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Title: Effect of Ultrasonic Pretreatment on Emulsion Polymerization of Styrene

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Abstract

This study investigated the effect of pretreatment of ultrasonic irradiation on emulsion polymerization of styrene to propose a process intensification method which gives high conversion, high reaction rate, and high energy efficiency. The solution containing styrene monomer was irradiated by a horn mounted on the ultrasonic transducer with the diameter of 5 mm diameter and the frequency of 28 kHz before starting polymerization. The pretreatment of ultrasound irradiation as short as 1 min drastically improved monomer dispersion and increased reaction rate even under the agitation condition with low rotational speed of impeller. Furthermore, the ultrasonic pretreatment resulted in higher monomer concentration in polymer particles and produced larger polymer particles than conventional polymerization without ultrasonic pretreatment.

Keywords: Emulsion polymerization; Process intensification; Function modules; Compartment reactor; Smith-Ewart theory; Partition equilibrium

1. Introduction

Process intensification brings technological innovations to drastically enhance energy efficiency and process performance, thus contributing toward a sustainable society. In chemical industries, reactors, which are the heart of chemical processes, have received more attention than other unit operations in the context of intensification. Stankiewicz and Moulijn [1] divided process intensification into two areas, i.e. process-intensifying equipment and process-intensifying methods. Among the process-intensifying methods, alternative energy sources such as centrifugal fields, ultrasound, solar energy, microwaves etc. are one of the promising methods for future process intensification. Particularly, the use of ultrasound as a source of energy for chemical processing has the potential for development of an innovative chemical process. Cavitation causing the formation, growth and implosion collapse of microbubbles can create high local energy with temperature of up to 5000 K and negative pressure of up to 10000 atm [1-3]. Furthermore, low-frequency ultrasound can exert some physical effects such as enhanced mass transport, emulsification and so on.

Emulsion polymerization which is a heterogeneous reaction system can be intensified by ultrasound irradiation. The cavitation produces radicals and emulsion polymerization can be conducted without adding initiator. Ooi and Biggs [4] showed that the monomer conversion could be achieved up to 90% without initiator using a horn-type ultrasound device in the emulsion polymerization of styrene. Kobayashi *et al.* [5] evaluated performance of emulsion polymerization of styrene using a bath-type ultrasonic equipment under no initiator conditions. Although applying ultrasound is hopeful for emulsion polymerization, continuous irradiation is rather wasteful for energy consumption. Most of the input energy by ultrasound irradiation is converted to thermal energy to simply rise the liquid temperature. As Stankiewicz and Moulijn [1] pointed out, therefore, the maximum economically and technically feasible size and shape of the reactor are still unresolved issue. This problem is interfering industrial applications of ultrasound device for emulsion polymerization.

Conventional emulsion polymerization processes often encounter deceleration of reaction rate due to unstable monomer dispersion which results in enlargement of monomer droplet size and phase separation due to coalescence of monomer droplets. In order to avoid the deceleration of reaction rate, higher agitation speed is required. However, higher agitation speed causes another problem, i.e. polymer coagulation due to high shear. Yatomi *et al.* [6] showed that amount of coagulation in the emulsion polymerization depended on required power of an agitation impeller, and optimal required power existed. This indicates how to obtain stable monomer dispersion is a critical issue in the emulsion polymerization.

In this study, emulsification ability of ultrasound was focused on because even a short time irradiation could produce highly stable dispersion state of monomer droplets. Ultrasound irradiation for a very short time was carried out before emulsion polymerization as pretreatment. This operation leads to high energy efficiency. Monomer dispersion can be maintained even at low agitation speed by ultrasonic pretreatment. Furthermore, the effect of size and shape of reactor on emulsion polymerization are independent of ultrasound irradiation condition. This study investigated the effect of ultrasonic pretreatment on reaction kinetics of emulsion polymerization of styrene to propose a process intensification method which gives higher conversion, faster reaction rate, less coagulation and higher energy efficiency.

2. Experimental

Figure 1 presents a schematic of the experimental apparatus. Styrene monomer (special grade, Wako Pure Chemical Industries, Ltd.) was washed with 10% NaOH three times to remove the inhibitor (p-tert butylcatechol), followed by three washes with distilled water. Distilled water of 180 mL, sodium dodecyl sulfate of 0.5 g (first grade, Wako Pure Chemical Industries, Ltd.) and the styrene monomer of 10 mL were added into a beaker. Before starting each experiment, dissolved oxygen in aqueous mixture of emulsifier and initiator was completely expelled by feeding nitrogen gas for sufficient time. The solution in a beaker was irradiated by a horn type ultrasonic device (SONAC-150, Honda Electronics Co., Ltd.) with the diameter of 5 mm diameter and the frequency of 28 kHz. After this pretreatment, the solution was poured into the cylindrical glass reactor with volume of 200 mL. The reactor was equipped with a water jacket to keep the reaction temperature 60 ±1°C. Reaction was started by adding aqueous potassium persulfate of 10 mL (2.9 wt %) (special grade, Kanto Chemical Co., Inc.). The 2-bladed turbine impeller was used at all experiments. The rotational speed of the impeller was varied from 250 rpm to 1000 rpm. Samples were taken for analysis at predetermined time. Polymerization in each sample was stopped by adding hydroquinone (special grade, Wako Pure Chemical Industries, Ltd.).

