EFFECT OF ULTRASONIC IRRADIATION ON DISPERSED POLYMER DROPLETS IN WATER

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ABSTRACT

A condition of 30 to 50 % monomer conversion in styrene suspension polymerization was approximated by dispersing toluene containing 30 to 50 wt% polystyrene in water.
The size distribution of those polymer droplets, in which no polymerization occurs, was measured under conditions of ultrasonic irradiation and of no irradiation to obtain more detailed information about viscous droplets in a stirred tank reactor under ultrasonic irradiation.

The ultrasonics caused a comparatively strong cohesive effect on the droplets over the whole range of experimental conditions. The effects of viscosity and PVA concentration on the size of droplets, however, was found to be the same under ultrasonic irradiation as under no irradiation.

Introduction

In the suspension polymerization process, dispersed polymer droplets coalesce and re-disperse enormously in the reactor, and have a certain "stable" average size balanced by the coalescence and re-dispersion.[1,3,4]
Under insufficient mechanical mixing or too low interfacial stabilizer concentration, however, polymer droplets would be unstable, proceeding to a sticking to the impeller and reactor wall, and/or proceeding to a caking phenomena, in which they lump together. Ultrasonic irradiation seems to be an effective method to prevent such phenomena.
In the previous reports,[2] such an effect has been demonstrated by carring out the styrene suspension polymerization under ultrasonic irradiation. At the same time the ultrasonics have been revealed to have an agglomeration effect over the whole range of the operating conditions. However, it is considered that the effect of changes of physical properties occuring with polymerization, especially such as the effect of viscosity of dispersed droplets on size distribution of polymer droplets, is not negligible. The size distribution of polymer droplets on the way of polymerization might be different from that at steady state.

In this study, to know the effect of the ultrasonics on the polymer droplets at steady state, the droplets size distribution in the system of dispersed toluene containing a fixed amount of polystyrene in water was measured under ultrasonic irradiation and no irradiation conditions.
The effects of viscosity and polyvinyl alcohol (PVA) concentration on the size of droplets were also investigated under both ultrasonic irradiation and no irradiation.

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1. Experimental

Styrene (St) , water, toluene, N, N'-azobisisobutyronitrile (AIBN) used as reagent were purified by the same method as mentioned previously.[21] The schematic diagram of the experimental apparatus is shown in Fig. 1. The source of ultrasonics employed was a Cho-Onpa Kogyo

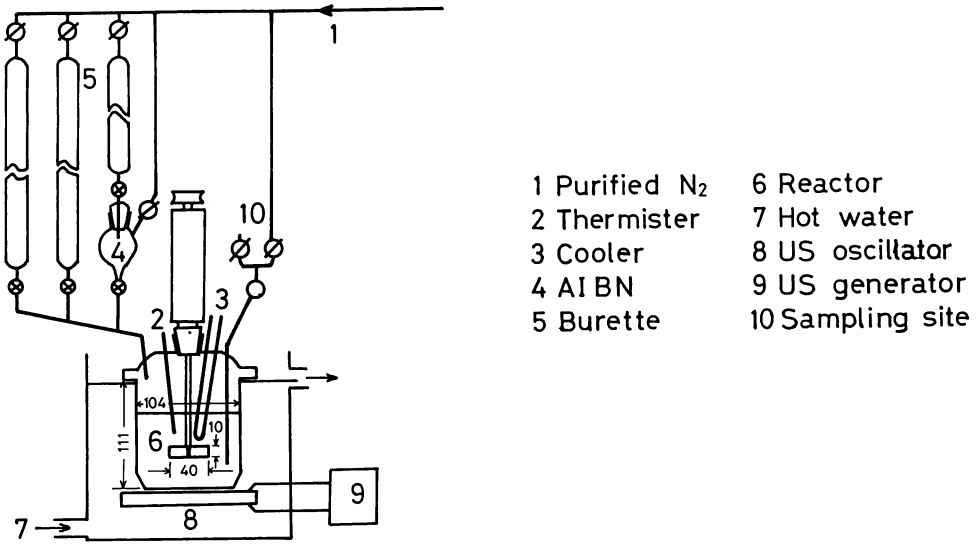

Fig. 1 Experimental apparatus

Co. Ultrasonics Generator, Model USV-500V, and the transducer element was barium-titanate disk. The reactor used was a separable flask of inner volume 600 ml. Ultrasonic radiation was irradiated from the transducer element to the bottom of the reactor.

