

KINETICS OF SUSPENDED EMULSION POLYMERIZATION OF METHYL METHACRYLATE*

Yong-zhong Bao**, Cheng-xi Wang, Zhi-ming Huang and Zhi-xue Weng
Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

Abstract The kinetics of suspended emulsion polymerization of methyl methacrylate (MMA), in which water acted as the dispersed phase and the mixture of MMA and cyclohexane as the continuous phase, was investigated. It showed that the initial polymerization rate (R_{p0}) and steady-state polymerization rate (R_p) were proportional to the mass ratio between water and oil phase, and increased as the polymerization temperature, the potassium persulphate concentration ($[I]$) and the Tween20 emulsifier concentration ($[S]$) increased. The relationships between the polymerization rate and $[I]$ and $[S]$ were obtained as follows: $R_{p0} \propto [I]^{0.73}[S]^{0.32}$ and $R_p \propto [I]^{0.71}[S]^{0.23}$. The above exponents were close to those obtained from normal MMA emulsion polymerization. It also showed that the average molecular weight of the resulting poly(methyl methacrylate) decreased as the polymerization temperature, $[I]$ and $[S]$ increased. Thus, MMA suspended emulsion polymerization could be considered as a combination of many miniature emulsion polymerizations proceeding in water drops and obeyed the classical kinetics of MMA emulsion polymerization.

Keywords Suspended emulsion polymerization, Methyl methacrylate, Polymerization rate, Average molecular weight and molecular weight distribution

INTRODUCTION

Suspended emulsion polymerization is a new polymerization process in which water acts as the dispersed phase and oil as the continuous phase. The polymerization starts in the water droplets as monomer dissolved in water and is initiated by a water-soluble initiator. The primary particles are formed through the emulsion polymerization mechanism and coagulate at the later polymerization stage due to the low colloidal stability of primary particles. As a result, porous polymer particles in supermicron size would be formed. Vindevoghel *et al.*^[1, 2] proposed the suspended emulsion polymerization process and applied this process to prepare porous poly(vinyl chloride) (PVC) and poly(acrylonitrile-butyl acrylate) particles. Bao *et al.*^[3] investigated the particle features and formation mechanism of PVC resin prepared by the suspended emulsion polymerization.

No efforts have been directed to the suspended emulsion polymerization of a monomer in which the corresponding polymer is soluble in its monomer. Methyl methacrylate (MMA) is a typical monomer which can dissolve its polymer and has a relatively high solubility in water^[4]. Thus, it is worth investigating the suspended emulsion polymerization of MMA.

The preparation of porous poly(methyl methacrylate) (PMMA) resin by the suspended emulsion polymerization process was reported in our previous paper^[5]. Influences of polymerization variables on the rate of MMA suspended emulsion polymerization and the average molecular weight of PMMA resin will be investigated in the present paper.

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** Corresponding author: Yong-zhong Bao (包永忠), E-mail: baoyz@che.zju.edu.cn

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EXPERIMENTAL

Materials

MMA was purchased from Dongfang Chemical Factory, Beijing, and distilled under reduced pressure before use. Cyclohexane (Hangzhou Shuanglin Chemical Factory) of analytical purity was used as a porogen. Potassium persulfate (KPS) with analytical purity was used as the initiator. Tween20 (Wenzhou Qingming Chemical Factory) with chemical purity was used as an emulsifier.

Polymerization

MMA polymerization was carried out in a 500 mL reactor equipped with a helix-belt agitator, a thermometer, a nitrogen inlet and a reflux condenser. Water, mixture of MMA/cyclohexane (mass ratio 1.0/1.2) and Tween20 were placed in the reactor and stirred for 15 min before polymerization. KPS solution was fed into the reactor when the content in the reactor reached the designed polymerization temperature, and polymerization proceeded under a nitrogen atmosphere. Samples of the reaction mixture were taken at suitable polymerization time intervals using a glass syringe for measuring the conversion of MMA by a weighing method.

Measurement of Average Molecular Weight and Molecular Weight Distribution of PMMA

The molecular weight and molecular weight distribution of PMMA was measured by using a Waters 150C GPC, equipped with three polystyrene gel columns (10^3 , 10^4 , 10^5 nm), at a flow rate of 1 mL/min in tetrahydrofuran at 25°C. Polystyrene standard samples with narrow molecular weight distribution were used as standards.

RESULTS AND DISCUSSION

Influence of the Initial Water/Oil Mass Ratio

Water acted as the dispersed phase suspended in the continuous oil phase with a drop size of 10 to 60 μm in the typical MMA suspended emulsion polymerization system^[5]. MMA polymerization mainly proceeded in the dispersed water drops through the emulsion polymerization mechanism because of the solubility of MMA in water and use of the water-soluble initiator. Although the final conversion of MMA was greater than 90% in most polymerizations, only at the initial and middle stages, polymerization conversions could be accurately determined by a weighing method, it is because the primary particles may coagulate at the later stage of polymerization.