Monomer conversion was determined by measuring the mass of coagulated latex particles after adding an aqueous solution of aluminum (III) chloride hexahydrate (2.5 $kg\cdot m^{-3}$) (special grade, Wako Pure Chemical Indstries, Ltd.), rinsing with distilled water and drying. The PSD was obtained using a laser-diffraction particle-size analyzer (ELSZ-2, Otsuka Electronics Co., Ltd.) on a number basis for percentage.

3. Results

3.1 Stability of emulsified monomer solution

Figure 2 shows the pictures of emulsified monomer solution at different elapsed time after ultrasonic irradiation. The ultrasonic pretreatment made fine droplets of styrene monomer and the emulsified solution became completely clouded. Although coalescence of monomer droplets occurred and phase separation between monomer and water gradually proceeded, sufficient monomer dispersion can be obtained even after 8 h since ultrasonic irradiation. Monomer droplets gradually floated on water with time courses. After about 48 h, water and monomer almost completely separated. Figure 3 shows time variation of monomer droplets diameter, d_m [μm], as a function of irradiation time. The diameter of monomer droplets slightly increased for 30 min in all cases. As shown in Fig. 3, the longer ultrasound was irradiated, the finer monomer droplets became. Consequently, the growth rate of droplet diameter in the case of longer irradiation was slower. Although slight difference of droplet size could be seen among three cases, even short irradiation made the droplet diameter sufficiently small to obtain stable emulsified state when reaction time of emulsion polymerization was taken into consideration.

3.2 Reaction rate and estimation of energy consumption

Figure 4 shows the time variation of monomer conversion as functions of ultrasound irradiation time and rotational speed of impeller. In the case without ultrasonic pretreatment (Fig. 4 a)), at lower rotational speed of impeller than 750 rpm, weak shear force by the slow impeller rotation induced rapid coalescence of monomer droplets and floating layer of monomer was formed. As a result, final monomer conversion did not reach 100%. On the other hand, at higher rotational speed of impeller than 750 rpm, monomer floating layer was not formed and the monomer was completely consumed and the conversion reached 100%. Although the final conversion values were different between lower and higher rotational speed of impeller, the initial reaction rate was almost the same. One should note that reaction rate was also increased by ultrasonic pretreatment. In the case of the various ultrasonic pretreatment time (Fig. 4 b)), the insufficient dispersion resulted in lower conversion when the irradiation time was less than 30 s. In contrast, ultrasonic pretreatment more than 1 min led to the 100 % conversion of monomer even at 250 rpm due to good dispersion of monomer, and there was little difference for the longer pretreatment than 1 min. Furthermore, in the case with ultrasonic pretreatment, the reaction rate was independent of rotational speed of impeller.

Here we measured electric power supplied to the system, E [g/J], defined as the following equation:

$$E = \frac{x}{e_{\mathrm{u}} t_{\mathrm{u}} + e_{\mathrm{r}} t_{\mathrm{r}}} \tag{1}$$

where x [g] is polymer yield, e_{u} [W] and e_{r} [W] are the electric power consumption rates required by ultrasonic irradiation and agitation respectively, and t_u [s], t_r [s] are the duration time of ultrasonic irradiation and agitation respectively. The electric power consumption rates were measured by an electrical power meter (TAP-TST5, SANWA SUPPLY). Figure 5 shows the polymer yield per consumption energy when the monomer conversion reached 80%. As can be seen from Fig. 5, 1 min ultrasonic pretreatment gave the highest polymer yield per energy consumption. With increasing irradiation time, the polymer yield decreased due to large energy consumption of ultrasonic irradiation. On the other hand, with decreasing irradiation time from 1 min to 30 s, the polymer yield was also decreased, because it took more time to reach 80% conversion due to the formation of thin monomer floating layer. Although the growth rate of droplet diameter was fast in a case when the irradiation time was 1 min, as shown in Fig. 3, the stability of the monomer droplets was guaranteed within the time range of polymerization when the diameter was less than 2.0 micrometers. Thus the optimum value of ultrasonic irradiation time could be regarded as 1 min.