Preparation of polymer solution Using toluene as solvent, whose physical property is very similar to that of styrene monomer, solution polymerization of styrene was carried out for about 20 hrs at 70 ℃ to complete the polymerization under the conditions shown in Table 1.

Table 1 Reaction conditions for the preparation of polymer solution

Reaction temperature	=70℃
Styrene mole fraction in solution	=0.37, 0.47, 0.60 and 0.69 [−]
Initiator concentration in solution	=0.0600 kmol/m³

The polymer weight fraction was calculated by regarding the residual St as a solvent as well as toluene.

Experimental procedure A toluene solution of 85.7 ml containing a fixed amount of polystyrene prepared by the method mentioned above, PVA aqueous solution of concentration of 10 kg/m³ and water were poured into the separable flask. (Volume ratio of the dispersed phase to the continuous one was 1/6.) After the system attained steady state operational conditions, a sample was taken and rapidly moved by pipette to a watch-glass containing PVA aqueous solution of concentration 50 kg/m³. Photographs of the sample were taken directly by camera or through the microscope to obtain the size distribution of polymer droplets.

2. Result and Discussion

The measurements of the net ultrasonic energy were carried out by the calorimetric method in the range of 200 to 800 KHz in frequency. 400 KHz was found to show a maximum. The observed rates of input energy at 400 and 200 KHz adopted here as ultrasonic frequencies were respectively 69.8 and 23.2 J/s.

The experimental conditions are shown in Table 2.

Table 2 Experimental conditions

Temperature	=70℃
Ultrasonic frequency	=200 and 400 KHz
PVA concentration	=0.03, 0.05 and 0.1 wt%
Rotational speed	=6.17, 8.83 and 10.7 s^{-1}

2.1. Measurement of size distribution of dispersed toluene droplets containing polystyrene

The physical properties of the solutions are listed in Table 3. From preliminary experiments, it was confirmed that steady state size distributions of polymer droplets are attained 30 min after stirring.[4]

Table 3 Physical properties of polymer solutions at 70℃

Liquid	ϕ* [−]	ρ [kg/m³]	μ [g·cm/s]	σ [g/s²]	PVA conc [wt%]
A	0.36	0.8939	0.0683	28.8	0
				14.6	0.03
				12.1	0.05
				11.4	0.10
B	0.45	0.9175	0.274	27.8	0
				14.1	0.03
				11.1	0.05
				9.05	0.10
Toluene		0.8200	0.00438	30.7	0
				15.5	0.01
				14.0	0.03
				12.6	0.05
				10.4	0.10
Styrene		0.8638	0.00461	30.9	0
				12.4	0.03
				10.8	0.05
				10.4	0.10
Water		0.9779	0.00406		0
		0.9785	0.00440		0.10

* : Polystyene weight fraction in solution

Relation between the Sauter average size of droplets and rotational speed under both ultrasonic irradiation and no irradiation for a PVA concentration of 0.1 wt% is shown in Fig. 2.

The dotted lines in the figure represent values calculated from the following correlation representing the average size of droplets under no irradiation.[5]

$$\frac{\bar{d}_{p32}}{D}=\frac{0.0583}{f\cdot f_{\phi}}N_{we}^{-0.75}N_{Fr}^{-0.2}\left(\frac{\mu_d}{\mu_c}\right)^{0.13} \quad (1)$$

It is found from the figure that the size of droplets under ultrasonic irradiation is considerable larger due to the cohesion effect of ultrasonics compared with that under no irradiation, and that the effect

