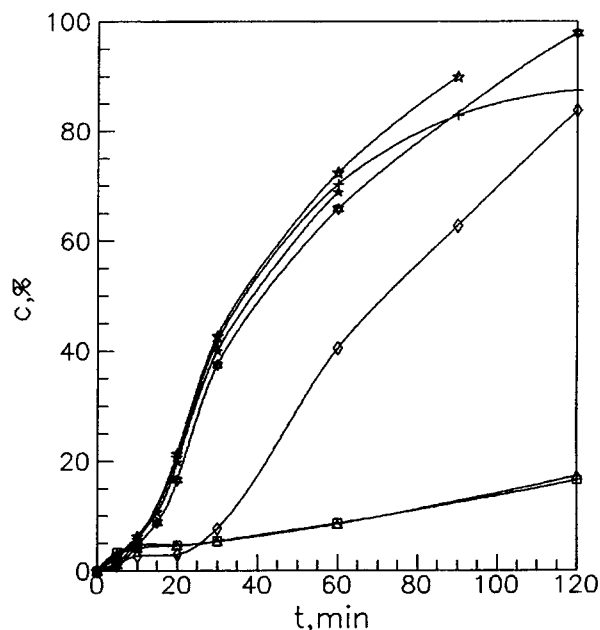


Figure 8 The effect of stirring speed on rate of emulsion polymerization: M , 100; H_2O , 500; I , 0.6; E , 0.8; $55^\circ C$. N (rpm): ($\square \square \square$) 600; ($\triangle \triangle \triangle$) 500; ($\diamond \diamond \diamond$) 450; ($\star \star \star$) 400; ($+++$) 350; ($\star \star \star$) 300; ($\odot \odot \odot$) 200.

1. The concentration of initiator has an insignificant effect on polymerization rate and particle size. As an increase in concentration of the emulsifier, the polymerization rate is faster and particle size is smaller. The ratio of H_2O /monomer and the temperature of polymerization exhibits a great influence on the polymerization rate and particle size. Increasing the ratio of H_2O/M and decreasing the temperature make the polymerization rate slower and particle size smaller. A suitable stirring speed is important for the polymerization and the stability of the latex.

Table VII The Effect of Stirring Speed on Particle Size and Particle-Size Distribution^a

	Stirring Speed (rpm)						
	200	300	350	400	450	500	600
dz (nm)	93.9	98.4	119.2	175.3	157.8	56.5	37.4
poly	0.068	0.054	0.059	0.024	0.062	0.124	0.266
dw/dn	1.190	1.123	1.178	1.075	1.180	1.350	1.820

^a Polymerization conditions are the same as in Figure 8.

2. The PMMA latex with monodisperse particles in size about 100–200 nm can be obtained by the emulsion polymerization of MMA in an emulsifier concentration below its CMC value.
3. A mechanism that the amount of MMA in an aqueous medium is the key factor to influence on polymerization rate and particle size is suggested.

This work was supported by the National Natural Science Foundation of China.

REFERENCES

1. S. Chen, J. Li, and Q. Ji, *Bull. Polym. (China)*, **3**, 129 (1991).
2. S. V. Bogdanova, Yu. V. Solovev, V. L. Eliseeva, and A. V. Zuikov, *Koll. Zh.*, **7**(4), 781–782 (1985).
3. D. Engel and H. Rinno, *Ger. Offen. DE 3,313,922* (1984).
4. W.-J. Wang, B.-G. Li, B.-F. Li, K. Cao, and Z.-Z. Yu, *Indust. Surfactants (China)*, to appear.

Received June 19, 1994

Accepted September 19, 1994