3.3 Polymer particle size

Figure 6 shows mode diameter of polymer particles. Comparing Figs. 6 a) and b), the mode diameter in the case with ultrasonic pretreatment was slightly larger than in the case without ultrasonic pretreatment. In Fig. 6 solid line is theoretical particle size as the function of monomer conversion using Smith-Ewart theory [7]. As shown in Fig. 6 a), in the case without ultrasonic pretreatment, the mode particle size showed relatively good agreement with theoretical particle size. According to Smith-Ewart theory [7], reaction rate is in proportion to the number of polymer particles as shown in the following reaction rate equation, r_M [mol/(m^3･s)]:

$$r_{\mathrm{M}} = -k_{\mathrm{p}} M_{\mathrm{p}} \bar{n}\, N / N_{\mathrm{A}} \tag{2}$$

where k_p [m^3/(mol･s)] is the reaction rate constant, M_p [mol/m^3] is the monomer concentration in the particle, $\bar{n}$ [-] is the average number of free radicals per particle, N [1/m^3] is the number of particle per volume and N_A [1/mol] is Avogadro’s number. In a batch process, polymer yield W [kg] is given by the following equation:

$$W = \frac{\pi}{6}\rho_{\mathrm{p}}\bar{d}^{3}N \qquad (3)$$

where ρ_{p} [kg/m^3] is the density of polymer particle and $\bar{d}$ [m] is mean particle size. Eq. (3) indicates that larger particle diameter results in smaller number of particles under the same polymer yield. Consequently, from Eq. (2), when larger particles are obtained, the reaction rate should be slower. Contrary to the above relation that the larger polymer particle generation results in the lower reaction rate, the experimental results indicate that growth of particle as well as the reaction rate was enhanced by ultrasonic pretreatment.

4. Discussion

In this section, the reason for these unexpected results will be discussed. According to Eq. (2), if the reaction rate in the case with ultrasonic pretreatment becomes larger in spite of increasing particle size, M_{p} or $\bar{n}$ must take much larger value than conventional emulsion polymerization of styrene. Emulsion polymerization of styrene belongs to Smith-Ewart Case2 kinetics and the average number of free radicals per particle $\bar{n}$ is 0.5. Consequently, the monomer concentration in the particle M_{p} is the only parameter making possible to increase the reaction rate. On the other hand, as for the particle growth rate, the volumetric growth rate of particle, μ [m^3/s] is expressed by the following equation [8]:

$$\mu = \frac{k_{\mathrm{p}}\rho_{\mathrm{m}}M_{\mathrm{p}}M_{\mathrm{m}}}{4N_{\mathrm{A}}\rho_{\mathrm{p}}\left(\rho_{\mathrm{m}} - M_{\mathrm{m}}M_{\mathrm{p}}\right)} \qquad (4)$$

where ρ_{m} [kg/m^3] is the density of monomer, M_{m} [g/mol] is the molecular weight of monomer. In Eq. (4), M_{p} is the only valuable and the others take constant values. Thus M_{p} is also the only parameter making possible to increase the particle growth rate. From the above discussion, theoretical particle diameter was recalculated by changing the value of M_{p} from 5.48 mol/L [9] which is the value for conventional emulsion polymerization of styrene to 7.80 mol/L. As shown in Fig. 7, the recalculated theoretical curve shows relatively good agreement with experimental data in the case with ultrasonic pretreatment.

Monomer concentrations in polymer particles and water phase are determined by their partition equilibrium. This partition equilibrium depends on the solubility and interfacial tension among water, monomer and polymer particles. Higher monomer solubility to water phase brings higher concentration of monomer in polymer particles. Kim *et al.* [9] reported that the swelling capacity of the seed particles depends on the size of monomer droplets. The effect of the size of monomer droplets can be negligible if monomer droplets are much larger than seed particles. On the other hand, the swelling capacity of the seed particle increases by the diameter of monomer droplets when very fine monomer droplets are prepared by ultrasonic irradiation. Yoshimatsu *et al.* [10] also reported that the solubility of monomer from monomer droplets to water is represented by following equation:

$$C_d = C_\infty \exp\left(\frac{2\gamma M_\mathrm{m}}{d\rho_\mathrm{m} RT}\right) \tag{5}$$

where C_d [kg/L] is the apparent solubility of monomer to water phase in the droplet of size d, C_∞ [kg/L] is the original solubility of monomer for water, γ [N/m] is the interfacial tension between monomer and water, R [J/(mol·K)] is gas constant and T [K] is temperature. According to Eq. 5, the apparent solubility increased when the diameter of monomer droplets decreases. These papers suggest that the monomer solubility for water phase goes up and the concentration in polymer particles also goes up due to the partition equilibrium.