The concentrations of KPS and Tween20 in water and the polymerization temperature were kept constant and the initial water/oil (including MMA and cyclohexane) mass ratio ($M_{\text{H}_2\text{O}}/M_{\text{oil}}$) was varied. Variations of polymerization conversion versus time with $M_{\text{H}_2\text{O}}/M_{\text{oil}}$ are shown in Fig. 1.

It can be seen that the polymerization rate is relatively low at the early stage of polymerization at different $M_{\text{H}_2\text{O}}/M_{\text{oil}}$. This is mainly caused by the dispersion of KPS in the monomer-containing water droplets since water is the dispersed phase in the suspended polymerization process. The polymerization is gradually accelerated after a short initial polymerization stage, due to the accumulation of free radicals. But the acceleration is not as obvious as that of normal emulsion polymerization of MMA since the volume fraction of water phase in the suspended emulsion polymerization process is lower than that in normal emulsion polymerization. After the polymerization conversion has become greater than 10%–15%, the polymerization enters into the steady state, in which polymerization time and conversion have a good linear relationship and the polymerization rate is almost constant. The initial polymerization rate (R_{p0}) and steady-state polymerization rate (R_p) could be obtained by fitting the experimental data. Dependences of R_{p0} and R_p on $M_{\text{H}_2\text{O}}/M_{\text{oil}}$ are shown in Fig. 2.

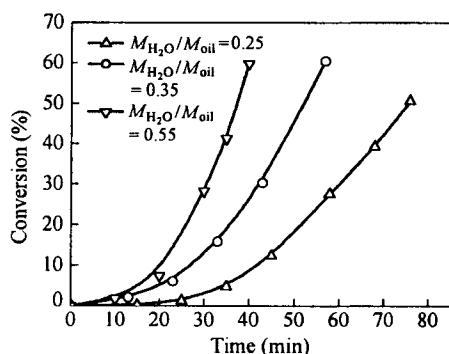


Fig. 1 Variations of polymerization conversion with time at different M_{H_2O}/M_{oil}
 $[KPS] = 8.89 \text{ mmol/L}$, $[Tween20] = 4.76 \text{ mmol/L}$,
 Temperature = 70°C

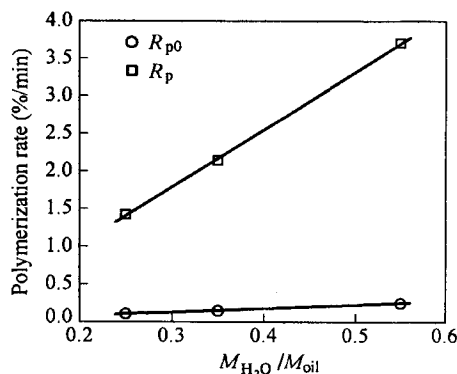


Fig. 2 Dependences of R_{p0} and R_p on M_{H_2O}/M_{oil}
 $[KPS] = 8.89 \text{ mmol/L}$, $[Tween20] = 4.76 \text{ mmol/L}$,
 Temperature = 70°C

It can be seen that R_{p0} and R_p are proportional to M_{H_2O}/M_{oil} , which means that polymerization proceeds separately in the dispersed water drops that acted as micro-reactors, and the overall polymerization rate is the sum of the polymerization rates of all water drops.

Influences of Polymerization Temperature

Variations of polymerization conversion versus time with the polymerization temperature are shown in Fig. 3. It can be seen that the polymerization rate increases with increasing temperature. This is caused by the increasing decomposition rate of initiator and increasing monomer solubility in the aqueous phase on raising the temperature.

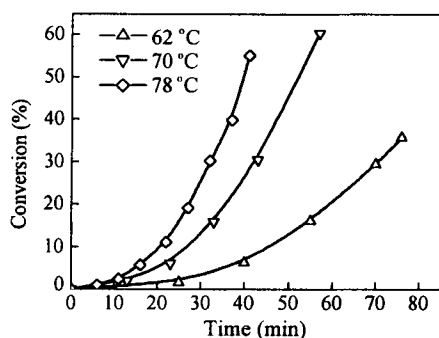


Fig. 3 Variation of polymerization conversion versus time at different polymerization temperatures
 $M_{H_2O}/M_{oil} = 0.35$; $[KPS] = 8.89 \text{ mmol/L}$;
 $[Tween20] = 4.76 \text{ mmol/L}$