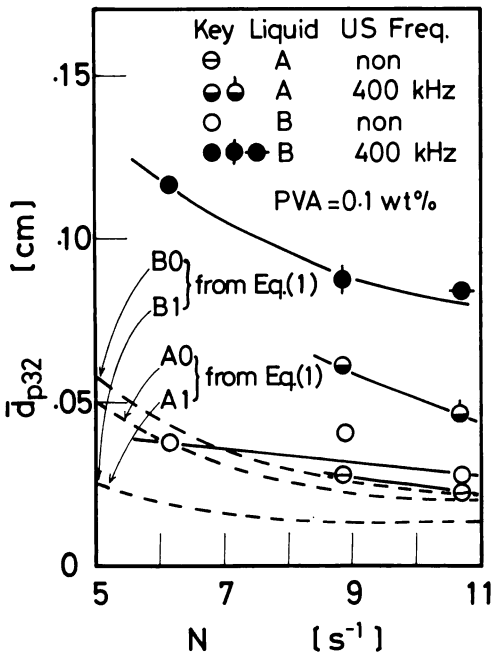

Fig. 2 Effect of ultrasonic irradiation on $\bar{d}_{p32}$ using polymer solutions as dispersed phase (A0, A1 : Solution A, and no PVA and 0.1 wt% PVA, respectively, B0, B1:Solution B, and no PVA andl 0.1 wt% PVA, respectively)

of viscosity on the size of droplets under ultrasonic irradiation is more profound than that under no irradiation. For each plot under ultrasonic irradiation in Fig. 2, the normal probability plot is examined in Fig. 3. From the figure, the size distribution of toluene droplets containing polystyrene

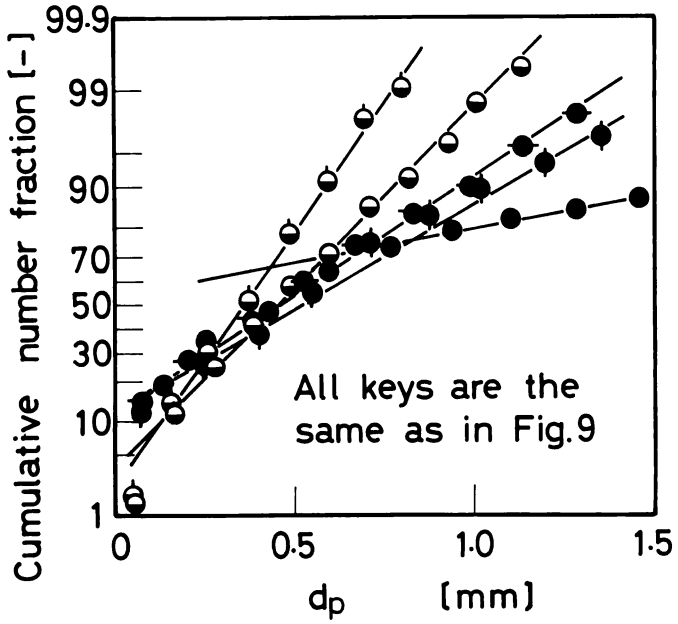

Fig. 3 Normal probability plot of droplets size distribution under ultrasonic irradiation

at steady state under ultrasonic irradiation is found to be approximated by the normal distribution as well as that of polymer droplets in progress of polymerization except for the case of N=6.17 rps.

The effect of PVA concentration on the average size of droplets under both ultrasonic irradiation and no irradiation is shown in Fig. 4 with polymer solution A. It is found from the figure that the average size of droplets is scarcely affected by PVA concentrations in the range of this

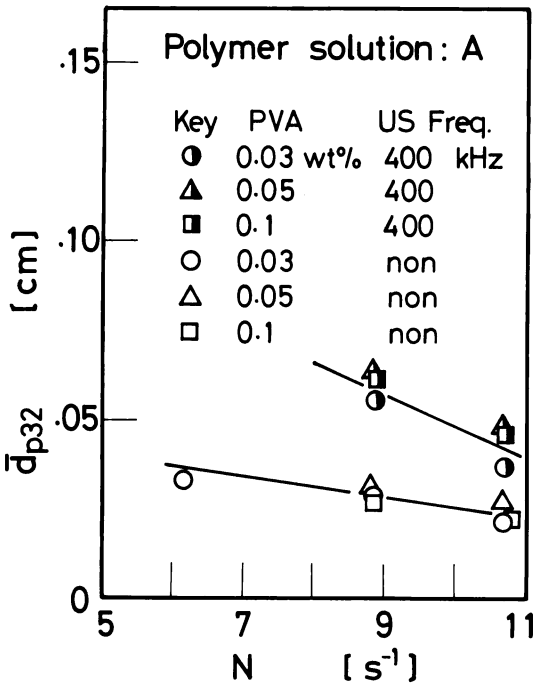

Fig. 4 Effect of PVA concentration on $\bar{d}_{p32}$ using Solution A as dispersed phase

experiment. As might be expected from Eq. (1), the size of droplets is significantly affected by the interfacial tension. From the fact that the interfacial tension of the polymer solution is scarcely affected by the PVA concentrations in the range 0.03～0.1 wt% as shown in Table 3, the above mentioned tendency of average droplet size seems to be not so surprising.