5. Conclusion

This study investigated the effect of pretreatment of ultrasonic irradiation on emulsion polymerization of styrene to propose a process intensification method which gives high conversion, fast reaction rate, and high energy efficiency. The pretreatment of ultrasound irradiation as short as 1 min drastically improved monomer dispersion and increased reaction rate even at low rotational speed of impeller. Furthermore, the ultrasonic pretreatment resulted in higher monomer concentration in polymer particles and produced larger polymer particles than conventional polymerization without ultrasonic pretreatment. From the viewpoint of process intensification, such very short irradiation time can drastically reduce the size of pretreatment device, which brings smaller energy consumption. Taking into account relatively long stable monomer dispersion in the case with ultrasonic pretreatment, one possible process is a conventional stirred tank combining with a plug-flow-type ultrasonic pretreatment device, as shown in Fig. 8 [12-14]. It can be concluded that this ultrasonic pretreatment is a hopeful tool for process intensification of emulsion polymerization.

Acknowledgments

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Figure captions

Fig.1 Experimental apparatus (1) horn-type ultrasonic device (2) beaker of 200 mL (3) magnet stirrer (4) stirrer (5) 2 - bladed turbine impeller (6) batch reactor (L = 60 mm, D = 20 mm, H = 73 mm, X = 10 mm) with a jacket

Fig.2 Stability of monomer droplets from the macroperspective after ultrasound (US) irradiation

Fig.3 Time variation of monomer droplet diameter, dm, depending on the various ultrasound irradiation time: ◆ 1min , ■ 2min , ▲ 4 min

Fig.4 Time variation of monomer conversion a) at a variety of rotational speed of impeller (noted in brackets) : ■ without US (250 rpm), ● without US (500 rpm), × without US (750 rpm), ▲ without US (1000 rpm), ◆ with US 2 min (250 rpm) b) at a variety of US irradiation time followed by agitation of 250 rpm: ∗ US 10 s, + US 30 s, ● US 1 min, ◆ US 2 min

Fig.5 Comparison of polymer yield per consumption energy, E, when monomer conversion reached 80%

Fig.6 Polymer particle mode diameter, d_M, along with monomer conversion a) at various rotational speeds of impeller (noted in brackets) : ■ without US (250 rpm), ● without US (500 rpm), × without US (750 rpm), ▲ without US (1000 rpm), ◆ with US 2 min (250 rpm) b) at various US irradiation time followed by agitation of 250 rpm: ∗10 s, + 30 s, ● 1 min,◆ 2 min, - Theoretical particle size

Fig.7 Parameter fitting result for M_p with respect to Fig. 6 b): ∗ 10 s, + 30 s, ●1 min, ◆2 min, - Theoretical particle size