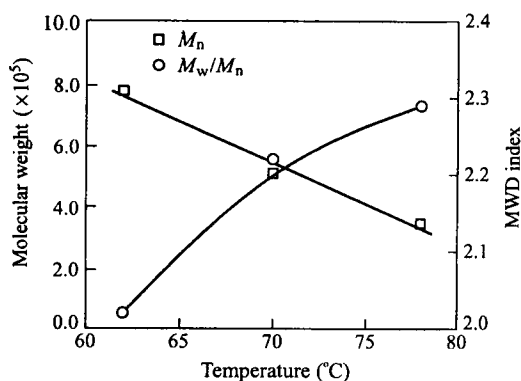


Fig. 4 Influence of polymerization temperature on M_n and M_w/M_n of PMMA
 $M_{H_2O}/M_{oil} = 0.35$; $[KPS] = 8.89 \text{ mmol/L}$;
 $[Tween20] = 4.76 \text{ mmol/L}$

Influences of polymerization temperature on the number average molecular weight (M_n) and molecular weight distribution (MWD) index (M_w/M_n) of resulting PMMA are shown in Fig. 4. From Fig. 4, it can be seen that the M_n of the resulting PMMA is high and close to that of PMMA prepared by the normal emulsion polymerization, and M_n decreases as the polymerization temperature increases. It can also be seen that the MWD index is close to 2.0 and increases slowly as the polymerization temperature increases.

Influence of KPS Concentration

The polymerization temperature, M_{H_2O}/M_{oil} and the concentration of Tween20 were kept constant, and the concentration of KPS initiator was varied. Influences of the KPS concentration on polymerization conversion versus time curves, and on R_{p0} and R_p , are shown in Fig. 5 and Fig. 6, respectively.

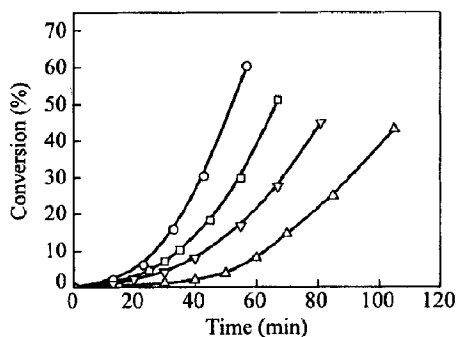


Fig. 5 Variation of polymerization conversion versus time at different KPS concentrations
[Tween20] = 4.76 mmol/L; Temperature = 70°C;
 M_{H_2O}/M_{oil} = 0.35

○ $K_2S_2O_8$ 8.89 mmol/L; □ $K_2S_2O_8$ 4.44 mmol/L;
▽ $K_2S_2O_8$ 2.96 mmol/L; △ $K_2S_2O_8$ 1.48 mmol/L

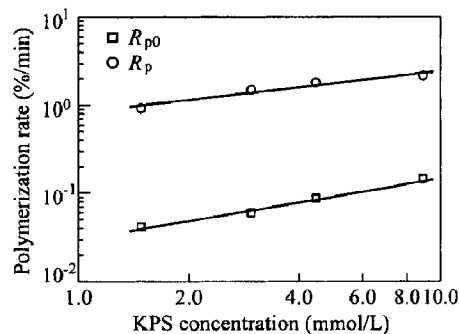


Fig. 6 Effect of KPS concentration on R_{p0} and R_p
[Tween20] = 4.76 mmol/L; Temperature = 70°C;
 M_{H_2O}/M_{oil} = 0.35

From Fig. 5, it can be seen that the polymerization rate increases as the KPS concentration ($[I]$) increases. Since increasing $[I]$ increases the radical to monomer molar ratio, this trend is expected. From Fig. 6, it can be seen that $\lg R_{p0}$ and $\lg R_p$ have good linear relationships with $\lg [I]$ and the following relationships can be obtained:

$$R_{p0} \propto [I]^{0.73}, R_p \propto [I]^{0.71}$$

The obtained exponents are very close to that obtained from normal MMA emulsion polymerization^[6], which indicates that MMA suspended emulsion polymerization obeys the classical mechanism of normal MMA emulsion polymerization.

Influences of KPS concentration on M_n and M_w/M_n of resulting PMMA are shown in Fig. 7. It can be seen that M_n decreases as the KPS concentration increases. MWD indexes of PMMA are close to 2.0 and increase slowly as the KPS concentration increases.