2. 2. Effect of micro-dispersion on size distribution of droplets

Because the size distributions of droplets described so far were obtained from camera photographs, the information on small droplets of 10－20 μm in size is doubtful.

The physical properties of the polymer solution used for microscopic measurements are shown in Table 4. Representative examples of size distribution of droplets obtaines by microscopy are shown in Fig. 5. As seen in this figure, it is found a considerable amount of micro-dispersion dro-

Table 4 Property of a polymer solution used for a micro photography

Polymer wt. fraction*	=0.40	[－]
Density at 70℃	=0.9077	kg／m^3
Viscosity at 70℃	=0.448	g·cm／s
Interfacial tension against water containing 0.1 wt% PVA at 70℃		
	=11.3	g／s^2

* Prepared from diluting the polymer solution containing 0.72 polystyrene in weight as shown in Table 1 with toluene

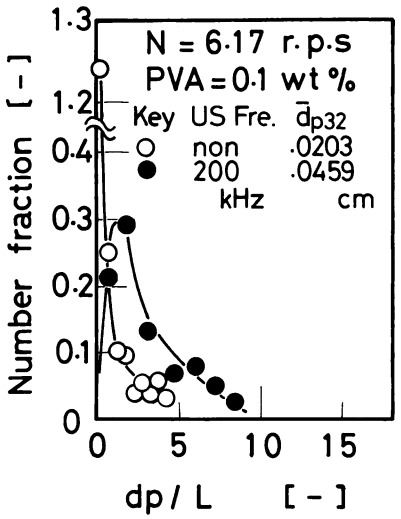

Fig. 5 Comparison of droplets size distribution under ultrasonic irradiation with that under no irradiation by microscopy

plets of 10~20 μm exist, and that the distribution might have a tendency to show a twin peak.[3]

The size distribution of polymer droplet in this case is complicated and it conforms to neither normal distribution nor logarithmic normal distribution. As expressed above, the result obtained by microscopy is apparently considerably different from that by direct photography using a camera.

However, considering that the polymer droplets under ultrasonic irradiation range from 0.5 to 1.0 mm in average size, the difference between microscopy and direct photgraphy is not of practical importance except in microscopy the number of micro-dispersion droplets below 10 μm can be detected.

Conclusion

Effects of ultrasonic irradiation on the size distribution of polymer droplets at steady state were investigated using polymer solution of polystyrene content of 36 and 45 weight percent.

The following results were obtained.

1) The size of droplets under ultrasonic irradiation is considerable larger due to the cohesion effect of ultrasonics compared with that under no irradiation.

2) The size distribution of polymer droplets conforms approximately to a normal distribution as well as that of polymer droplets in progress of polymerization.

3) The effects of viscosity and PVA concentration on the size of droplets are the same under ultrasonnics irradiation as under no irradiation.

Nomenclature

A, B= polymer solutions

D= impeller diameter [cm]

d_p= droplet size [mm]

$\bar{d}_{p32}$= Sauter average size [cm]

f= a factor related to the effect of the size limit in dispersion [−]
f_ϕ= a factor related to the effect of the volume fraction of dispersed phase [−]
g= gravitational acceleration [cm/s^2]
L= length for normalization (=0.1 mm) [mm]
N= rotational speed [s^{-1}]
N_{Fr}= Froude number ($=DN^2/g$) [−]
N_{we}= Wever number ($=DN\rho/\sigma$) [−]
μ_c, μ_d= viscosities of continuous and dispersed phases, respectively [g·cm/s]
ρ_c, ρ_d= densities of continuous and dispersed phases, respectively [g/cm^3]
σ= interfacial tension [g/s^2]

Acknowledgment

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