Fig.8 Possible emulsion polymerization process

Figure1

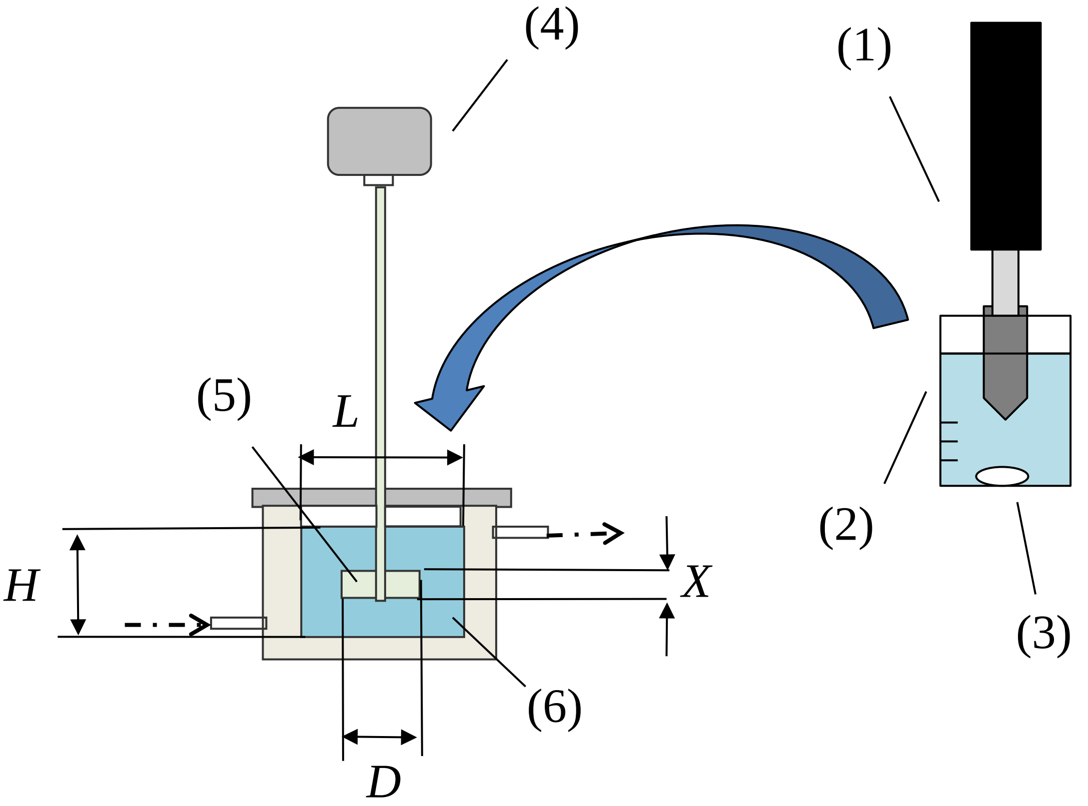

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Figure2

After 2min irradiation

8 h

24 h

32 h

48 h

Fig.2 Stability of monomer droplets from the macroperspective after ultrasound (US) irradiation

Figure3

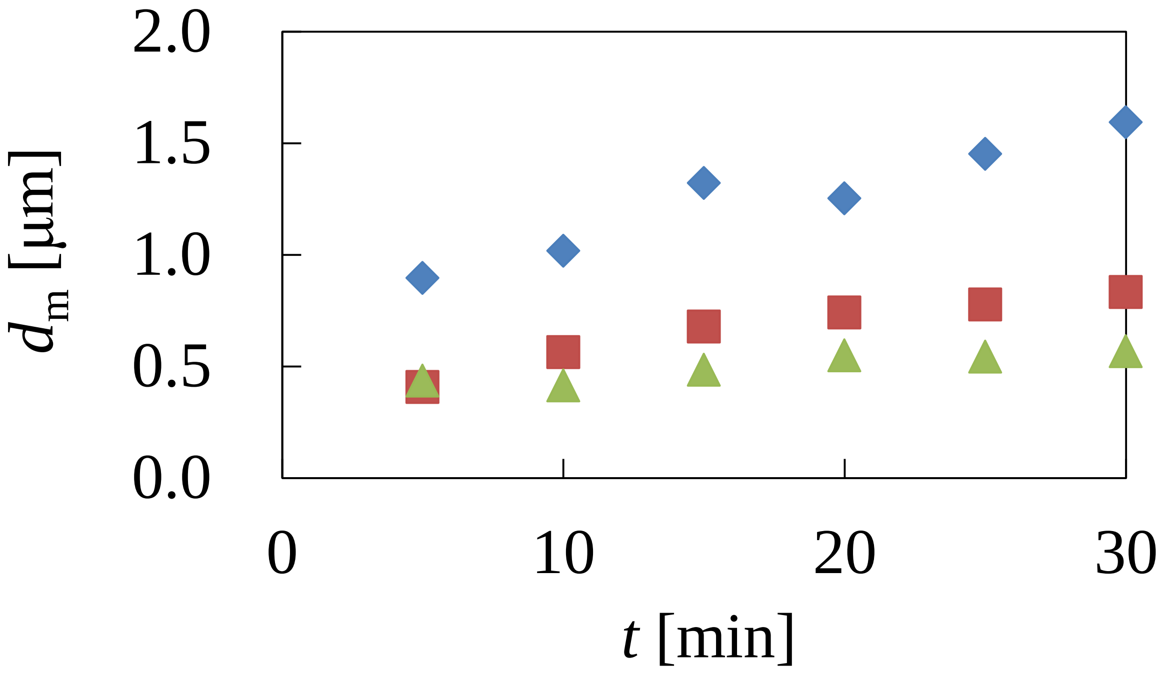
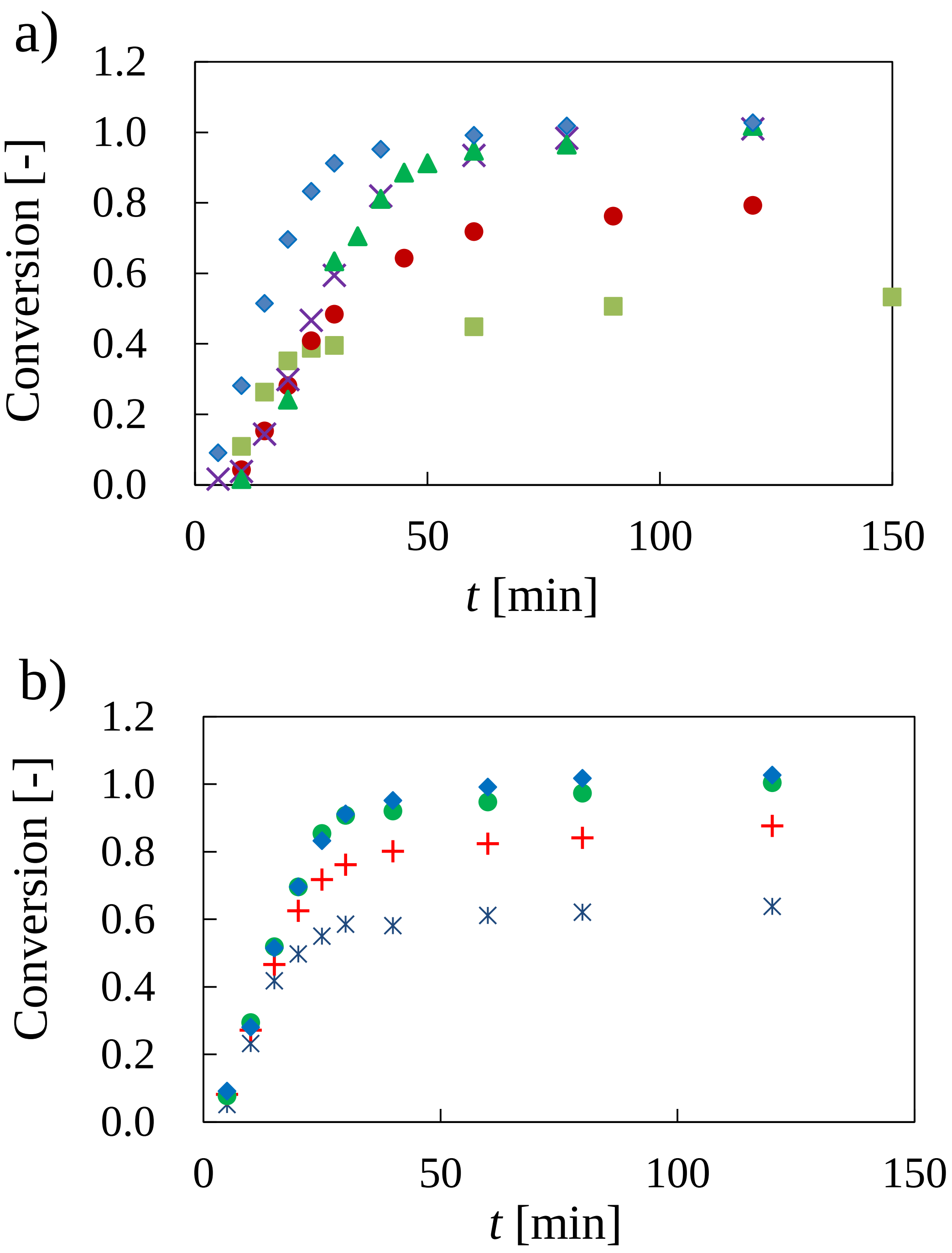