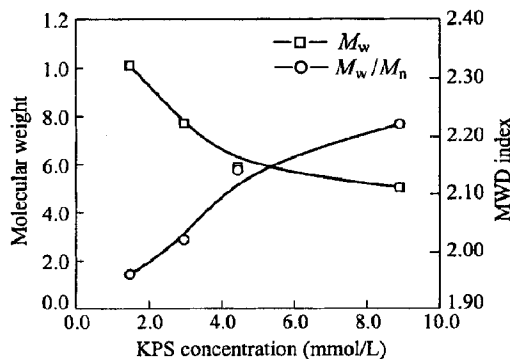


Fig. 7 Influences of KPS concentration on M_n and M_w/M_n of PMMA
[Tween20] = 4.76 mmol/L; Temperature = 70°C; M_{H_2O}/M_{oil} = 0.35

Influence of Tween20 Concentration

MMA suspended emulsion polymerizations were carried out with no emulsifier and at different Tween20 concentrations. The polymerization conversion versus time plots and the influence of Tween20 concentration ([E]) on R_{p0} and R_p are shown in Fig. 8 and Fig. 9, respectively.

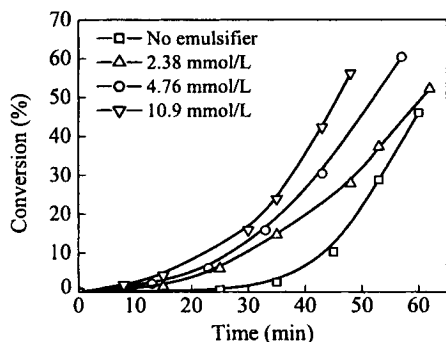


Fig. 8 Variations of polymerization conversion versus time at different Tween20 concentrations $[K_2S_2O_8] = 8.89$ mmol/L; Temperature = 70°C; $M_{H_2O}/M_{oil} = 0.35$

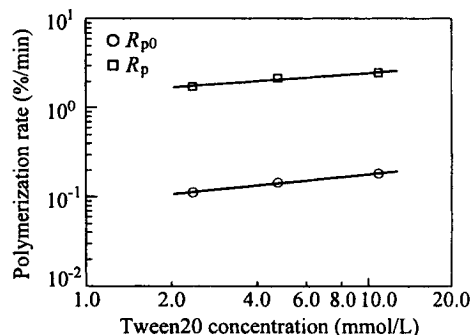


Fig. 9 Influence of Tween20 concentration on R_{p0} and R_p $[K_2S_2O_8] = 8.89$ mmol/L; Temperature = 70°C; $M_{H_2O}/M_{oil} = 0.35$

Compared to the polymerization system with Tween20, R_{p0} of the emulsifier-free MMA suspended emulsion polymerization is lower and R_p is higher. The colloidal stability of PMMA primary particles was poor in emulsifier-free polymerization and they were coagulated at a relatively low conversion. The lifetime of radicals would be increased and the acceleration of polymerization becomes significant.

From Fig. 9, it can be seen that $\lg R_{p0}$ and $\lg R_p$ have good linear relationships with $\lg[E]$ and the following relationships can be obtained:

$$R_{p0} \propto [E]^{0.32}, R_p \propto [E]^{0.23}$$

The obtained exponent is also close to that obtained from normal MMA emulsion polymerization^[6], and it means that the influence of Tween20 concentration on polymerization rate is not significant.

Influences of Tween20 concentration on M_n and M_w/M_n of resulting PMMA are shown in Fig. 10. It can be seen that M_n and M_w/M_n of PMMA decreases as Tween20 concentration increases.

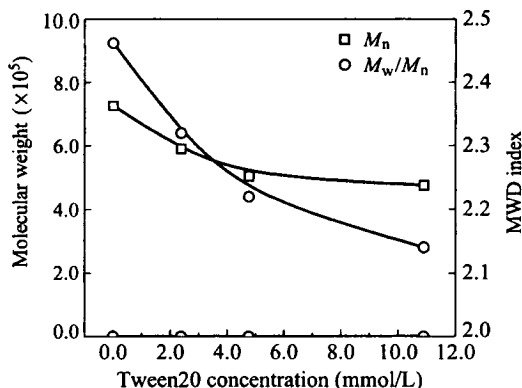


Fig. 10 Influence of Tween20 concentration on M_n and M_w/M_n of PMMA $[K_2S_2O_8] = 8.89$ mmol/L; Temperature = 70°C; $M_{H_2O}/M_{oil} = 0.35$

CONCLUSIONS

The kinetics study on MMA suspended emulsion polymerization showed that the initial and steady-state polymerization rates were proportional to M_{H_2O}/M_{oil} , and had the following relationships with KPS concentration ([I]) and Tween20 concentration ([S]): $R_{p0} \propto [I]^{0.73}[S]^{0.32}$ and $R_p \propto [I]^{0.71}[S]^{0.23}$. The polymerization rate also increased with increasing polymerization temperature. The average molecular weight of the resulting PMMA resins decreased as the polymerization temperature, [I] and [S] increased. MMA suspended emulsion polymerization can be considered as a combination of many miniature emulsion polymerizations proceeding in the dispersed water drops and obeys a polymerization mechanism similar to that of normal MMA emulsion polymerization.

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