CHANGE OF SIZE DISTRIBUTION OF POLYMER DROPLETS DURING THE SLURRY POLYMERIZATION OF STYRENE WITHIN ISOCTANE DROPLETS SUSPENDED IN WATER

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Introduction

Styrene slurry polymerization within isooctane droplets suspended in water would be a useful microcapsule preparation method by *in situ* polymerization.¹⁾ At the present time, this procedure shows no reproducible result at complete monomer conversion. This is caused by extremely low polymerization rates above 90% monomer conversion and the fluid property of the polymer shell of microcapsules. However, such a defect would be overcome by a charging initiator and/or hardening agent in the course of the polymerization. So, it is very important to know the behavior of polymer droplets during this polymerization.

In this study, the effect of important operating variables such as mixing rate and volume fraction of dispersed organic phase on the change of size distribution of polymer droplets with conversion were investigated to clarify the quantitative relationship between operating conditions and polymer droplets.

1. Experimental

1.1 Reagent

Reagents used in this work were prepared by the same method as mentioned previously.^{1,2)}

1.2 Experimental apparatus and procedure

The same experimental apparatus as described in the previous paper¹⁾ was employed, where the reactor was a 1000-ml separable flask with four baffle blades having a width of 1/10 the reactor diameter.

The experimental procedure is described below. Prescribed amounts of water and isooctane were charged into the reactor and the temperature in the reactor was raised to 70°C at a given rotation rate.

The initiator α, α' -azobisisobutyronitrile (AIBN) was dissolved in a prescribed amount of styrene and was rapidly introduced into the reactor. From this time samples were taken at regular intervals. Microphotographs of the samples were taken to obtain the size distribution of polymer droplets. That is, the sample dropped in 5 wt% PVA aqueous solution on a glass plate was photographed with a microscope of 150-fold magnification. Each droplet in the photo was directly measured with a ruler. About 500 droplets were inspected for each sample. The Sauter average diameter of droplets was determined from the following equation.

$$\bar{d}_{p32} = \frac{\sum n_i d_{pi}^3}{\sum n_i d_{pi}^2} \quad (1)$$

Size distribution of polymer droplets based on weight was calculated.

2. Results and Discussion

Experimental conditions are shown in Table 1.

To investigate the effect of rotation rate on the Sauter average diameter, the relations of $\bar{d}_{p32}$ vs. conversion under the range of rotation rates from 450 to 1400 rpm are shown in Fig. 1. $\bar{d}_{p32}$ values of 30–60 μm were obtained in the initial part of the reaction, which is reasonable in the range from 1400 to 450 rpm according to the following equation of Vermeulen *et al.*⁵⁾

$$\frac{\bar{d}_{p32}}{D} = 0.055(1 + 3.3\psi)We^{-0.6} \quad (2)$$

It is evident that the average diameter decreases clearly with increasing revolution rate and the average diameter increases with conversion except for the experiment at 1400 rpm. This peculiar relationship at 1400 rpm may be due to the increasing production of extremely minute droplets with polymerization.

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Table 1. Experimental conditions

Run No.	A_0 [mol/l]	I_0 [mol/l]	ψ_0 [—]	Rev. rate [min ⁻¹]	PVA [wt%]	Recipe for each run			
						Styrene [g]	Isooctane [g]	AIBN [g]	Water [g]
3	5.15	0.051	0.16	650	0.1	77.2	35.9	1.21	739
9	5.13	0.051	0.038	650	0.1	18.3	8.58	0.286	941
4	3.01	0.060	0.14	650	0.1	39.5	52.8	1.24	841
58	3.00	0.060	0.14	450	0.1	39.4	52.9	1.24	841
59	3.00	0.060	0.14	1000	0.1	39.4	52.9	1.24	841
60	3.00	0.060	0.14	1400	0.1	39.4	52.9	1.24	841

Fig. 1. Effect of rotation rate on average diameter. (Square keys are calculated by Eq. (2) using initial conditions. Each rotation rate used for calculation is shown for each key.)

The effects of rotation rate on size distribution of droplets at $A_0 = 3.0$ mol/l are shown in Fig. 2. Here, IS, MS and FS represent the initial reaction stage (conversion 0–10%), medial reaction stage (conversion 50–60%) and final reaction stage (conversion 80–90%), respectively. As predicted from the above-mentioned result of the average diameter, the size distributions of droplets shift to the left with increasing rotation rate. At 1400 rpm, extremely minute droplets are found to occupy a much larger part at the medial stage of reaction than at the initial stage. The droplet size distribution in the initial reaction stage exhibits the sharp normal distribution. However, the normal distribution could not be predominant in the later stage because of the complicated coalescence and redispersion behavior of viscous droplets with increasing conversion.

The relations of $\bar{d}_{p32}$ vs. conversion in the range of dispersion phase volume fraction from 0.04 to 0.16 is shown in Fig. 3 to demonstrate the effect of dispersion

Fig. 2. Effect of rotation rate on droplet size distribution.

Fig. 3. Effect of dispersion phase volume fraction on average diameter. (Square keys are calculated by Eq. (2) using initial conditions. Each dispersion phase volume fraction is shown for each key.)

phase volume fraction on the average diameter. It is evident that the average diameter increases with increasing dispersion phase volume fraction and monomer conversion.

The effect of dispersion phase volume fraction on droplet size distributions at $A_0 = 5.1$ mol/l is shown in

Fig. 4. Effect of dispersion phase volume fraction on droplet size distribution.

Fig. 4. The size distribution shifts to the right with increasing dispersion phase volume fraction, and becomes broader as the polymerization proceeds.

Conclusions

To clarify the behavior of polymer droplets in styrene slurry polymerization within suspended isooc-tane droplets in water, the Sauter average diameter and size distribution of polymer droplets were studied. The following results were obtained.

1) Although a polymer shell would be formed around each droplet in the course of the polymerization,¹⁾ almost the same effects of rotation rate and dispersion phase volume fraction as in suspension polymerization^{3,4)} were observed for the change of droplet size with conversion. The average diameter greatly decreases with rotation rate and slightly increases with dispersion phase volume fraction.

2) The normal size distribution is predominant for droplets in the initial reaction stage. However, in the later stage of reaction, such a normal size distribution is not maintained any longer due to complicated behavior of droplets with different redisper-

sion and coalescence rates and polymerization rates.

Nomenclature

A	= monomer concentration in dispersed phase	[mol/l]
D	= 0.05, impeller diameter	[m]
$\bar{d}_{p32}$	= Sauter average diameter	[μ m]
I	= initiator concentration in dispersed phase	[mol/l]
PVA	= polyvinyl alcohol concentration in water phase	[mol/l]
We	= Weber number	[—]
ψ	= dispersion phase volume fraction	[—]

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