Fig.3 Time variation of monomer droplet diameter, d_m, depending on the various ultrasound irradiation time: ◆ 1min , ■ 2min , ▲ 4 min

Figure4



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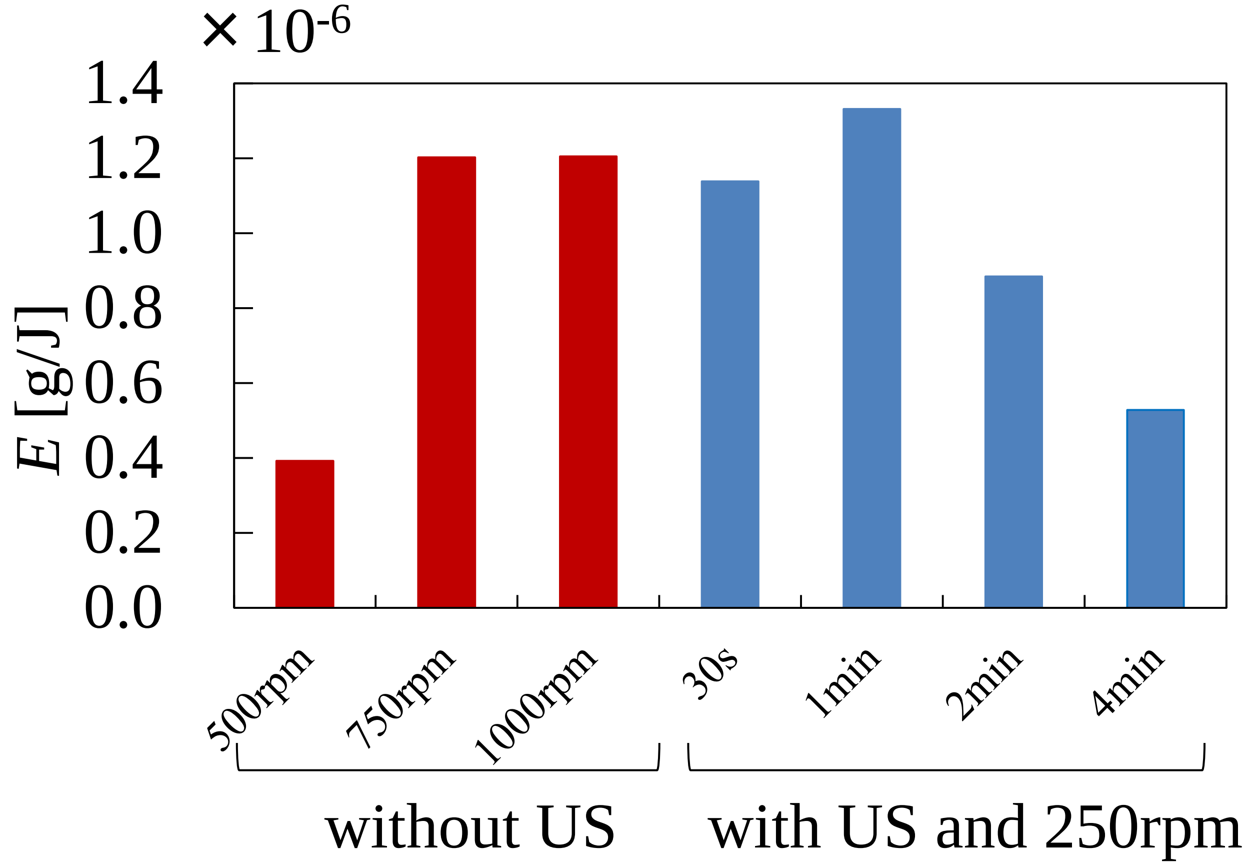

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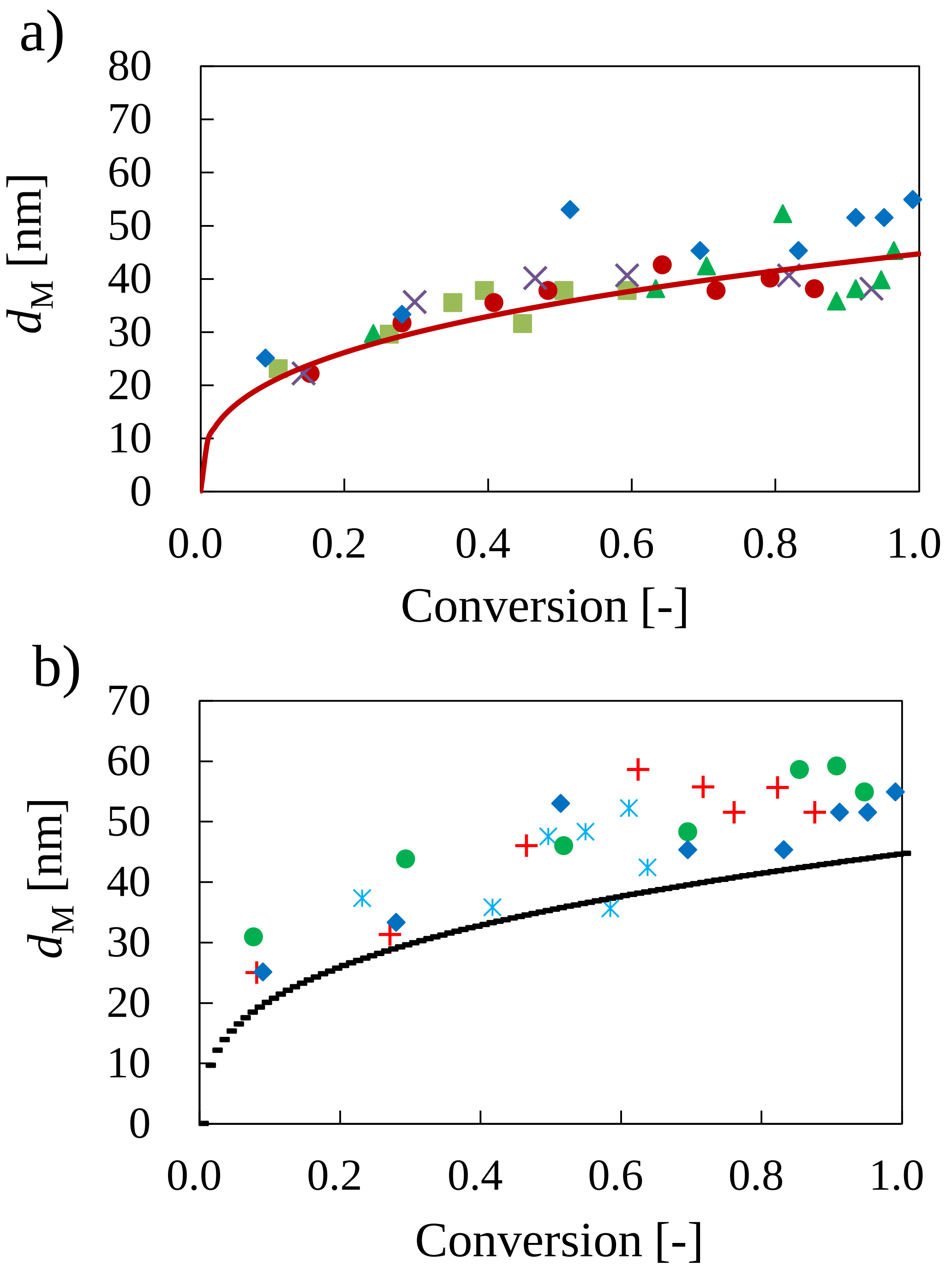
Figure6



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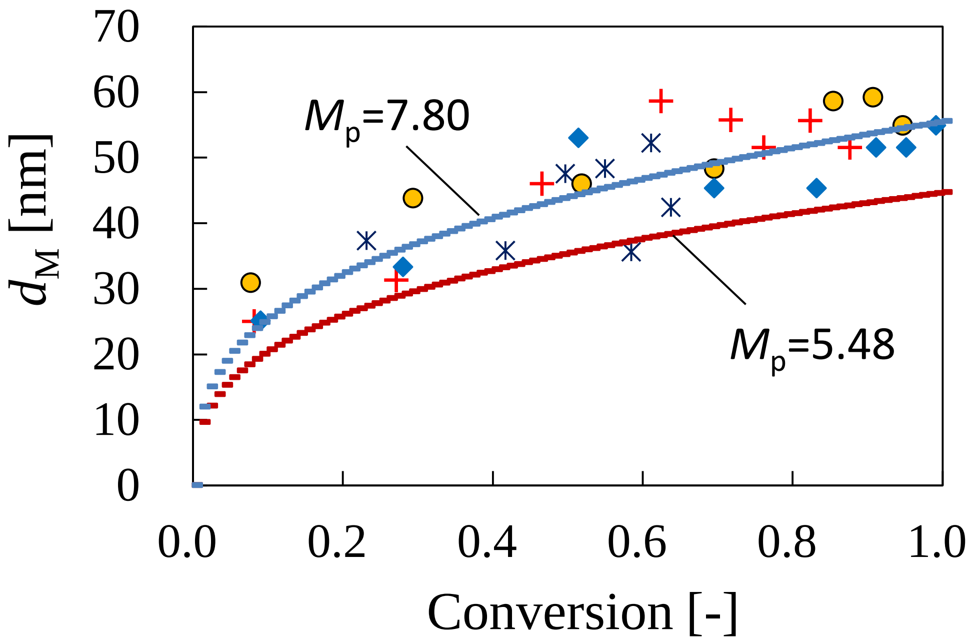

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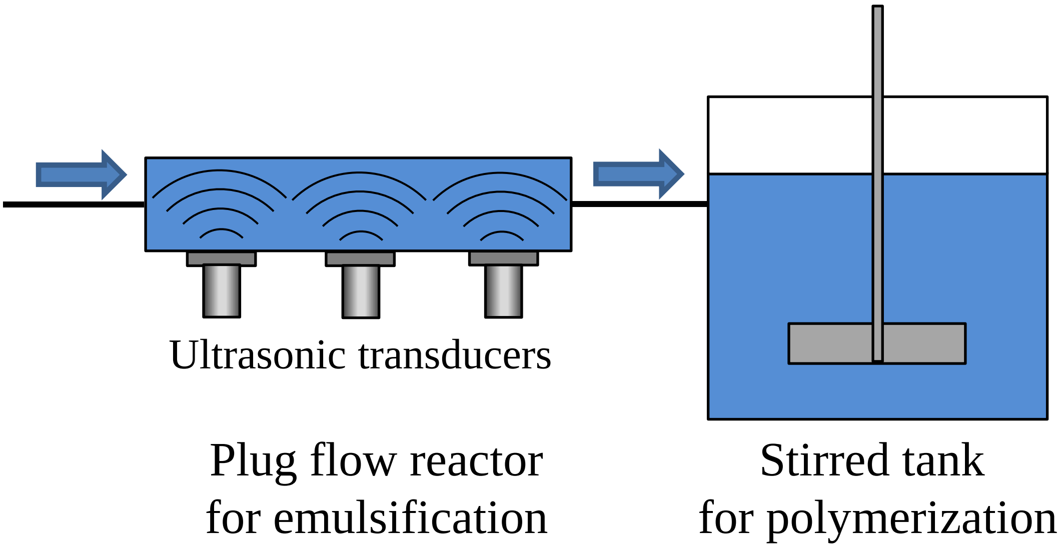
Figure8



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